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REVIEW

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Recent Advances in Wave Function-Based Methods of Molecular-Property Calculations

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1. INTRODUCTION

Our understanding of the electronic structure of molecules often comes from spectroscopic investigations in which electromagnetic radiation is applied to a molecule and the scattering or absorption of the radiation is measured.[1,2] These experimental techniques probe the structure of molecules by observing their response to applied electromagnetic perturbations. Such measurements provide a detailed picture of molecular systems, often rich in detail and sometimes difficult to interpret.

Over the last few decades, molecular electronic-structure theory has developed to a stage where it can provide invaluable help in the interpretation of experimental measurements of a broad range of molecular properties of importance in rotational and vibrational spectroscopies,[3] ultraviolet−visible spectroscopies,[4,5] magnetic-resonance spectroscopies,[6−8] linear and nonlinear optics,[1,9,10] and so on. In all these fields, spectroscopic constants can be calculated at various levels of electronic-structure theory, capable of approaching the exact value in a controlled, systematic manner, using established hierarchical levels of theory. At the same time, methodological developments toward larger systems are being made in different laboratories, promising to make calculations of molecular properties of systems containing hundreds and thousands of atoms routine in the near future.[11−14] In the present review, we discuss these developments in computational molecular electronic-structure theory. Our emphasis is on molecular response theory based on construction of a many-electron wave function, concentrating on developments during the past decade. As such, we do not discuss the various electronic-structure models themselves in any depth nor do we consider optimization of the energy and wave functions. Also, we do not discuss here calculations of molecular properties based on density-functional theory (DFT) except indirectly in our discussion of techniques for Hartree−Fock theory.

This review is divided into eight sections. Following the Introduction, we discuss in section 2 the molecular electronic Hamiltonian, including an overview of the Breit−Pauli Hamiltonian and the second-quantization formalism, extensively used in the remaining sections. Next, in section 3, we review response theory for exact states, providing a flexible quasi-energy framework subsequently used for approximate states in section 4, which contains detailed expositions of response theory for Hartree−Fock self-consistent field (SCF) theory, multiconfigurational SCF (MCSCF) theory, coupled-cluster theory, and Møller−Plesset theory. Following this exposition of response theory, we give a survey of molecular properties in section 5, covering geometrical properties and spectroscopic constants, magnetic resonance parameters, linear and nonlinear electromagnetic properties including nonlinear optics and birefringences, excitation energies, and excited-state properties. Following discussions of pure vibrational corrections in section 6 and molecular properties in liquids and solids in section 7, some concluding remarks are given in section 8.

2. ELECTRONIC HAMILTONIAN

In the present section, we discuss the electronic Hamiltonian with emphasis on those aspects that are important for evaluation of molecular properties. First, in section 2.1, we discuss the nonrelativistic electronic Hamiltonian in an external electromagnetic field and survey the Breit−Pauli relativistic corrections to second order in the fine-structure constant. In section 2.2, we introduce nuclear electromagnetic fields into the electronic Hamiltonian, thereby arriving at the molecular electronic Breit−Pauli Hamiltonian appropriate for molecular response calculations. Much of the exposition of molecular response theory given in the present review is presented using the formalism of second quantization. In section 2.3, we give a brief introduction to this formalism, in particular, we transform the molecular electronic Breit−Pauli Hamiltonian developed in section 2.2 to the second-quantization representation. Finally, in section 2.4, we discuss the effects of perturbation-dependent basis sets for the second-quantization representation of the molecular Hamiltonian and calculation of molecular properties.

2.1. Many-Electron Hamiltonian

In this subsection, we discuss the nonrelativistic Hamiltonian of an electronic system in the presence of an electromagnetic field and its relativistic corrections within the framework of the Breit−Pauli Hamiltonian. Particular attention is paid to the description of electromagnetic interactions and introduction of electron spin. The electronic Hamiltonian developed in this subsection forms the basis for the molecular electronic Hamiltonian discussed in section 2.2, where we introduce the effects of nuclear charges and nuclear magnetic moments. For a more thorough discussion of the electronic Hamiltonian, see ref 15.

2.1.1. Classical Particles in an Electromagnetic Field. In the presence of an electric field $\mathbf{E}(\mathbf{r},t)$ and a magnetic field (or magnetic induction) $\mathbf{B}(\mathbf{r},t)$, a classical particle of charge z moving with velocity $\mathbf{v}$ experiences the Lorentz force $\mathbf{F}$ (in Cartesian coordinates)

$$\mathbf{F} = z(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \tag{1}$$

which is velocity dependent and hence nonconservative. The motion of the particle is determined by Newton's equation of motion (subject to boundary conditions)

$$\mathbf{F} = m\mathbf{a} \tag{2}$$

where m is the mass of the particle and $\mathbf{a}$ its acceleration. The electric and magnetic fields $\mathbf{E}$ and $\mathbf{B}$ satisfy Maxwell's equations

$$\nabla \cdot \mathbf{E} = 4\pi\rho \tag{3}$$

$$\nabla \times \mathbf{B} - c^{-2}\partial_t\mathbf{E} = 4\pi c^{-2}\mathbf{J} \tag{4}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{5}$$

$$\nabla \times \mathbf{E} + \partial_t\mathbf{B} = \mathbf{0} \tag{6}$$

in the short-hand notation $\partial_t = \partial/\partial t$. Here and in the following, we employ SI-based atomic units[16] where $m_e = 1$, $e = 1$, and $\hbar = 1$. In addition, the electric and magnetic constants satisfy $4\pi\varepsilon_0 = 1$ and $4\pi\mu_0 = c^2$, respectively. When the sources, that is, the charge density $\rho(\mathbf{r},t)$ and the current density $\mathbf{J}(\mathbf{r},t)$ generated by all particles in the system, are known, Maxwell's equations can be solved for $\mathbf{E}(\mathbf{r},t)$ and $\mathbf{B}(\mathbf{r},t)$. Conversely, since the particles are driven by the Lorentz force, $\rho(\mathbf{r},t)$ and $\mathbf{J}(\mathbf{r},t)$ depend on $\mathbf{E}(\mathbf{r},t)$ and $\mathbf{B}(\mathbf{r},t)$. In principle, therefore, we must simultaneously solve Maxwell's equations for the electromagnetic field and the classical equations of motion for the particles.

Maxwell's equations consist of two distinct pairs of equations: the inhomogeneous equations in eqs 3 and 4 and the homogeneous equations in eqs 5 and 6. The homogeneous equations are exact relations between the components of $\mathbf{E}$ and $\mathbf{B}$, independent of the charges and currents in the system. Indeed, the homogeneous equations are automatically satisfied by expressing the fields in terms of a scalar potential $\phi(\mathbf{r},t)$ and a vector potential $\mathbf{A}(\mathbf{r},t)$ such that

$$\mathbf{E}(\mathbf{r}, t) = -\nabla\phi(\mathbf{r}, t) - \partial_t\mathbf{A}(\mathbf{r}, t) \tag{7}$$

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t) \tag{8}$$

The potentials $(\phi,\mathbf{A})$, which contain four rather than six components as in $(\mathbf{E},\mathbf{B})$, are subsequently obtained by solving the first, inhomogeneous pair of Maxwell's equations subject to boundary conditions (usually that the fields go to zero at an infinite distance from the sources). However, the scalar and vector potentials ϕ and $\mathbf{A}$ are not unique in the sense that gauge transformations of the potentials

$$\phi' = \phi - \partial_t f \tag{9}$$

$$\mathbf{A}' = \mathbf{A} + \nabla f \tag{10}$$

where the gauge function $f(\mathbf{r},t)$ depends on $\mathbf{r}$ and t, do not affect the physical fields generated from the potentials by eqs 7 and 8. We are thus free to choose f so as to make ϕ and $\mathbf{A}$ satisfy additional conditions. In the Coulomb gauge, the gauge function is chosen such that the vector potential becomes divergenceless

$$\nabla\cdot\mathbf{A} = 0 \tag{11}$$

In the following, we shall always work in the Coulomb gauge, in which the scalar potential is given by the instantaneous Coulomb interaction, corresponding to the strict nonrelativistic limit of electrodynamics.[17] Retardation and magnetic interactions appear as relativistic corrections through the purely solenoidal (divergenceless) vector potential. Indeed, as the speed of light c tends to infinity in Maxwell's equations in eqs 3−6, the divergence and curl of the magnetic field vanish, which combined with the boundary conditions suggests that, in the strict nonrelativistic limit, the magnetic field is zero everywhere. Non-Coulomb gauges have been explored for ab initio calculation of magnetic properties,[18−21] but these have not gained widespread use.

2.1.2. Classical Hamiltonian. In classical Hamiltonian mechanics, a system of particles is described in terms of their positions q_i and conjugate momenta p_i. For each system, there exists a scalar Hamiltonian function $H(q_i,p_i)$ such that the classical equations of motion are given by

$$\dot{q}_i = \partial_{p_i}H, \; \dot{p}_i = -\partial_{q_i}H \tag{12}$$

where $\partial p_i = \partial/\partial p_i$ and $\partial q_i = \partial/\partial q_i$. The corresponding equations for continuous systems are obtained by replacing the Hamiltonian function with the Hamiltonian density, the positions and momenta by the corresponding field variables, and the partial derivatives with functional derivatives. For a system of particles and fields, the Hamiltonian separates into three parts

$$H = H_{\mathrm{p}} + H_{\mathrm{f}} + H_{\mathrm{int}} \tag{13}$$

corresponding to the particles, the fields, and their interaction. The corresponding equations of motion are rarely solved self-consistently. Rather, the degrees of freedom associated with either particles or fields are frozen, that is, treated as parameters, and the equations of motions are developed for the remaining variables. If the particles are treated as sources, then the particle term H_{p} drops out of the equations of motion, which then reduce to Maxwell's equations. When calculating molecular properties, on the other hand, we consider the response of molecules to externally applied electromagnetic fields and so the field term H_{f} drops out of the equations of motion.

The classical Hamiltonian for a single particle of mass m and charge z moving in an external electromagnetic field $\mathbf{E}$ and $\mathbf{B}$ is obtained from the free-particle Hamiltonian by the substitutions

$$\mathbf{p} \rightarrow \boldsymbol{\pi} = \mathbf{p} - z\mathbf{A}, \; H \rightarrow H + z\phi(\mathbf{r}, t) \tag{14}$$

corresponding to the principle of minimal electromagnetic coupling[22,23] based on a relativistic coupling of particles and fields.[17] The coupling is minimal in the sense that it is the minimal coupling of particles and fields consistent with gauge invariance of the corresponding Lagrangian density.[24] In the nonrelativistic case, we then obtain the Hamiltonian

$$H(\mathbf{r}, \mathbf{p}) = \frac{\pi^2}{2m} + z\phi(\mathbf{r}, t) \tag{15}$$

The first of Hamilton's equations in eq 12 allows identification of the nonrelativistic kinetic momentum as

$$\boldsymbol{\pi} = m\mathbf{v} \tag{16}$$

Its total time derivative is the Lorentz force in eq 1, as can be shown from the second of Hamilton's equations.

2.1.3. Schrödinger Hamiltonian. To arrive at a quantum-mechanical description of the electron (i.e., a particle with charge $z = -e = -1$ au and mass $m = m_{\mathrm{e}} = 1$ au) in an electromagnetic field, we perform the substitutions $\mathbf{p} \rightarrow -\mathrm{i}\nabla$ and $H \rightarrow \mathrm{i}\partial_t$ in eq 15 followed by multiplication with the wave function $\Psi(\mathbf{r})$ from the right, yielding the time-dependent Schrödinger equation

$$\mathrm{i}\partial_t\Psi = H_{1\mathrm{c}}\Psi \tag{17}$$

with the electronic Schrödinger Hamiltonian

$$H_{1\mathrm{c}} = \frac{\pi^2}{2} - \phi, \; \boldsymbol{\pi} = -\mathrm{i}\nabla + \mathbf{A} \tag{18}$$

We may expand the kinetic-energy operator $\pi^2/2$ in eq 18, yielding the following expression for the electronic Hamiltonian in the Coulomb gauge

$$H_{1\mathrm{c}} = \frac{1}{2}p^2 + \mathbf{A}\cdot\mathbf{p} + \frac{1}{2}A^2 - \phi \tag{19}$$

In an electromagnetic field, the vector potential thus makes both a linear paramagnetic contribution $\mathbf{A}\cdot\mathbf{p}$ and a quadratic diamagnetic contribution $A^2/2$ to the Hamiltonian. The diamagnetic contribution may be viewed as a small positive correction $A^2/2$ to the interaction $-\phi$ of the electron with the scalar potential.

Consider now a uniform magnetic field $\mathbf{B}$. In the Coulomb gauge, such a field may be represented by the vector potential

$$\mathbf{A}_{\mathrm{O}}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r}_{\mathrm{O}} = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) \tag{20}$$

which vanishes at the gauge origin $\mathbf{O}$. Using this potential, we may write the paramagnetic interaction in the form

$$\mathbf{A}_{\mathrm{O}}\cdot\mathbf{p} = \frac{1}{2}\mathbf{B}\cdot\mathbf{l}_{\mathrm{O}}, \; \mathbf{l}_{\mathrm{O}} = \mathbf{r}_{\mathrm{O}} \times \mathbf{p} \tag{21}$$

Thus, the paramagnetic interaction is proportional to the component of the orbital angular momentum $\mathbf{l}_{\mathrm{O}}$ of the electron about the gauge origin $\mathbf{O}$ and along the direction of the external magnetic field $\mathbf{B}$. It turns out, however, that this treatment of the interaction of the electron with the external magnetic field is inadequate as it ignores a fundamental property of the electron, namely, its spin.

2.1.4. Pauli Hamiltonian. The two-by-two Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\ \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix},\ \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{22}$$

were introduced by Pauli in 1927[25] and are matrix representations of twice the spin operator **s** for $s = 1/2$. They satisfy the algebra

$$\sigma_i \sigma_j = \delta_{ij} + \mathrm{i}\varepsilon_{ijk}\sigma_k \tag{23}$$

where the Kronecker delta δ_{ij} is 1 for identical indices and 0 otherwise whereas the Levi−Civita antisymmetric symbol ε_{ijk} is +1 for even permutations of the indices, −1 for odd permutations, and 0 if two or more indices are identical. Using the relation in eq 23, we easily deduce the Dirac identity

$$(\boldsymbol{\sigma}\cdot\mathbf{A})(\boldsymbol{\sigma}\cdot\mathbf{B}) = \mathbf{A}\cdot\mathbf{B} + \mathrm{i}\boldsymbol{\sigma}\times(\mathbf{A}\times\mathbf{B}) \tag{24}$$

of which a particular instance is the simple relation

$$(\boldsymbol{\sigma}\cdot\mathbf{p})^2 = p^2 \tag{25}$$

It suggests that spin is hidden in the nonrelativistic free-particle Hamiltonian. However, a difference between the left- and the right-hand sides of the above identity occurs when external electromagnetic fields are introduced through the minimal substitutions, eq 14. Starting from the left-hand side of the identity, we obtain a Hamiltonian of the form

$$H_{2c} = \frac{1}{2}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2 - \phi = \frac{1}{2}\pi^2 + \frac{1}{2}(\boldsymbol{\sigma}\cdot\mathbf{B}) - \phi \tag{26}$$

whereas the right-hand side leads to a Hamiltonian in which the spin−Zeeman interaction (the second term above) is absent.

For a proper quantum-mechanical description of the electron, we therefore need a two-component wave function, which in the Pauli representation of eq 22 satisfies the Schrödinger equation

$$\mathrm{i}\partial_t \begin{pmatrix} \Psi_\alpha(\mathbf{r}) \\ \Psi_\beta(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} \frac{1}{2}\pi^2 - \phi + B_z & B_x - \mathrm{i}B_y \\ B_x + \mathrm{i}B_y & \frac{1}{2}\pi^2 - \phi - B_z \end{pmatrix} \begin{pmatrix} \Psi_\alpha(\mathbf{r}) \\ \Psi_\beta(\mathbf{r}) \end{pmatrix} \tag{27}$$

The two components are coupled only in the presence of an external magnetic field. Alternatively, we may equip the electron with an additional discrete coordinate $\sigma = \pm 1/2$ in the manner $\Psi(\mathbf{x}) = \Psi(\mathbf{r},\sigma)$, where $\Psi(\mathbf{r}, \pm 1/2)$ are two states whose lower and upper components vanish, respectively. The spin interaction is interpreted by associating a magnetic moment with the spin of the electron

$$\mathbf{m} = g_e \mu_B \mathbf{s},\ g_e = -2,\ \mu_B = \frac{e}{2m_e} = \frac{1}{2}\,\mathrm{au} \tag{28}$$

where we introduced the electron g factor g_e and the Bohr magneton μ_B. Here, we set the electron g factor equal to the value predicted by the Dirac equation, whereas its recommended value, including quantum-electrodynamics corrections, is $g_e = -2.0023193043622(15)$.[26] The spin paramagnetic term may now be written as a Zeeman interaction $-\mathbf{B}\cdot\mathbf{m}$ of the external induction with the magnetic moment of the electron. Thus, the two-component Hamiltonian eq 26 differs from the one-component Hamiltonian eq 18 only in the presence of the Zeeman term

$$H_{2c} = H_{1c} - \mathbf{B}\cdot\mathbf{m} \tag{29}$$

In the absence of an external magnetic field, the one- and two-component nonrelativistic Hamiltonians are equivalent and the two components of the wave function are not coupled. The total paramagnetic Zeeman interaction with a uniform magnetic field may therefore be written in the form

$$H_z = -\mathbf{B}\cdot\mathbf{m}_{\mathrm{tot}},\ \mathbf{m}_{\mathrm{tot}} = -\frac{1}{2}(\mathbf{l}_O + 2\mathbf{s}) \tag{30}$$

where $\mathbf{l}_O$ is the orbital-angular momentum of the electron about the gauge origin **O**, see eq 21. We note the anomalous double weight of the spin angular momentum in the magnetic dipole-moment operator $\mathbf{m}_{\mathrm{tot}}$ in eq 30.

From the one-electron Pauli Hamiltonian in eq 26, we obtain the N-electron Pauli Hamiltonian by adding pairwise Coulomb interactions to the sum of N one-electron Hamiltonians

$$\begin{aligned} H^{\mathrm{NR}} &= \sum_{i=1}^{N}\left(\frac{1}{2}(\boldsymbol{\sigma}_i\cdot\boldsymbol{\pi}_i)^2 - \phi_i\right) + \sum_{i>j=1}^{N}\frac{1}{r_{ij}} \\ &= \sum_{i=1}^{N}\left(\frac{1}{2}p_i^2 + \mathbf{A}_i\cdot\mathbf{p}_i + \mathbf{B}_i\cdot\mathbf{s}_i + \frac{1}{2}A_i^2 - \phi_i\right) \\ &\quad + \sum_{i>j=1}^{N}\frac{1}{r_{ij}} \end{aligned} \tag{31}$$

adopting the short-hand notation $\phi_i = \phi(\mathbf{r}_i,t)$ and so on for the potentials and fields at the position of electron i. In nonrelativistic quantum mechanics, a many-electron system is described by an antisymmetric N-particle wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N)$ that satisfies the time-dependent Schrödinger equation

$$\mathrm{i}\partial_t\Psi(\mathbf{x}_1, ...\mathbf{x}_N, t) = H^{\mathrm{NR}}\Psi(\mathbf{x}_1, ...\mathbf{x}_N, t) \tag{32}$$

using the nonrelativistic electronic Pauli Hamiltonian of eq 31. Before we consider the potentials ϕ and **A** characteristic of molecular systems, we shall briefly consider the relativistic corrections to this Hamiltonian.

2.1.5. Breit−Pauli Hamiltonian. In a relativistic treatment of many-electron systems, the Dirac−Coulomb−Breit Hamiltonian is often used[15,27]

$$\begin{aligned} H^{\mathrm{DCB}} &= \sum_i [c(\boldsymbol{\alpha}_i\cdot\boldsymbol{\pi}_i) - \phi_i + \beta_i c^2] \\ &\quad + \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}} - \frac{1}{2}\sum_{i\neq j}\left[\frac{c\boldsymbol{\alpha}_i\cdot c\boldsymbol{\alpha}_j}{c^2 r_{ij}} + \frac{(c\boldsymbol{\alpha}_i\cdot\nabla_i)(c\boldsymbol{\alpha}_j\cdot\nabla_j)}{2c^2}\right] \end{aligned} \tag{33}$$

where $\boldsymbol{\alpha}$ and β are the four-by-four Dirac matrices, which in terms of two-by-two submatrices take the form

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix},\ \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \tag{34}$$

For a fully relativistic treatment of the electronic system, we may now solve the Dirac−Coulomb−Breit equation

$$\mathrm{i}\partial_t\Psi(\mathbf{r}_i, t) = H^{\mathrm{DCB}}\Psi(\mathbf{r}_i, t) \tag{35}$$

which, due to the presence of negative-energy states, is done with the explicit or implicit use of projection operators onto the positive-energy states defined with respect to the current or some reference potential.[27] We note that this equation is only approximately Lorentz invariant, the two-electron part being correct only to second order in the fine-structure constant

$$\alpha = \frac{e^2}{c} \approx 7.297 \times 10^{-3} \tag{36}$$

The zero-order two-electron term in eq 33 is the Coulomb term, which is constructed from the interaction of one electron with the scalar potential of another electron defined with respect to the nuclear framework; it has the form of an instantaneous charge–charge interaction. Although it has the same form as in the nonrelativistic domain, the physical content is different in that it gives rise to the spin–same-orbit interaction. The second-order term in eq 33, the Breit term, arises from the interaction of one electron with the lowest order contribution of the corresponding vector potential and gives rise to the spin–other-orbit interaction. It has the form of a current–current interaction, as seen from the presence of the relativistic velocity operator $c\boldsymbol{\alpha}$.

Reducing the Dirac–Coulomb–Breit Hamiltonian to two-component form, we obtain the Breit–Pauli operator

$$H^{\mathrm{BP}} = H^{\mathrm{NR}} + H^{\mathrm{MV}} + H^{\mathrm{DW}} + H^{\mathrm{SsO}} + H^{\mathrm{SoO}} + H^{\mathrm{SS}} + H^{\mathrm{OO}} + O(\alpha^4) \tag{37}$$

where the leading term is the usual Pauli Hamiltonian in eq 31

$$H^{\mathrm{NR}} = \sum_i \frac{1}{2}\pi_i^2 + \sum_i \mathbf{B}_i \cdot \mathbf{s}_i - \sum_i \phi_i + \frac{1}{2}\sum_{i \neq j} \frac{1}{r_{ij}} \tag{38}$$

and the lowest order relativistic corrections are given by

$$H^{\mathrm{MV}} = -\frac{\alpha^2}{8}\sum_i (\pi_i^4 + B_i^2) - \frac{\alpha^2}{4}\sum_i (\pi_i^2 \mathbf{B}_i \cdot \mathbf{s}_i + \mathbf{B}_i \cdot \mathbf{s}_i \pi_i^2) \tag{39}$$

$$H^{\mathrm{DW}} = \frac{\alpha^2}{8}\sum_i (\nabla_i \cdot \mathbf{E}_i) - \frac{\alpha^2 \pi}{2}\sum_{i \neq j} \delta(\mathbf{r}_{ij}) \tag{40}$$

$$H^{\mathrm{SsO}} = \frac{\alpha^2}{4}\sum_i \mathbf{s}_i \cdot (\mathbf{E}_i \times \boldsymbol{\pi}_i - \boldsymbol{\pi}_i \times \mathbf{E}_i) - \frac{\alpha^2}{2}\sum_{i \neq j} \frac{\mathbf{s}_i \cdot \mathbf{r}_{ij} \times \boldsymbol{\pi}_i}{r_{ij}^3} \tag{41}$$

$$H^{\mathrm{SoO}} = -\alpha^2 \sum_{i \neq j} \frac{\mathbf{s}_j \cdot \mathbf{r}_{ij} \times \boldsymbol{\pi}_i}{r_{ij}^3} \tag{42}$$

$$H^{\mathrm{SS}} = \frac{\alpha^2}{2}\sum_{i \neq j} \frac{r_{ij}^2 \mathbf{s}_i \cdot \mathbf{s}_j - 3\mathbf{s}_i \cdot \mathbf{r}_{ij}\mathbf{r}_{ij} \cdot \mathbf{s}_j}{r_{ij}^5} - \frac{4\alpha^2 \pi}{3}\sum_{i \neq j} \delta(\mathbf{r}_{ij})\mathbf{s}_i \cdot \mathbf{s}_j \tag{43}$$

$$H^{\mathrm{OO}} = -\frac{\alpha^2}{4}\sum_{i \neq j} \frac{\boldsymbol{\pi}_i \cdot r_{ij}^2 \boldsymbol{\pi}_j + \boldsymbol{\pi}_i \cdot \mathbf{r}_{ij}\mathbf{r}_{ij} \cdot \boldsymbol{\pi}_j}{r_{ij}^3} \tag{44}$$

Whereas the mass–velocity operator in eq 39 provides a correction to the kinetic energy, the Darwin operator in eq 40 corrects the potential energy of the electrons and their two-electron repulsion energy for the charge smearing caused by their Zitterbewegung.[15] The spin–same-orbit operator or simply spin–orbit operator in eq 41 couples the spin of each electron to its own orbital motion in the presence of the external potential and the other electrons. The last three terms in eqs 42–44 couple different electrons to each other: the spin–other-orbit operator in eq 42, the spin–spin operator in eq 43, and the orbit–orbit operator in eq 44.

2.2. Molecular Electronic Breit–Pauli Hamiltonian

Thus far, we have treated the electrons without specifying the scalar and vector potentials ϕ and $\mathbf{A}$ in which these particles move. In molecular systems, the most important contributions to these potentials are from the nuclei. In addition, there may be contributions from externally applied electromagnetic fields. To arrive at the molecular electronic Hamiltonian, we shall identify the nuclear contributions to the potentials ϕ_{nuc} and $\mathbf{A}_{\mathrm{nuc}}$ and then perform the substitutions

$$\phi(\mathbf{r}) \rightarrow \phi_{\mathrm{nuc}}(\mathbf{r}) + \phi(\mathbf{r}) \tag{45}$$

$$\mathbf{A}(\mathbf{r}) \rightarrow \mathbf{A}_{\mathrm{nuc}}(\mathbf{r}) + \mathbf{A}(\mathbf{r}) \tag{46}$$

in the Breit–Pauli Hamiltonian eq 37, yielding the molecular electronic Breit–Pauli Hamiltonian.[15] On a phenomenological basis, we also include in this Hamiltonian purely nuclear terms, which involve internuclear interactions or interactions of the nuclei with external electromagnetic fields. However, staying within the Born–Oppenheimer approximation, we treat the nuclei as stationary particles and do not introduce terms that involve the motion of the nuclei.

2.2.1. Nuclear Electromagnetic Potentials and Fields.

Nuclei are complicated many-body systems. For our purposes, they are sufficiently well characterized by their charges Z_K, their radial extents $\mathscr{R}_K$, their traceless quadrupole moments $\boldsymbol{\Theta}_K$, and their magnetic moments $\mathbf{M}_K$. From these charges and moments, we arrive at the following multipole expansions of the nuclear contributions to the potentials in eqs 45 and 46

$$\phi_{\mathrm{nuc}}(\mathbf{r}) = \sum_K \frac{Z_K}{r_K} - \frac{2\pi}{3}\sum_K Z_K \mathscr{R}_K^2 \delta(\mathbf{r}_K) + \frac{1}{3}\sum_K \frac{\mathrm{tr}\Theta_K(3\mathbf{r}_K\mathbf{r}_K^{\mathrm{T}} - r_K^2 \mathbf{I}_3)}{r_K^5} \tag{47}$$

$$\mathbf{A}_{\mathrm{nuc}}(\mathbf{r}) = \alpha^2 \sum_K \frac{\mathbf{M}_K \times \mathbf{r}_K}{r_K^3} \tag{48}$$

where we ignored higher order moments as well as all non-electromagnetic interactions such as those arising from parity violation, see ref 28 and references therein. To leading orders, the corresponding nuclear electric and magnetic fields are given by

$$\mathbf{E}_{\mathrm{nuc}}(\mathbf{r}) = \sum_K \frac{Z_K \mathbf{r}_K}{r_K^3} \tag{49}$$

$$\mathbf{B}_{\mathrm{nuc}}(\mathbf{r}) = \alpha^2 \sum_K \frac{3(\mathbf{M}_K \cdot \mathbf{r}_K)\mathbf{r}_K - r_K^2 \mathbf{M}_K}{r_K^5} + \frac{8\pi}{3}\alpha^2 \sum_K \delta(\mathbf{r}_K)\mathbf{M}_K \tag{50}$$

For symmetry (parity) reasons, there are no odd-order electric moments and no even-order magnetic moments in the expansions of the nuclear potentials.[15] Among the different contributions to the nuclear potentials in eqs 47 and 48, by far the largest is the electrostatic contribution from the nuclear charge Z_K; indeed, the resulting nuclear point-charge potential is responsible for generating stable molecular structures. The remaining contributions to the potentials are orders of magnitude smaller, representing small corrections to the point-charge nuclear model and being responsible for the hyperfine interactions in atoms and molecules.

The contact and quadrupolar interactions in eq 47 depend on the size and shape of the nucleus as represented by the radial extent and traceless quadrupolar moments

$$Z_K \mathscr{R}_K^2 = \int r^2 \rho_K(\mathbf{r})\mathrm{d}\mathbf{r} \tag{51}$$

$$\Theta_K = \frac{1}{2}\int (3\mathbf{r}\mathbf{r}^{\mathrm{T}} - r^2\mathbf{I}_3)\rho_K(\mathbf{r})\mathrm{d}\mathbf{r} \tag{52}$$

where $\rho_K(\mathbf{r})$ is the nuclear charge distribution. From eq 51, we note that the finite size reduces the potential at the nucleus, increasing the total energy. Since nuclear sizes are of the order of 1 fm, the correction is small, in particular, for light nuclei. The finite nuclear size may alternatively be corrected for by representing the nucleus by a Gaussian charge distribution[27,29]

$$\rho_K(r_K) = Z_K\left(\frac{\eta_K}{\pi}\right)^{3/2}\exp(-\eta_K r_K^2) \tag{53}$$

where $\eta_K = (3/2)\mathscr{R}_K^{-2}$. Gaussian distributions or linear combinations of such distributions are used since they simplify calculation of integrals over Gaussian atomic orbitals (AOs).[30] Integrated over all space, the potential from the Gaussian nucleus becomes

$$\int \frac{\rho_K(r_K)}{r_K}\mathrm{d}\mathbf{r} = \frac{Z_K \mathrm{erf}(\sqrt{\eta_K} r_K)}{r_K} \tag{54}$$

where the strictly increasing error function $0 \leq \mathrm{erf}(x) \leq 1$ reduces the potential at the nucleus. The traceless quadrupolar moments in eq 52 interact with the field gradients at the position of the nuclei in eq 47, providing a correction for nonspherical charge distribution.[31]

The nuclear magnetic moments $\mathbf{M}_K$ in eq 48 arise from the nuclear spins $\mathbf{I}_K$, to which they are related as

$$\mathbf{M}_K = g_K \mu_{\mathrm{N}} \mathbf{I}_K = \gamma_K \hbar \mathbf{I}_K \tag{55}$$

where $\mu_{\mathrm{N}} = e\hbar/2m_{\mathrm{p}}$ is the nuclear magneton, g_K is the nuclear g value, and γ_K is the magnetogyric ratio of the nucleus. The nuclear magneton is numerically small, about 2.7×10^{-4} au. The nuclear g value g_K is a dimensionless empirical constant, different for each nucleus. It is on the order of unity (its absolute value never exceeds six) and may be positive or negative. The nuclear magnetic moments are therefore roughly 3 orders of magnitude smaller than the electronic magnetic moment $\mathbf{m}$ in eq 28. Only nuclei with spin 1/2 or greater have a nonvanishing magnetic dipole moment.

Finally, we take the purely nuclear contributions to the electronic Hamiltonian to be of the form

$$\begin{aligned} H^{\mathrm{nuc}} = {} & \frac{1}{2}\sum_{K\neq L}\frac{Z_K Z_L}{R_{KL}} + \sum_K Z_K \phi_K - \sum_K \mathbf{B}\cdot\mathbf{M}_K \\ & + \frac{\alpha^2}{2}\sum_{K\neq L}\frac{R_{KL}^2(\mathbf{M}_K\cdot\mathbf{M}_L) - 3(\mathbf{M}_K\cdot\mathbf{R}_{KL})(\mathbf{R}_{KL}\cdot\mathbf{M}_L)}{R_{KL}^5} \end{aligned} \tag{56}$$

where we included the pairwise Coulomb repulsion between nuclei of charges Z_K and Z_L and separation R_{KL}, the interaction with an external scalar potential $\phi_K = \phi(\mathbf{R}_K)$ at the nuclear position $\mathbf{R}_K$, the Zeeman interaction of the nuclear magnetic moments $\mathbf{M}_K$ with a uniform external magnetic induction $\mathbf{B}$, and the pairwise dipolar magnetic interactions between nuclei of magnetic moments $\mathbf{M}_K$ and $\mathbf{M}_L$ and relative positions $\mathbf{R}_{KL} = \mathbf{R}_K - \mathbf{R}_L$. Unlike in the electronic spin−spin operator in eq 43, there is no nuclear−nuclear contact term since the stationary nuclei never occupy the same point in space.

2.2.2. Molecular Electronic Breit−Pauli Hamiltonian.

Substituting the nuclear potentials in eqs 47 and 48 and the fields in eqs 49 and 50 into the electronic Breit−Pauli Hamiltonian in eq 37 and adding the purely nuclear contributions in eq 56 we arrive at the molecular electronic Breit−Pauli Hamiltonian. There are many ways to collect the terms in the resulting Hamiltonian. Our classification is based on the nature of the physical mechanisms and interactions rather than on the number and kinds of particles involved in each interaction, giving

$$H_{\mathrm{mol}}^{\mathrm{BP}} = \begin{cases} H_{\mathrm{kin}} & \leftarrow \text{kinetic energy} \\ +H_{\mathrm{cou}} & \leftarrow \text{Coulomb interactions} \\ +H_{\mathrm{ef}} & \leftarrow \text{external electric interactions} \\ +H_{\mathrm{z}} & \leftarrow \text{Zeeman interactions} \\ +H_{\mathrm{so}} & \leftarrow \text{spin−orbit interactions} \\ +H_{\mathrm{ss}} & \leftarrow \text{spin− spin interactions} \\ +H_{\mathrm{oo}} & \leftarrow \text{orbit−orbit interactions} \\ +H_{\mathrm{dia}} & \leftarrow \alpha^4 \text{ diamagnetic interactions} \end{cases} \tag{57}$$

Before considering the individual terms, we recall that the nuclei are treated as stationary sources of electromagnetic fields, thereby excluding all terms involving nuclear motion. Moreover, although the electrons are treated relativistically only to order α^2, we retain diamagnetic terms (which are on the order of α^4, assuming that the external fields are on the order of α^2) since they are spectroscopically important and needed for calculation of molecular magnetic properties as well as to maintain formal gauge invariance. With these remarks, we are ready to survey the various contributions to the molecular electronic Breit−Pauli Hamiltonian.

2.2.3. Kinetic Energy.

The Breit−Pauli kinetic-energy operator in eq 57 is given by

$$H_{\mathrm{kin}} = -\frac{1}{2}\sum_i \nabla_i^2 - \frac{\alpha^2}{8}\sum_i \nabla_i^4 \tag{58}$$

The first term is the usual Newtonian kinetic-energy operator. The second term is the mass−velocity term, which arises because of the relativistic dependence of mass on velocity. The mass−velocity correction is always negative and represents, together with the one-electron Darwin correction described shortly, the major contribution to the relativistic energy correction for slow electrons. The mass−velocity term is unbounded from below. It (and the other small terms in the Breit−Pauli Hamiltonian) should therefore not be used in variational calculations.[32,33]

2.2.4. Coulomb Interactions. In the Breit–Pauli Hamiltonian in eq 57, the Coulomb interactions are represented by

$$\begin{aligned} H_{\mathrm{cou}} = & -\sum_{iK}\frac{Z_K}{r_{iK}} + \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}} + \frac{1}{2}\sum_{K\neq L}\frac{Z_K Z_L}{R_{KL}} \\ & + \frac{\alpha^2\pi}{2}\sum_{iK} Z_K\delta(\mathbf{r}_{iK}) - \frac{\alpha^2\pi}{2}\sum_{i\neq j}\delta(\mathbf{r}_{ij}) \\ & + \frac{2\pi}{3}\sum_{iK} Z_K R_K^2\delta(\mathbf{r}_{iK}) - \frac{1}{3}\sum_{iK}\frac{\mathrm{tr}\Theta_K(3\mathbf{r}_{iK}\mathbf{r}_{iK}^{\mathrm{T}} - r_{iK}^2\mathbf{I}_3)}{r_{iK}^5} \end{aligned} \tag{59}$$

The first three operators are the usual nonrelativistic point-charge interactions among electrons of charge -1 and nuclei of charge Z_K, followed by the Darwin corrections (fourth and fifth operators) caused by the Zitterbewegung of the electrons. The one-electron Darwin correction provides, together with the mass–velocity correction in eq 58, the dominant relativistic correction to the total energies of light systems—it is almost as large as the mass–velocity correction but positive, increasing the total energy. The negative two-electron Darwin term is much less important (by about 2 orders of magnitude)[34] since the repulsion between the electrons reduces their probability of occupying the same point in space. There is no nuclear–nuclear Darwin correction in eq 59 since the nuclei are treated as stationary in the Born–Oppenheimer approximation.

As noted in section 2.2.1, the nuclear point-charge model is not always adequate. The finite size and nonspherical charge distributions of the nuclei may then be corrected for by using the second last and last operators in eq 59, respectively. In these operators, R_K represents the nuclear extent as defined in eq 51 and $\mathbf{\Theta}_K$ is the nuclear quadrupole moment, interacting with the field gradient at the nucleus. Nonspherical nuclear charge distributions are observed in nuclear quadrupole resonance (NQR) studies[35] as well as hyperfine interactions in high-resolution rotational spectra.[3] They are also important in magnetic resonance studies since the quadrupole moment is aligned with the nuclear magnetic moment, thereby providing a coupling between nuclear spins and electronic field gradients, thus providing an important relaxation pathway in nuclear magnetic resonance (NMR) spectroscopy.[36]

2.2.5. External Electric-Field Interactions. The interactions of a molecule with an externally applied scalar potential $\phi(\mathbf{r})$ are in the Breit–Pauli Hamiltonian in eq 57 represented by the operator

$$H_{\mathrm{ef}} = -\sum_i \phi_i + \sum_K Z_K\phi_K + \frac{\alpha^2}{8}\sum_i(\nabla_i\cdot\mathbf{E}_i) \tag{60}$$

According to Coulomb's law in eq 3, the Darwin correction vanishes in vacuum. Since macroscopically applied fields are fairly uniform on a molecular scale, it is expedient to expand the Hamiltonian in eq 60 in multipoles

$$H_{\mathrm{ef}} = Q_{\mathrm{tot}}\phi_0 - \boldsymbol{\mu}_{\mathrm{tot}}\cdot\mathbf{E}_0 - \frac{1}{2}\,\mathrm{tr}\,\mathbf{Q}_{\mathrm{tot}}\mathbf{V}_0 + \ldots \tag{61}$$

where q_{tot} is the total charge of the molecule while $\boldsymbol{\mu}_{\mathrm{tot}}$ and $\mathbf{Q}_{\mathrm{tot}}$ are the dipole and second moments, respectively

$$\mu_{\mathrm{tot},\,\alpha} = -\sum_i r_{i\alpha} + \sum_K Z_K R_{K\alpha} \tag{62}$$

$$Q_{\mathrm{tot},\,\alpha\beta} = -\sum_i r_{i\alpha}r_{i\beta} + \sum_K Z_K R_{K\alpha}R_{K\beta} \tag{63}$$

Since the field gradient generated by an external source is traceless, the traceless quadrupole moment

$$\Theta = \frac{3}{2}\mathbf{Q} - \frac{1}{2}(\mathrm{tr}\,\mathbf{Q})\mathbf{I}_3 \tag{64}$$

is often used instead of $\mathbf{Q}$. In the multipole expansion of eq 61, the electric potential ϕ_0, the electric field $\mathbf{E}_0$, and the electric field gradient $\mathbf{V}_0$ are evaluated at the origin of the expansion. Higher order multipoles are rarely needed to describe macroscopic fields but are needed for the highly nonuniform fields generated by neighboring molecular systems, in particular, for calculation of weak intermolecular interactions and long-range Coulomb interactions.[37] The external scalar potential ϕ also contributes to the spin–orbit interaction, as discussed in section 2.2.7.

2.2.6. Zeeman Interactions. The Zeeman term in the Breit–Pauli Hamiltonian in eq 57 describes the paramagnetic interactions of the molecule with an externally applied magnetic field $\mathbf{B}$

$$H_z = -\mathbf{B}\cdot\sum_i\left(-\frac{1}{2}\mathbf{l}_{iO} - \mathbf{s}_i + \frac{1}{2}\alpha^2\mathbf{s}_i\nabla_i^2\right) - \mathbf{B}\cdot\sum_K\mathbf{M}_K \tag{65}$$

Since the nuclear moments are on the order of 10^{-3} in atomic units, the nuclear part is much smaller than the electronic part but it is important in NMR spectroscopy, where it determines the position of the (unshielded) resonance lines in the spectra. We also note that, in the Breit–Pauli Hamiltonian in eq 57, there is, apart from the paramagnetic interactions in H_z discussed here, a corresponding set of diamagnetic (quadratic) interactions in H_{dia} discussed later.

There are three distinct contributions to the electronic part of H_z in eq 65, the first of which represents the Zeeman interaction with the magnetic moment generated by the orbital angular momentum of the electrons relative to the gauge origin $\mathbf{l}_{iO} = \mathbf{r}_{iO} \times \mathbf{p}_i$. The second and third electronic contributions to H_z constitute the Zeeman interaction with the spin of the electrons. In addition to a dominant nonrelativistic contribution from eq 38, there is a small relativistic correction from eq 39, which contributes to the g shift of electron paramagnetic resonance (EPR) spectroscopy. Note that because of its dependence on the gauge origin $\mathbf{O}$ the Zeeman operator is not uniquely defined.

The expectation value of an imaginary Hermitian operator Ω vanishes for orbitally nondegenerate states, since their wave function may be chosen real

$$\begin{aligned} \langle\mathrm{real}|\Omega|\mathrm{real}\rangle &= \langle\mathrm{real}|\Omega|\mathrm{real}\rangle^* = \langle\mathrm{real}|\Omega^\dagger|\mathrm{real}\rangle \\ &= -\langle\mathrm{real}|\Omega|\mathrm{real}\rangle \end{aligned} \tag{66}$$

For such states, the expectation value of $\mathbf{L}_O = \Sigma_i\mathbf{l}_{iO}$ therefore vanishes and the orbital angular momentum is said to be quenched. Likewise, the expectation value of any triplet operator such as the spin angular momentum operator $\mathbf{S} = \Sigma_i\mathbf{s}_i$ vanishes for singlet states. Closed-shell molecules therefore do not interact with external magnetic fields to first order, but the second-order diamagnetic interactions never vanish.

2.2.7. Spin–Orbit Interactions. Collecting those terms in the Breit–Pauli Hamiltonian of eq 57 that, to second order in the fine-structure constant, couple the motion of the electrons to particle spins (magnetic moments), we obtain

$$\begin{aligned} H_{\mathrm{so}} = {} & \frac{\alpha^2}{2}\sum_{iK}\frac{Z_K\mathbf{s}_i\cdot\mathbf{l}_{iK}}{r_{iK}^3} - \frac{\alpha^2}{2}\sum_{i\neq j}\frac{\mathbf{s}_i\cdot\mathbf{l}_{ij}}{r_{ij}^3} - \alpha^2\sum_{i\neq j}\frac{\mathbf{s}_j\cdot\mathbf{l}_{ij}}{r_{ij}^3} \\ & + \alpha^2\sum_{iK}\frac{\mathbf{M}_K\cdot\mathbf{l}_{iK}}{r_{iK}^3} + \frac{\alpha^2}{4}\sum_i \mathbf{s}_i\cdot(\mathbf{E}_i\times\mathbf{p}_i - \mathbf{p}_i\times\mathbf{E}_i) \end{aligned} \tag{67}$$

The spin−orbit interaction arises from the coupling of electron spin to the magnetic fields induced by other charges in relative motion. In the Born−Oppenheimer approximation, all particle motion is with respect to the nuclear framework. The first term in eq 67 is the nuclear spin−orbit operator arising from the motion of the electrons relative to the nuclei. It should be emphasized that the angular momentum operator $\mathbf{l}_{iK}$ accordingly represents the relative motion of the electron and nucleus. The second term above is the spin−same-orbit operator arising from the orbital motion of the reference electron with respect to the nuclear frame, whereas the third term is the spin−other-orbit operator, which arises from the relative motion of the other electron with the respect to the nuclear frame.

Because of their triplet nature, the spin−orbit operators do not contribute to the total energy of closed-shell systems to order α^2. On the other hand, they are responsible for the splitting of otherwise degenerate states in open-shell systems, producing, for example, the fine structure of atomic spectra. The spin−orbit operators are also important in providing a mechanism for intersystem crossings and phosphorescence, that is, spin-forbidden radiationless and radiative transitions between molecular electronic energy levels. Finally, in magnetic-resonance spectroscopies, the spin−orbit operators contribute to second order to *g* values and hyperfine coupling constants and to zero-field splittings in EPR and often provide the leading order relativistic corrections to heavy-atom effects on the shielding constants of light nuclei.

The fourth operator in eq 67, which arises from substitution of $\mathbf{A}_{\mathrm{nuc}}$ of eq 48 into the $\sum_i\mathbf{A}_i\cdot\mathbf{p}_i$ part of eq 38, provides a mechanism for coupling the nuclear magnetic moments $\mathbf{M}_K$ to the orbital motion of the electrons. It is known as the orbital hyperfine operator or the paramagnetic spin−orbit operator; it is similar to the spin−other-orbit operator, which likewise couples the spin and orbital motion of different particles. Like all hyperfine operators, the orbital hyperfine interaction is weak (10^{-8} au). It contributes to nuclear shielding constants and indirect nuclear spin−spin coupling constants in NMR and in second order to hyperfine coupling constants in EPR. The last term in eq 67 depends on the external electric field and is unimportant for free molecules.

2.2.8. Spin−Spin Interactions. Collecting all terms in the Breit−Pauli operator of eq 57 that involve interactions between the spins (magnetic moments) of two particles, we obtain

$$\begin{aligned} H_{\mathrm{ss}} = {} & \frac{\alpha^2}{2}\sum_{i\neq j}\left[\frac{r_{ij}^2\mathbf{s}_i\cdot\mathbf{s}_j - 3\mathbf{s}_i\cdot\mathbf{r}_{ij}\mathbf{r}_{ij}\cdot\mathbf{s}_j}{r_{ij}^5} - \frac{8\pi}{3}\delta(\mathbf{r}_{ij})\mathbf{s}_i\cdot\mathbf{s}_j\right] \\ & -\alpha^2\sum_{iK}\left[\frac{r_{iK}^2\mathbf{s}_i\cdot\mathbf{M}_K - 3\mathbf{s}_i\cdot\mathbf{r}_{iK}\mathbf{r}_{iK}\cdot\mathbf{M}_K}{r_{iK}^5} - \frac{8\pi}{3}\delta(\mathbf{r}_{iK})\mathbf{s}_i\cdot\mathbf{M}_K\right] \\ & +\frac{\alpha^2}{2}\sum_{K\neq L}\frac{R_{KL}^2(\mathbf{M}_K\cdot\mathbf{M}_L) - 3(\mathbf{M}_K\cdot\mathbf{R}_{KL})(\mathbf{R}_{KL}\cdot\mathbf{M}_L)}{R_{KL}^5} \end{aligned} \tag{68}$$

consisting of classical dipolar and Fermi-contact interaction terms. Together with the Darwin operator of eq 59, the two-electron Fermi-contact operator in the first line of eq 68 provides the largest two-electron relativistic correction to the energy of light systems. The two-electron spin−spin operator also contributes to the zero-field splitting observable in EPR spectroscopy of triplet species (biradicals)[38,39] discussed in section 5.3.2. Whereas the two-electron spin−spin interaction dominates the zero-field splittings in organic biradicals, the spin−orbit interaction dominates the splittings in systems containing heavier elements, eq 612.

The hyperfine interaction operator in the second line of eq 68 couples the electronic and nuclear spins and arises from substitution of $\mathbf{B}_{\mathrm{nuc}}$ of eq 50 into $\sum_i\mathbf{B}_i\cdot\mathbf{s}_i$ of eq 38. Together with the orbital hyperfine operator in eq 67 it contributes to the indirect coupling of nuclear spins observed in NMR for liquids, as discussed in section 5.2. The isotropic Fermi-contact term is particularly important, coupling the rapidly tumbling nuclear moments in high-resolution NMR. Finally, the dipolar nuclear spin−spin operator in the last line of eq 68 is responsible for important direct coupling of nuclear spins observed in NMR in solids but makes no contribution to the isotropic coupling in liquids. We omitted the nuclear−nuclear contact term, which does not contribute for stationary nuclei.

2.2.9. Orbit−Orbit Interactions. The two-electron orbit−orbit operator in eq 57 arises from eq 44 and represents a relativistic correction to the two-electron Coulomb interaction due to the relative motion of the electrons

$$H_{\mathrm{oo}} = -\frac{\alpha^2}{4}\sum_{i\neq j}\frac{\mathbf{p}_i\cdot r_{ij}^2\mathbf{p}_j + \mathbf{p}_i\cdot\mathbf{r}_{ij}\mathbf{r}_{ij}\cdot\mathbf{p}_j}{r_{ij}^3}. \tag{69}$$

The orbit−orbit correction is smaller than the two-electron Darwin and spin−spin corrections but becomes more important in heavier atoms.[34] Moreover, the orbit−orbit interaction does not split levels and does not cause transitions. It is therefore usually of less interest than the two-electron spin−orbit and spin−spin interactions.

2.2.10. Diamagnetic Interactions. The diamagnetic interactions in the Breit−Pauli Hamiltonian of eq 57 are terms of order α^4 or smaller (keeping in mind that the external magnetic induction is typically of order α^2), arising from expansion of the vector potential in the kinetic-momentum operators of eq 37. Although the Breit−Pauli Hamiltonian as such is correct only to order α^2, the small diamagnetic interactions are included in our discussion since they are important for many spectroscopic parameters

$$H_{\mathrm{dia}} = \left\{\begin{array}{lll} H_{\mathrm{BB}} & \leftarrow & \text{magnetizability} \\ +H_{\mathrm{BM}} & \leftarrow & \text{nuclear shielding (NMR)} \\ +H_{\mathrm{MM}} & \leftarrow & \text{indirect nuclear spin−spin coupling (NMR)} \\ +H_{\mathrm{MVBs}} & \leftarrow & \text{electronic } g \text{ factor shift (EPR)} \\ +H_{\mathrm{Bs}} & \leftarrow & \text{electronic } g \text{ factor shift (EPR)} \\ +H_{\mathrm{Ms}} & \leftarrow & \text{hyperfine coupling (EPR)} \end{array}\right. \tag{70}$$

The first three operators in H_{dia} arise from expansion of $A^2/2$ with the vector potential given by eq 46

$$H_{\mathrm{BB}} = \frac{1}{8}\sum_i(\mathbf{B}\times\mathbf{r}_{iO})^2 \tag{71}$$

$$H_{\mathrm{BM}} = \frac{\alpha^2}{2}\sum_{iK}\frac{(\mathbf{B}\times\mathbf{r}_{iO})\cdot(\mathbf{M}_K\times\mathbf{r}_{iK})}{r_{iK}^3} \tag{72}$$

$$H_{\mathrm{MM}} = \frac{\alpha^4}{2}\sum_{iKL}\frac{(\mathbf{M}_K\times\mathbf{r}_{iK})\cdot(\mathbf{M}_L\times\mathbf{r}_{iL})}{r_{iK}^3 r_{iL}^3} \tag{73}$$

They contribute diamagnetically to the magnetizability tensor, to the nuclear shielding tensor, and to the indirect nuclear spin−spin tensor, respectively. The fourth operator in H_{dia} is the spin-dependent part of the mass−velocity operator in eq 39

$$H_{\mathrm{MVBs}} = -\frac{\alpha^2}{4}\sum_i(\pi_i^2\mathbf{B}_i\cdot\mathbf{s}_i + \mathbf{B}_i\cdot\mathbf{s}_i\pi_i^2) \tag{74}$$

Finally, the last two operators in H_{dia} arise from expansion of eq 46 in the spin−orbit and spin−other-orbit operators in eqs 41 and 42 with a simultaneous substitution of the nuclear electric field in eq 49

$$\begin{aligned} H_{\mathrm{Bs}} = {} & \frac{\alpha^2}{4}\sum_{iK}\frac{Z_K(\mathbf{B}\times\mathbf{r}_{iO})\cdot(\mathbf{s}_i\times\mathbf{r}_{iK})}{r_{iK}^3} \\ & -\frac{\alpha^2}{4}\sum_{i\neq j}\frac{(\mathbf{B}\times\mathbf{r}_{iO})\cdot(\mathbf{s}_i + 2\mathbf{s}_j)\times\mathbf{r}_{ij}}{r_{ij}^3} \end{aligned} \tag{75}$$

$$\begin{aligned} H_{\mathrm{Ms}} = {} & \frac{\alpha^4}{2}\sum_{i,\,KL}\frac{Z_K(\mathbf{M}_L\times\mathbf{r}_{iL})\cdot(\mathbf{s}_i\times\mathbf{r}_{iK})}{r_{iK}^3 r_{iL}^3} \\ & -\frac{\alpha^4}{2}\sum_{K,\,i\neq j}\frac{(\mathbf{M}_K\times\mathbf{r}_{iK})\cdot(\mathbf{s}_i + 2\mathbf{s}_j)\times\mathbf{r}_{ij}}{r_{iK}^3 r_{ij}^3} \end{aligned} \tag{76}$$

These operators couple the spin of the electron to the external magnetic field and the nuclear magnetic moments, respectively, contributing in second order to the g shifts and nuclear hyperfine coupling constants in EPR spectroscopy[40] as well as often being the leading order relativistic correction in heavy-element shieldings.[41−43]

2.3. Second Quantization

We introduce in this subsection second quantization with emphasis on the representation of the molecular electronic Breit−Pauli operator in this formalism. For a more extensive treatment of second quantization in quantum chemistry, see the monograph by Helgaker, Olsen, and Jørgensen.[30]

2.3.1. Second Quantization in the Spin−Orbital Basis.

In second quantization, the elementary operators are the creation and annihilation operators $a_P^\dagger$ and a_P, respectively. The annihilation operator a_P annihilates an electron in spin orbital ψ_P, whereas the creation operator $a_P^\dagger$ creates an electron in the same spin orbital. In a basis of orthonormal spin orbitals, these operators satisfy the anticommutation relations

$$[a_P^\dagger, a_Q^\dagger]_+ = 0 \tag{77}$$

$$[a_P, a_Q]_+ = 0 \tag{78}$$

$$[a_P^\dagger, a_Q]_+ = \delta_{PQ} \tag{79}$$

From these simple relations all other algebraic properties of the second-quantization formalism follow. In a nonorthonormal basis of spin orbitals, the anticommutation relations would be the same except for the last relation, which becomes

$$[a_P^\dagger, a_Q]_+ = \langle\psi_Q|\psi_P\rangle \tag{80}$$

where $\langle\psi_Q|\psi_P\rangle$ is the overlap between the two spin orbitals.

In the Fock space generated by an orthonormal basis of M spin orbitals ψ_P, the basis vectors are the occupation-number vectors $|\mathbf{k}\rangle$, where k_P is the occupation number of spin orbital P in $|\mathbf{k}\rangle$. The simplest such state is the vacuum state $|\mathrm{vac}\rangle$, which contains no electrons, that is, all occupation numbers k_P are zero. Any occupation-number vector can be generated from the vacuum state by application of a string of creation operators to the vacuum state

$$|\mathbf{k}\rangle = [\prod_{k=1}^{M}(a_P^\dagger)^{k_P}]|\mathrm{vac}\rangle \tag{81}$$

whereas application of an annihilation operator to the vacuum state yields

$$a_P|\mathrm{vac}\rangle = 0 \tag{82}$$

A general N-electron state is represented as a linear combination of such occupation-number vectors, each containing N electrons. By applying strings of creation and annihilation operators to a given N-electron state, we generate new states, possibly containing more or fewer particles, the anticommutation relations in eqs 77−79 ensuring that all such manipulations are consistent with the Pauli principle.

An important class of operators is the number-conserving operators, containing the same number of creation and annihilation operators, in particular, the single- and double-excitation operators $a_P^\dagger a_Q$ and $a_P^\dagger a_Q^\dagger a_R a_S$, in terms of which we may, for example, construct the nonrelativistic field-free Hamiltonian operator

$$\hat{H} = \sum_{PQ} h_{PQ}a_P^\dagger a_Q + \frac{1}{2}\sum_{PQRS} g_{PQRS}a_P^\dagger a_R^\dagger a_S a_Q + h_{\mathrm{nuc}} \tag{83}$$

where

$$h_{PQ} = \int \psi_P^*(\mathbf{x})\left(-\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{r_I}\right)\psi_Q(\mathbf{x})\mathrm{d}\mathbf{x} \tag{84}$$

$$g_{PQRS} = \iint \frac{\psi_P^*(\mathbf{x}_1)\psi_R^*(\mathbf{x}_2)\psi_Q(\mathbf{x}_1)\psi_S(\mathbf{x}_2)}{r_{12}}\mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2 \tag{85}$$

$$h_{\mathrm{nuc}} = \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{R_{IJ}} \tag{86}$$

The form of this second-quantization operator may be interpreted in the following way: When applied to an electronic state, the Hamiltonian produces a linear combination of the original state with states generated by single- and double-electron excitations from this state; with each such excitation there is an associated probability amplitude h_{PQ} and g_{PQRS} calculated from spin orbitals according to eqs 84 and 85, respectively. The expectation value with respect to the state $|0\rangle$ is given by

$$\langle 0|H|0\rangle = \sum_{PQ} D_{PQ}h_{PQ} + \frac{1}{2}\sum_{PQRS}\mathrm{d}_{PQRS}g_{PQRS} + h_{\mathrm{nuc}} \tag{87}$$

where the one- and two-electron density-matrix elements

$$D_{PQ} = \langle 0|a_P^\dagger a_Q|0\rangle \tag{88}$$

$$\mathrm{d}_{PQRS} = \langle 0|a_P^\dagger a_R^\dagger a_S a_Q|0\rangle \tag{89}$$

are expectation values of the excitation operators.

2.3.2. Second Quantization in the Orbital Basis. In eq 87, the energy is calculated in a basis of spin orbitals. Often it is more convenient to work in a basis of orthonormal orbitals, typically molecular orbitals (MOs) expanded in AOs. A general spin orbital may be written as a linear combination of two orbitals multiplied by spin functions

$$\psi_P(\mathbf{r}, m_s) = \phi_P^{\alpha}(\mathbf{r})\alpha(m_s) + \phi_P^{\beta}(\mathbf{r})\beta(m_s) \tag{90}$$

where the spin functions α and β are eigenfunctions of the total- and projected-spin angular-momentum operators

$$S^2\alpha(m_s) = \frac{3}{4}\alpha(m_s),\ \ S_z\alpha(m_s) = \frac{1}{2}\alpha(m_s) \tag{91}$$

$$S^2\beta(m_s) = \frac{3}{4}\beta(m_s),\ \ S_z\beta(m_s) = -\frac{1}{2}\beta(m_s) \tag{92}$$

and where $m_s = \pm 1/2$ is a discrete spin coordinate such that $\alpha(1/2) = \beta(-1/2) = 1$ and $\alpha(-1/2) = \beta(1/2) = 0$.[30] In nonrelativistic theory, it is common to use spin orbitals in the more restricted form

$$\psi_{p\sigma}(\mathbf{r}, m_s) = \phi_p(\mathbf{r})\sigma(m_s) \tag{93}$$

so that a given spin orbital consists of an orbital multiplied by a spin function. Spin orbitals with different spins are orthogonal.

In the orbital basis the elementary creation and annihilation operators are $a_{p\sigma}^{\dagger}$ and $a_{p\sigma}$, from which all other operators can be constructed. It is then convenient to classify all second quantization operators according to their spin properties. A spin-tensor operator of integral or half-integral rank S is a set of $2S + 1$ operators $T^{S,M}$, where M runs from $-S$ to S in unit increments and which fulfill the relations

$$[S_{\pm}, T^{S,\ M}] = \sqrt{S(S+1) - M(M \pm 1)}T^{S,\ M \pm 1} \tag{94}$$

$$[S_z, T^{S,\ M}] = MT^{S,\ M} \tag{95}$$

where we assume that $T^{S,S+1} = T^{S,-S-1} = 0$. A tensor operator working on the vacuum state generates a set of spin eigenfunctions with total and projected spins S and M (provided it does not annihilate the vacuum state). Two examples of doublet spin-tensor operators $\{T^{1/2,1/2},T^{1/2,-1/2}\}$ are the creation operators $\{a_{p\alpha}^{\dagger},a_{p\beta}^{\dagger}\}$ and the annihilation operators $\{-a_{p\beta},a_{p\alpha}\}$. Important singlet and triplet spin-tensor operators $\{T^{0,0}\}$ and $\{T^{1,1},T^{1,0},T^{1,-1}\}$ are the singlet single-excitation operators

$$S_{pq}^{0,\ 0} = \frac{1}{\sqrt{2}}(a_{p\alpha}^{\dagger}a_{q\alpha} + a_{p\beta}^{\dagger}a_{q\beta}) \tag{96}$$

and the triplet single-excitation operators

$$T_{pq}^{1,\ 1} = -a_{p\alpha}^{\dagger}a_{q\beta} \tag{97}$$

$$T_{pq}^{1,\ 0} = \frac{1}{\sqrt{2}}(a_{p\alpha}^{\dagger}a_{q\alpha} - a_{p\beta}^{\dagger}a_{q\beta}) \tag{98}$$

$$T_{pq}^{1,-1} = a_{p\beta}^{\dagger}a_{q\alpha} \tag{99}$$

From the triplet spin-tensor operators we may, for example, construct the spin-shift and spin-projection operators $S_+ = -\Sigma_p T_{pp}^{1,1}$, $S_- = \Sigma_p T_{pp}^{1,-1}$, and $S_z = (1/2)^{1/2}\Sigma_p T_{pp}^{1,0}$. For the representation of the electronic Hamiltonian, we shall use the singlet excitation operators in the form

$$E_{pq} = \sqrt{2}S_{pq}^{0,\ 0} = a_{p\alpha}^{\dagger}a_{q\alpha} + a_{p\beta}^{\dagger}a_{q\beta} \tag{100}$$

and also the triplet operators in the Cartesian form

$$\begin{aligned} T_{pq} = \begin{pmatrix} T_{pq}^{x} \\ T_{pq}^{y} \\ T_{pq}^{z} \end{pmatrix} &= \begin{pmatrix} \frac{1}{2}(a_{p\alpha}^{\dagger}a_{q\beta} + a_{p\beta}^{\dagger}a_{q\alpha}) \\ \frac{1}{2\mathrm{i}}(a_{p\alpha}^{\dagger}a_{q\beta} - a_{p\beta}^{\dagger}a_{q\alpha}) \\ \frac{1}{2}(a_{p\alpha}^{\dagger}a_{q\alpha} - a_{p\beta}^{\dagger}a_{q\beta}) \end{pmatrix} \\ &= \begin{pmatrix} -\frac{1}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2\mathrm{i}} & -\frac{1}{2\mathrm{i}} & 0 \\ 0 & 0 & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} T_{pq}^{1,\ 1} \\ T_{pq}^{1,\ -1} \\ T_{pq}^{1,\ 0} \end{pmatrix} \end{aligned} \tag{101}$$

In terms of these excitation operators the second-quantization representation of the Breit–Pauli Hamiltonian of eqs 38–44 becomes

$$\begin{aligned} H^{\mathrm{NR}} &= \sum_{pq} \left\langle p \middle| \frac{1}{2}\pi^2 - \phi \middle| q \right\rangle E_{pq} + \sum_{pq} \mathbf{B}\cdot\mathbf{T}_{pq} \\ &\quad + \frac{1}{2}\sum_{pqrs} \langle pr|r_{12}^{-1}|qs\rangle(E_{pq}E_{rs} - \delta_{qr}E_{ps}) \end{aligned} \tag{102}$$

$$H^{\mathrm{MV}} = -\frac{\alpha^2}{8}\sum_{pq} \langle p|\pi^4 + B^2|q\rangle E_{pq} - \frac{\alpha^2}{2}\sum_{pq} \langle p|\pi^2|q\rangle \mathbf{B}\cdot\mathbf{T}_{pq} \tag{103}$$

$$\begin{aligned} H^{\mathrm{DW}} &= \frac{\alpha^2}{8}\sum_{pq} \langle p|(\nabla\cdot\mathbf{E})|q\rangle E_{pq} \\ &\quad - \frac{\alpha^2\pi}{2}\sum_{pqrs} \langle pr|\delta(r_{12})|qs\rangle(E_{pq}E_{rs} - \delta_{qr}E_{ps}) \end{aligned} \tag{104}$$

$$\begin{aligned} H^{\mathrm{SsO}} &= \frac{\alpha^2}{4}\sum_{pq} \langle p|\mathbf{E}\times\boldsymbol{\pi} - \boldsymbol{\pi}\times\mathbf{E}|q\rangle\cdot\mathbf{T}_{pq} \\ &\quad + \frac{\alpha^2}{4}\sum_{pqrs} \langle pr|(\nabla_1 r_{12}^{-1})\times\boldsymbol{\pi}_1|qs\rangle\cdot(\mathbf{T}_{pq}E_{rs} - \delta_{qr}\mathbf{T}_{ps}) \end{aligned} \tag{105}$$

$$H^{\mathrm{SoO}} = -\frac{\alpha^2}{2}\sum_{pqrs} \langle pr|(\nabla_1 r_{12}^{-1})\times\boldsymbol{\pi}_2|qs\rangle\cdot(\mathbf{T}_{pq}E_{rs} - \delta_{qr}\mathbf{T}_{ps}) \tag{106}$$

$$H^{\mathrm{SS}} = \frac{\alpha^2}{8}\sum_{pqrs}\sum_{\mu\nu} \langle pr|[(\mathbf{I}_3\nabla_1^2 - \nabla_1\nabla_1^{\mathrm{T}})r_{12}^{-1}]_{\mu\nu}|qs\rangle(4T_{pq}^{\mu}T_{rs}^{\nu} - \delta_{\mu\nu}\delta_{qr}E_{ps}) \tag{107}$$

$$H^{\mathrm{OO}} = -\frac{\alpha^2}{4}\sum_{pqrs}\langle pr|\boldsymbol{\pi}_1^{\mathrm{T}}[(\mathbf{I}_3\nabla_1^2 - \nabla_1\nabla_1^{\mathrm{T}})r_{12}]\boldsymbol{\pi}_2|qs\rangle(E_{pq}E_{rs} - \delta_{qr}E_{ps}) \tag{108}$$

For a discussion of these operators and their integral evaluation, see Coriani et al.[34]

2.4. Perturbation-Dependent Basis Sets

In second quantization, the electronic Hamiltonian is expressed in terms of one- and two-electron integrals over MOs expanded in AOs, see eqs 102−108. In calculations of molecular properties, the use of this Hamiltonian presents a complication not encountered in energy calculations, namely, that the AOs employed often depend explicitly on the external parameters representing the perturbations. In this section we discuss the second-quantization Hamiltonian with emphasis on the consequences of such perturbation-dependent basis sets.

2.4.1. Perturbation-Dependent Atomic Orbitals. In calculations of molecular properties the AOs often depend explicitly on the external parameters that describe the system. Here, the AOs are taken to be solid-harmonic Gaussian functions with angular-momentum quantum numbers l and m and exponent a fixed to an atomic position $\mathbf{K}$ and equipped with a complex phase factor that depends on the external magnetic field $\mathbf{B}$ and the gauge origin $\mathbf{O}$[44] in the manner

$$\chi_{lm}(\mathbf{r};\, a,\, \mathbf{K},\, \mathbf{B},\, \mathbf{O}) = \mathrm{e}^{\mathrm{i}(1/2)\mathbf{B}\times\mathbf{O}_K\cdot\mathbf{r}}S_{lm}(\mathbf{r}_K)\mathrm{e}^{-ar_K^2} \tag{109}$$

where $\mathbf{O}_K = \mathbf{O} - \mathbf{K}$, $\mathbf{r}_K = \mathbf{r} - \mathbf{K}$, and $S_{lm}(\mathbf{r}_K)$ is a solid-harmonic function. By fixing the AOs to the nuclei we obtain a balanced treatment of the electronic system at different molecular geometries, introducing into the AOs the observed strong coupling of the atomic charge distributions to the nuclei. By including a field-dependent phase factor in the AOs we ensure that our results become independent of the gauge origin $\mathbf{O}$ and furthermore improve basis-set convergence by introducing into the AOs the correct first-order response of the electrons to an applied external magnetic field, as discussed in section 2.4.5. We note here that AOs with an explicit dependence on the external electric field have also been proposed[45,46] but are much less widespread, as the added computational complexity does not compensate for the rather moderate improvements in basis-set convergence observed.

Use of perturbation-dependent AOs is essential for reducing the AO basis sets to a manageable size while maintaining high accuracy in the calculations. However, their use also introduces certain complications, in particular, in the evaluation of molecular integrals. Moreover, since the AOs change with the external parameters ε, we are in fact at each value of ε faced with a different second-quantization representation $H(\varepsilon)$ of the Hamiltonian. To calculate molecular properties with such basis sets we must establish a connection between Hamiltonians at different values of ε.[47]

2.4.2. Orbital Connections. Consider the second-quantization representation of an electronic Hamiltonian in a basis of perturbation-dependent AOs $\chi_\mu(\mathbf{r};\varepsilon)$, where ε represents the external parameters (e.g., the molecular geometry or the magnetic field strength) upon which the AOs in eq 109 depend. For the unperturbed system, for which we conventionally set $\varepsilon = 0$, we calculate a set of orthonormal MOs

$$\phi_p(\mathbf{r};0) = \sum_\mu C_{p\mu}^{(0)}\chi_\mu(\mathbf{r};0) \tag{110}$$

from which the Hamiltonian operator is constructed in the usual manner

$$H(0) = \sum_{pq} h_{pq}(0)E_{pq}(0) + \frac{1}{2}\sum_{pqrs} g_{pqrs}(0)[E_{pq}(0)E_{rs}(0) - \delta_{rs}E_{ps}(0)] \tag{111}$$

The one- and two-electron integrals are obtained by integration over the orthonormal MOs in eq 110

$$h_{pq}(0) = \langle\phi_p(0)|h_1(0)|\phi_q(0)\rangle \tag{112}$$

$$g_{pqrs}(0) = \langle\phi_p(0)\phi_r(0)|r_{12}^{-1}|\phi_q(0)\phi_s(0)\rangle \tag{113}$$

whereas the excitation operators

$$E_{pq}(0) = a_{p\alpha}^\dagger(0)a_{q\alpha}(0) + a_{p\beta}^\dagger(0)a_{q\beta}(0) \tag{114}$$

are constructed in the usual manner from the creation and annihilation operators that obey the anticommutation relations in eqs 77−79.

Let us now consider a perturbed system with $\varepsilon \neq 0$. For this system we would like to set up a second-quantization representation that connects smoothly with the representation of the unperturbed system.[48,49] We define a set of nonorthogonal unmodified MOs (UMOs) by retaining the MO coefficients of the unperturbed system

$$\phi_p(\mathbf{r};\varepsilon) = \sum_\mu C_{p\mu}^{(0)}\chi_\mu(\mathbf{r};\varepsilon) \tag{115}$$

This UMO basis connects smoothly with the unperturbed basis of eq 110 at $\varepsilon = 0$ but is nonorthonormal at $\varepsilon \neq 0$ since the overlap integrals of the AOs depend on the perturbation

$$S_{pq}(\varepsilon) = \langle\phi_p(\varepsilon)|\phi_q(\varepsilon)\rangle = \sum_{\mu\nu} C_{p\mu}^{(0)}C_{q\nu}^{(0)}\langle\chi_\mu(\varepsilon)|\chi_\nu(\varepsilon)\rangle \neq \delta_{pq} \tag{116}$$

We therefore cannot represent our Hamiltonian in this basis at $\varepsilon \neq 0$ without affecting the algebra of the creation and annihilation operators, having to replace the simple anticommutation relation in eq 79 with the more complicated relation in eq 80. To avoid this complication we construct a set of orthonormalized MOs (OMOs) by an orthonormalization of the UMOs

$$\tilde{\phi}_p(\varepsilon) = \sum_q \phi_q(\varepsilon)T_{qp}(\varepsilon) \tag{117}$$

where $\mathbf{T}(\varepsilon)$ is the connection matrix,[47−49] taken to satisfy the relation

$$\mathbf{T}^\dagger(\varepsilon)\mathbf{S}(\varepsilon)\mathbf{T}(\varepsilon) = \mathbf{I} \tag{118}$$

The connection matrix can be chosen in infinitely many ways, each of which establishes a particular orbital connection between orthonormalized MOs at different ε. For example, by decomposing $\mathbf{T}$ into its real and imaginary parts $\mathbf{T} = \mathbf{T}^{\mathrm{R}} + \mathrm{i}\mathbf{T}^{\mathrm{I}}$ with $T_{pq}^{\mathrm{R}} = 0$ for $p > q$ and $T_{pq}^{\mathrm{I}} = 0$ for $p \geq q$ we arrive at the Gram−Schmidt connection.[47,50] A physically better motivated connection is obtained by requiring the OMOs $\tilde{\phi}_p(\mathbf{r};\varepsilon)$ to resemble as closely as possible some target functions $f_p(\mathbf{r};\varepsilon)$. Introducing the overlap matrix between the UMOs and the target functions

$$W_{pq}(\varepsilon) = \langle f_p(\varepsilon)|\phi_q(\varepsilon)\rangle \tag{119}$$

it can be shown that the connection matrix is given by

$$\mathbf{T}(\varepsilon) = \mathbf{W}^{-1}(\varepsilon)[\mathbf{W}(\varepsilon)\mathbf{S}^{-1}(\varepsilon)\mathbf{W}^{\dagger}(\varepsilon)]^{1/2} \tag{120}$$

Requiring the OMOs to resemble the perturbed UMOs by setting $f_p(\mathbf{r};\varepsilon) = \phi_p(\mathbf{r};\varepsilon)$,[48] we obtain the symmetric orthonormalization[51]

$$\mathbf{T}(\varepsilon) = \mathbf{S}^{-1/2}(\varepsilon) \tag{121}$$

Alternatively, we may require the OMOs to resemble the unperturbed UMOs by setting $f_p(\mathbf{r};\varepsilon) = \phi_p(\mathbf{r};0)$, yielding instead the natural connection.[47] The natural connection ensures that the OMOs in terms of which the Hamiltonian is constructed change as little as possible with ε, improving numerical stability.[52]

In the OMO basis of eq 117 we may now construct a Hamiltonian operator that is defined for all ε in the usual manner

$$H(\varepsilon) = \sum_{\widetilde{pq}} \tilde{h}_{\tilde{p}\tilde{q}}(\varepsilon)E_{\tilde{p}\tilde{q}}(\varepsilon) + \frac{1}{2}\sum_{\widetilde{pqrs}} \tilde{g}_{\tilde{p}\tilde{q}\tilde{r}\tilde{s}}(\varepsilon)[E_{\tilde{p}\tilde{q}}(\varepsilon)E_{\tilde{r}\tilde{s}}(\varepsilon) - \delta_{\tilde{r}\tilde{s}}E_{\tilde{p}\tilde{s}}(\varepsilon)] \tag{122}$$

where the OMO integrals are denoted by the tilde and may be expanded in UMO integrals

$$\begin{aligned}\tilde{h}_{\tilde{p}\tilde{q}}(\varepsilon) &= \sum_{pq} h_{pq}(\varepsilon)T_{\tilde{p}p}(\varepsilon)T^{*}_{\tilde{q}q}(\varepsilon) \\ &= \sum_{pq} \langle\phi_p(\varepsilon)|h_1(\varepsilon)|\phi_q(\varepsilon)\rangle T_{\tilde{p}p}(\varepsilon)T^{*}_{\tilde{q}q}(\varepsilon)\end{aligned} \tag{123}$$

$$\begin{aligned}\tilde{g}_{\tilde{p}\tilde{q}\tilde{r}\tilde{s}}(\varepsilon) &= \sum_{pqrs} g_{pqrs}(\varepsilon)T_{\tilde{p}p}(\varepsilon)T^{*}_{\tilde{q}q}(\varepsilon)T_{\tilde{r}r}(\varepsilon)T^{*}_{\tilde{s}s}(\varepsilon) \\ &= \sum_{pqrs} \langle\phi_p(\varepsilon)\phi_r(\varepsilon)|r_{12}^{-1}|\phi_q(\varepsilon)\phi_s(\varepsilon)\rangle T_{\tilde{p}p}(\varepsilon)T^{*}_{\tilde{q}q}(\varepsilon)T_{\tilde{r}r}(\varepsilon)T^{*}_{\tilde{s}s}(\varepsilon)\end{aligned} \tag{124}$$

The excitation operators are constructed in the usual manner

$$E_{\tilde{p}\tilde{q}}(\varepsilon) = a^{\dagger}_{\tilde{p}\alpha}(\varepsilon)a_{\tilde{q}\alpha}(\varepsilon) + a^{\dagger}_{\tilde{p}\beta}(\varepsilon)a_{\tilde{q}\beta}(\varepsilon) \tag{125}$$

from the creation and annihilation operators that obey the anticommutation relations in eqs 77−79. Above, we restricted ourselves to singlet perturbations; the corresponding expressions for triplet perturbations are obtained by a simple generalization of the scheme for singlet perturbations.

2.4.3. Perturbation Dependence of the Creation and Annihilation Operators.

The dependence of the creation and annihilation operators $a^{\dagger}_P(\varepsilon)$ and $a_P(\varepsilon)$ on ε in eq 125 arises from the dependence of the OMOs in eq 117 on ε. However, for the purpose of calculating derivatives of electronic energies we may treat these operators as being independent of ε because the creation and annihilation operators always appear in transition expectation values such as

$$\langle\mathbf{K}|a^{\dagger}_P a_Q|\mathbf{L}\rangle = \langle\mathrm{vac}|a_{K_1}a_{K_2}...a_{K_N}a^{\dagger}_P a_Q a^{\dagger}_{L_N}...a^{\dagger}_{L_2}a^{\dagger}_{L_1}|\mathrm{vac}\rangle \tag{126}$$

which, by means of the anticommutation relations in eqs 77−79, may be reduced to sums of products of Kronecker deltas. Since these are independent of ε we may ignore the perturbation dependence of the creation and annihilation operators altogether

$$H(\varepsilon) = \sum_{\widetilde{pq}} \tilde{h}_{\tilde{p}\tilde{q}}(\varepsilon)E_{\tilde{p}\tilde{q}} + \frac{1}{2}\sum_{\widetilde{pqrs}} \tilde{g}_{\tilde{p}\tilde{q}\tilde{r}\tilde{s}}(\varepsilon)(E_{\tilde{p}\tilde{q}}E_{\tilde{r}\tilde{s}} - \delta_{\tilde{r}\tilde{s}}E_{\tilde{p}\tilde{s}}) \tag{127}$$

If instead the Hamiltonian had been constructed from nonorthonormal spin orbitals, the vacuum expectation values would reduce to sums of products of perturbation-dependent overlap integrals $S_{pq}(\varepsilon)$, making it necessary to account for the perturbation dependence of the creation and annihilation operators in calculation of energies and other properties of the system.

The above arguments are no longer valid when we consider, for example, nonadiabatic coupling matrix elements,[53] the intensities of electronic circular dichroism (ECD),[54] and vibrational circular dichroism (VCD).[55,56] We are then interested in calculating elements of the form $\langle\mathbf{K}|\mathrm{d}/\mathrm{d}\varepsilon|\mathbf{L}\rangle$, where $\langle\mathbf{K}|$ and $|\mathbf{L}\rangle$ are different electronic states. The creation and annihilation operators in the bra and ket states are no longer the same, and transition densities cannot be reduced to simple Kronecker deltas. In such calculations the perturbation dependence of the excitation operators cannot be neglected. In these cases, the natural connection provides a particularly attractive approach for calculating the relevant matrix elements.[47,54,56]

2.4.4. One-Index Transformations.

For calculation of molecular properties, we need to expand the OMO integrals in eqs 123 and 124 in orders of the perturbation. To express these expansions in a compact form we introduce the integrals (restricting ourselves to the one-electron case and omitting the argument ε for ease of presentation)

$$h_{pq}(t) = \sum_{rs} h_{rs}[\exp(t\ln\mathbf{T})]_{pr}[\exp(t\ln\mathbf{T}^{*})]_{qs} \tag{128}$$

which include the UMO integrals $(t = 0)$ and the OMO integrals $(t = 1)$ as special cases. Expanding around $t = 0$ and setting $t = 1$ we obtain an expansion of the OMO integrals in the UMO integrals

$$\tilde{\mathbf{h}} = \mathbf{h} + \{\ln\mathbf{T}, \mathbf{h}\} + \frac{1}{2}\{\ln\mathbf{T}, \ln\mathbf{T}, \mathbf{h}\} + ... \tag{129}$$

where we introduced a brace notation for one-index transformations

$$\{\mathbf{M}, \mathbf{h}\}_{pq} = \sum_{o}(M_{po}h_{oq} + M^{*}_{qo}h_{po}) \tag{130}$$

with the following notation for symmetrized multiple one-index transformations

$$\{\mathbf{M}_1, \mathbf{M}_2, \mathbf{h}\} = \frac{1}{2}\{\mathbf{M}_1, \{\mathbf{M}_2, \mathbf{h}\}\} + \frac{1}{2}\{\mathbf{M}_2, \{\mathbf{M}_1, \mathbf{h}\}\} \tag{131}$$

An order-by-order expansion in the perturbation now yields to second order[48,57−59]

$$\tilde{\mathbf{h}}(\varepsilon) = \mathbf{h}^{(0)} + \mathbf{h}^{(1)}\varepsilon + \frac{1}{2}\mathbf{h}^{(2)}\varepsilon^2 + ... \tag{132}$$

with the expansion coefficients

$$\tilde{\mathbf{h}}^{(0)} = \mathbf{h}^{(0)} \tag{133}$$

$$\tilde{\mathbf{h}}^{(1)} = \mathbf{h}^{(1)} + \left\{\mathbf{T}^{(1)}, \mathbf{h}^{(0)}\right\} \tag{134}$$

$$\tilde{\mathbf{h}}^{(2)} = \mathbf{h}^{(2)} + \frac{1}{2}\left\{\mathbf{T}^{(2)} - \mathbf{T}^{(1)}\mathbf{T}^{(1)}, \mathbf{h}^{(0)}\right\} + \left\{\mathbf{T}^{(1)}, \mathbf{h}^{(1)}\right\} + \left\{\mathbf{T}^{(1)}, \mathbf{T}^{(1)}, \mathbf{h}^{(0)}\right\} \tag{135}$$

where we used the expansion

$$\ln \mathbf{T} = (\mathbf{T} - \mathbf{I}) - \frac{1}{2}(\mathbf{T} - \mathbf{I})^2 + \frac{1}{3}(\mathbf{T} - \mathbf{I})^3 - \ldots \qquad (136)$$

to re-express $\ln \mathbf{T}$ in terms of the derivatives of $\mathbf{T}$, noting that $\mathbf{T}(\mathbf{0}) = \mathbf{I}$. The advantage of the expressions in eqs 133−135 over those obtained by a straightforward expansion of the OMO integrals in eq 123 is that they maintain the symmetry of the integrals upon differentiation. The two-electron integrals are obtained in the same manner using the one-index transformations

$$\{\mathbf{M}, \mathbf{g}\}_{pqrs} = \sum_{o} (M_{po}g_{oqrs} + M^{*}_{qo}g_{pors} + M_{ro}g_{pqos} + M^{*}_{so}g_{pqro}) \qquad (137)$$

as a generalization of the one-index transformations for one-electron integrals in eq 130. Finally, we note that the lowest order connection matrices are given by[47]

$$\mathbf{T}^{(1)} = \begin{cases} -\frac{1}{2}\mathbf{S}^{(1)}, & \text{symmetric connection} \\ -\mathbf{W}^{(1)}, & \text{natural connection} \end{cases} \qquad (138)$$

$$\mathbf{T}^{(2)} = \begin{cases} -\frac{1}{2}\mathbf{S}^{(2)} + \frac{3}{4}\mathbf{S}^{(1)}\mathbf{S}^{(1)}, & \text{symmetric connection} \\ -\frac{1}{2}\mathbf{S}^{(2)} - \frac{1}{2}(\mathbf{W}^{(2)\dagger} - \mathbf{W}^{(2)}) & \\ + 2\mathbf{W}^{(1)}\mathbf{W}^{(1)} + \mathbf{W}^{(1)\dagger}\mathbf{W}^{(1)}, & \text{natural connection} \end{cases} \qquad (139)$$

where

$$W_{pq}(\varepsilon) = \langle \phi_p(0) | \phi_q(\varepsilon) \rangle \qquad (140)$$

in the symmetric and natural connections.

2.4.5. London Atomic Orbitals.

We recall from section 2.1.4 that, in calculations involving an externally applied uniform magnetic field $\mathbf{B}$, the field is represented by a vector potential $\mathbf{A}_{\mathbf{O}}(\mathbf{r})$ that vanishes at the gauge origin $\mathbf{O}$

$$\mathbf{B} = \nabla \times \mathbf{A}_{\mathbf{O}}(\mathbf{r}), \ \mathbf{A}_{\mathbf{O}}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) \qquad (141)$$

The representation of the magnetic field is not unique, being dependent on our choice of gauge origin $\mathbf{O}$. The translation of the gauge origin from $\mathbf{O}$ to $\mathbf{K}$ represents a gauge transformation of eqs 9 and 10

$$\mathbf{A}_{\mathbf{K}}(\mathbf{r}) = \mathbf{A}_{\mathbf{O}}(\mathbf{r}) - \mathbf{A}_{\mathbf{O}}(\mathbf{K}) = \mathbf{A}_{\mathbf{O}}(\mathbf{r}) + \nabla f(\mathbf{r}) \qquad (142)$$

with the gauge function

$$f(\mathbf{r}) = -\mathbf{A}_{\mathbf{O}}(\mathbf{K}) \cdot \mathbf{r} \qquad (143)$$

In exact calculations, such gauge transformations do not affect the value of the calculated observables. To see this invariance we note that a general gauge transformation, eqs 9 and 10, with gauge function f represents a unitary transformation of the operator $H - \mathrm{i}\partial_t$

$$H^{'} - \mathrm{i}\partial_t = \mathrm{e}^{-\mathrm{i}f(r)}(H - \mathrm{i}\partial_t)\mathrm{e}^{\mathrm{i}f(r)} \qquad (144)$$

In order for the Schrödinger equation to still be satisfied

$$(H' - \mathrm{i}\partial_t)\Psi'(\mathbf{r}) \Leftrightarrow (H - \mathrm{i}\partial_t)\Psi(\mathbf{r}) \qquad (145)$$

the new wave function must be related to the old one by a compensating unitary transformation

$$\Psi'(\mathbf{r}) = \mathrm{e}^{-\mathrm{i}f(\mathbf{r})}\Psi(\mathbf{r}) \qquad (146)$$

No observable properties such as the electron density are then affected by the transformation

$$\begin{aligned} \rho^{'}(\mathbf{r}) &= \Psi^{'}(\mathbf{r})^{*}\Psi^{'}(\mathbf{r}) = (\Psi(\mathbf{r})\mathrm{e}^{-\mathrm{i}f(\mathbf{r})})^{*}(\mathrm{e}^{-\mathrm{i}f(\mathbf{r})}\Psi(\mathbf{r})) \\ &= \Psi^{*}(\mathbf{r})\Psi(\mathbf{r}) = \rho(\mathbf{r}) \end{aligned} \qquad (147)$$

In exact calculations the wave function has the ability to perform the transformation in eq 146, leaving all observables unaffected. In particular, for the gauge transformation in eq 143 the exact wave function transforms as

$$\Psi^{\text{exact}}_{\mathbf{K}}(\mathbf{r}) = \mathrm{e}^{\mathrm{i}\mathbf{A}_{\mathbf{O}}(\mathbf{K})\cdot\mathbf{r}}\Psi^{\text{exact}}_{\mathbf{O}}(\mathbf{r}) \qquad (148)$$

giving gauge-invariant results. By contrast, approximate wave functions are in general unable to perform this transformation

$$\Psi^{\text{approx}}_{\mathbf{K}}(\mathbf{r}) \neq \mathrm{e}^{\mathrm{i}\mathbf{A}_{\mathbf{O}}(\mathbf{K})\cdot\mathbf{r}}\Psi^{\text{approx}}_{\mathbf{O}}(\mathbf{r}) \qquad (149)$$

As a result, different gauge origins may give different results. We note that attaching an explicit phase factor to the approximate wave function

$$\Psi^{\text{approx}}_{\mathbf{K}}(\mathbf{r}) \overset{\text{def}}{=} \mathrm{e}^{\mathrm{i}\mathbf{A}_{\mathbf{O}}(\mathbf{K})\cdot\mathbf{r}}\Psi^{\text{approx}}_{\mathbf{O}}(\mathbf{r}) \qquad (150)$$

does not solve this problem; it merely produces the same result as with the gauge origin at $\mathbf{O}$.[60] However, no natural, best gauge origin can usually be identified (except for atoms). In any case, we might as well have carried out the calculation with the origin at $\mathbf{O}$.

By contrast, when applied to individual AOs, this approach becomes useful, as can be seen by first assuming that we have AOs positioned at $\mathbf{K}$ with the properties[55]

$$\begin{aligned} H_0\psi^{\mathbf{K}}_{lm} &= E_0\psi^{\mathbf{K}}_{lm}, \quad L^{\mathbf{K}}_z\psi^{\mathbf{K}}_{lm} = m_l\psi^{\mathbf{K}}_{lm}, \\ \mathbf{L}^{\mathbf{K}} &= -\mathrm{i}(\mathbf{r} - \mathbf{K}) \times \nabla \end{aligned} \qquad (151)$$

Typical examples of such AOs are traditional field-independent spherical-harmonic Gaussians. With the gauge origin at $\mathbf{K}$ and vector potential $\mathbf{A}_{\mathbf{K}}(\mathbf{r})$ these AOs are correct to first order in $\mathbf{B}$

$$\begin{aligned} H_{\mathbf{K}}(\mathbf{B})\psi^{\mathbf{K}}_{lm} &= \left[H_0 + \frac{1}{2}BL^{\mathbf{K}}_z + O(B^2)\right]\psi^{\mathbf{K}}_{lm} \\ &= \left[E_0 + \frac{1}{2}m_lB + O(B^2)\right]\psi^{\mathbf{K}}_{lm} \end{aligned} \qquad (152)$$

where we omitted the Zeeman spin contribution BS_z. On the other hand, with the gauge origin at $\mathbf{O} \neq \mathbf{K}$ and vector potential $\mathbf{A}_{\mathbf{O}}(\mathbf{r})$ the AOs at $\mathbf{K}$ are correct only to zero order in $\mathbf{B}$

$$\begin{aligned} H_{\mathbf{O}}(\mathbf{B})\psi^{\mathbf{K}}_{lm} &= \left[H_0 + \frac{1}{2}BL^{\mathbf{O}}_z + O(B^2)\right]\psi^{\mathbf{K}}_{lm} \\ &\neq \left[E_0 + \frac{1}{2}m_lB + O(B^2)\right]\psi^{\mathbf{K}}_{lm} \end{aligned} \qquad (153)$$

Clearly, standard AOs positioned at **K** are biased toward the gauge origin at **K** in the sense that they give a better description of the electronic system with this origin than with all other gauge origins. Therefore, by attaching to each AO a phase factor that represents the transformation of the gauge origin from the global origin **O** to the AO center **K**

$$\chi_{lm}^{\mathbf{K}} = \mathrm{e}^{\mathrm{i}\mathbf{A}_{\mathbf{K}}(\mathbf{O})\cdot\mathbf{r}}\psi_{lm}^{\mathbf{K}} = \mathrm{e}^{\mathrm{i}(1/2)\mathbf{B}\times(\mathbf{O}-\mathbf{K})\cdot\mathbf{r}}\psi_{lm}^{\mathbf{K}} \tag{154}$$

we obtain a basis set where the AOs are correct to first order in the perturbation[55] for any gauge origin

$$\begin{aligned} H_{\mathbf{O}}(\mathbf{B})\chi_{lm}^{\mathbf{K}} &= \left[H_0 + \frac{1}{2}BL_z^{\mathbf{O}} + O(B^2)\right]\chi_{lm}^{\mathbf{K}} \\ &= \left[E_0 + \frac{1}{2}m_lB + O(B^2)\right]\chi_{lm}^{\mathbf{K}} \end{aligned} \tag{155}$$

The calculations become gauge-origin independent, and uniform (good) quality follows. These are the London orbitals (1937),[44,61,62] also known as GIAOs (gauge-origin independent AOs or gauge-origin including AOs), widely used in molecular calculations involving an external magnetic field.

3. RESPONSE THEORY FOR EXACT STATES

In the present section we develop molecular response theory for exact wave functions, in particular, we derive response functions and study their properties. In section 4, the results obtained here for exact wave functions will be used to develop response theory for approximate electronic-structure models.

We begin our development in section 3.1 by studying various forms of the time-dependent electronic Schrödinger equation and introducing the time-dependent quasi-energy, which is a generalization of the energy of standard time-independent perturbation theory. Two formulations for the quasi-energy are developed: a formulation analogous to the standard Hermitian expectation value of the energy and a formulation based on a non-Hermitian Lagrangian. For periodic Hamiltonians it is shown that the time-dependent Schrödinger equation may be written as a variation principle for the time-averaged quasi-energy. In section 3.2, the time-dependent wave function is expanded in orders of the perturbation and expressions are developed for the wave function corrections of different orders. This development is followed in section 3.3 by perturbation expansions of the time-dependent and time-averaged quasi-energy in the Hermitian form. In section 3.4, the response functions associated with an observable are identified from expansion of the expectation value of the corresponding operator. It is shown how the response functions may be identified with terms in the perturbation expansion of the quasi-energy. Using the Hermitian formulation of the quasi-energy, explicit expressions for the lowest order response functions are given; in section 3.5, alternative expressions for the response functions are given, based on the Lagrangian formulation of the quasi-energy.

In developing these Hermitian and Lagrangian expressions for the response functions, a generalization of Wigner's $2n + 1$ rule to time-dependent theory is repeatedly invoked; this generalization is discussed in section 3.6. Finally, in section 3.7, a phenomenological treatment is given to describe the broadening of absorption spectra arising from the finite lifetimes of excited states and from interactions with other molecules.

3.1. Quasi-Energy Formulation

A convenient framework for molecular response theory is the quasi-energy formulation,[63−66] which provides a uniform treatment of periodic time-dependent perturbations and time-independent perturbations. In the present subsection we introduce the time-dependent and time-averaged quasi-energies and develop the variation principles for these quantities, laying the foundation for our development of response functions in later subsections. Importantly, our treatment is not restricted to the quasi-energy calculated as an expectation value from a normalized wave function; we also consider the quasi-energy calculated by projection from an intermediately normalized wave function. The general framework developed here is therefore equally applicable to variational model theories such as MCSCF theory and to nonvariational model theories such as coupled-cluster theory, both of which are treated in section 4.

3.1.1. Time-Dependent Quasi-Energy and Its Variation Principle.

The time development of the electronic wave function $|0\rangle$ is determined by the time-dependent Schrödinger equation

$$H|0\rangle = \mathrm{i}\partial_t|0\rangle \tag{156}$$

where the Hermitian Hamiltonian consists of a dominant time-independent part H_0 and a time-dependent perturbation $V(t)$

$$H = H_0 + V(t) \tag{157}$$

From the Hermiticity of the Hamiltonian it follows from eq 156 that the norm $\langle 0|0\rangle$ is independent of time; here, we assume normalization to unity

$$\langle 0|0\rangle = 1 \tag{158}$$

In the following it will be convenient to separate the wave function into a product of a phase factor and a regular wave function $|\tilde{0}\rangle$[63]

$$|0\rangle = \mathrm{e}^{-\mathrm{i}F(t)}|\tilde{0}\rangle \tag{159}$$

where the phase $F(t)$ is a real-valued function that depends only on time. The regular wave function $|\tilde{0}\rangle$ is taken to be a normalized wave function whose overlap with a chosen time-independent normalized reference state $|\mathrm{R}\rangle$ is real and positive: $\langle \mathrm{R}|\tilde{0}\rangle > 0$. Neither the reference state $|\mathrm{R}\rangle$ nor the states $|i\rangle$ are required to be eigenfunctions of H_0. Introducing an orthonormal basis $\{|\mathrm{R}\rangle, |i\rangle\}$, we may write the regular wave function as

$$|\tilde{0}\rangle = \frac{|\mathrm{R}\rangle + \sum_i c_i|i\rangle}{\sqrt{1 + \sum_i |c_i|^2}} \tag{160}$$

The restriction that the overlap $\langle \mathrm{R}|\tilde{0}\rangle$ is nonzero means that the above ansatz is not fully general. However, this restriction does not pose any problems in the current context, where we are only interested in perturbation expansions rather than in the explicit time development for an arbitrary time-dependent perturbation. We note that the separation in eq 159 is not unique, depending on our choice of regular wave function and phase factor. Consider an alternative separation, $|0\rangle = \mathrm{e}^{-\mathrm{i}F'(t)}|\tilde{0}'\rangle$, different from that in eq 159. Comparing with eq 159, we find that $|\tilde{0}\rangle$ and $|\tilde{0}'\rangle$ are related by a time-dependent phase factor

$$|\tilde{0}'\rangle = \mathrm{e}^{\mathrm{i}(F'(t) - F(t))}|\tilde{0}\rangle \tag{161}$$

We shall later see that this nonuniqueness does not affect the central quantity of response theory: the time-averaged quasi-energy.

Let us now consider the Schrödinger equation for the phase-separated wave function. By substituting eq 159 into eq 156 we obtain the time-dependent Schrödinger equation for $|\tilde{0}\rangle$ and $F(t)$

$$(H - \mathrm{i}\partial_t - \dot{F}(t))|\tilde{0}\rangle = 0 \tag{162}$$

Introducing in eq 162 the projection operator P_x for the space orthogonal to x

$$P_x = 1 - \frac{|x\rangle\langle x|}{\langle x|x\rangle} \tag{163}$$

we arrive at the time-dependent Schrödinger equation for the regular wave function

$$P_{\tilde{0}}(H - \mathrm{i}\partial_t)|\tilde{0}\rangle = 0 \tag{164}$$

If we instead project eq 162 onto $|\tilde{0}\rangle$, we obtain an equation for the phase factor

$$Q(t) = \dot{F}(t) = \langle\tilde{0}|H - \mathrm{i}\partial_t|\tilde{0}\rangle \tag{165}$$

By first solving eq 164 for the regular wave function and subsequently determining the phase factor by integrating eq 165 we obtain the full solution to the Schrödinger equation in eq 156. In the time-independent case, with $V(t) = 0$ and $H_0|\tilde{0}\rangle = E_0|\tilde{0}\rangle$, we obtain $Q(t) = E_0$ and hence $F(t) = E_0t + k$. For this reason $Q(t)$ is known as the time-dependent quasi-energy. To distinguish the expression for the time-dependent quasi-energy in eq 165 from other expressions derived later, this form is termed the Hermitian form of the time-dependent quasi-energy. The time-dependent quasi-energy is a real quantity, being the derivative of the real function $F(t)$; alternatively, the real valuedness of $Q(t)$ follows explicitly from the Hermiticity of H and the constant norm of $|\tilde{0}\rangle$ in eq 165. The quasi-energy is not a unique quantity; it depends on the choice of the regular wave function and phase factor: $Q(t) = \dot{F}(t)$. However, in section 3.1.2 it is demonstrated that, for periodic perturbations, the time-averaged quasi-energy is uniquely defined.

For the development of response theory we need to characterize the quasi-energy and regular wave function in terms of a variation principle. From eq 162 we obtain the Frenkel variation principle[67] for an arbitrary variation $|\delta\tilde{0}\rangle$ in the regular wave function

$$\langle\delta\tilde{0}|H - \mathrm{i}\partial_t - Q(t)|\tilde{0}\rangle = 0 \tag{166}$$

Taking the complex conjugate of eq 166 and adding it to the same equation we obtain

$$\delta\langle\tilde{0}|H - \mathrm{i}\partial_t|\tilde{0}\rangle + \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\langle\tilde{0}|\delta\tilde{0}\rangle = 0 \tag{167}$$

where we used $\delta\langle\tilde{0}|Q(t)|\tilde{0}\rangle = Q(t)\delta\langle\tilde{0}|\tilde{0}\rangle = 0$, which follows from the fixed normalization of the regular wave function. To simplify eq 167 it is useful to separate a general variation $|\delta\tilde{0}\rangle$ into a component $|\delta\tilde{0}^{\perp}\rangle$ orthogonal to $|\tilde{0}\rangle$ and a component $\mathrm{i}\alpha|\tilde{0}\rangle$ parallel to $|\tilde{0}\rangle$

$$|\delta\tilde{0}\rangle = |\delta\tilde{0}^{\perp}\rangle + \mathrm{i}\alpha|\tilde{0}\rangle \tag{168}$$

From the normalization of the regular wave function it follows that the amplitude α in eq 168 is real. Inserting eq 168 into eq 167, we obtain the variation principle

$$\begin{aligned}&\langle\tilde{0}|H - \mathrm{i}\partial_t|\delta\tilde{0}^{\perp}\rangle + \langle\delta\tilde{0}^{\perp}|H - \mathrm{i}\partial_t|\tilde{0}\rangle + \dot{\alpha}\langle\tilde{0}|\tilde{0}\rangle - \dot{\alpha}\langle\tilde{0}|\tilde{0}\rangle\\&\quad = \langle\tilde{0}|H - \mathrm{i}\partial_t|\delta\tilde{0}^{\perp}\rangle + \langle\delta\tilde{0}^{\perp}|H - \mathrm{i}\partial_t|\tilde{0}\rangle = 0\end{aligned} \tag{169}$$

similar to the standard variation principle of time-independent quantum mechanics. The variation principles in eqs 167 and 169 are equivalent, and either may be used to determine the time-dependent wave function. In particular, eq 167 constitutes the time-dependent variation principle of Langhoff, Epstein, and Karplus.[63] Note that it is not a variation principle in the usual sense in which the variation in the function to be determined vanishes at the solution. To establish such a variation principle we shall henceforth restrict our attention to periodic perturbations.

3.1.2. Time-Averaged Quasi-Energy and Its Variation Principle.

Let us now consider a periodic time-dependent perturbation of period T and frequency ω

$$V(t + T) = V(t),\ \omega = \frac{2\pi}{T} \tag{170}$$

noting that this periodicity does not require all components of $V(t)$ to oscillate with the same frequency ω, only to oscillate with a frequency $n\omega$, where n is an integer (negative, zero, or positive). It may be shown that the regular wave function oscillates with the same period T

$$|\tilde{0}(t + T)\rangle = |\tilde{0}(t)\rangle \tag{171}$$

For such periodic perturbations, we introduce the time-averaged quasi-energy or simply the quasi-energy as

$$\mathcal{Q} = \{Q\}_T = \{\langle\tilde{0}|H - \mathrm{i}\partial_t|\tilde{0}\rangle\}_T \tag{172}$$

where the time average of a periodic function $g(t)$ is defined by

$$\{g\}_T = \frac{1}{T}\int_0^T g(t)\mathrm{d}t \tag{173}$$

Importantly, the time-averaged quasi-energy $\mathcal{Q}$ is independent of our choice of regular wave function. To see this, let $\mathcal{Q}'$ and $\mathcal{Q}$ be associated with the two representations $|\tilde{0}'\rangle$ and $|\tilde{0}\rangle$, which are connected via eq 161. From eqs 161 and 171 it follows that $F'(t) - F(t)$ and hence $\dot{F}'(t) - \dot{F}(t)$ are periodic in t, yielding

$$\begin{aligned}\mathcal{Q}' - \mathcal{Q} &= \{Q'(t) - Q(t)\}_T = \{\dot{F}'(t) - \dot{F}(t)\}_T\\&= 0\end{aligned} \tag{174}$$

demonstrating that the choice of regular wave function does not affect the time-averaged quasi-energy.

Let us now consider the variation principle for the time-averaged quasi-energy. Taking the time average of the variation principle in eq 167 and invoking the periodicity of $|\tilde{0}\rangle$ and $|\delta\tilde{0}\rangle$, we obtain the variation principle for the quasi-energy[63]

$$\delta\mathcal{Q} = 0 \tag{175}$$

Conversely, to see that the time-dependent variation principle in eq 169 follows from that in eq 175 we introduce eq 168 into eq 175, obtaining

$$\{\langle\tilde{0}|H - \mathrm{i}\partial_t|\delta\tilde{0}^{\perp}\rangle\}_T + \{\langle\delta\tilde{0}^{\perp}|H - \mathrm{i}\partial_t|\tilde{0}\rangle\}_T + \{\dot{\alpha}\}_T = 0 \tag{176}$$

As α is periodic, the term $\{\dot{\alpha}\}_T$ vanishes. Furthermore, as $|\delta\tilde{0}^{\perp}\rangle$ may have an arbitrary time dependence in the interval $[0,T]$, eq 176 shows that $\langle\tilde{0}|H - \mathrm{i}\partial_t|\delta\tilde{0}^{\perp}\rangle + \langle\delta\tilde{0}^{\perp}|H - \mathrm{i}\partial_t|\tilde{0}\rangle$ vanishes at all times, giving eq 169. For periodic perturbations, the time-dependent variation principles in eqs 167 and 169 are thus equivalent to the time-averaged variation principle of eq 175.

Assume next that the Hamiltonian contains a term that depends on the perturbation strength ε. By differentiating the quasi-energy of eq 172 and using the stationary condition in eq 175 we obtain

$$\begin{aligned}\frac{\mathrm{d}\mathcal{Q}}{\mathrm{d}\varepsilon} &= \{\langle\tilde{0}\,|\partial_\varepsilon H|\tilde{0}\rangle\}_T + \{\langle\partial_\varepsilon\tilde{0}|H - \mathrm{i}\partial_t|\tilde{0}\rangle\}_T \\ &+ \{\langle\tilde{0}|H - \mathrm{i}\partial_t|\partial_\varepsilon\tilde{0}\rangle\}_T \\ &= \{\langle\tilde{0}|\partial_\varepsilon H|\tilde{0}\rangle\}_T + \delta\mathcal{Q}|_{\partial\tilde{0}=\partial_\varepsilon\tilde{0}} = \{\langle\tilde{0}|\partial_\varepsilon H|\tilde{0}\rangle\}_T\end{aligned} \tag{177}$$

which constitutes a generalization of the Hellmann–Feynman theorem[68,69] to time-dependent perturbations.[63] The quasi-energy variation principle eq 175 and the associated Hellmann–Feynman theorem in eq 177 will play an important role in our development of perturbation theory; formally, they are equivalent to the variation principle and Hellmann–Feynman theorem for time-independent perturbations, respectively, greatly simplifying development of response theory.

3.1.3. Quasi-Energy Lagrangian and Its Variation Principle. In the theory developed in sections 3.1.1 and 3.1.2 the time-dependent quasi-energy was calculated as an expectation value according to eq 165 from the explicitly normalized wave function $|\tilde{0}\rangle$ in eq 160. Often a different formulation is more convenient, where the energy is calculated by projection rather than as an expectation value, from an intermediately normalized wave function $|\hat{0}\rangle$ with unit overlap with the reference state

$$\langle \mathrm{R}|\hat{0}\rangle = 1 \tag{178}$$

Such an approach is taken in many-body perturbation theory and in coupled-cluster theory, for example. By analogy with the normalized wave function $|\tilde{0}\rangle$ in eq 160 the intermediately normalized wave function is expanded in the orthonormal basis $\{|\mathrm{R}\rangle,|i\rangle\}$

$$|\hat{0}\rangle = |\mathrm{R}\rangle + \sum_{\mathrm{i}} c_i|i\rangle \tag{179}$$

and is related to the regular wave function in eq 160 by a real normalization constant N_R

$$\begin{aligned}&|\tilde{0}\rangle = N_\mathrm{R}|\hat{0}\rangle, \\ &N_\mathrm{R} = \langle\mathrm{R}|\tilde{0}\rangle = (1 + \sum_i |c_i|^2)^{-1/2} = \langle\hat{0}|\hat{0}\rangle^{-1/2}\end{aligned} \tag{180}$$

As the normalization constant N_R varies with time, the intermediately normalized wave function does not fulfill the usual time-dependent Schrödinger equation. Instead, inserting eq 180 into eq 162 we obtain the following Schrödinger equation for the intermediately normalized wave function

$$\left(H - \mathrm{i}\partial_t - Q(t) - \mathrm{i}\frac{\dot{N}_R(t)}{N_R(t)}\right)|\hat{0}\rangle = 0 \tag{181}$$

where the quasi-energy $Q(t)$ is defined in terms of $|\tilde{0}\rangle$, see eq 165. To express $Q(t)$ in terms of $|\hat{0}\rangle$ we multiply eq 181 with $\langle\mathrm{R}|$ from the left. From the intermediate normalization in eq 178 we obtain

$$\langle\mathrm{R}|H|\hat{0}\rangle - Q(t) - \mathrm{i}\frac{\dot{N}_R(t)}{N_R(t)} = 0 \tag{182}$$

Given that $\mathrm{i}\dot{N}_R(t)/N_R(t)$ is imaginary and $Q(t)$ is real we may identify the time-dependent quasi-energy in the intermediate normalization with the real part of the complex quantity $\langle\mathrm{R}|H|\hat{0}\rangle$

$$Q(t) = \mathrm{Re}\langle\mathrm{R}|H|\hat{0}\rangle \tag{183}$$

where $|\hat{0}\rangle$ is a solution to the time-dependent Schrödinger equation in eq 181. The form of the time-dependent quasi-energy given in eq 183 is termed the non-Hermitian form in contrast to the Hermitian form of eq 165.

Let us now consider the solution of the Schrödinger equation in the intermediate normalization. Using the definition of the time-dependent quasi-energy in eq 165 and the relation between the regular and the intermediately normalized wave functions in eq 180 it follows from projection of $|\hat{0}\rangle$ onto the time-dependent Schrödinger equation, eq 181, that

$$\begin{aligned}&\langle\hat{0}|H - \mathrm{i}\partial_t - Q(t) - \mathrm{i}\frac{\dot{N}_\mathrm{R}(t)}{N_\mathrm{R}(t)}|\hat{0}\rangle = N_\mathrm{R}^{-1}\langle\hat{0}|H - \mathrm{i}\partial_t - Q(t)|\tilde{0}\rangle \\ &= N_\mathrm{R}^{-2}\langle\tilde{0}|H - \mathrm{i}\partial_t - Q(t)|\tilde{0}\rangle = 0\end{aligned} \tag{184}$$

We therefore need to solve eq 181 only in the space orthogonal to the intermediately normalized wave function. Projecting the Schrödinger equation in eq 181 from the left with the projector of eq 163 with $x = \hat{0}$ we obtain the following Schrödinger equation for the intermediately normalized wave function

$$P_{\hat{0}}(H - \mathrm{i}\partial_t)|\hat{0}\rangle = 0 \tag{185}$$

similar to that for the regular wave function in eq 164. Alternatively, we can use the coefficients $\mathbf{c}$ of eq 179 to introduce a nonorthogonal basis $|\hat{i}\rangle$ for the space orthogonal to $|\hat{0}\rangle$

$$|\hat{i}\rangle = |i\rangle - c_i^*|\mathrm{R}\rangle,\ \langle\hat{i}|\hat{0}\rangle = 0 \tag{186}$$

and write the projected Schrödinger equation as

$$\langle\hat{i}|H - \mathrm{i}\partial_t|\hat{0}\rangle = 0 \tag{187}$$

To establish a variation principle for the quasi-energy in the intermediate normalization we note that the quasi-energy is calculated from eq 183 subject to the constraint that the intermediately normalized state satisfies the projected Schrödinger equation in eq 187. Invoking Lagrange's method we construct a Lagrangian by adding to $\langle\mathrm{R}|H|\hat{0}\rangle$ the constraints in eq 187 multiplied by the undetermined multipliers $\bar{c}_j$. Introducing the notation

$$\langle\bar{0}| = \sum_i \bar{c}_i^{\,*}\langle\hat{i}| \tag{188}$$

we obtain the time-dependent complex-valued quasi-energy Lagrangian

$$L^\mathrm{c}(t) = \langle\mathrm{R}|H|\hat{0}\rangle + \langle\bar{0}|H - \mathrm{i}\partial_t|\hat{0}\rangle \tag{189}$$

By taking the real part of $L^\mathrm{c}(t)$ we obtain the time-dependent quasi-energy Lagrangian

$$L(t) = \mathrm{Re}(\langle\mathrm{R}|H|\hat{0}\rangle + \langle\bar{0}|H - \mathrm{i}\partial_t|\hat{0}\rangle) \tag{190}$$

which is equal to the quasi-energy $Q(t)$ in eq 183 when the projected equations in eq 187 are satisfied. The Lagrangian is required to be stationary with respect to variations of the Lagrange multipliers $\bar{c}_i$, which implies eq 187. To show this implication, we assume stationarity of eq 190 with respect to variations in the real and imaginary parts of the multipliers, $\bar{c}_i = \bar{c}_i^\mathrm{R} + \mathrm{i}\bar{c}_i^\mathrm{I}$, yielding the stationary conditions

$$\frac{\partial L(t)}{\partial\bar{c}_i^\mathrm{R}} = \mathrm{Re}\langle\hat{i}|H - \mathrm{i}\partial_t|\hat{0}\rangle = 0 \tag{191}$$

$$\frac{\partial L(t)}{\partial \bar{c}_i^{\mathrm{I}}} = \mathrm{Re}(\mathrm{i}\langle \hat{i}|H - \mathrm{i}\partial_t|\hat{0}\rangle) = -\mathrm{Im}\langle \hat{i}|H - \mathrm{i}\partial_t|\hat{0}\rangle = 0 \qquad (192)$$

which are equivalent to eq 187.

The stationary conditions above are to be solved at each time t. By analogy with eq 175, we now introduce the time-averaged quasi-energy Lagrangian

$$\begin{aligned}\mathscr{L} &= \{L\}_T \\ &= \mathrm{Re}(\{\langle \mathrm{R}|H|\hat{0}\rangle\}_T + \{\langle \bar{0}|H - \mathrm{i}\partial_t|\hat{0}\rangle\}_T)\end{aligned} \qquad (193)$$

where $\langle \bar{0}|\hat{0}\rangle = 0$, as follows from eqs 186 and 188. Henceforth, $\mathscr{L}$ will be called the quasi-energy Lagrangian or the non-Hermitian form of the quasi-energy. The Lagrange multipliers and the intermediately normalized state are now determined from the time-averaged stationary condition

$$\delta \mathscr{L} = 0 \qquad (194)$$

corresponding to the stationary conditions

$$\frac{\partial \mathscr{L}}{\partial c_i} = \frac{\partial \mathscr{L}}{\partial \bar{c}_i} = 0 \qquad (195)$$

However, for eq 194 to be a valid stationary condition we must also show that it implies the time-dependent equation, eq 187. Consider in eq 194 a variation $\langle \delta\bar{0}|$, yielding the condition

$$\delta \mathscr{L} = \mathrm{Re}\{\langle \delta\bar{0}|H - \mathrm{i}\partial_t|\hat{0}\rangle\}_T = 0 \qquad (196)$$

As the variation $\langle \delta\bar{0}|$ may have an arbitrary time dependence in the interval $[0,T]$, eq 196 implies that the equation

$$\mathrm{Re}\langle \delta\bar{0}|H - \mathrm{i}\partial_t|\hat{0}\rangle = 0 \qquad (197)$$

holds at all times. Finally, using the fact that $\langle \delta\bar{0}|$ and $\mathrm{i}\langle \delta\bar{0}|$ are both allowed variations in $\langle \delta\bar{0}|$, eq 187 is obtained from eq 197. We have thus shown that eqs 194 and 187 are equivalent. The time-averaged Lagrangian variation principle of eq 194 will later be used to derive compact expressions for the response functions in coupled-cluster theory.

From the stationarity of the Lagrangian with respect to $\boldsymbol{c}$ and $\bar{\mathbf{c}}$, we obtain for the derivative of the Lagrangian with respect to a perturbation parameter ε in the Hamiltonian the relation

$$\frac{\mathrm{d}\mathscr{L}}{\mathrm{d}\varepsilon} = \mathrm{Re}(\{\langle \mathrm{R}|\partial_\varepsilon H|\hat{0}\rangle\}_T + \{\langle \bar{0}|\partial_\varepsilon H|\hat{0}\rangle\}_T) \qquad (198)$$

which constitutes an alternative form of the Hellmann–Feynman theorem, eq 177.

3.2. Perturbation Expansion of the Wave Function

The development in section 3.1 allows us to determine the solution to the time-dependent Schrödinger equation in the time domain. Although such a scheme is needed to treat the interaction between a molecule and an arbitrarily strong external field in a general manner, we now restrict ourselves to cases where the interaction with the external field may be treated by perturbation theory, expanding the wave function in orders of a periodic time-dependent perturbation $V(t)$.

We begin by specifying the form of the perturbation operator. Allowing for several periodic components we write $V(t)$ in the general form

$$V(t) = \sum_B \varepsilon_B V_B \mathrm{e}^{-\mathrm{i}\omega_B t} \qquad (199)$$

where the summation over B runs symmetrically over both positive and negative indices. From the Hermiticity requirement, $V(t) = V^\dagger(t)$, it follows that all components of nonzero frequency occur in pairs of opposite frequencies $\omega_{\pm B}$, where we adopted the notation

$$\omega_{-B} = -\omega_B \qquad (200)$$

Allowing for complex perturbation strengths, the Hermiticity of $V(t)$ gives the following symmetry relations

$$V_B^\dagger = V_{-B} \qquad (201)$$

$$\varepsilon_B^* = \varepsilon_{-B} \qquad (202)$$

Instead of using the real and imaginary parts of ε_B as the independent parameters, it will be convenient to consider ε_B and $\varepsilon_B{}^*$ as independent parameters. For symmetry reasons, static perturbations ($\omega = 0$) are also included with both a positive and a negative perturbation index. In this way, all perturbations entering eq 199 are treated on the same footing and satisfy the relations in eqs 200–202. When evaluating response functions we shall later examine expectation values of the specific perturbation component with index B_0 (frequency ω_{B_0}, perturbation strength ε_{B_0}, and operator V_{B_0}).

To ensure that $V(t)$ is periodic, all ω_B must be equal to some chosen frequency ω multiplied by an integer. In general, the frequencies ω_B correspond to some experimental setup and are not multiples of some common frequency ω. However, for an arbitrarily small $\tau \geq 0$ we can always find integers n_B and a frequency ω such that $|n_B\omega_B - \omega| \leq \tau$.

3.2.1. Perturbation Expansion with a General Reference State. Having specified $V(t)$, we now consider the expansion of the wave function defined by eq 187, which by substitution of the Hamiltonian of eq 157 becomes

$$\langle \hat{i}|H_0 + V(t) - \mathrm{i}\partial_t|\hat{0}\rangle = 0 \qquad (203)$$

Using intermediate normalization, the coefficients $\mathbf{c}(t)$ of the wave function $|\hat{0}\rangle$ in eq 179 may be written as the sum of a perturbation-independent zero-order part $\mathbf{c}^{(0)} = \{1, c_i^0\}$ and a perturbation-dependent correction

$$\Delta\mathbf{c}(t) = \mathbf{c}(t) - \mathbf{c}^{(0)} \qquad (204)$$

with coefficients $\{0, c_i(t) - c_i^{(0)}\}$. The zero-order wave function and a basis for its orthogonal complement are then given by

$$|\hat{0}^{(0)}\rangle = |\mathrm{R}\rangle + \sum_i c_i^{(0)}|i\rangle \qquad (205)$$

$$|\hat{i}^{(0)}\rangle = |i\rangle - c_i^{(0)*}|\mathrm{R}\rangle \qquad (206)$$

where $\langle \hat{\mathrm{i}}^{(0)}|\hat{0}^{(0)}\rangle = 0$ follows from $\langle i|\mathrm{R}\rangle = 0$. Retaining only the zero-order terms in eq 203 we obtain the zero-order equation

$$\langle \hat{i}^{(0)}|H_0|\hat{0}^{(0)}\rangle = 0 \qquad (207)$$

demonstrating that $H_0|\hat{0}^{(0)}\rangle$ has no components orthogonal to $|\hat{0}^{(0)}\rangle$ and hence that $|\hat{0}^{(0)}\rangle$ is an eigenfunction of H_0 with eigenvalue E_0

$$H_0|\hat{0}^{(0)}\rangle = E_0|\hat{0}^{(0)}\rangle \qquad (208)$$

Usually the zero-order state is taken to be the ground-state wave function. However, in the following we do not make this assumption, requiring only that the zero-order state is an eigenstate of H_0 with a nonzero overlap with $|\mathrm{R}\rangle$, not necessarily the ground state.

We now consider the perturbation-dependent correction to the zero-order wave function. Inserting $|\hat{i}\rangle$ written as the sum of a zero-order part and a correction term

$$|\hat{i}\rangle = |\hat{i}^{(0)}\rangle + \left(|\hat{i}\rangle - |\hat{i}^{(0)}\rangle\right) = |\hat{i}^{(0)}\rangle - \Delta c_i^*(t)|\mathrm{R}\rangle \tag{209}$$

into eq 203 and using eq 207 we obtain the following equations for the corrections $\Delta c_j(t)$

$$\begin{aligned}&\langle\hat{i}^{(0)}|V(t)|\hat{0}^{(0)}\rangle - \mathrm{i}\partial_t\Delta c_i(t) + \sum_j \left(\langle\hat{i}^{(0)}|H_0|j\rangle - \delta_{ij}E_0\right)\Delta c_j(t)\\ &+ \sum_j \left(\langle\hat{i}^{(0)}|V(t)|j\rangle - \delta_{ij}\langle\mathrm{R}|V(t)|\hat{0}^{(0)}\rangle\right)\Delta c_j(t)\\ &-\Delta c_i(t)\sum_j \langle\mathrm{R}|V(t)|j\rangle\Delta c_j(t) - \Delta c_i(t)\sum_j\langle\mathrm{R}|H_0|j\rangle\Delta c_j(t) = 0\end{aligned} \tag{210}$$

Next, by inserting the expansion of the perturbation $V(t)$ given in eq 199 and introducing the vectors

$$\left(\hat{H}^{\mathrm{R}[1]}\right)_i = \langle\hat{i}^{(0)}|H_0|\mathrm{R}\rangle \tag{211}$$

$$\left(\hat{V}_B^{[1]}\right)_i = \langle\hat{i}^{(0)}|V_B|\hat{0}^{(0)}\rangle \tag{212}$$

$$\left(\hat{V}_B^{\mathrm{R}[1]}\right)_i = \langle\hat{i}^{(0)}|V_B|\mathrm{R}\rangle \tag{213}$$

and the matrices

$$A_{ij} = \langle\hat{i}^{(0)}|H_0|j\rangle - \delta_{ij}E_0 \tag{214}$$

$$\left(\hat{V}_B^{[2]}\right)_{ij} = \langle\hat{i}^{(0)}|V_B|j\rangle - \delta_{ij}\langle R|V_B|\hat{0}^{(0)}\rangle \tag{215}$$

where $\mathbf{A}$ is the Jacobian matrix, we arrive at the Schrödinger equation for $\Delta\mathbf{c}(t)$

$$\begin{aligned}(\mathbf{A} - \mathrm{i}\partial_t)\Delta\mathbf{c}(t) = &-\sum_B \varepsilon_B \mathrm{e}^{-\mathrm{i}\omega_B t}\left[\hat{\mathbf{V}}_B^{[1]} + \hat{\mathbf{V}}_B^{[2]}\Delta\mathbf{c}(t)\right.\\ &\left.- \Delta\mathbf{c}(t)\left(\hat{\mathbf{V}}_{-B}^{\mathrm{R}[1]\dagger}\Delta\mathbf{c}(t)\right)\right] + \Delta\mathbf{c}(t)\left(\hat{\mathbf{H}}^{\mathrm{R}[1]\dagger}\Delta\mathbf{c}(t)\right)\end{aligned} \tag{216}$$

All terms in this equation follow straightforwardly from eq 210 except the term containing $\hat{\mathbf{V}}_{-\mathrm{B}}^{\mathrm{R}[1]\dagger}$, which is obtained in the following manner

$$\begin{aligned}\sum_j \langle R|V|j\rangle\Delta c_j(t) &= \sum_j \langle j|V|R\rangle^*\Delta c_j(t)\\ &= \sum_{j,\,B} \varepsilon_B^*\langle j|V_B|R\rangle^*\Delta c_j(t)\mathrm{e}^{\mathrm{i}\omega_B t}\\ &= \sum_{j,\,-B} \varepsilon_B\langle j|V_{-B}|R\rangle^*\Delta c_j(t)\mathrm{e}^{-\mathrm{i}\omega_B t}\\ &= \sum_B \varepsilon_B \mathrm{e}^{-\mathrm{i}\omega_B t}\left(\hat{\mathbf{V}}_{-B}^{\mathrm{R}[1]\dagger}\Delta\mathbf{c}(t)\right)\end{aligned} \tag{217}$$

where the Hermiticity of $V(t)$ and eqs 200 and 202 have been used.

From the Schrödinger equation in eq 216 we may now determine equations for the wave function parameters to different orders in the perturbation

$$\begin{aligned}\Delta\mathbf{c}(t) = &\sum_{B_1} \varepsilon_{B_1}\mathbf{c}_{B_1}^{(1)}\mathrm{e}^{-\mathrm{i}\omega_{B_1}t} + \sum_{B_1B_2}\varepsilon_{B_1}\varepsilon_{B_2}\mathbf{c}_{B_1,\,B_2}^{(2)}\,\mathrm{e}^{-\mathrm{i}(\omega_{B_1}+\omega_{B_2})t} + \ldots\\ &+ \sum_{B^n}\left(\prod_{k=1}^{n}\varepsilon_{B_k}\right)\mathbf{c}_{B^n}^{(n)}\,\mathrm{e}^{-\mathrm{i}\sum_{k=1}^{n}\omega_{B_k}t} + \ldots\end{aligned} \tag{218}$$

where B^n is an n-dimensional multi-index of perturbation indices B_i

$$B^n = (B_1, B_2, \ldots, B_n) \tag{219}$$

The multi-index B^n is not ordered; consequently, there are, for instance, six third-order corrections B^3 corresponding to the six permutations of B_1, B_2, and B_3. However, corrections referring to the same set of indices are required to be identical, for example, $\mathbf{c}_{B_1,B_2}^{(2)} = \mathbf{c}_{B_2,B_1}^{(2)}$. By inserting the expansion of the wave function parameters in eq 218 in the Schrödinger equation eq 216 and collecting terms proportional to ε_{B1} and to $\varepsilon_{B_1}\varepsilon_{B_2}$ we obtain the first- and second-order corrections, respectively

$$\mathbf{c}_{B_1}^{(1)} = -(\mathbf{A} - \omega_{B_1}\mathbf{I})^{-1}\hat{\mathbf{V}}_{B_1}^{[1]} \tag{220}$$

$$\begin{aligned}\mathbf{c}_{B_1,\,B_2}^{(2)} = &-P_{[1,\,2]}[\mathbf{A} - (\omega_{B_1} + \omega_{B_2})\mathbf{I}]^{-1}\\ &\times\left[\hat{\mathbf{V}}_{B_1}^{[2]}\mathbf{c}_{B_2}^{(1)} - \mathbf{c}_{B_1}^{(1)}\left(\hat{\mathbf{H}}^{\mathrm{R}[1]\dagger}\mathbf{c}_{B_2}^{(1)}\right)\right]\end{aligned} \tag{221}$$

where we used the identity $\mathbf{c}_{B_1,B_2}^{(2)} = \mathbf{c}_{B_2,B_1}^{(2)}$ and introduced $P_{[1,2]}$, which averages over the two permutations of 1 and 2

$$P_{[1,\,2]}f_{B_1B_2} = \frac{1}{2!}\left(f_{B_1B_2} + f_{B_2B_1}\right) \tag{222}$$

In a similar way, the general correction of order $n \geq 2$ becomes

$$\begin{aligned}\mathbf{c}_{B^n}^{(n)} = &-P_{[1,\,n]}\left(\mathbf{A} - \sum_{k=1}^{n}\omega_{B_k}\mathbf{I}\right)^{-1}\\ &\times\left(\hat{\mathbf{V}}_{B_1}^{[2]}\mathbf{c}_{B_2,\,\ldots,\,B_n}^{(n-1)} - \sum_{m=1}^{n-2}\mathbf{c}_{B_2,\,\ldots,\,B_{m+1}}^{(m)}\hat{\mathbf{V}}_{-B_1}^{\mathrm{R}[1]\dagger}\mathbf{c}_{B_{m+2},\,\ldots,\,B_n}^{(n-m-1)}\right.\\ &\left.-\sum_{m=1}^{n-1}\mathbf{c}_{B_1,\,\ldots,\,B_m}^{(m)}\hat{\mathbf{H}}^{\mathrm{R}[1]\dagger}\mathbf{c}_{B_{m+1},\,\ldots,\,B_n}^{(n-m)}\right)\end{aligned} \tag{223}$$

where $P_{[1,n]}$ averages over the n! permutations of the integers 1, 2, ..., n, imposing the required permutational symmetry on the wave function corrections.

3.2.2. Jacobian Matrix.

In the preceding subsection the Jacobian was introduced in eq 214 and the wave function corrections were obtained as solutions to linear equations involving this matrix, see, for example, eq 223. We shall now study the Jacobian in more detail and, in particular, show that its eigenvalues are the excitation energies from the zero-order state.

Consider an eigenstate $|n^{(0)}\rangle$ of the Hamiltonian H_0 with energy E_n, assuming that this eigenstate has a nonzero overlap with the reference state $|\mathrm{R}\rangle$. Using the nonorthogonal basis $\{|\hat{0}^{(0)}\rangle, |i\rangle\}$ rather than the orthonormal basis $\{|\mathrm{R}\rangle,|i\rangle\}$, this eigenvector can be expanded as

$$|n^{(0)}\rangle = |\hat{0}^{(0)}\rangle + \sum_i C_i^n|i\rangle \tag{224}$$

The condition that $|n^{(0)}\rangle$ is an eigenstate of H_0 with eigenvalue E_n may then be written as

$$(H_0 - E_0)\left(|\hat{0}^{(0)}\rangle + \sum_i C_i^n|i\rangle\right) = (E_n - E_0)\left(|\hat{0}^{(0)}\rangle + \sum_i C_i^n|i\rangle\right) \qquad (225)$$

Projecting eq 225 from the left against the complete basis $\{|\mathrm{R}\rangle, |\hat{i}^{(0)}\rangle\}$ we obtain the matrix eigenvalue problem

$$\mathbf{H}^{\mathrm{b}}\begin{pmatrix} 1 \\ \mathbf{C}^n \end{pmatrix} = (E_n - E_0)\mathbf{S}^{\mathrm{b}}\begin{pmatrix} 1 \\ \mathbf{C}^n \end{pmatrix} \qquad (226)$$

where the shifted Hamiltonian and overlap matrices are given by (in a shorthand sub-block notation)

$$\mathbf{H}^{\mathrm{b}} = \begin{pmatrix} \langle \mathrm{R}|H_0 - E_0|\hat{0}^{(0)}\rangle & \langle \mathrm{R}|H_0 - E_0|j\rangle \\ \langle \hat{i}^{(0)}|H_0 - E_0|\hat{0}^{(0)}\rangle & \langle \hat{i}^{(0)}|H_0 - E_0|j\rangle \end{pmatrix} = \begin{pmatrix} 0 & \langle \mathrm{R}|H_0 - E_0|j\rangle \\ 0 & A_{ij} \end{pmatrix} \qquad (227)$$

$$\mathbf{S}^{\mathrm{b}} = \begin{pmatrix} \langle \mathrm{R}|\hat{0}^{(0)}\rangle & \langle \mathrm{R}|j\rangle \\ \langle \hat{i}^{(0)}|\hat{0}^{(0)}\rangle & \langle \hat{i}^{(0)}|j\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & \delta_{ij} \end{pmatrix} \qquad (228)$$

The first column of the Hamiltonian $\mathbf{H}^{\mathrm{b}}$ vanishes because of eq 208; in the overlap matrix $\mathbf{S}^{\mathrm{b}}$ the off-diagonal blocks vanish because of the orthonormality of $\{|\mathrm{R}\rangle, |i\rangle\}$ and $\{|0^{(0)}\rangle, |\hat{i}^{(0)}\rangle\}$, whereas the unity of the diagonal blocks follows from eqs 205 and 206. Expansion of the Schrödinger equation in eq 226 now gives the Jacobian eigenvalue problem

$$\mathbf{A}\mathbf{C}^n = (E_n - E_0)\mathbf{C}^n \qquad (229)$$

whose eigenvalues are the excitation energies $E_n - E_0$ and whose eigenvectors define the excited eigenstates $|n^{(0)}\rangle$. In approximate theories the eigenvalues of the approximate Jacobian will be used to define excitation energies.

3.2.3. Perturbation Expansion with an Eigenvector Reference State.

In the standard formulation of time-dependent perturbation theory, the reference state $|\mathrm{R}\rangle$ is chosen as a normalized eigenfunction $|0^{(0)}\rangle$ of the unperturbed Hamiltonian H_0 with energy E_0. The zero-order amplitudes then vanish, $\mathbf{c}^{(0)} = \mathbf{0}$, yielding $|\hat{0}^{(0)}\rangle = |0^{(0)}\rangle$ and $|\hat{i}^{(0)}\rangle = |i\rangle$ so that the vectors and matrices in eqs 211−215 reduce to

$$\left(\hat{H}^{\mathrm{R}[1]}\right)_i = 0 \qquad (230)$$

$$\left(\hat{V}_B^{[1]}\right)_i = \left(\hat{V}_B^{\mathrm{R}[1]}\right)_i = \left(V_B^{[1]}\right)_i = \langle i|V_B|0^{(0)}\rangle \qquad (231)$$

$$A_{ij} = E_{ij}^{[2]} = \langle i|H_0|j\rangle - \delta_{ij}E_0 \qquad (232)$$

$$\left(\hat{V}_B^{[2]}\right)_{ij} = \left(V_B^{[2]}\right)_{ij} = \langle i|V_B|j\rangle - \delta_{ij}\langle 0^{(0)}|V_B|0^{(0)}\rangle \qquad (233)$$

Note, in particular, how the asymmetric Jacobian matrix $\mathbf{A}$ of the general theory now becomes the Hermitian Hessian matrix $\mathbf{E}^{[2]}$. Inserting the identifications of eqs 230 and 233 into the wave function corrections in eqs 220, 221, and 223, which are valid for any reference state, we obtain the following wave function corrections valid for an eigenvector reference state

$$\mathbf{c}_{B_1}^{(1)} = -\left(\mathbf{E}^{[2]} - \omega_{B_1}\mathbf{I}\right)^{-1}\mathbf{V}_{B_1}^{[1]} \qquad (234)$$

$$\mathbf{c}_{B_1,\ B_2}^{(2)} = -P_{[1,\ 2]}\left(\mathbf{E}^{[2]} - \left(\omega_{B_1} + \omega_{B_2}\right)\mathbf{I}\right)^{-1}\mathbf{V}_{B_1}^{[2]}\mathbf{c}_{B_2}^{(1)} \qquad (235)$$

$$\mathbf{c}_{B^n}^{(n)} = -P_{[1,\ n]}\left(\mathbf{E}^{[2]} - \sum_{k=1}^{n}\omega_{B_k}\mathbf{I}\right)^{-1} \times \left(\mathbf{V}_{B_1}^{[2]}\mathbf{c}_{B_2,\ \ldots,\ B_n}^{(n-1)} - \sum_{m=1}^{n-2}\mathbf{c}_{B_2,\ \ldots,\ B_{m+1}}^{(m)}\mathbf{V}_{-B_1}^{[1]\dagger}\mathbf{c}_{B_{m+2},\ \ldots,\ B_n}^{(n-m-1)}\right) \qquad (236)$$

For static perturbations with $\omega_{B_k} = 0$ these responses reduce to the standard time-independent perturbation corrections.

3.2.4. Wave Function Corrections As Functions of the Reference State.

The corrections to the wave function depend on the choice of reference state $|\mathrm{R}\rangle$. However, all observables must be independent of this choice. In section 3.5.2, we will show explicitly that the lowest order observables are independent of the reference state. To prepare for this analysis we here study the relations for the zero-order state and also examine the first-order wave function corrections obtained using different reference states.

We first note that the intermediately normalized zero-order wave function $|\hat{0}^{(0)}(\mathrm{R})\rangle$ of eq 205 (whose dependence on the reference state is now made explicit) and the normalized zero-order state $|0^{(0)}\rangle$ are related as

$$|\hat{0}^{(0)}(\mathrm{R})\rangle = \sqrt{\langle \hat{0}^{(0)}(\mathrm{R})|\hat{0}^{(0)}(\mathrm{R})\rangle}\,|0^{(0)}\rangle \qquad (237)$$

Consider next the first-order corrections, where we examine the relation between the first-order correction using $|\mathrm{R}\rangle$ and the normalized eigenstate $|0^{(0)}\rangle$ as reference states. For this purpose the expressions in eqs 220, 221, and 223 are inconvenient as they refer to expansions in the orthonormal basis $\{|\mathrm{R}\rangle, |i\rangle\}$, which depends on the choice of the reference state $|\mathrm{R}\rangle$. To avoid this dependence we work instead directly in terms of the first-order state expressed as

$$|\hat{0}_{B_1}^{(1)}(\mathrm{R})\rangle = \sum_i c_{B_1,\ i}^{(1)}(\mathrm{R})|i\rangle \qquad (238)$$

To obtain the state representation of the first-order correction we note that the wave function corrections by construction are orthogonal to the reference state. The first-order correction $|\hat{0}_{B_1}^{(1)}(\mathrm{R})\rangle$ of eq 238 is therefore orthogonal to the reference state, $\langle \mathrm{R}|\hat{0}_{B_1}^{(1)}(\mathrm{R})\rangle = 0$, giving the condition

$$P_{\mathrm{R}}|\hat{0}_{B_1}^{(1)}(\mathrm{R})\rangle = |\hat{0}_{B_1}^{(1)}(\mathrm{R})\rangle \qquad (239)$$

The first-order equation in eq 220 may be expanded using the definitions of $\mathbf{A}$ and $\hat{\mathbf{V}}_{B_1}^{[1]}$ in eqs 212 and 214, respectively, giving

$$\langle \hat{i}^{(0)}|\left[\left(H_0 - E_0 - \omega_{B_1}\right)\sum_j c_{B_1,\ j}^{(1)}|j\rangle + V_{B_1}|\hat{0}^{(0)}\rangle\right] = 0 \qquad (240)$$

The first-order equations are thus solved in the space spanned by $\{\langle\hat{i}^{(0)}|\}$, which is the space orthogonal to $\langle\hat{0}^{(0)}|$. The first-order equations can therefore be recast in the basis-independent form

$$\begin{aligned} &P_{\hat{0}^{(0)}}(H_0 - E_0 - \omega_{B_1})|\hat{0}_{B_1}^{(1)}(\mathrm{R})\rangle \\ &\quad = -\sqrt{\langle\hat{0}^{(0)}(\mathrm{R})|\hat{0}^{(0)}(\mathrm{R})\rangle}P_{\hat{0}^{(0)}}V_{B_1}|0^{(0)}\rangle \end{aligned} \tag{241}$$

where we used eq 237. The action of the matrix $\mathrm{P}_{\hat{0}^{(0)}}(H_0{-}E_0{-}\omega_{\mathrm{B}_1})$ on the eigenvector $|0^{(0)}\rangle$ vanishes; thus, eq 241 determines $|\hat{0}_{B_1}^{(1)}(\mathrm{R})\rangle$ to within a component of $|0^{(0)}\rangle$, which is subsequently determined by eq 239. To find the form of $|\hat{0}_{B_1}^{(1)}(\mathrm{R})\rangle$ that fulfills eqs 239 and 241 we first note that the ansatz

$$|\hat{0}_{B_1}^{(1)}(\mathrm{R})\rangle = \sqrt{\langle\hat{0}^{(0)}(\mathrm{R})|\hat{0}^{(0)}(\mathrm{R})\rangle}(|\hat{0}_{B_1}^{(1)}(0^{(0)})\rangle + \alpha|0^{(0)}\rangle) \tag{242}$$

solves the first-order equations in eq 241 for any α. Insertion of the ansatz in eq 242 into eq 239 identifies α, yielding the first-order correction

$$\begin{aligned} |\hat{0}_{B_1}^{(1)}(\mathrm{R})\rangle &= \sqrt{\langle\hat{0}^{(0)}(\mathrm{R})|\hat{0}^{(0)}(\mathrm{R})\rangle} \\ &\quad \times (|\hat{0}_{B_1}^{(1)}(0^{(0)})\rangle - \langle\mathrm{R}|0^{(0)}\rangle^{-1}\langle\mathrm{R}|0_{B_1}^{(1)}(0^{(0)})\rangle|0^{(0)}\rangle) \end{aligned} \tag{243}$$

3.3. Perturbation Expansion of the Quasi-Energy

Having determined the perturbation expansion of the wave function parameters in section 3.2 we are now ready to consider the expansion of the quasi-energy (in the Hermitian form) in orders of the external perturbations. We thereby obtain the time-dependent analogue of the standard perturbation expansion of the energy in time-independent perturbation theory; this expansion is subsequently used in section 3.4 to identify expressions for the response functions.

We assume that the reference state is the eigenstate $|0^{(0)}\rangle$ of the zero-order Hamiltonian, giving the wave function corrections of eqs 234−236 rather than the somewhat more complicated wave function corrections for a general reference state in eqs 220, 221, and 223. In terms of the intermediately normalized wave function the quasi-energy of eq 172 becomes

$$\mathcal{Q} = \left\{\frac{\langle\hat{0}|H - \mathrm{i}\partial_t|\hat{0}\rangle}{\langle\hat{0}|\hat{0}\rangle}\right\}_T \tag{244}$$

Remembering that $\mathbf{c}^{(0)}$ is the expansion for the state $|0^{(0)}\rangle$, here $\{1,0\}$ and introducing the matrices $\mathbf{H}_0$ and $\mathbf{V}_B$ for the operators H_0 and V_B, respectively, in the orthonormal basis $\{|0^{(0)}\rangle, |i\rangle\}$, the numerator and denominator of the time-dependent quasi-energy may be written in the form

$$\begin{aligned} E(t) &= \langle\hat{0}|H - \mathrm{i}\partial_t|\hat{0}\rangle \\ &= \left(\mathbf{c}^{(0)} + \Delta\mathbf{c}\right)^\dagger\left(\mathbf{H}_0 + \sum_B \varepsilon_B\mathbf{V}_B e^{-\mathrm{i}\omega_B t} - \mathrm{i}\partial_t\right)\left(\mathbf{c}^{(0)} + \Delta\mathbf{c}\right) \end{aligned} \tag{245}$$

$$S(t) = \langle\hat{0}|\hat{0}\rangle = 1 + \Delta\mathbf{c}^\dagger\Delta\mathbf{c} \tag{246}$$

The time-dependent quasi-energy $Q(t)$ and the quantities $E(t)$ and $S(t)$ may be expanded in the external perturbations as

$$Q(t) = \sum_{n=0}^{\infty}\sum_{B^n}\left(\prod_{k=1}^{n}\varepsilon_{B_k}\right)Q_{B^n}^{(n)}\, e^{-\mathrm{i}\sum_{k=1}^{n}\omega_{B_k}t} \tag{247}$$

$$E(t) = \sum_{n=0}^{\infty}\sum_{B^n}\left(\prod_{k=1}^{n}\varepsilon_{B_k}\right)E_{B^n}^{(n)}\, e^{-\mathrm{i}\sum_{k=1}^{n}\omega_{B_k}t} \tag{248}$$

$$S(t) = \sum_{n=0}^{\infty}\sum_{B^n}\left(\prod_{k=1}^{n}\varepsilon_{B_k}\right)S_{B^n}^{(n)}\, e^{-\mathrm{i}\sum_{k=1}^{n}\omega_{B_k}t} \tag{249}$$

To accommodate the zero-order terms in these expressions we conventionally set $\prod_{k=1}^{0}\varepsilon_{B_k} = 1$. We furthermore require that the corrections $Q_{B^n}^{(n)}$, $E_{B^n}^{(n)}$, and $S_{B^n}^{(n)}$ are permutationally symmetric, for instance, $Q_{B_1,B_2}^{(2)} = Q_{B_2,B_1}^{(2)}$. The nth-order corrections are then proportional to the nth-order derivatives of the quasi-energy

$$\frac{\mathrm{d}^n Q}{\mathrm{d}\varepsilon_{B_1}\ldots\mathrm{d}\varepsilon_{B_n}} = \frac{1}{n!}Q_{B^n}^{(n)} \tag{250}$$

and likewise for $E_{B^n}^{(n)}$ and $S_{B^n}^{(n)}$.

Inserting the expansion of the intermediate wave function from eq 218 in eqs 248 and 249, the expansions of $E(t)$ and $S(t)$ become

$$\begin{aligned} E_{B^n}^{(n)} &= P_{[1,\,n]}\sum_{m=0}^{n}\mathbf{c}_{-B_1,\,\ldots,\,-B_m}^{(m)\dagger}\left(\mathbf{H}_0 - \sum_{k=m+1}^{n}\omega_{B_k}\mathbf{I}\right)\mathbf{c}_{B_{m+1},\,\ldots,\,B_n}^{(n-m)} \\ &\quad + P_{[1,\,n]}\sum_{m=0}^{n-1}\mathbf{c}_{-B_2,\,\ldots,\,-B_{m+1}}^{(m)\dagger}\mathbf{V}_{B_1}\mathbf{c}_{B_{m+2},\,\ldots,\,B_n}^{(n-m-1)} \end{aligned} \tag{251}$$

$$S_{B^n}^{(n)} = P_{[1,\,n]}\sum_{m=0}^{n}\mathbf{c}_{-B_1,\,\ldots,\,-B_m}^{(m)\dagger}\mathbf{c}_{B_{m+1},\,\ldots,\,B_n}^{(n-m)} \tag{252}$$

Using eq 178 we obtain for the lowest order terms in the expansion of $S(t)$ the contributions

$$S^{(0)} = \mathbf{c}^{(0)\dagger}\mathbf{c}^{(0)} = 1 \tag{253}$$

$$S_{B_1}^{(1)} = \mathbf{c}_{-B_1}^{(1)\dagger}\mathbf{c}^{(0)} + \mathbf{c}^{(0)\dagger}\mathbf{c}_{B_1}^{(1)} = 0 \tag{254}$$

Expansion of the time-dependent quasi-energy $Q(t)$ is most conveniently determined from $Q(t)S(t) = E(t)$, which by eqs 253 and 254 leads to the identification

$$Q_{B^n}^{(n)} = P_{[1,\,n]}\left(E_{B^n}^{(n)} - \sum_{m=0}^{n-2}Q_{B_1,\,\ldots,\,B_m}^{(m)}S_{B_{m+1},\,\ldots,\,B_n}^{(n-m)}\right) \tag{255}$$

For the zero-order correction we trivially obtain that

$$Q^{(0)} = E_0 \tag{256}$$

Next, given that $\mathbf{c}^{(0)}$ is an eigenvector of $\mathbf{H}_0$ and that the wave function correction $\mathbf{c}_{B_1}^{(1)}$ is orthogonal to the zero-order state $\mathbf{c}^{(0)}$, we obtain the following first-order correction to the quasi-energy

$$\begin{aligned} Q_{B_1}^{(1)} &= E_{B_1}^{(1)} = \mathbf{c}^{(0)\dagger}(\mathbf{H}_0 - \omega_{B_1}\mathbf{I})\mathbf{c}_{B_1}^{(1)} + \mathbf{c}_{-B_1}^{(1)\dagger}\mathbf{H}_0\mathbf{c}^{(0)} \\ &\quad + \mathbf{c}^{(0)\dagger}\mathbf{V}_{B_1}\mathbf{c}^{(0)} = \mathbf{c}^{(0)\dagger}\mathbf{V}_{B_1}\mathbf{c}^{(0)} \end{aligned} \tag{257}$$

To obtain the second-order correction to the time-dependent quasi-energy we first write

$$\begin{aligned} Q^{(2)}_{B_1,\,B_2} &= P_{[1,\,2]}(\mathbf{c}^{(0)\dagger}(\mathbf{H}_0 - (\omega_{B_1} + \omega_{B_2})\mathbf{I})\mathbf{c}^{(2)}_{B_1,\,B_2} \\ &\quad + \mathbf{c}^{(2)\dagger}_{-B_1,\,-B_2}\mathbf{H}_0\mathbf{c}^{(0)} + \mathbf{c}^{(1)\dagger}_{B_1}(\mathbf{H}_0 - \omega_{B_2}\mathbf{I})\mathbf{c}^{(1)}_{B_2} \\ &\quad + \mathbf{c}^{(0)\dagger}\mathbf{V}_{B_2}\mathbf{c}^{(1)}_{B_1} + \mathbf{c}^{(1)\dagger}_{-B_1}\mathbf{V}_{B_2}\mathbf{c}^{(0)} \\ &\quad - E_0\left(\mathbf{c}^{(0)\dagger}\mathbf{c}^{(2)}_{B_1,\,B_2} + \mathbf{c}^{(2)\dagger}_{-B_1,\,-B_2}\mathbf{c}^{(0)} + \mathbf{c}^{(1)\dagger}_{B_1}\mathbf{c}^{(1)}_{B_2})\right) \\ &= P_{[1,\,2]}\left(\mathbf{c}^{(1)\dagger}_{-B_1}\left(\mathbf{E}^{[2]} - \omega_{B_2}\mathbf{I}\right)\mathbf{c}^{(1)}_{B_2} + \mathbf{c}^{(1)\dagger}_{-B_1}\mathbf{V}^{[1]}_{B_2} + \mathbf{V}^{[1]\dagger}_{-B_2}\mathbf{c}^{(1)}_{B_1}\right) \end{aligned} \tag{258}$$

where we used the definitions of $\mathbf{E}^{[2]}$ and $\mathbf{V}_B{}^{[1]}$ of eq 233 and the orthogonality of the wave function corrections to the zero-order state. From the first-order equations in eq 234 we find that the first two terms in the final expression in eq 258 cancel, yielding the following simple expression for the second-order time-dependent quasi-energy

$$Q^{(2)}_{B_1,\,B_2} = P_{[1,\,2]}\mathbf{V}^{[1]\dagger}_{-B_1}\mathbf{c}^{(1)}_{B_2} \tag{259}$$

We note that the second-order energy depends only on the first-order wave function, while the zero- and first-order energies in eqs 256 and 257 depend only on the zero-order wave function.

We next consider the corresponding perturbation expansion of the time-averaged quasi-energy $\mathcal{Q}$. From the relation

$$\frac{1}{T}\int_0^T e^{in\omega t}\,dt = \frac{1}{T}\int_0^T e^{in2\pi t/T}\,dt = \delta_{n,\,0} \tag{260}$$

we observe that the time average of $Q^{(n)}_{B^n}e^{i\Sigma_k\omega_{B_k}t}$ vanishes unless $\Sigma_k\omega_{Bk} = 0$. We therefore obtain the following expansion of the time-averaged quasi-energy

$$\mathcal{Q} = \sum_n \sum_{B^n:\,\sum\limits_k \omega_{B_k}=0} \left(\prod_k \varepsilon_{B_k}\right)\mathcal{Q}^{(n)}_{B^n} \tag{261}$$

with trivial relations between the time-averaged and time-dependent quasi-energy corrections

$$\mathcal{Q}^{(n)}_{B^n} = \begin{cases} Q^{(n)}_{B^n} & \text{if } \sum\limits_k \omega_{B_k} = 0 \\ 0 & \text{otherwise} \end{cases} \tag{262}$$

The time-averaged quasi-energy $\mathcal{Q}$ is variational in each of the nonvanishing components of the perturbation expansion. In particular, because $\mathcal{Q}^{(2n)}_{B^{2n}}$ and $\mathcal{Q}^{(2n+1)}_{B^{2n+1}}$ are linear in the wave function corrections $\mathbf{c}^{(k)}$ of orders $k > n$, these corrections do not contribute. Thus, to determine the time-averaged quasi-energy to order $2n + 1$ it is only necessary to include the wave function corrections up to order n. This is an example of the $2n + 1$ rule, which is proved in section 3.6.

With this observation we are ready to develop compact forms for the lower order corrections to the quasi-energy. In the following we consider the perturbation component with index B_0 since the expectation value of the V_{B_0} operator will be the central quantity when identifying the response functions in section 3.4. The corresponding frequency ω_{B_0} is chosen such that the sum of all the frequencies for a given correction vanishes. The first- and second-order quasi-energies become

$$\mathcal{Q}^{(1)}_{B_0} = \mathbf{c}^{(0)\dagger}\mathbf{V}_{B_0}\mathbf{c}^{(0)}, \qquad \omega_{B_0} = 0 \tag{263}$$

$$\mathcal{Q}^{(2)}_{B_0,\,B_1} = P_{[0,\,1]}\mathbf{V}^{[1]\dagger}_{-B_0}\mathbf{c}^{(1)}_{B_1},\ \omega_{B_0} = -\omega_{B_1} \tag{264}$$

Using the first-order equations in eq 220 and $\omega_{-B_0} = \omega_{B_1}$ the second-order quasi-energy correction may alternatively be written in the form

$$\begin{aligned} \mathcal{Q}^{(2)}_{B_0,\,B_1} &= P_{[0,\,1]}\mathbf{V}^{[1]\dagger}_{-B_0}\mathbf{c}^{(1)}_{B_1} = P_{[0,\,1]}\mathbf{V}^{[1]\dagger}_{-B_0}(\mathbf{E}^{[2]} - \omega_{-B_0}\mathbf{I})^{-1}\mathbf{V}^{[1]}_{B_1} \\ &= P_{[0,\,1]}\mathbf{c}^{(1)\dagger}_{-B_0}\mathbf{V}^{[1]}_{B_1} \end{aligned} \tag{265}$$

To obtain the third-order quasi-energy we expand eq 255, including only wave function corrections to first order, and then use the expression for $\mathbf{V}^{[2]}$ in eq 233

$$\begin{aligned} \mathcal{Q}^{(3)}_{B_0,\,B_1,\,B_2} &= P_{[0,\,2]}\left(\mathbf{c}^{(1)\dagger}_{-B_0}\mathbf{V}_{B_1}\mathbf{c}^{(1)}_{B_2} - E^{(1)}_{B_1}\mathbf{c}^{(1)\dagger}_{-B_0}\mathbf{c}^{(1)}_{B_2}\right) \\ &= P_{[0,\,2]}\mathbf{c}^{(1)\dagger}_{-B_0}\mathbf{V}^{[2]}_{B_1}\mathbf{c}^{(1)}_{B_2},\ \omega_{B_0} = -(\omega_{B_1} + \omega_{B_2}) \end{aligned} \tag{266}$$

The fourth-order energy is obtained by first expanding eq 255 using only wave function corrections to second order and then the definitions of $\mathbf{E}^{[2]}$ and $\mathbf{V}^{[2]}$ in eqs 232 and 233 yielding

$$\begin{aligned} \mathcal{Q}^{(4)}_{B_0,\,B_1,\,B_2,\,B_3} &= P_{[0,\,3]}\left(\mathbf{c}^{(2)\dagger}_{-B_0,\,-B_1}(\mathbf{H}_0 - (\omega_{B_2} + \omega_{B_3})\mathbf{I})\mathbf{c}^{(2)}_{B_2,\,B_3}\right. \\ &\quad + \mathbf{c}^{(2)\dagger}_{-B_0,\,-B_1}\mathbf{V}_{B_2}\mathbf{c}^{(1)}_{B_3} + \mathbf{c}^{(1)\dagger}_{-B_0}\mathbf{V}_{B_1}\mathbf{c}^{(2)}_{B_2,\,B_3} \\ &\quad - E^{(0)}\mathbf{c}^{(2)\dagger}_{-B_0,\,-B_1}\mathbf{c}^{(2)}_{B_2,\,B_3} - E^{(1)}_{B_1}\mathbf{c}^{(1)\dagger}_{-B_0}\mathbf{c}^{(2)}_{B_2,\,B_3} \\ &\quad - E^{(1)}_{B_2}\mathbf{c}^{(2)\dagger}_{-B_0,\,-B_1}\mathbf{c}^{(1)}_{B_3} - Q^{(2)}_{B_0,\,B_1}S^{(2)}_{B_2,\,B_3}) \\ &= P_{[0,\,3]}\left(\mathbf{c}^{(2)\dagger}_{-B_0,\,-B_1}\left(\mathbf{E}^{[2]} - (\omega_{B_2} + \omega_{B_3})\mathbf{I}\right)\mathbf{c}^{(2)}_{B_2,\,B_3}\right. \\ &\quad + P_{[2,\,3]}\mathbf{c}^{(2)\dagger}_{-B_0,\,-B_1}\mathbf{V}^{[2]}_{B_2}\mathbf{c}^{(1)}_{B_3} \\ &\quad \left. + \mathbf{c}^{(1)\dagger}_{-B_0}\mathbf{V}^{[2]}_{B_1}\mathbf{c}^{(2)}_{B_2,\,B_3} - Q^{(2)}_{B_0,\,B_1}S^{(2)}_{B_2,\,B_3}\right) \end{aligned} \tag{267}$$

which by eq 235 simplifies to the following expression

$$\begin{aligned} \mathcal{Q}^{(4)}_{B_0,\,B_1,\,B_2,\,B_3} &= P_{[0,\,3]}\left(\mathbf{c}^{(1)\dagger}_{-B_0}\mathbf{V}^{[2]}_{B_1}\mathbf{c}^{(2)}_{B_2,\,B_3} - Q^{(2)}_{B_0,\,B_1}S^{(2)}_{B_2,\,B_3}\right), \\ \omega_{B_0} &= -(\omega_{B_1} + \omega_{B_2} + \omega_{B_3}) \end{aligned} \tag{268}$$

for the fourth-order quasi-energy.

3.4. Response Functions

To introduce response functions we now consider the expectation value of the operator V_{B_0} and the expansion of this expectation value in orders of the external perturbation. Subsequently, we identify the response functions with derivatives of the quasi-energy and use these identifications to obtain explicit expressions for response functions to third order. Having examined the symmetries of the response functions we finally examine their residues.

3.4.1. Definition of Response Functions. To introduce response functions we consider the Hamiltonian eq 157, where terms with indices B_0 and $-B_0$ are omitted from the perturbation

$$V(t) = \sum_{B\neq\pm B_0} \varepsilon_B V_B e^{-i\omega_B t} = \sum_B{}' \varepsilon_B V_B e^{-i\omega_B t} \tag{269}$$

Here and in the following the prime indicates that terms with indices B_0 and $-B_0$ are omitted, unlike the perturbation in eq 199. The response functions are now defined as terms in the perturbation expansion of the expectation value of an operator V_{B_0}

$$\begin{aligned}\langle V_{B_0}\rangle'(t) = \langle\langle V_{B_0}\rangle\rangle \quad &+ \sum_{B_1}{}'\varepsilon_{B_1}\langle\langle V_{B_0}; V_{B_1}\rangle\rangle_{\omega_{B_1}} \mathrm{e}^{-\mathrm{i}\omega_{B_1}t} \\ &+\frac{1}{2!}\sum_{B_1,\ B_2}{}'\ \varepsilon_{B_1}\varepsilon_{B_2}\langle\langle V_{B_0}; V_{B_1},\ V_{B_2}\rangle\rangle_{\omega_{B_1},\ \omega_{B_2}} \mathrm{e}^{-\mathrm{i}(\omega_{B_1}+\omega_{B_2})t} \\ &+\frac{1}{3!}\sum_{B_1,\ B_2,\ B_3}{}'\ \varepsilon_{B_1}\varepsilon_{B_2}\varepsilon_{B_3}\langle\langle V_{B_0}; V_{B_1},\ V_{B_2},\ V_{B_3}\rangle\rangle_{\omega_{B_1},\ \omega_{B_2},\ \omega_{B_3}} \\ &\times \mathrm{e}^{-\mathrm{i}(\omega_{B_1}+\omega_{B_2}+\omega_{B_3})t} + \ldots\end{aligned} \tag{270}$$

The terms $\langle\langle V_{B_0}\rangle\rangle$, $\langle\langle V_{B_0};V_{B_1}\rangle\rangle_{\omega_{B_1}}$, $\langle\langle V_{B_0};V_{B_1},V_{B_2}\rangle\rangle_{\omega_{B_1},\ \omega_{B_2}}$, and $\langle\langle V_{B_0};V_{B_1},V_{B_2},V_{B_3}\rangle\rangle_{\omega_{B1},\omega_{B2},\omega_{B3}}$ are the zero-order, linear, quadratic, and cubic response functions, respectively,[70] which describe how the expectation value of an operator V_{B_0} responds to a set of external perturbations to zero, first, second, and third orders in the perturbation strengths. Note that the response functions do not depend on the representation of the wave function, in particular, they do not depend on whether a Hermitian (eq 177) or a non-Hermitian (eq 198) form of the expectation value is used. For example, using the Hermitian form it follows that $\langle V_{B_0}\rangle'(t) = \langle 0|V_{B_0}|0'\rangle$, where $|0\rangle$ is the time-dependent wave function in eq 156 for the perturbation in eq 269, while the zero-order response function is a simple expectation value for the normalized eigenfunction of the unperturbed state: $\langle\langle V_{B_0}\rangle\rangle = \langle 0^{(0)}|V_{B_0}|0^{(0)}\rangle$.

3.4.2. Response Functions As Derivatives of the Quasi-Energy.

To establish a connection between the expansion of the expectation value in response functions and the expansion of the quasi-energy we first take the time average of the expectation value of $V_{B_0}\mathrm{e}^{-\mathrm{i}\omega_{B_0}t}$. Using eq 260 we obtain

$$\begin{aligned}\left\{\langle V_{B_0}\rangle' e^{-\mathrm{i}\omega_{B_0}t}\right\}_T = \langle\langle V_{B_0}\rangle\rangle \quad &+ \sum_{\substack{B_1:\\ \omega_{B_0}+\omega_{B_1}=0}}{}' \varepsilon_{B_1}\langle\langle V_{B_0}; V_{B_1}\rangle\rangle_{\omega_{B_1}} \\ +\frac{1}{2!} &\sum_{\substack{B_1,\ B_2:\\ \omega_{B_0}+\omega_{B_1}+\omega_{B_2}=0}}{}' \varepsilon_{B_1}\varepsilon_{B_2}\langle\langle V_{B_0}; V_{B_1},\ V_{B_2}\rangle\rangle_{\omega_{B_1},\ \omega_{B_2}} \\ +\frac{1}{3!} &\sum_{\substack{B_1,\ B_2,\ B_3:\\ \omega_{B_0}+\omega_{B_1}+\omega_{B_2}+\omega_{B_3}=0}}{}' \varepsilon_{B_1}\varepsilon_{B_2}\varepsilon_{B_3}\langle\langle V_{B_0}; V_{B_1},\ V_{B_2},\ V_{B_3}\rangle\rangle_{\omega_{B_1},\ \omega_{B_2},\ \omega_{B_3}} + \ldots\end{aligned} \tag{271}$$

An alternative identification of the time-averaged expectation value $\{\langle V_{B_0}\rangle\mathrm{e}^{-\mathrm{i}\omega_{B_0}t}\}_T$ is obtained using the time-dependent Hellmann–Feynman theorem eq 177 for the perturbation of eq 199 followed by eq 261

$$\begin{aligned}\left\{\langle V_{B_0}\rangle'\mathrm{e}^{-\mathrm{i}\omega_{B_0}t}\right\}_T &= \left.\frac{\mathrm{d}\mathscr{Q}}{\mathrm{d}\varepsilon_{B_0}}\right|_{\varepsilon_{B_0}=\varepsilon_{-B_0}=0} = \mathscr{Q}^{(1)}_{B_0}\delta_{\omega_{B_0},\ 0} \\ &+2\sum_{\substack{B_1:\\ \omega_{B_0}+\omega_{B_1}=0}}{}' \varepsilon_{B_1}\mathscr{Q}^{(2)}_{B_0,\ B_1} + 3\sum_{\substack{B_1,\ B_2:\\ \omega_{B_0}+\omega_{B_1}+\omega_{B_2}=0}}{}' \varepsilon_{B_1}\varepsilon_{B_2}\mathscr{Q}^{(3)}_{B_0,\ B_1,\ B_2} \\ &+4\sum_{\substack{B_1,\ B_2,\ B_3:\\ \omega_{B_0}+\omega_{B_1}+\omega_{B_2}+\omega_{B_3}=0}}{}' \varepsilon_{B_1}\varepsilon_{B_2}\varepsilon_{B_3}\mathscr{Q}^{(4)}_{B_0,\ B_1,\ B_2,\ B_3}\end{aligned} \tag{272}$$

Comparing eqs 271 and 272 we obtain the identifications

$$\langle\langle V_{B_0}\rangle\rangle = \frac{\mathrm{d}\mathscr{Q}}{\mathrm{d}\varepsilon_{B_0}} = \mathscr{Q}^{(1)}_{B_0} \tag{273}$$

$$\langle\langle V_{B_0}; V_{B_1}\rangle\rangle_{\omega_{B_1}} = \frac{\mathrm{d}^2\mathscr{Q}}{\mathrm{d}\varepsilon_{B_0}\mathrm{d}\varepsilon_{B_1}} = 2\mathscr{Q}^{(2)}_{B_0,\ B_1} \tag{274}$$

$$\begin{aligned}\langle\langle V_{B_0}; V_{B_1},\ V_{B_2}\rangle\rangle_{\omega_{B_1},\ \omega_{B_2}} &= \frac{\mathrm{d}^3\mathscr{Q}}{\mathrm{d}\varepsilon_{B_0}\mathrm{d}\varepsilon_{B_1}\mathrm{d}\varepsilon_{B_2}} \\ &= 3!\mathscr{Q}^{(3)}_{B_0,\ B_1,\ B_2}\end{aligned} \tag{275}$$

$$\begin{aligned}&\langle\langle V_{B_0}; V_{B_1},\ V_{B_2},\ V_{B_2}\rangle\rangle_{\omega_{B_1},\ \omega_{B_2},\ \omega_{B_3}} \\ &= \frac{\mathrm{d}^4\mathscr{Q}}{\mathrm{d}\varepsilon_{B_0}\mathrm{d}\varepsilon_{B_1}\mathrm{d}\varepsilon_{B_2}\mathrm{d}\varepsilon_{B_3}} = 4!\mathscr{Q}^{(4)}_{B_0,\ B_1,\ B_2,\ B_3}\end{aligned} \tag{276}$$

and conclude that the response functions are the derivatives of the quasi-energy (in the Hermitian form) with respect to the perturbation parameters. We shall later extend this identification to the quasi-energy in the Lagrangian form.

3.4.3. Explicit Expressions for the Linear, Quadratic, and Cubic Response Functions.

In section 3.4.2, we expressed the response functions in terms of the quasi-energy corrections $Q^{(n)}_{B^n}$. We now combine these identifications with the results of section 3.3 to express the response functions in terms of wave function corrections.

If we are only interested in lower order response functions, up to the cubic response function, for instance, then it is convenient to introduce a more compact notation for the operators and frequencies. We use A, B, C, and D for the operators V_{B_0}, V_{B_1}, V_{B_2}, and V_{B_3}, respectively, and ω_A, ω_B, ω_C, and ω_D for the frequencies ω_{B_0}, ω_{B_1}, ω_{B_2}, and ω_{B_3}, respectively. The paired operators occur again with opposite frequencies, for example, $\omega_{A^\dagger} = -\omega_A$. We furthermore assume that the basis vectors $|i\rangle$ are eigenfunctions of H_0 with energies E_i, in which case the matrix $\mathbf{E}^{[2]}$ in eq 232 becomes diagonal

$$E^{[2]}_{ij} = \delta_{ij}\omega_i,\ \omega_i = E_i - E_0 \tag{277}$$

Using eq 276 and the form of the response functions in eqs 264, 266, and 268 we arrive at the spectral representation of the response functions[71]

$$\begin{aligned}\langle\langle A; B\rangle\rangle_{\omega_B} &= 2!P^{\omega_A}_{[A,\ B]}\mathbf{V}^{[1]\dagger}_{A^\dagger}\mathbf{c}^{(1)}_B \\ &= 2!P^{\omega_A}_{[A,\ B]}\sum_i \frac{\langle 0^{(0)}|A|i\rangle\langle i|B|0^{(0)}\rangle}{\omega_B - \omega_i}\end{aligned} \tag{278}$$

$$\begin{aligned}\langle\langle A; B,\ C\rangle\rangle_{\omega_B,\ \omega_C} &= 3!P^{\omega_A}_{[A,\ B,\ C]}\mathbf{c}^{(1)\dagger}_{A^\dagger}\mathbf{V}^{[2]}_B\mathbf{c}^{(1)}_C \\ &= -3!P^{\omega_A}_{[A,\ B,\ C]}\sum_{ij}\frac{\langle 0^{(0)}|A|i\rangle\langle i|\overline{B}|j\rangle\langle j|C|0^{(0)}\rangle}{(\omega_A + \omega_i)(\omega_C - \omega_j)}\end{aligned} \tag{279}$$

$$\langle\langle A; B, C, D\rangle\rangle_{\omega_B, \omega_C, \omega_D} = 4! P^{\omega_A}_{[A, B, C, D]} \left(\mathbf{c}^{(1)\dagger}_{A^\dagger} \mathbf{V}^{[2]}_B \mathbf{c}^{(2)}_{C, D} - \mathcal{Q}^{(2)}_{A, B} S^{(2)}_{C, D} \right)$$

$$= -4! P^{\omega_A}_{[A, B, C, D]} \left(\sum_{ijk} \frac{\langle 0^{(0)}|A|i\rangle\langle i|\bar{B}|j\rangle\langle j|\bar{C}|k\rangle\langle k|D|0^{(0)}\rangle}{(\omega_A + \omega_i)(\omega_C + \omega_D - \omega_j)(\omega_D - \omega_k)} - \sum_{ij} \frac{\langle 0^{(0)}|A|i\rangle\langle i|B|0^{(0)}\rangle}{\omega_B - \omega_i} \frac{\langle 0^{(0)}|C|j\rangle\langle j|D|0^{(0)}\rangle}{(\omega_C + \omega_j)(\omega_D - \omega_j)} \right) \tag{280}$$

where we introduced the shorthand notation

$$\bar{X} = X - \langle 0^{(0)}|X|0^{(0)}\rangle \tag{281}$$

and where $P^{\omega_A}_{[A,B,C,D]}$ averages over all permutations of A, B, C, D and adjusts the frequency ω_A such that all frequencies add up to zero: $\omega_A + \omega_B + \omega_C + \omega_D = 0$. As a result, we obtain from eq 278 the following well-known expression for the linear response function in the spectral representation

$$\langle\langle A; B\rangle\rangle_{\omega_B} = \sum_i \frac{\langle 0^{(0)}|A|i\rangle\langle i|B|0^{(0)}\rangle}{\omega_B - \omega_i} - \sum_i \frac{\langle 0^{(0)}|B|i\rangle\langle i|A|0^{(0)}\rangle}{\omega_B + \omega_i} \tag{282}$$

3.4.4. Symmetry Properties of Response Functions.

A number of symmetry relations and identities exist between response functions of the same order. First, as the response functions are symmetric in the permutation of the indices we have

$$\langle\langle A; B\rangle\rangle_{\omega_B} = \langle\langle B; A\rangle\rangle_{\omega_A} = \langle\langle B; A\rangle\rangle_{-\omega_B} \tag{283}$$

$$\begin{aligned}\langle\langle A; B, C\rangle\rangle_{\omega_B, \omega_C} &= \langle\langle A; C, B\rangle\rangle_{\omega_C, \omega_B} \\ &= \langle\langle C; A, B\rangle\rangle_{\omega_A, \omega_B}\end{aligned} \tag{284}$$

$$\begin{aligned}\langle\langle A; B, C, D\rangle\rangle_{\omega_B, \omega_C, \omega_D} &= \langle\langle A; C, B, D\rangle\rangle_{\omega_C, \omega_B, \omega_D} \\ &= \langle\langle D; A, B, C\rangle\rangle_{\omega_A, \omega_B, \omega_C}\end{aligned} \tag{285}$$

Next, assuming that the operators A, B, C, D are Hermitian, additional relations are obtained by setting $\langle A\rangle^* = \langle A\rangle$ in eq 270. Using eqs 200 and 202 we then obtain the following relations

$$\langle\langle A; B\rangle\rangle_{\omega_B} = \langle\langle A; B\rangle\rangle^*_{-\omega_B} \tag{286}$$

$$\langle\langle A; B, C\rangle\rangle_{\omega_B, \omega_C} = \langle\langle A; B, C\rangle\rangle^*_{-\omega_B, -\omega_C} \tag{287}$$

$$\langle\langle A; B, C, D\rangle\rangle_{\omega_B, \omega_C, \omega_D} = \langle\langle A; B, C, D\rangle\rangle^*_{-\omega_B, -\omega_C, -\omega_D} \tag{288}$$

between response functions at positive and negative frequencies.

3.4.5. Residues of Response Functions.

From the spectral representations of the linear, quadratic, and cubic response functions given in eqs 278−280 it is seen that these tend to $\pm\infty$ when the frequency parameters ω_A, ω_B, ... tend to plus or minus an excitation energy, $\pm\omega_f$, of the unperturbed system. For example, the linear response function of eq 278 becomes infinite for $\omega_B \rightarrow \omega_f$. However, if the linear response function is multiplied by $\omega_B - \omega_f$, then the resulting function $(\omega_B - \omega_f)\langle\langle A;B\rangle\rangle_{\omega_B}$ is finite for $\omega_B \rightarrow \omega_f$ and the linear response function is said to have a first-order pole with an associated residue $\lim_{\omega_B\rightarrow\omega_f}(\omega_B - \omega_f)\langle\langle A;B\rangle\rangle_{\omega_B}$. Higher order response functions have a more complicated pole structure, for example, the cubic response function $\langle\langle A;B,C,D\rangle\rangle_{\omega_B,\omega_C,\omega_D}$ has poles at $\omega_C + \omega_D = \pm\,\omega_f$, see eq 280.

The residues of the response functions provide important information about the unperturbed system. From eq 278 we obtain the single residues of the linear response function as

$$\lim_{\omega_B \rightarrow \omega_i} (\omega_B - \omega_i)\langle\langle A; B\rangle\rangle_{\omega_B} = \langle 0^{(0)}|A|i\rangle\langle i|B|0^{(0)}\rangle \tag{289}$$

$$\lim_{\omega_B \rightarrow -\omega_i} (\omega_B + \omega_i)\langle\langle A; B\rangle\rangle_{\omega_B} = -\langle 0^{(0)}|B|i\rangle\langle i|A|0^{(0)}\rangle \tag{290}$$

From these residues we obtain transition-matrix elements $\langle 0^{(0)}|A|i\rangle$ of an operator A between the reference state $|0^{(0)}\rangle$ and states $|i\rangle$ different from the reference state. Assuming that these transition moments are known, the transition moments of an operator A between two states $|i\rangle$ and $|j\rangle$ both different from the reference state $|0^{(0)}\rangle$ are obtained from the double residues of the quadratic response function in eq 279

$$\lim_{\omega_B \rightarrow -\omega_i} (\omega_B + \omega_i) \lim_{\omega_C \rightarrow \omega_j} (\omega_C - \omega_j)\langle\langle A; B, C\rangle\rangle_{\omega_B, \omega_C} = -\langle 0^{(0)}|B|i\rangle\langle i|\bar{A}|j\rangle\langle j|C|0^{(0)}\rangle \tag{291}$$

Finally, the following single residue of the quadratic response function

$$\lim_{\omega_C \rightarrow \omega_i} (\omega_C - \omega_i)\langle\langle A; B, C\rangle\rangle_{\omega_B, \omega_C} = -P^{\omega_A}_{[A, B]} \sum_j \frac{\langle 0^{(0)}|A|j\rangle\langle j|\bar{B}|i\rangle\langle i|C|0^{(0)}\rangle}{\omega_A + \omega_j} \tag{292}$$

is important for calculation of induced transitions.

3.4.6. Equations of Motion for Response Functions.

In this subsection we consider a set of relations between response functions known as the equations of motion.[72] To obtain these relations we use the time-dependent Schrödinger equation in eq 156 to write the total time derivative of an expectation value of a time-independent operator V_{B_0} in the form

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle 0(t)|V_{B_0}|0(t)\rangle &= \langle \partial_t 0(t)|V_{B_0}|0(t)\rangle + \langle 0(t)|V_{B_0}|\partial_t 0(t)\rangle \\ &= -\mathrm{i}\langle 0(t)|[V_{B_0}, H]|0(t)\rangle\end{aligned} \tag{293}$$

which constitutes the Ehrenfest equation for the operator V_{B_0}.[73] Assuming that neither V_{B_0} nor any terms in the Hamiltonian contains terms involving time differentiation, eq 159 may be used to write the expectation values of eq 293 in terms of the regular wave function $|\tilde{0}\rangle$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle \tilde{0}|V_{B_0}|\tilde{0}\rangle &= \langle \partial_t\tilde{0}|V_{B_0}|\tilde{0}\rangle + \langle \tilde{0}|V_{B_0}|\partial_t\tilde{0}\rangle \\ &= -\mathrm{i}\langle \tilde{0}|[V_{B_0}, H]|\tilde{0}\rangle\end{aligned} \tag{294}$$

Expanding the expectation values in eq 294 in response functions using eq 270 we obtain

$$
\begin{aligned}
&-\mathrm{i}\sum_{B_1}\omega_{B_1}\varepsilon_{B_1}\langle\langle V_{B_0};V_{B_1}\rangle\rangle_{\omega_{B_1}}\mathrm{e}^{-\mathrm{i}\omega_{B_1}t}\\
&-\frac{\mathrm{i}}{2}\sum_{B_1,\,B_2}\varepsilon_{B_1}\varepsilon_{B_2}(\omega_{B_1}+\omega_{B_2})\langle\langle V_{B_0};V_{B_1},V_{B_2}\rangle\rangle_{\omega_{B_1},\,\omega_{B_2}}\mathrm{e}^{-\mathrm{i}(\omega_{B_1}+\omega_{B_2})t}+\ldots\\
&=-\mathrm{i}\sum_{B_1}\varepsilon_{B_1}\left(\langle 0^{(0)}|[V_{B_0},V_{B_1}]|0^{(0)}\rangle+\langle\langle[V_{B_0},H_0];V_{B_1}\rangle\rangle_{\omega_{B_1}}\right)\mathrm{e}^{-\mathrm{i}\omega_{B_1}t}\\
&-\frac{\mathrm{i}}{2}\sum_{B_1,\,B_2}\varepsilon_{B_1}\varepsilon_{B_2}\Big(2\langle\langle[V_{B_0},V_{B_1}];V_{B_2}\rangle\rangle_{\omega_{B_2}}\\
&+\langle\langle[V_{B_0},H_0];V_{B_1},V_{B_2}\rangle\rangle_{\omega_{B_1},\,\omega_{B_2}}\Big)\mathrm{e}^{-\mathrm{i}(\omega_{B_1}+\omega_{B_2})t}+\ldots
\end{aligned}
\tag{295}
$$

By equating terms of the same order in the perturbation strength we obtain the following equations of motion

$$
\begin{aligned}
\omega_{B_1}\langle\langle V_{B_0};V_{B_1}\rangle\rangle_{\omega_{B_1}}&=\langle 0^{(0)}|[V_{B_0},V_{B_1}]|0^{(0)}\rangle\\
&+\langle\langle[V_{B_0},H_0];V_{B_1}\rangle\rangle_{\omega_{B_1}}
\end{aligned}
\tag{296}
$$

$$
\begin{aligned}
&(\omega_{B_1}+\omega_{B_2})\langle\langle V_{B_0};V_{B_1},V_{B_2}\rangle\rangle_{\omega_{B_1},\,\omega_{B_2}}\\
&\quad=P_{[1,\,2]}\langle\langle[V_{B_0},V_{B_1}];V_{B_2}\rangle\rangle_{\omega_{B_2}}\\
&\qquad+\langle\langle[V_{B_0},H_0];V_{B_1},V_{B_2}\rangle\rangle_{\omega_{B_1},\,\omega_{B_2}}
\end{aligned}
\tag{297}
$$

for the linear and quadratic response functions.

The equations of motion for the response functions may be used to obtain relations between transition-matrix elements. Consider, for example, the linear response function. The equation of motion in eq 296 and the finiteness of $\langle 0^{(0)}|[A,B]|0^{(0)}\rangle$ give the relation

$$
\begin{aligned}
&\lim_{\omega_B\longrightarrow\omega_i}(\omega_B-\omega_i)\omega_B\langle\langle A;B\rangle\rangle_{\omega_B}\\
&\quad=\omega_i\lim_{\omega_B\longrightarrow\omega_i}(\omega_B-\omega_i)\langle\langle[A,H_0];B\rangle\rangle_{\omega_B}
\end{aligned}
\tag{298}
$$

which in combination with eq 290 yields

$$
\omega_i\langle 0^{(0)}|A|i\rangle=\langle 0^{(0)}|[A,H_0]|i\rangle
\tag{299}
$$

This relation also follows trivially from the fact that $|0^{(0)}\rangle$ and $|i\rangle$ are both eigenfunctions of H_0. However, the important point is that eq 299 was here obtained only by assuming that the time development fulfills the Ehrenfest equation in eq 294. Therefore, in any approximate theory that fulfills the Ehrenfest equation, transition moments and energies identified from the poles and residues of the linear response function satisfy the equation of motion, eq 299.

3.5. Response Functions As Derivatives of the Quasi-Energy Lagrangian

In section 3.4, response functions were developed from expansion of the quasi-energy in the Hermitian form, eq 244. However, in the development of response theory for coupled-cluster theory it is important to use the quasi-energy in the non-Hermitian form, eq 193. In section 3.5.1, we therefore study the expansion of the time-dependent quasi-energy Lagrangian of eq 190 and the time-averaged quasi-energy Lagrangian of eq 193 in orders of the external perturbation.

Using an approach similar to that of section 3.4, the theory may be developed to arbitrary order in the external perturbation, see refs 74 and 75 for examples from coupled-cluster theory. We here restrict our treatment to terms up to second order in the perturbation, which allows us to identify the linear response function. It will not be assumed that the reference state is an eigenstate of the zero-order Hamiltonian, so the wave function expressions will be those of eqs 220, 221, and 223. Although the expressions for the quasi-energy corrections and the response functions obtained in section 3.5.1 differ from those developed in section 3.3, they are equivalent, as may be demonstrated explicitly by a (tedious) comparison of terms.

3.5.1. Perturbation Expansions of the Lagrangian Quasi-Energies. By analogy with the expansion of the time-dependent quasi-energy and the averaged quasi-energy in the Hermitian form, we have the following expansions for the corresponding quasi-energy Lagrangians

$$
L^{\mathrm{c}}(t)=\sum_{n=0}^{\infty}\sum_{B^n}\left(\prod_{k=1}^{n}\varepsilon_{B_k}\right)L_{B^n}^{\mathrm{c}(n)}\mathrm{e}^{-\mathrm{i}\sum_{k=1}^{n}\omega_{B_k}t}
\tag{300}
$$

$$
L(t)=\sum_{n=0}^{\infty}\sum_{B^n}\left(\prod_{k=1}^{n}\varepsilon_{B_k}\right)L_{B^n}^{(n)}\mathrm{e}^{-\mathrm{i}\sum_{k=1}^{n}\omega_{B_k}t}
\tag{301}
$$

$$
\mathscr{L}=\sum_{n}\sum_{B^n:\,\sum_k\omega_{B_k}=0}\left(\prod_{k}\varepsilon_{B_k}\right)\mathscr{L}_{B^n}^{(n)}
\tag{302}
$$

Given that $L(t)$ is the real part of $L^{\mathrm{c}}(t)$ we obtain from eqs 300 and 301 the simple relation

$$
L_{B^n}^{(n)}=\frac{1}{2}\left(L_{B^n}^{\mathrm{c}(n)}+L_{-B^n}^{\mathrm{c}(n)*}\right)=\frac{1}{2}C^{\pm}L_{B^n}^{\mathrm{c}(n)}
\tag{303}
$$

where $-B^n$ contains the elements $-B_i$ and where the operator $C^{\pm}$ is defined by

$$
C^{\pm}X_{B_n}=X_{B^n}+X_{-B^n}^{*}
\tag{304}
$$

By analogy with eq 262, the terms in the time-dependent and time-averaged quasi-energy Lagrangian are related as

$$
\mathscr{L}_{B^n}^{(n)}=\begin{cases}\frac{1}{2}C^{\pm}L_{B^n}^{\mathrm{c}(n)} & \text{if }\sum_k\omega_{B_k}=0\\ 0 & \text{otherwise}\end{cases}
\tag{305}
$$

The expansions of the quasi-energy in the Hermitian and non-Hermitian forms in eqs 261 and 302, respectively, are identical for all field strengths. The two expansions must therefore be identical term by term and have the same derivatives

$$
\mathscr{L}_{B^n}^{(n)}=\mathscr{Q}_{B^n}^{(n)}
\tag{306}
$$

Furthermore, as the expansion coefficients $\mathscr{Q}_{B^n}^{(n)}$ are proportional to the response functions, see eqs 274−276, the response functions may also be expressed in terms of $\mathscr{L}_{B^n}^{(n)}$, yielding the following linear, quadratic, and cubic response functions in the Lagrangian form

$$
\langle\langle V_{B_0};V_{B_1}\rangle\rangle_{\omega_{B_1}}=\frac{\mathrm{d}^2\mathscr{L}}{\mathrm{d}\varepsilon_{B_0}\mathrm{d}\varepsilon_{B_1}}=2\mathscr{L}_{B_0,\,B_1}^{(2)}=C^{\pm}L_{B_0,\,B_1}^{\mathrm{c}(2)}
\tag{307}
$$

$$
\langle\langle V_{B_0};V_{B_1},V_{B_2}\rangle\rangle_{\omega_{B_1},\,\omega_{B_2}}=\frac{\mathrm{d}^3\mathscr{L}}{\mathrm{d}\varepsilon_{B_0}\mathrm{d}\varepsilon_{B_1}\mathrm{d}\varepsilon_{B_2}}=\frac{3!}{2}C^{\pm}L_{B_0,\,B_1,\,B_2}^{\mathrm{c}(3)}
\tag{308}
$$

$$\langle\langle V_{B_0}; V_{B_1}, V_{B_2}, V_{B_2}\rangle\rangle_{\omega_{B_1}, \omega_{B_2}, \omega_{B_3}} = \frac{\mathrm{d}^4\mathscr{L}}{\mathrm{d}\varepsilon_{B_0}\mathrm{d}\varepsilon_{B_1}\mathrm{d}\varepsilon_{B_2}\mathrm{d}\varepsilon_{B_3}} = \frac{4!}{2}C^{\pm}L^{\mathrm{c}(4)}_{B_0, B_1, B_2, B_3} \tag{309}$$

to be compared with the expressions for response functions in the Hermitian form in eqs 274−276.

To obtain the expressions for the terms in the expansion of the quasi-energy Lagrangian, the coefficients of the multiplier state $|\bar{0}\rangle$ of eq 188 must be expanded in the perturbation. By analogy with the expansion of the wave function parameters the multipliers are expanded as

$$\begin{aligned}\bar{\mathbf{c}}(t) = {} & \bar{\mathbf{c}}^{(0)} + \sum_{B_1}\varepsilon_{B_1}\bar{\mathbf{c}}^{(1)}_{B_1}\mathrm{e}^{-\mathrm{i}\omega_{B_1}t} \\ & + \sum_{B_1B_2}\varepsilon_{B_1}\varepsilon_{B_2}\bar{\mathbf{c}}^{(2)}_{B_1, B_2}\mathrm{e}^{-\mathrm{i}(\omega_{B_1}+\omega_{B_2})t} + \ldots \\ & + \sum_{n}\sum_{B^n}\left(\prod_{k=1}^{n}\varepsilon_{B_k}\right)\bar{\mathbf{c}}^{(n)}_{B^n}\mathrm{e}^{-\mathrm{i}\sum_{k=1}^{n}\omega_{B_k}t} + \ldots\end{aligned} \tag{310}$$

We are now ready to derive the expressions for the zero-, first-, and second-order terms in the expansion of $\mathscr{L}$. As the Lagrangian quasi-energy $\mathscr{L}$ is variational in the wave function and multiplier parameters, these parameters to order n determine $\mathscr{L}$ to order $2n + 1$. Furthermore, the multiplier parameters occur linearly in $\mathscr{L}$, allowing for an additional reduction discussed in section 3.6: the multiplier parameters to order n determine the time-averaged Lagrangian quasi-energy to order $2n + 2$. In short, to obtain the Lagrangian to second order, we need the wave function parameters to first order and the multipliers to zero order.

Introducing the expansion of eq 310 in the multiplier state $\langle\bar{0}|$ of eq 188 and the expansion of eq 218 in $\langle\hat{0}|$ we may expand the time-averaged quasi-energy in orders of the perturbation. Using this result we obtain from the expansion of eq 189 and from eq 305 the terms contributing to the lowest order quasi-energy terms as

$$\mathscr{L}^{(0)}_{0} = Re\left(\langle\mathrm{R}|H_0|\hat{0}^{(0)}\rangle + \langle\bar{0}^{(0)}|H_0|\hat{0}^{(0)}\rangle\right) \tag{311}$$

$$\mathscr{L}^{(1)}_{B_0} = \frac{1}{2}C^{\pm}\left(\langle\mathrm{R}|V_{B_0}|\hat{0}^{(0)}\rangle + \langle\bar{0}^{(0)}|V_{B_0}|\hat{0}^{(0)}\rangle\right) \tag{312}$$

$$\begin{aligned}\mathscr{L}^{(2)}_{B_0, B_1} = {} & \frac{1}{2}C^{\pm}P_{[0, 1]}\Bigg[\langle\mathrm{R}|V_{B_0}|\hat{0}^{(1)}_{B_1}\rangle + \langle\bar{0}^{(0)}|V_{B_0}|\hat{0}^{(1)}_{B_1}\rangle \\ & - \left(\sum_i \bar{c}_i^{(0)*}c^{(1)}_{B_1, i}\right)\left(\langle\mathrm{R}|H_0 - \omega_{B_0}|\hat{0}^{(1)}_{B_0}\rangle + \langle\mathrm{R}|V_{B_0}|\hat{0}^{(0)}\rangle\right)\Bigg]\end{aligned} \tag{313}$$

These expressions provide alternative forms for the lowest order corrections to the time-averaged quasi-energy, which by definition are identical to those obtained previously. As the zero-order state is an eigenstate of H_0 (eq 208), the zero-order term becomes

$$\mathscr{L}^{(0)}_{0} = E_0 \tag{314}$$

The first-order correction of eq 312 must similarly be identical to that of eq 263, and insertion of eq 313 into eq 307 gives an alternative form of the linear response equation of eq 278. The equivalence between the forms of the first-order corrections is explicitly demonstrated in the following subsection, where we derive the expression for the zero-order Lagrange multipliers.

3.5.2. Zero-Order Lagrange Multipliers.

The zero-order Lagrange multipliers, which determine the quasi-energy Lagrangian to second order, are most conveniently identified by invoking the stationarity of the time-averaged zero-order Lagrangian of eq 311 with respect to the variations in the zero-order wave function parameters

$$\frac{\partial}{\partial c_k^{(0)}}\left(\sum_j\langle\mathrm{R}|H_0|j\rangle c_j^{(0)} + \sum_{ij}\bar{c}_i^{(0)*}\langle i|H_0|j\rangle c_j^{(0)} - \left(\sum_i\bar{c}_i^{(0)*}c_i^{(0)}\right)\sum_j\langle\mathrm{R}|H_0|j\rangle c_j^{(0)}\right) = 0 \tag{315}$$

which in terms of the Jacobian **A** of eq 214 may be written in the form

$$\langle\mathrm{R}|H_0|k\rangle + \sum_i\bar{c}_i^{(0)*}A_{ik} = 0 \tag{316}$$

Introducing the shifted Hamiltonian $\mathbf{H}^{\mathrm{b}}$ of eq 227, the zero-order multiplier equations may be written in matrix form

$$\begin{pmatrix}1 & \bar{\mathbf{c}}^{(0)\dagger}\end{pmatrix}\mathbf{H}^{\mathrm{b}} = \mathbf{0} \tag{317}$$

showing that $\begin{pmatrix}1\\ \bar{\mathbf{c}}^{(0)}\end{pmatrix}$ is a left eigenvector of the shifted Hamiltonian $\mathbf{H}^{\mathrm{b}}$ with zero eigenvalue, corresponding to an eigenvalue E_0 of the unshifted Hamiltonian H_0. Assuming that this eigenvalue is nondegenerate, we conclude that the state defined by $\begin{pmatrix}1\\ \bar{\mathbf{c}}^{(0)}\end{pmatrix}$ is proportional to the zero-order state

$$|\mathrm{R}\rangle + \sum_i\bar{c}_i^{(0)}|\hat{i}^{(0)}\rangle = \alpha\left(|\mathrm{R}\rangle + \sum_i c_i^{(0)}|i\rangle\right) \tag{318}$$

where α is some scalar. To determine α we insert the expansion in eq 206 into eq 318, enabling us to make the identifications

$$\bar{c}_i^{(0)} = \alpha c_i^{(0)}, \; \alpha = \frac{1}{1 + \sum_i|c_i^{(0)}|^2} = \frac{1}{\langle\hat{0}^{(0)}|\hat{0}^{(0)}\rangle} \tag{319}$$

The zero-order multiplier state $|\bar{0}^{(0)}\rangle$ occurs in the following together with the reference state, making it convenient to introduce the (zero-order) lambda state

$$|\Lambda^{(0)}\rangle = |\mathrm{R}\rangle + \sum_i\bar{c}_i^{(0)}|\hat{i}^{(0)}\rangle \tag{320}$$

which from eq 319 may be written in the form

$$|\Lambda^{(0)}\rangle = \frac{1}{\langle\hat{0}^{(0)}|\hat{0}^{(0)}\rangle}|\hat{0}^{(0)}\rangle \tag{321}$$

which shows that $\langle\Lambda^{(0)}|\hat{0}^{(0)}\rangle = 1$.

As a first use of the explicit forms of the Lagrange multipliers we show that $\mathscr{L}^{(1)}$ of eq 312 is identical to $\mathscr{Q}^{(1)}$ of eq 263, thereby also demonstrating that $\mathscr{L}^{(1)}$ is independent of the choice of the reference state even though the left- and right-hand states of eq 312 both depend on this state. The equivalence is easily established using eqs 237, 320, and 321 and the identification in eq 263

$$\begin{aligned}\mathscr{L}^{(1)}_{B_0} & = \frac{1}{2}C^{\pm}\langle\Lambda^{(0)}(\mathrm{R})|V_{B_0}|\hat{0}^{(0)}(R)\rangle = \frac{\langle\hat{0}^{(0)}(\mathrm{R})|V_{B_0}|\hat{0}^{(0)}(\mathrm{R})\rangle}{\langle\hat{0}^{(0)}(\mathrm{R})|\hat{0}^{(0)}(\mathrm{R})\rangle} \\ & = \langle 0^{(0)}|V_{B_0}|0^{(0)}\rangle = \mathbf{c}^{(0)}\mathbf{V}_{B_0}\mathbf{c}^{(0)} = \mathscr{Q}^{(1)}_{B_0}\end{aligned} \tag{322}$$

The higher order terms, such as the second-order corrections $\mathcal{L}^{(2)}$ of eq 313 and $\mathcal{Q}^{(2)}$in eq 264, may similarly be shown to be identical.

3.6. Elimination Rules

In the calculation of the terms in the expansion of the quasi-energy in sections 3.3 and 3.5 we made repeated use of the $2n + 1$ and $2n + 2$ rules, which state that wave function parameters and Lagrange multipliers to order n determine the quasi-energy to order $2n + 1$ and $2n + 2$, respectively. These rules are developed in this section, where we also briefly discuss alternative elimination rules. We adopt a formalism that includes both exact and approximate wave functions. For an early exposition of these rules, see ref 76.

3.6.1. $2n + 1$ Rule. Consider a time-averaged quasi-energy $\mathcal{Q}(\varepsilon,\lambda)$ that depends on the external parameters ε and the wave function parameters λ. The optimized quasi-energy is given by

$$\mathcal{Q}(\varepsilon) = \mathcal{Q}(\varepsilon, \lambda(\varepsilon)) \tag{323}$$

where the optimized wave function parameters $\lambda(\varepsilon)$ are determined from the variational condition

$$\frac{\partial \mathcal{Q}(\varepsilon, \lambda(\varepsilon))}{\partial \lambda(\varepsilon)} = 0 \tag{324}$$

In response theory, we are interested in the expansion of $\mathcal{Q}(\varepsilon,\lambda(\varepsilon))$ in orders of ε

$$\mathcal{Q}(\varepsilon) = \mathcal{Q}^{(0)} + \mathcal{Q}^{(1)}\varepsilon + \frac{1}{2}\mathcal{Q}^{(2)}\varepsilon^2 + ... \tag{325}$$

In particular, we wish to determine expressions for the perturbed quasi-energies $\mathcal{Q}^{(n)}$ in terms of the perturbed wave function parameters $\lambda^{(k)}$ of the expansion

$$\lambda(\varepsilon) = \lambda^{(0)} + \lambda^{(1)}\varepsilon + \frac{1}{2}\lambda^{(2)}\varepsilon^2 + ... \tag{326}$$

To determine the perturbed quasi-energies, we expand the quasi-energy in orders of ε and λ

$$\begin{aligned}\mathcal{Q}(\varepsilon, \lambda) = {} & \mathcal{Q}^{(00)} + \mathcal{Q}^{(10)}\varepsilon + \mathcal{Q}^{(01)}\lambda \\ & + \frac{1}{2}\mathcal{Q}^{(20)}\varepsilon^2 + \mathcal{Q}^{(11)}\varepsilon\lambda + \frac{1}{2}\mathcal{Q}^{(02)}\lambda^2 + ...\end{aligned} \tag{327}$$

where we introduced a short-hand notation for quasi-energy derivatives

$$\mathcal{Q}^{(mn)} = \frac{\partial^{m+n}\mathcal{Q}(\varepsilon, \lambda)}{\partial\varepsilon^m \partial\lambda^n}\Big|_{\varepsilon=0,\ \lambda=0} \tag{328}$$

By inserting the expansion in eq 326 into eq 327 and collecting terms of the same order of ε we obtain to lowest orders

$$\mathcal{Q}^{(0)} = \mathcal{Q}^{(00)} + \mathcal{Q}^{(01)}\lambda^{(0)} + ... \tag{329}$$

$$\begin{aligned}\mathcal{Q}^{(1)} = {} & \mathcal{Q}^{(10)} + \mathcal{Q}^{(11)}\lambda^{(0)} + \mathcal{Q}^{(01)}\lambda^{(1)} \\ & + \mathcal{Q}^{(02)}\lambda^{(0)}\lambda^{(1)} + ...\end{aligned} \tag{330}$$

$$\begin{aligned}\mathcal{Q}^{(2)} = {} & \mathcal{Q}^{(20)} + 2\mathcal{Q}^{(21)}\lambda^{(0)} + 2\mathcal{Q}^{(11)}\lambda^{(1)} \\ & + 2\mathcal{Q}^{(12)}\lambda^{(0)}\lambda^{(1)} + \mathcal{Q}^{(01)}\lambda^{(2)} \\ & + \mathcal{Q}^{(02)}\lambda^{(0)}\lambda^{(2)} + \mathcal{Q}^{(02)}\lambda^{(1)}\lambda^{(1)} \\ & + \mathcal{Q}^{(03)}\lambda^{(0)}\lambda^{(1)}\lambda^{(1)} + ...\end{aligned} \tag{331}$$

where the omitted terms are of second and higher orders in $\lambda^{(0)}$. From order considerations we note that $\lambda^{(n)}$ does not occur in quasi-energies of orders less than n, that $\lambda^{(n)}$ occurs only linearly in quasi-energies up to order $2n - 1$, and that $\lambda^{(n)}$ appears nonlinearly in quasi-energies of order $2n$ and greater. The zero-order parameters $\lambda^{(0)}$ have a special status and may appear to infinite order, depending on the form of $\mathcal{Q}(\varepsilon,\lambda)$. The structure of the perturbed quasi-energies is therefore

$$\mathcal{Q}^{(n)} = \mathcal{Q}^{(n)}(\underbrace{\lambda^{(0)}}_{\substack{\text{infinite}\\ \text{order}}}, \underbrace{\lambda^{(1)}, \ldots \lambda^{([n/2])}}_{\substack{\text{nonlinear}\\ \text{parameters}}}, \underbrace{\lambda^{([n/2]+1)}, \ldots \lambda^{(n)}}_{\substack{\text{linear}\\ \text{parameters}}}) \tag{332}$$

where $[n/2]$ is the greatest integer less than or equal to $n/2$. The quasi-energy $\mathcal{Q}^{(n)}$ thus depends linearly on $\lambda^{(k)}$ for $[n/2] < k \leq n$.

We now wish to identify the stationary conditions for $\mathcal{Q}^{(n)}$ with respect to variations in the perturbed wave functions $\lambda^{(k)}$. Using the chain rule and the fact that $\lambda^{(k)}$ is independent of ε we obtain

$$\begin{aligned}\frac{\partial \mathcal{Q}^{(n)}}{\partial \lambda^{(k)}} &= \frac{\partial^{n+1}\mathcal{Q}(\varepsilon, \lambda(\varepsilon))}{\partial\lambda^{(k)}\partial\varepsilon^n}\Bigg|_{\varepsilon=0} = \frac{\partial^n}{\partial\varepsilon^n}\frac{\partial\mathcal{Q}(\varepsilon, \lambda(\varepsilon))}{\partial\lambda^{(k)}}\Bigg|_{\varepsilon=0} \\ &= \frac{\partial^n}{\partial\varepsilon^n}\frac{\partial\lambda(\varepsilon)}{\partial\lambda^{(k)}}\frac{\partial\mathcal{Q}(\varepsilon, \lambda(\varepsilon))}{\partial\lambda(\varepsilon)}\Bigg|_{\varepsilon=0} = \frac{\partial^n}{\partial\varepsilon^n}\frac{\varepsilon^k}{k!}\frac{\partial\mathcal{Q}(\varepsilon, \lambda(\varepsilon))}{\partial\lambda(\varepsilon)}\Bigg|_{\varepsilon=0}\end{aligned} \tag{333}$$

where we inserted eq 326. From the variational condition in eq 324 it now follows that the nth-order quasi-energy $\mathcal{Q}^{(n)}$ is stable toward variations in all perturbed parameters $\lambda^{(k)}$

$$\frac{\partial \mathcal{Q}^{(n)}}{\partial \lambda^{(k)}} = 0 \tag{334}$$

According to eq 332 $\mathcal{Q}^{(n)}$ depends linearly on $\lambda^{(k)}$ with $k > [n/2]$, while according to eq 334 $\mathcal{Q}^{(n)}$ is stationary with respect to $\lambda^{(k)}$. The coefficient multiplying $\lambda^{(k)}$ in the expression for $\mathcal{Q}^{(n)}$ must therefore be zero. We conclude that $\mathcal{Q}^{(n)}$ must be independent of $\lambda^{(k)}$ for $k > [n/2]$

$$\mathcal{Q}^{(n)} = \mathcal{Q}^{(n)}(\lambda^{(0)}, \lambda^{(1)}, ...\lambda^{([n/2])}) \tag{335}$$

We have now established the $2n + 1$ rule: the wave function to order n determines the quasi-energy to order $2n + 1$. Applied to the lower order quasi-energies in eqs 329−331 we obtain (in a parametrization with $\lambda^{(0)} = 0$) the following simplified expressions for the energies

$$\mathcal{Q}^{(0)} = \mathcal{Q}^{(00)} \tag{336}$$

$$\mathcal{Q}^{(1)} = \mathcal{Q}^{(10)} \tag{337}$$

$$\mathcal{Q}^{(2)} = \mathcal{Q}^{(20)} + 2\mathcal{Q}^{(11)}\lambda^{(1)} + \mathcal{Q}^{(02)}\lambda^{(1)}\lambda^{(1)} \tag{338}$$

$$\mathcal{Q}^{(3)} = \mathcal{Q}^{(30)} + 3\mathcal{Q}^{(21)}\lambda^{(1)} + 3\mathcal{Q}^{(12)}\lambda^{(1)}\lambda^{(1)} + \mathcal{Q}^{(03)}\lambda^{(1)}\lambda^{(1)}\lambda^{(1)} \tag{339}$$

We note how the first-order wave function determines the quasi-energy to third order.

Having established the structure of the quasi-energies $\mathcal{Q}^{(n)}$ in eq 335, we shall now use the variational conditions in eq 334 to determine $\lambda^{(k)}$. First, assuming that $k \leq n$ we obtain from eqs 333 and 334 the stationary conditions

$$\frac{\partial \mathcal{Q}^{(n)}}{\partial \lambda^{(k)}} = \frac{\partial^n}{\partial \varepsilon^n} \frac{\varepsilon^k}{k!} \frac{\partial \mathcal{Q}(\varepsilon, \lambda(\varepsilon))}{\partial \lambda(\varepsilon)}\bigg|_{\varepsilon=0} = \binom{n}{k} \frac{\partial^{n-k}}{\partial \varepsilon^{n-k}} \frac{\partial \mathcal{Q}(\varepsilon, \lambda(\varepsilon))}{\partial \lambda(\varepsilon)}\bigg|_{\varepsilon=0} = 0 \tag{340}$$

where we used the Leibniz rule for the differentiation of a product of two functions

$$\frac{\partial^n [f(\varepsilon)g(\varepsilon)]}{\partial \varepsilon^n} = \sum_{i=0}^{n} \binom{n}{i} \frac{\partial^i f(\varepsilon)}{\partial \varepsilon^i} \frac{\partial^{n-i} g(\varepsilon)}{\partial \varepsilon^{n-i}} \tag{341}$$

Next, we note that the stationary conditions in eq 340 are not all independent, depending only on the value of $n - k$ rather than separately on n and k. We therefore only need to consider the conditions

$$\frac{\partial \mathcal{Q}^{(n)}}{\partial \lambda^{(0)}} = \frac{\partial^n}{\partial \varepsilon^n} \frac{\partial \mathcal{Q}(\varepsilon, \lambda(\varepsilon))}{\partial \lambda(\varepsilon)}\bigg|_{\varepsilon=0} = 0 \tag{342}$$

By satisfying the stationary conditions with respect to $\lambda^{(0)}$ in eq 342 for all $n \geq 0$ we ensure that the expansion of $\partial \mathcal{Q}(\varepsilon, \lambda(\varepsilon))/\partial \lambda(\varepsilon)$ about $\varepsilon = 0$ vanishes to all orders. The conditions in eq 342 for all $n \geq 0$ are therefore equivalent to the conditions in eq 324 for all values of ε.

Let us now consider the structure of the nth-order response equations $\partial \mathcal{Q}^{(n)}/\partial \lambda^{(0)} = 0$ of eq 342 in more detail. Differentiating eq 342 with respect to $\lambda^{(k)}$, using the chain rule, and inserting eq 326 we obtain

$$\frac{\partial}{\partial \lambda^{(k)}} \frac{\partial \mathcal{Q}^{(n)}}{\partial \lambda^{(0)}}\bigg|_{\varepsilon=0} = \frac{\partial^n}{\partial \varepsilon^n} \left(\frac{\partial \lambda(\varepsilon)}{\partial \lambda^{(k)}} \frac{\partial}{\partial \lambda(\varepsilon)} \frac{\partial \mathcal{Q}(\varepsilon, \lambda(\varepsilon))}{\partial \lambda(\varepsilon)} \right)\bigg|_{\varepsilon=0} = \frac{\partial^n}{\partial \varepsilon^n} \left(\frac{\varepsilon^k}{k!} \frac{\partial^2 \mathcal{Q}(\varepsilon, \lambda(\varepsilon))}{\partial \lambda(\varepsilon)^2} \right)\bigg|_{\varepsilon=0} \tag{343}$$

which may be simplified by application of the Leibniz rule in eq 341 to give

$$\frac{\partial}{\partial \lambda^{(k)}} \frac{\partial \mathcal{Q}^{(n)}}{\partial \lambda^{(0)}}\bigg|_{\varepsilon=0} = \begin{cases} \binom{n}{k} \dfrac{\partial^{n-k}}{\partial \varepsilon^{n-k}} \dfrac{\partial^2 \mathcal{Q}(\varepsilon, \lambda(\varepsilon))}{\partial \lambda(\varepsilon)^2}\bigg|_{\varepsilon=0} & (k < n) \\ \mathcal{Q}^{(02)} & (k = n) \\ 0 & (k > n) \end{cases} \tag{344}$$

We conclude that the stationary conditions in eq 342 may be written in the form[76]

$$\frac{\partial \mathcal{Q}^{(n)}}{\partial \lambda^{(0)}} = \mathcal{Q}^{(02)}\lambda^{(n)} + R^{(n)}(\lambda^{(0)}, ..., \lambda^{(n-1)}) = 0 \tag{345}$$

where $R^{(n)}$ is a polynomial in $\lambda^{(k)}$ with $k < n$. To a given order n in the perturbation the response equations

$$\mathcal{Q}^{(02)}\lambda^{(k)} = -R^{(k)}(\lambda^{(0)}, ..., \lambda^{(k-1)}) \tag{346}$$

are solved recursively for $k \leq n$ beginning with $\lambda^{(1)}$, the solution $\lambda^{(k)}$ depending on the solutions $\lambda^{(l)}$ with $l < k$.

3.6.2. 2*n* + 2 Rule.

In the intermediate normalization, the time-dependent quasi-energy $Q(t)$ in eq 183 is not variationally determined and is therefore not suited for calculation of response functions. In contrast, the time-dependent Lagrangian $L(t)$ in eq 190 provides us with an equivalent, variational formulation of the energy in the intermediate normalization, suitable for response theory, noting that the corresponding time-averaged quasi-energy $\mathcal{L}$ in eq 193 satisfies the stationary conditions in eq 194. Likewise, in approximate theories the approximate quasi-energy is often not variational.[66] Rather, the wave function parameters satisfy some subsidiary condition $e(\varepsilon,\lambda(\varepsilon)) = 0$ such as the amplitude equations in coupled-cluster theory. In such cases, a variational quasi-energy Lagrangian may be constructed of the general form[66,77]

$$\mathcal{L}(\varepsilon) = \mathcal{L}(\varepsilon, \lambda(\varepsilon), \bar{\lambda}(\varepsilon)) = \mathcal{Q}(\varepsilon, \lambda(\varepsilon)) + \bar{\lambda}(\varepsilon)e(\varepsilon, \lambda(\varepsilon)) \tag{347}$$

where $\bar{\lambda}(\varepsilon)$ is a collection of Lagrange multipliers. For the Lagrangian in the intermediate normalization in eq 193, $e(\varepsilon,\lambda(\varepsilon))$ and $\bar{\lambda}(\varepsilon)$ correspond to eqs 185 and 188, respectively. The Lagrangian is by construction stationary in the multipliers as well as in the original wave function parameters (omitting arguments for brevity)

$$\frac{\partial \mathcal{L}}{\partial \bar{\lambda}} = e = 0 \tag{348}$$

$$\frac{\partial \mathcal{L}}{\partial \lambda} = \frac{\partial \mathcal{Q}}{\partial \lambda} + \bar{\lambda}\frac{\partial e}{\partial \lambda} = 0 \tag{349}$$

The variation with respect to $\bar{\lambda}$ in eq 348 gives the equation for λ and is trivially satisfied, whereas the variation in λ in eq 349 yields a set of linear equations that determine the multipliers. By analogy with the quasi-energy expansion in eq 325 we expand the Lagrangian in the perturbation strength

$$\mathcal{L}(\varepsilon) = \mathcal{L}^{(0)} + \mathcal{L}^{(1)}\varepsilon + \frac{1}{2}\mathcal{L}^{(2)}\varepsilon^2 + ... \tag{350}$$

By construction, perturbation-strength derivatives of a quasi-energy and its corresponding Lagrangian function are identical. However, by constructing a Lagrangian function we have the freedom to eliminate computationally expensive parameters by means of the variational conditions in eqs 348 and 349. We shall now examine the elimination rules for the quasi-energy expressed as a Lagrangian in eq 347.

Since the Lagrangian satisfies the variational conditions in eq 349 with respect to the wave function parameters λ, the $2n + 1$ rule for these parameters follow in the same way as for the variational quasi-energy in section 3.6.1. Thus, the responses $\lambda^{(k)}$

with $k \le [n/2]$ are sufficient to evaluate the nth-order Lagrangian $\mathscr{L}^{(n)}$. Likewise, it is possible to eliminate some of the perturbed multipliers $\bar{\lambda}^{(i)}$ from $\mathscr{L}^{(n)}$, noting that the Lagrangian is both linear and stationary in the multipliers, see eqs 347 and 348. However, we cannot eliminate all multipliers $\bar{\lambda}^{(i)}$ independently because the preceding elimination of $\lambda^{(k)}$ (in accordance with the $2n + 1$ rule) has modified some of the terms containing $\bar{\lambda}^{(i)}$ ($i \le n - k$) in eq 347. For example, elimination of $\lambda^{(k)}$ with $[n/2] < k \le n$ removes the factor multiplying $\lambda^{(k)}$ from $\mathscr{L}^{(n)}$. Since this factor contains $\bar{\lambda}^{(i)}$ and $\lambda^{(i)}$ with $i \le n - k$, $\mathscr{L}^{(n)}$ is no longer variational in these parameters. In short, removal of $\lambda^{(k)}$ with $[n/2] < k \le n$ from $\mathscr{L}^{(n)}$ precludes subsequent removal of $\bar{\lambda}^{(i)}$ with $i \le n - k$, binding them to $\mathscr{L}^{(n)}$.

Having made this observation we now examine which multipliers $\bar{\lambda}^{(i)}$ are affected when the perturbed wave function parameters $\lambda^{(k)}$ are eliminated from the quasi-energy Lagrangian in accordance with the $2n + 1$ rule, following Kristensen et al.[78] For clarity of presentation, we consider even- and odd-order quasi-energies separately.

- $\mathscr{L}^{(2n+1)}$: Application of the $2n + 1$ rule to $\mathscr{L}^{(2n+1)}$ removes $\lambda^{(n+1)}$ and higher order parameters, binding $\bar{\lambda}^{(k)}$ with $k \le 2n + 1 - (n + 1) = n$ to $\mathscr{L}^{(2n+1)}$. Since $\bar{\lambda}^{(k)}$ with $k > n$ may still be removed from $\mathscr{L}^{(2n+1)}$ by the $2n + 1$ rule, $\bar{\lambda}^{(k)}$ with $k \le n$ are sufficient to determine $\mathscr{L}^{(2n+1)}$.
- $\mathscr{L}^{(2n+2)}$: Application of the $2n + 1$ rule to $\mathscr{L}^{(2n+2)}$ removes $\lambda^{(n+2)}$ and higher order parameters, binding $\bar{\lambda}^{(k)}$ with $k \le 2n + 2 - (n + 2) = n$ to $\mathscr{L}^{(2n+2)}$. Since $\bar{\lambda}^{(k)}$ with $k > n$ may still be removed from $\mathscr{L}^{(2n+2)}$ by the $2n + 1$ rule, $\bar{\lambda}^{(k)}$ with $k \le n$ are sufficient to determine $\mathscr{L}^{(2n+2)}$.

We have now established the $2n + 2$ rule for Lagrange multipliers: the multipliers to order n determine the Lagrangian to order $2n + 2$.[76,77] Together with the $2n + 1$ rule, the $2n + 2$ rule is important in reducing the cost of calculating perturbed quasi-energies of variational and nonvariational methods.

3.6.3. Alternative Elimination Schemes. In the discussion of the $2n + 1$ and $2n + 2$ rules we eliminated response parameters for the full set of N perturbations responsible for a given molecular property. Alternatively, these elimination rules may be applied to a subset K of the full set of N perturbations that determine the property of interest.[78] In this way, we eliminate as many parameters as possible for the first subset of K perturbations at the price of calculating higher order parameters for the remaining subset of $N - K$ perturbations. Such a strategy is useful when the molecular property involves a mixture of extensive and intensive perturbations.

For extensive perturbations the number of components is proportional to the system size (e.g., the $3N_{\mathrm{atoms}}$ geometric or nuclear-magnetic perturbations of a molecule), whereas the number of intensive perturbations is system independent (e.g., the three electric or magnetic dipole operators of a molecule). It is then advantageous to eliminate as many response parameters as possible involving the computationally expensive extensive perturbations. Consider, for example, a third-order molecular property expressed as a quasi-energy Lagrangian derivative involving one extensive differentiation (with $3N_{\mathrm{atoms}}$ components) and two intensive differentiations (with 3 components), schematically denoted as $\mathscr{L}^{\mathrm{eii}}$. Applying the $2n + 1$ rule to all perturbations, all $2(3N_{\mathrm{atoms}} + 3)$ first-order parameters λ^{e}, λ^{i}, $\bar{\lambda}^{\mathrm{e}}$, and $\bar{\lambda}^{\mathrm{i}}$ must be determined (disregarding zero-order parameters), making the calculations expensive for large molecules. Instead, by applying the $2n + 1$ rule to the extensive perturbations only, we may eliminate all occurrences of λ^{e} and $\bar{\lambda}^{\mathrm{e}}$ from L^{eii} at the small cost of not being able to remove any intensive perturbations and therefore having to determine 6 first-order parameters λ^{i} and $\bar{\lambda}^{\mathrm{i}}$ and 12 second-order parameters λ^{ii} and $\bar{\lambda}^{\mathrm{ii}}$. In this manner the number of response equations to be solved is 18 (rather than $6N_{\mathrm{atoms}} + 6$), independently of the number of atoms in the system, reducing the computational cost for large molecules.[79,80]

The above development described the formal analysis required to minimize the number of response equations to be solved. For even-order response functions we may alternatively develop expressions that ensure that the errors of these response functions are quadratic in the error of the highest wave function corrections. Following the development of Sellers for time-independent perturbations[81] this has been discussed for the linear response function by Koch and Harrison.[82]

3.7. Damped Response Theory

Molecular response functions become singular when one or more of the optical frequencies are equal to an excitation energy, as discussed in section 3.5.2. These singularities give an unphysical behavior of the calculated molecular properties in the resonance region such as divergent dispersion curves and infinitely narrow absorption peaks, reflecting the infinite lifetime of excited states in standard molecular response theory. For a rigorous treatment of molecular properties near resonance, the finite lifetime of excited states must be accounted for. However, this is not readily achieved in traditional response theory. Instead, finite lifetimes are in damped response theory imposed by multiplying the excited states by a damping factor.[71] The resulting phenomenological lifetimes are related to the widths of the absorption peaks by the energy—time uncertainty principle.

From a practical point of view, introduction of finite excited-state lifetimes in damped response theory allows broadened absorption (or dispersion) spectra in any frequency region to be calculated directly, without explicit reference to the transition strengths of individual excited states. The damped response functions describe standard absorption transition strengths, such as the residue of the linear response function in eq 290, with superimposed absorption (or dispersion) line-shape functions. Direct calculation of absorption spectra in damped response theory is particularly advantageous when many transitions need to be addressed in the traditional residue approach. Important cases include electronic transitions to high-lying excited states, for example, in X-ray spectra,[83,84] and absorption spectra of large molecules in general,[85] where the excited-state density is particularly high. Another important use of damped response theory is calculation of the polarizability at different imaginary frequencies, giving direct access to the C_6 dispersion coefficients that govern weak intermolecular interactions.[82,86−88]

In their complex propagator approach, Norman et al.[89] introduced a damping term into the Liouville equation to account for finite lifetimes and identified damped response functions from this equation. Using a quasi-energy formulation Kristensen et al.[90] introduced finite lifetimes directly into the response functions in terms of complex excitation energies. The two formulations are equivalent, giving the same damped response functions. We note in passing that Jensen, Autschbach, and coworkers also presented linear response functions using finite lifetimes at the time-dependent density-functional level of theory,[91] applying it, for instance, to the study of resonance Raman scattering.[92] In all formulations finite excited-state lifetimes are introduced by means of an empirical damping parameter. This parameter is input to the response calculation; the theory provides no recipe for determining the damping parameter. Below, we discuss damped response theory in terms of complex excitation energies.

3.7.1. Phenomenological Damping of Excited States.

Let us assume that the excited-state wave function $|n\rangle$ is a solution to the time-independent Schrödinger equation

$$H_0|n\rangle = E_n|n\rangle \tag{351}$$

The corresponding time-dependent excited state given by

$$|n(t)\rangle = \mathrm{e}^{-\mathrm{i}E_n t}|n\rangle \tag{352}$$

then trivially satisfies the time-dependent Schrödinger equation

$$\mathrm{i}\partial_t|n(t)\rangle = H_0|n(t)\rangle = E_n|n(t)\rangle \tag{353}$$

In particular, the norm of $|n(t)\rangle$ is constant in time

$$\langle n(t)|n(t)\rangle = \langle n|n\rangle = 1 \tag{354}$$

Therefore, no decay occurs from the excited state to the ground state (or to other excited states). In other words, the lifetime of the excited state $|n(t)\rangle$ is infinite.

In reality, an excited state has a finite lifetime but this lifetime cannot be accounted for by the Hamiltonian H_0. Instead, a phenomenological description of the lifetime may be obtained by introducing a damped excited state $|\overline{n}(t)\rangle$ according to

$$|\overline{n}(t)\rangle = \mathrm{e}^{-\gamma t}|n(t)\rangle = \mathrm{e}^{-\mathrm{i}(E_n - \mathrm{i}\gamma)t}|n\rangle \tag{355}$$

The norm of the damped excited state $|\overline{n}(t)\rangle$ decays exponentially in time

$$\langle\overline{n}(t)|\overline{n}(t)\rangle = \mathrm{e}^{-2\gamma t} \tag{356}$$

and $(2\gamma)^{-1}$ may therefore be interpreted as the effective lifetime of the excited state. Unlike the undamped state $|n(t)\rangle$ in eq 353, the damped state $|\overline{n}(t)\rangle$ does not possess a well-defined real energy

$$\mathrm{i}\partial_t|\overline{n}(t)\rangle = (E_n - \mathrm{i}\gamma)|\overline{n}(t)\rangle \tag{357}$$

Comparing eqs 353 and 357 we see that damped excited states may be introduced through complex excited-state energies

$$E_n \rightarrow E_n - \mathrm{i}\gamma \tag{358}$$

In the absence of external perturbations the ground-state lifetime is infinite and the damping parameter associated with the ground-state energy E_0 is zero. Substitution in eq 358 is therefore equivalent to introduction of complex excitation energies

$$\omega_n \rightarrow \omega_n - \mathrm{i}\gamma, \quad \omega_n = E_n - E_0 \tag{359}$$

Conceptually, damped response theory only requires the substitutions in eq 359 to be performed in the standard response-function expressions to introduce finite exited-state lifetimes. The empirical damping parameter γ is an effective inverse lifetime common to all excited states, leading to broadening that in reality has a number of physical origins: spontaneous-emission broadening, Doppler broadening, vibrational broadening, and collisional broadening. It is difficult, if at all possible, to devise an accurate ab initio model that takes into account the different broadening effects and provides a γ value tailored to each excited state; instead, finite lifetimes are treated empirically by means of the single damping parameter γ common to all excited states.

Damped response functions are complex and describe broadened dispersion and absorption spectra, as illustrated for the complex polarizability in section 3.7.2. In section 3.7.3 we briefly discuss higher order damped response theory.

3.7.2. Damped Linear Response theory.

By introducing complex excitation energies into the standard linear response function expression in eq 282 according to eq 359 the resulting damped linear response function $\overline{\langle\langle A;B\rangle\rangle}_{\omega_B}$ may be written as

$$\overline{\langle\langle A;B\rangle\rangle}_{\omega_B} = -\sum_j \left(\frac{\langle 0^{(0)}|A|j\rangle\langle j|B|0^{(0)}\rangle}{(\omega_j - \mathrm{i}\gamma) - \omega_B} + \frac{\langle j|A|0^{(0)}\rangle\langle 0^{(0)}|B|j\rangle}{(\omega_j - \mathrm{i}\gamma)^* + \omega_B} \right) \tag{360}$$

Note that the excitation energies in the second term are complex conjugated. Formally this is done to retain with the underlying structure of the Hessian matrix $\mathbf{E}^{[2]}$ in eq 232 also in damped response theory, see ref 90 for details. By performing the complex conjugation of the second term in eq 360 we obtain

$$\overline{\langle\langle A;B\rangle\rangle}_{\omega_B + \mathrm{i}\gamma} = -\sum_j \left(\frac{\langle 0^{(0)}|A|j\rangle\langle j|B|0^{(0)}\rangle}{\omega_j - (\omega_B + \mathrm{i}\gamma)} + \frac{\langle j|A|0^{(0)}\rangle\langle 0^{(0)}|B|j\rangle}{\omega_j + (\omega_B + \mathrm{i}\gamma)} \right) \tag{361}$$

where the imaginary iγ term in eq 360 is now effectively associated with the frequency ω_B rather than with the excitation energy ω_j. For this reason we added the iγ term to the frequency argument of the linear response function. Thus, damped linear response theory effectively corresponds to introducing a complex optical frequency

$$\omega_B \rightarrow \omega_B + \mathrm{i}\gamma \tag{362}$$

Damped response theory therefore requires solving response equations with complex frequencies.[89,93,90] By construction the damped linear response function in eq 361 satisfies the symmetry relation for the standard linear response function in eq 283

$$\overline{\langle\langle A;B\rangle\rangle}_{\omega_B + \mathrm{i}\gamma} = \overline{\langle\langle B;A\rangle\rangle}_{-(\omega_B + \mathrm{i}\gamma)} \tag{363}$$

Thus, phenomenological introduction of complex excitation energies as described above preserves this fundamental symmetry property of the linear response function.

To illustrate the underlying structure of the damped response function in eq 361 we consider the case where $A = B = \mu_\alpha$ is a component of the electric dipole operator, writing the real and imaginary components of the damped response function out in detail

$$\begin{aligned}\overline{\langle\langle \mu_\alpha;\mu_\alpha\rangle\rangle}_{\omega_B} = -\sum_j \Big(&\langle 0^{(0)}|\mu_\alpha|j\rangle\langle j|\mu_\alpha|0^{(0)}\rangle D_j(\omega_B) \\ &+ \langle 0^{(0)}|\mu_\alpha|j\rangle\langle j|\mu_\alpha|0^{(0)}\rangle D_j(-\omega_B) \\ &+ \mathrm{i}\Big[\langle 0^{(0)}|\mu_\alpha|j\rangle\langle j|\mu_\alpha|0^{(0)}\rangle A_j(\omega_B) \\ &- \langle 0^{(0)}|\mu_\alpha|j\rangle\langle j|\mu_\alpha|0^{(0)}\rangle A_j(-\omega_B)\Big]\Big)\end{aligned} \tag{364}$$

where the dispersion and absorption line-shape functions $D_j(\pm\omega)$ and $A_j(\pm\omega)$ are given by

$$\begin{aligned} D_j(\omega) &= \frac{\omega_j - \omega}{(\omega_j - \omega)^2 + \gamma^2}, \\ D_j(-\omega) &= \frac{\omega_j + \omega}{(\omega_j + \omega)^2 + \gamma^2} \\ A_j(\omega) &= \frac{\gamma}{(\omega_j - \omega)^2 + \gamma^2}, \end{aligned} \tag{365}$$

$$A_j(-\omega) = \frac{\gamma}{(\omega_j + \omega)^2 + \gamma^2}. \tag{366}$$

The dispersion and absorption line-shape functions are plotted in Figure 1. We note that γ determines the width of the line-shape functions, in particular, 2γ is the full width at half-maximum for the Lorentzian absorption line-shape function.

A plot of the real component of $\overline{\langle\langle \mu_\alpha;\mu_\alpha\rangle\rangle}_{\omega_B}$ against ω_B describes a spectrum of (minus) the polarizability, also close to resonance frequencies, where it has a physically correct dispersion shape D_j. In contrast, the standard response function in eq 278 diverges at resonance frequencies. The real part of the damped response function thus provides a physically motivated description of the polarizability at all frequencies, whereas the standard response function is well behaved only in the nonresonant region.

The imaginary part of $\overline{\langle\langle \mu_\alpha;\mu_\alpha\rangle\rangle}_{\omega_B}$ plotted against ω_B describes an absorption spectrum with Lorentzian line-shape functions A_j superimposed on electric-dipole transition strengths $\|\langle 0^{(0)}|\mu_\alpha|j\rangle\|^2$. We note that damped linear response functions may be evaluated in any frequency interval to obtain the corresponding absorption spectrum. Thus, damped response theory enables direct determination of absorption spectra also when application of standard response theory is difficult because it would require determination of a large number of individual transition dipole strengths, for example, in X-ray spectra and absorption spectra of large molecules.[83−85]

3.7.3. Higher Order Damped Response theory.

For the damped linear response function discussed above, introduction of complex excitation energies is equivalent to introduction of complex frequencies, see eq 362. Likewise, for higher order response functions complex frequencies are effectively introduced in accordance with eq 362 for each frequency that enters the response function.[89,90] However, the fundamental symmetry relations for higher order response functions, such as those in eqs 284 and 285, are in general not conserved in higher order damped response theory, as is the case in damped linear response theory, see eq 363.

Introduction of damping in quadratic and higher order response functions can be interpreted in a similar way as for the polarizability in section 3.7.2, where one component describes dispersion and the other absorption. For example, magnetic optical rotation (dispersion) and magnetic circular dichroism (MCD) (absorption) are described by the imaginary and real components, respectively, of the damped quadratic response function $\overline{\langle\langle \mu_\alpha;\mu_\beta,m_\gamma\rangle\rangle}_{\omega_B,0}$ where m_γ is a component of the magnetic dipole operator,[94−96] and two-photon absorption (TPA) spectra can be obtained from a damped cubic response function as described in ref 97. We note that, in general, the residue spectrum of a conventional response function can be obtained from the imaginary (or real in the case of an imaginary operator) component of the corresponding damped response function.

4. RESPONSE THEORY FOR APPROXIMATE STATES

In this section, we use the variation principles developed in the previous section to determine molecular response functions for approximate wave functions. From these response functions (and their poles and residues) we determine molecular properties for ground and excited states and transition matrix elements between these states, where the ground state is represented by an approximate wave function. For the variational Hartree−Fock and MCSCF models in sections 4.1 and 4.2 we use the variation principle for the time-averaged quasi-energy to determine the response functions. For the nonvariational coupled-cluster model in section 4.3 we use the time-averaged Lagrangian to determine the response functions. In section 4.3, we also describe how response functions may be obtained for a coupled-cluster wave function using the equation of motion formalism. Next, in section 4.4 we consider Møller−Plesset perturbation theory, in which only static ground-state properties can be calculated.

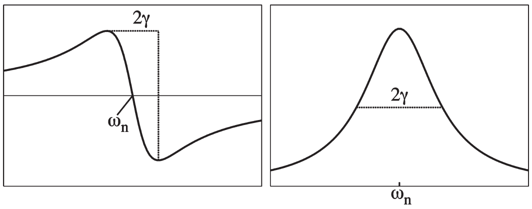

Figure 1. Dispersion $D_n(\omega)$ (left) and absorption $A_n(\omega)$ (right) line-shape functions of damped response theory.

In sections 4.1−4.4 we focus on the theoretical formulation of the wave function models mentioned above, where response functions are obtained as perturbation strength derivatives of the quasi-energy (or quasi-energy Lagrangian). Following the discussion of response functions for perturbation-dependent basis sets in section 4.5 we give in section 4.6 an overview of computational developments and implementations of response methods in a historical perspective.

4.1. Hartree−Fock Theory

The general theoretical basis for carrying out response theory at the SCF and MCSCF levels of theory was formulated by Olsen and Jørgensen in 1985,[70] followed by implementations of the linear,[98] quadratic,[99] and cubic[100,101] response functions in the MO basis in the 1980s and 1990s. Since 2000, developments in SCF response theory have been aimed at large molecular systems and a reformulation of response equations and response functions in the AO basis[13,14,102−106,141] using the elements of the AO density matrix as variational parameters instead of the MO coefficients. In the AO-based response formalism, all manipulations are reduced to elementary matrix operations such as additions and multiplications, making this formalism particularly convenient for developing linear-scaling algorithms when sparse matrix algebra can be applied.

Noting that the equations defining SCF response theory in the MO basis may be obtained as a special case of the MCSCF equations derived in section 4.2, we summarize in this section the AO-based quasi-energy formulation by Thorvaldsen et al.[106] The main advantage of this formulation is that perturbation-dependent basis sets (which may also depend on time) are an integral part of the formulation, treating perturbations with perturbation-dependent AOs (e.g., geometrical and magnetic perturbations with atom-fixed London orbitals, see section 2.4) on the same footing as perturbations where the field dependence is not included in the AOs (e.g., electric-field perturbations). This situation appears, for instance, when considering time-periodic London atomic orbitals.[107] Bearing in mind that DFT is not the focus of this review, we here restrict ourselves to Hartree−Fock theory but note that the same formulation applies to Kohn−Sham theory with the additional inclusion of exchange-correlation terms, which can be efficiently implemented and calculated using automatic differentiation techniques.[108] We also note that the quasi-energy formulation by Thorvaldsen et al.[106] has been generalized to two- and four-component wave functions in the basis of four-component spinors.[109]

4.1.1. Quasi-Energy Response Theory in a Density-Matrix Formulation. In the quasi-energy of eq 165 only the ket state is subject to time differentiation. The Hartree–Fock quasi-energy is therefore not symmetric with respect to operations on the bra and ket states

$$Q(t) = \langle\widetilde{\mathrm{HF}}|H - \mathrm{i}\partial_t|\widetilde{\mathrm{HF}}\rangle \tag{367}$$

In particular, the second term in eq 367 may be evaluated as

$$\langle\widetilde{\mathrm{HF}}| - \mathrm{i}\partial_t|\widetilde{\mathrm{HF}}\rangle = -\mathrm{i}\sum_J \int \phi_J^*(\mathbf{r}, t)\partial_t\phi_J(\mathbf{r}, t)\mathrm{d}\mathbf{r} \tag{368}$$

where the summation is over all occupied spin MOs (denoted with index J), differentiating only the ket MO $\phi_J(\mathbf{r},t)$. In contrast, the electron density

$$\rho(\mathbf{r}, t) = \sum_J \phi_J^*(\mathbf{r}, t)\phi_J(\mathbf{r}, t) \tag{369}$$

and its time derivative

$$\dot{\rho}(\mathbf{r}, t) = \sum_J (\phi_J^*(\mathbf{r}, t)\phi_J(\mathbf{r}, t) + \phi_J^*(\mathbf{r}, t)\phi_J(\mathbf{r}, t)) \tag{370}$$

are symmetric in $\phi_J{}^*(\mathbf{r},t)$ and $\phi_J(\mathbf{r},t)$. Given that the time-derivative contribution to the quasi-energy in eq 368 contains only the second term in the time-differentiated electron density, it is not straightforward to express the quasi-energy in terms of $\rho(\mathbf{r},t)$ and $\dot{\rho}(\mathbf{r},t)$.

Let us now consider the matrix representation of $\rho(\mathbf{r},t)$ in the AO basis. By expanding the MOs in the AOs χ_μ, which may depend on the external (possibly time-dependent) perturbation (see section 2.4)

$$\phi_J(\mathbf{r}, t) = \sum_\mu C_{\mu J}(t)\chi_\mu(\mathbf{r}, t) \tag{371}$$

we obtain

$$\rho(\mathbf{r}, t) = \sum_{\mu\nu} D_{\mu\nu}\dot{\chi}_\mu^*(\mathbf{r}, t)\chi_\nu(\mathbf{r}, t) \tag{372}$$

where we introduced the one-electron density matrix in the AO basis, $\mathbf{D}$, whose elements are given by

$$D_{\mu\nu}(t) = \sum_J C_{\mu J}^*(t)C_{\nu J}(t) \tag{373}$$

The time derivative of $\rho(\mathbf{r},t)$ may thus be expressed in terms of the time derivative of the density matrix

$$\dot{\rho}(\mathbf{r}, t) = \sum_{\mu\nu} (\dot{D}_{\mu\nu}\dot{\chi}_\mu^*(\mathbf{r}, t)\chi_\nu(\mathbf{r}, t) + D_{\mu\nu}\dot{\chi}_\mu^*(\mathbf{r}, t)\chi_\nu(\mathbf{r}, t)$$
$$+ D_{\mu\nu}\dot{\chi}_\mu^*(\mathbf{r}, t)\dot{\chi}_\nu(\mathbf{r}, t)) \tag{374}$$

with contributions from the density matrix as well as the AOs.

Even though the Hartree–Fock quasi-energy cannot be expressed in terms of $\rho(\mathbf{r},t)$ and its time derivative (or, equivalently, in terms of $\mathbf{D}$ and its time derivative) it is possible to express the perturbation-strength derivative of the time-averaged Hartree–Fock quasi-energy as a function of the density matrix $\mathbf{D}$ and its time derivative $\dot{\mathbf{D}}$[106]

$$\frac{\mathrm{d}\mathcal{Q}}{\mathrm{d}\varepsilon_A} = \frac{\mathrm{d}\mathcal{Q}(\mathbf{D}, \dot{\mathbf{D}})}{\mathrm{d}\varepsilon_A} \equiv \mathcal{Q}^A(\mathbf{D}, \dot{\mathbf{D}}) \tag{375}$$

where the quasi-energy derivative $\mathcal{Q}^A(\mathbf{D},\dot{\mathbf{D}})$ (whose explicit form is given in section 4.1.2) contains all information needed to determine the response functions by further differentiation with respect to the perturbation strengths, similarly to eqs 274–276

$$\langle\langle A; B\rangle\rangle_{\omega_B} = \frac{\mathrm{d}\mathcal{Q}^A(\mathbf{D}, \dot{\mathbf{D}})}{\mathrm{d}\varepsilon_B}\Big|_{\{\varepsilon\}=0}, \quad \omega_A = -\omega_B \tag{376}$$

$$\langle\langle A; B, C\rangle\rangle_{\omega_B, \omega_C} = \frac{\mathrm{d}^2\mathcal{Q}^A(\mathbf{D}, \dot{\mathbf{D}})}{\mathrm{d}\varepsilon_B\mathrm{d}\varepsilon_C}\Big|_{\{\varepsilon\}=0},$$
$$\omega_A = -\omega_B - \omega_C \tag{377}$$

and so on. The quasi-energy derivative $\mathcal{Q}^A(\mathbf{D},\dot{\mathbf{D}})$ therefore provides an alternative starting point to the quasi-energy for identifying response functions in terms of perturbed density matrices. Extending the notation in eq 375, we write the derivatives of a general function or matrix f in the manner

$$f^{B_1\ldots B_m} = \frac{\mathrm{d}^m f}{\mathrm{d}\varepsilon_{B_1}\ldots\mathrm{d}\varepsilon_{B_m}} \tag{378}$$

$$f^{n,\ B_1\ldots B_m} = \frac{\partial^{n+m} f}{\partial(\mathbf{D}^\mathrm{T})^n\partial\varepsilon_{B_1}\ldots\partial\varepsilon_{B_m}} \tag{379}$$

with special cases $f^{0,B_1\ldots B_m} = \partial^m f/\partial\varepsilon_{B_1}\ldots\partial\varepsilon_{B_m}$ and $f^{n,0} = \partial^n f/\partial(\mathbf{D}^\mathrm{T})^n$. In some cases, such derivatives are evaluated at zero perturbation strength, but this will always be clear from the context.

4.1.2. Quasi-Energy Gradient. When working with general time- and perturbation-dependent basis functions χ_μ, it is convenient to introduce the generalized Hartree–Fock energy[106]

$$E = \mathrm{tr}\left(\mathbf{h} + \mathbf{V} + \frac{1}{2}\mathbf{G}(\mathbf{D}) - \frac{\mathrm{i}}{2}\mathbf{T}\right)\mathbf{D} + h_\mathrm{nuc} \tag{380}$$

where $\mathbf{h}$ is the one-electron matrix without the external perturbation, $\mathbf{V}$ is the perturbation matrix (e.g., an electric dipole matrix), $\mathbf{G}(\mathbf{D})$ is the two-electron matrix containing Coulomb and exchange contributions, $\mathbf{T}$ is an anti-Hermitian time-differentiated overlap matrix

$$h_{\mu\nu} = \langle\chi_\mu| - \frac{1}{2}\nabla^2 - \sum_K Z_K r_K^{-1}|\chi_\nu\rangle \tag{381}$$

$$V_{\mu\nu} = \langle\chi_\mu|V(t)|\chi_\nu\rangle \tag{382}$$

$$G_{\mu\nu}(\mathbf{D}) = \sum_{\alpha\beta} D_{\beta\alpha}(g_{\mu\nu\alpha\beta} - g_{\mu\beta\alpha\nu}) \tag{383}$$

$$g_{\mu\nu\alpha\beta} = \iint \frac{\chi_\mu^*(\mathrm{r}_1)\chi_\alpha^*(\mathrm{r}_2)\chi_\nu(\mathrm{r}_1)\chi_\beta(\mathrm{r}_2)}{r_{12}}\mathrm{d}\mathrm{r}_1\ \mathrm{d}\mathrm{r}_2 \tag{384}$$

$$T_{\mu\nu} = \langle\chi_\mu|\dot{\chi}_\nu\rangle - \langle\dot{\chi}_\mu|\chi_\nu\rangle \tag{385}$$

while h_{nuc} is the nuclear repulsion term of eq 86. In the notation of eqs 378 and 379, the quasi-energy gradient $\mathcal{Q}^A = \mathcal{Q}^A(\mathbf{D},\dot{\mathbf{D}})$ may be written in terms of the partial derivatives of the generalized Hartree–Fock energy $E^{0,A}$ and a reorthonormalization term $\mathrm{tr}\mathbf{S}^A\mathbf{W}$[106]

$$\mathcal{Q}^A = E^{0,\,A} - \mathrm{tr}\mathbf{S}^A\mathbf{W} \tag{386}$$

where $E^{0,A}$ is given by

$$E^{0,\,A} = \mathrm{tr}\left(\mathbf{h}^A + \mathbf{V}^A + \frac{1}{2}\mathbf{G}^A(\mathbf{D}) - \frac{\mathrm{i}}{2}\mathbf{T}^A\right)\mathbf{D} + h^A_{\mathrm{nuc}} \tag{387}$$

because $\mathbf{h}^{0,A} = \mathbf{h}^A$ and so on. Note that in $\mathbf{G}^A(\mathbf{D})$ only the two-electron integrals $g_{\mu\nu\alpha\beta}$ are differentiated with respect to ε_A. The $\mathbf{S}^A$ matrix in eq 386 is the derivative of the AO overlap matrix

$$S_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle \tag{388}$$

and $\mathbf{W}$ is a generalized energy- and frequency-weighted density matrix

$$\mathbf{W} = \mathbf{DFD} + \frac{\mathrm{i}}{2}(\dot{\mathbf{D}}\mathbf{SD} - \mathbf{DS}\dot{\mathbf{D}}) \tag{389}$$

where $\mathbf{F}$ is the generalized time-dependent Fock matrix

$$\mathbf{F} = \mathbf{E}^{1,\,0} = \mathbf{h} + \mathbf{G}(\mathbf{D}) + \mathbf{V} - \frac{\mathrm{i}}{2}\mathbf{T} \tag{390}$$

We note the close relationship between eq 386 and the molecular gradient in the AO basis.[110] The main difference lies in the inclusion of time-dependent terms in eq 386, where $\mathbf{W}$ is a generalization of the energy-weighted density matrix.[111] Indeed, the molecular gradient is recovered in the time-independent limit, when the time-dependent terms (i.e., the terms involving $\mathbf{T}$, $\mathbf{T}^A$, and the two last terms in $\mathbf{W}$) vanish. If the perturbation A is not described using perturbation-dependent basis sets, most of the terms in eq 386 vanish and the following simple expression is obtained

$$\mathcal{Q}^A = \mathrm{tr}\,\mathbf{V}^A\mathbf{D} \tag{391}$$

which represents the expectation value of the one-electron perturbation operator V^A.

The quasi-energy gradient in eq 386 provides the starting point for generating response functions by further differentiation, according to eqs 376 and 377. However, before considering response functions in section 4.1.4, we discuss the parametrization of the density matrix in section 4.1.3.

4.1.3. Perturbed Density Matrix. The density matrix for a single-determinant Hartree–Fock state must satisfy the trace, Hermiticity, and idempotency conditions

$$\mathrm{tr}\,\mathbf{DS} = N \tag{392}$$

$$\mathbf{D}^\dagger = \mathbf{D} \tag{393}$$

$$\mathbf{DSD} = \mathbf{D} \tag{394}$$

where N is the number of electrons in the molecular system. Whereas the trace and Hermiticity conditions are automatically satisfied in the formulation given below, the idempotency relation requires special attention. Furthermore, the time-dependent density matrix must be a solution to the time-dependent SCF (TDSCF) matrix equation[106]

$$\left(\mathbf{F} - \frac{\mathrm{i}}{2}\mathbf{S}\partial_t\right)\mathbf{DS} - \left(\mathbf{SDF} + \frac{\mathrm{i}}{2}\partial_t(\mathbf{SD})\mathbf{S}\right) = \mathbf{0} \tag{395}$$

which, in the absence of a time-dependent perturbation, reduces to the usual Fock stationary conditions $\mathbf{FDS} = \mathbf{SDF}$ of Hartree–Fock theory.[30] We note that eq 395 was also derived in ref 102 but without taking into account the possible perturbation and time dependence of the AO basis functions.

The AO density matrix is now expanded in orders of the perturbation

$$\mathbf{D} = \mathbf{D}_0 + \mathbf{D}^{(1)} + \mathbf{D}^{(2)} + \ldots \tag{396}$$

where $\mathbf{D}_0$ is the optimized density matrix for the unperturbed system (the subscript 0 here and elsewhere denoting the unperturbed system) and where higher order density matrices are written in terms of their frequency and operator components following eq 218

$$\mathbf{D}^{(1)} = \sum_B \varepsilon_B\mathbf{D}^B\mathrm{e}^{-\mathrm{i}\omega_B t} \tag{397}$$

$$\mathbf{D}^{(2)} = \sum_{BC} \varepsilon_B\varepsilon_C\mathbf{D}^{BC}\mathrm{e}^{-\mathrm{i}(\omega_B + \omega_C)t} \tag{398}$$

The perturbed density matrices are partitioned into particular and homogeneous components.[106] The particular component is chosen such that the time-dependent density matrix satisfies the idempotency relation, whereas the homogeneous component ensures that the density matrix is a solution to the TDSCF equation.

To illustrate this partitioning scheme, we consider the first-order perturbed density matrix $\mathbf{D}^B$, which we decompose into particular and homogeneous components

$$\mathbf{D}^B = \mathbf{D}^B_{\mathrm{P}} + \mathbf{D}^B_{\mathrm{H}} \tag{399}$$

From eq 394 we find that the first-order idempotency relation is the inhomogeneous equation

$$\mathbf{D}^B\mathbf{S}_0\mathbf{D}_0 + \mathbf{D}_0\mathbf{S}_0\mathbf{D}^B - \mathbf{D}^B = \mathbf{N}^B,\quad \mathbf{N}^B = -\mathbf{D}_0\mathbf{S}^B\mathbf{D}_0 \tag{400}$$

A particular solution $\mathbf{D}^B_{\mathrm{P}}$ to this equation is given by

$$\mathbf{D}^B_{\mathrm{P}} = \mathbf{N}^B\mathbf{S}_0\mathbf{D}_0 + \mathbf{D}_0\mathbf{S}_0\mathbf{N}^B - \mathbf{N}^B = -\mathbf{D}_0\mathbf{S}^B\mathbf{D}_0 \tag{401}$$

The homogeneous component $\mathbf{D}^B_{\mathrm{H}}$ is parametrized in terms of an unknown matrix $\mathbf{X}^B$ in the form

$$\mathbf{D}^B_{\mathrm{H}} = \mathbf{D}_0\mathbf{S}_0\mathbf{X}^B - \mathbf{X}^B\mathbf{S}_0\mathbf{D}_0 \tag{402}$$

ensuring that $\mathbf{D}^B_{\mathrm{H}}$ is a solution to the homogeneous equation associated with eq 400

$$\mathbf{D}^B_{\mathrm{H}}\mathbf{S}_0\mathbf{D}_0 + \mathbf{D}_0\mathbf{S}_0\mathbf{D}^B_{\mathrm{H}} - \mathbf{D}^B_{\mathrm{H}} = \mathbf{0} \tag{403}$$

In this way, it is ensured that $\mathbf{D}^B$ in eq 399 satisfies the idempotency relation to first order. The matrix $\mathbf{X}^B$ in the homogeneous component $\mathbf{D}^B_{\mathrm{H}}$ is now determined so that $\mathbf{D}^B$ is also a solution to the first-order TDSCF equation. Differentiating eq 395 with respect to ε_B at zero perturbation strengths the following equation for $\mathbf{X}^B$ is obtained[106]

$$\left(\mathbf{E}^{[2]} - \omega_B\mathbf{S}^{[2]}\right)\mathbf{X}^B = \mathbf{R}^B \tag{404}$$

where $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ are generalized Hessian and metric matrices, respectively. As eq 404 is solved iteratively, it is not necessary to construct these matrices explicitly; it is sufficient to know their products with a general matrix $\mathbf{X}$

$$\begin{aligned}\mathbf{E}^{[2]}\mathbf{X} = {} & \mathbf{G}(\mathbf{X}\mathbf{S}_0\mathbf{D}_0 - \mathbf{D}_0\mathbf{S}_0\mathbf{X})\mathbf{D}_0\mathbf{S}_0 - \mathbf{S}_0\mathbf{D}_0\mathbf{G}(\mathbf{X}\mathbf{S}_0\mathbf{D}_0 - \mathbf{D}_0\mathbf{S}_0\mathbf{X}) \\ & + \mathbf{F}_0(\mathbf{X}\mathbf{S}_0\mathbf{D}_0 - \mathbf{D}_0\mathbf{S}_0\mathbf{X})\mathbf{S}_0 - \mathbf{S}_0(\mathbf{X}\mathbf{S}_0\mathbf{D}_0 - \mathbf{D}_0\mathbf{S}_0\mathbf{X})\mathbf{F}_0 \end{aligned} \tag{405}$$

$$\mathbf{S}^{[2]}\mathbf{X} = \mathbf{S}_0(\mathbf{X}\mathbf{S}_0\mathbf{D}_0 - \mathbf{D}_0\mathbf{S}_0\mathbf{X})\mathbf{S}_0 \tag{406}$$

where $\mathbf{F}_0$ is the Fock matrix of the unperturbed system. The right-hand-side matrix of the response equation in eq 404 is given by

$$\begin{aligned}\mathbf{R}^B = {} & \left[\mathbf{E}^{1,\,B} + \mathbf{E}^{2,\,0}(\mathbf{D}_\mathrm{P}^B)\right]\mathbf{D}_0\mathbf{S}_0 + \left(\mathbf{F}_0 - \frac{\omega_B}{2}\mathbf{S}_0\right)(\mathbf{D}_\mathrm{P}^B\mathbf{S}_0 + \mathbf{D}_0\mathbf{S}^B) \\ & - \mathbf{S}_0\mathbf{D}_0\left[\mathbf{E}^{1,\,B} + \mathbf{E}^{2,\,0}(\mathbf{D}_\mathrm{P}^B)\right] - (\mathbf{S}_0\mathbf{D}_\mathrm{P}^B + \mathbf{S}^B\mathbf{D}_0)\left(\mathbf{F}_0 - \frac{\omega_B}{2}\mathbf{S}_0\right)\end{aligned} \tag{407}$$

We note that the particular component $\mathbf{D}_\mathrm{P}^B$ only depends on the zero-order density matrix $\mathbf{D}_0$, whereas the homogeneous component $\mathbf{D}_\mathrm{H}^B$ requires solution of the response equation in eq 404.

The first-order analysis given above may be generalized to arbitrary orders, decomposing the mth-order density matrix into particular and homogeneous components

$$\mathbf{D}^{B_1\ldots B_m} = \mathbf{D}_\mathrm{P}^{B_1\ldots B_m} + \mathbf{D}_\mathrm{H}^{B_1\ldots B_m} \tag{408}$$

The mth-order idempotency condition can be written in the form

$$\mathbf{D}^{B_1\ldots B_m}\mathbf{S}\mathbf{D}_0 + \mathbf{D}_0\mathbf{S}\mathbf{D}^{B_1\ldots B_m} - \mathbf{D}^{B_1\ldots B_m} = \mathbf{N}^{B_1\ldots B_m} \tag{409}$$

where the inhomogeneity $\mathbf{N}^{B_1\ldots B_m}$ contains perturbed density matrices of order less than m. A particular solution $\mathbf{D}_\mathrm{P}^{B_1\ldots B_m}$ to eq 409 is given by

$$\mathbf{D}_\mathrm{P}^{B_1\ldots B_m} = \mathbf{N}^{B_1\ldots B_m}\mathbf{S}_0\mathbf{D}_0 + \mathbf{D}_0\mathbf{S}_0\mathbf{N}^{B_1\ldots B_m} - \mathbf{N}^{B_1\ldots B_m} \tag{410}$$

Note that $\mathbf{D}_\mathrm{P}^{B_1\ldots B_m}$ has the same structure as the first-order particular density matrix $\mathbf{D}_\mathrm{P}^B$ in eq 401. The mth-order homogeneous component $\mathbf{D}_\mathrm{H}^{B_1\ldots B_m}$ is parametrized as in eq 402

$$\mathbf{D}_\mathrm{H}^{B_1\ldots B_m} = \mathbf{D}_0\mathbf{S}\mathbf{X}^{B_1\ldots B_m} - \mathbf{X}^{B_1\ldots B_m}\mathbf{S}\mathbf{D}_0 \tag{411}$$

where $\mathbf{X}^{B_1\ldots B_m}$ is determined so that the total density matrix in eq 408 satisfies the TDSCF equation to order m by solving the mth-order response equation

$$[\mathbf{E}^{[2]} - (\omega_{B_1} + \ldots + \omega_{B_m})\mathbf{S}^{[2]}]\mathbf{X}^{B_1\ldots B_m} = \mathbf{R}^{B_1\ldots B_m} \tag{412}$$

This equation has the same form as the first-order equation in eq 404, with $\mathbf{R}^{B_1\ldots B_m}$ containing only lower order density matrices. Since the response equations have the same structure to all orders they can be determined using the same solver, for example, the linear-scaling solver of Coriani et al.,[14] making the formulation suitable for large molecular systems. We note that the partitioning of the density matrix presented here, where one component is a solution to the idempotency relation and another component solves the TDSCF equation, was first developed and implemented for molecular Hessians and magnetizabilities by Larsen et al.[112]

In summary, to determine the mth-order density matrices $\mathbf{D}^{B_1\ldots B_m}$ we first construct the mth-order inhomogeneity $\mathbf{N}^{B_1\ldots B_m}$ from lower order density matrices and determine the particular solutions $\mathbf{D}_\mathrm{P}^{B_1\ldots B_m}$. Next, the right-hand sides $\mathbf{R}^{B_1\ldots B_m}$ are constructed from $\mathbf{D}_\mathrm{P}^{B_1\ldots B_m}$ and from lower order density matrices followed by solution of the mth-order response equations to yield $\mathbf{X}^{B_1\ldots B_m}$ and the homogeneous components $\mathbf{D}_\mathrm{H}^{B_1\ldots B_m}$. Finally, $\mathbf{D}^{B_1\ldots B_m}$ is determined according to eq 408. We have thus established a recursive procedure for determining perturbed density matrices to arbitrary order, where perturbation-dependent basis sets are an integrated part of the formulation. With the perturbed density matrices at hand it is straightforward to evaluate response functions, as discussed in the next subsection.

4.1.4. Response Functions.

Response functions may be identified by differentiation of the quasi-energy gradient in eq 386 according to eqs 376 and 377. In the notation of eq 379 the derivative of the first term in eq 386 at zero interaction strength may be written as

$$\frac{\mathrm{d}E^{0,\,A}}{\mathrm{d}\varepsilon_B} = \frac{\partial E^{0,\,A}}{\partial \varepsilon_B} + \mathrm{tr}\,\frac{\partial E^{0,\,A}}{\partial \mathbf{D}^\mathrm{T}}\frac{\partial \mathbf{D}}{\partial \varepsilon_B} = E^{0,\,AB} + \mathrm{tr}\,\mathbf{E}^{1,\,A}\mathbf{D}^B \tag{413}$$

Including also the derivative of the second term in eq 386 we obtain the following expression for the linear response function

$$\langle\langle A; B\rangle\rangle_{\omega_B} = \mathcal{Q}^{AB} = E^{0,\,AB} + \mathrm{tr}\,\mathbf{E}^{1,\,A}\mathbf{D}^B - \mathrm{tr}\,\mathbf{S}^{AB}\mathbf{W}_0 - \mathrm{tr}\,\mathbf{S}^A\mathbf{W}^B \tag{414}$$

According to eq 390 the differentiated Fock matrix becomes

$$\mathbf{E}^{1,\,A} = \mathbf{F}^{0,\,A} = \mathbf{h}^A + \mathbf{G}^A(\mathbf{D}_0) + \mathbf{V}^A - \frac{\mathrm{i}}{2}\mathbf{T}^A \tag{415}$$

and using eq 389 the $\mathbf{W}$ matrices are given by

$$\mathbf{W}_0 = \mathbf{D}_0\mathbf{F}_0\mathbf{D}_0 \tag{416}$$

$$\mathbf{W}^B = \mathbf{D}_0\mathbf{F}^B\mathbf{D}_0 + \mathbf{D}^B\left(\mathbf{F}_0 + \frac{\omega_B}{2}\mathbf{S}_0\right)\mathbf{D}_0 + \mathbf{D}_0\left(\mathbf{F}_0 - \frac{\omega_B}{2}\mathbf{S}_0\right)\mathbf{D}^B \tag{417}$$

Although not immediately apparent from the expression in eq 414, the linear response function satisfies the general symmetry relation in eq 283. When the basis set does not depend on the external perturbations A and B only the contribution involving $\mathbf{V}^A$ in the second term of eq 414 remains, reducing the linear response function to the simple expression

$$\langle\langle A; B\rangle\rangle_{\omega_B} = \mathrm{tr}\,\mathbf{V}^A\mathbf{D}^B \tag{418}$$

also obtained by Larsen et al.[102]

The quadratic response function in eq 377 is given by[106]

$$\begin{aligned}\langle\langle A; B,\, C\rangle\rangle_{\omega_B,\,\omega_C} = {} & \mathcal{Q}^{ABC} = E^{0,\,ABC} \\ & + \mathrm{tr}(\mathbf{E}^{1,\,AC}\mathbf{D}^B + \mathbf{E}^{1,\,AB}\mathbf{D}^C + \mathbf{E}^{2,\,A}(\mathbf{D}^B)\mathbf{D}^C + 2\mathbf{E}^{1,\,A}\mathbf{D}^{BC}) \\ & - \mathrm{tr}(\mathbf{S}^{ABC}\mathbf{W}_0 + \mathbf{S}^{AC}\mathbf{W}^B + \mathbf{S}^{AB}\mathbf{W}^C + \mathbf{S}^A\mathbf{W}^{BC})\end{aligned} \tag{419}$$

where the first-order density matrices $\mathbf{D}^B$ and $\mathbf{D}^C$ and the second-order density matrices $\mathbf{D}^{BC}$ are required to determine the quadratic response function. We also note that $\mathbf{E}^{2,A}(\mathbf{D}^B)$ corresponds to the two-electron matrix in 383 with differentiated two-electron integrals. It is possible to obtain an expression for $\langle\langle A;B,C\rangle\rangle_{\omega_B,\omega_C}$ that complies with the $2n + 1$ rule so that only first-order density matrices $\mathbf{D}^A$, $\mathbf{D}^B$, and $\mathbf{D}^C$ are required; see ref 106 for details.

4.2. Multiconfigurational Self-Consistent Field Theory

The multiconfigurational self-consistent field (MCSCF) model[30,113,114] is a highly flexible electronic-structure model, well suited to systems not dominated by a single electronic configuration, for example, the ground-state ozone molecule, molecular dissociation processes, and symmetry-forbidden reactions. With its flexible multiconfigurational ansatz the MCSCF model is able to recover the static correlation necessary for a qualitatively correct description of such systems; for a quantitatively correct description some correction for dynamic correlation is also necessary, as can be achieved by perturbation theory (e.g., second-order complete-active-space perturbation theory, CASPT2,[115] or second-order *n*-electron valence-state perturbation theory, NEVPT2[116]) or by a multireference configuration interaction (MRCI)[114] treatment. In the following, we discuss the calculation of molecular properties for the MCSCF model, restricting ourselves to linear response theory.

4.2.1. MCSCF Quasi-Energy. In terms of the unperturbed MCSCF reference state $|\mathrm{MC}\rangle$, the regular time-dependent MCSCF wave function $|\widetilde{\mathrm{MC}}\rangle$ may be parametrized as[70]

$$|\widetilde{\mathrm{MC}}\rangle = \mathrm{e}^{\mathrm{i}\kappa(t)}\mathrm{e}^{\mathrm{i}S(t)}|\mathrm{MC}\rangle \tag{420}$$

where $|\mathrm{MC}\rangle$ is a linear combination of Slater determinants and $\kappa(t)$ and $S(t)$ are Hermitian orbital-rotation and state-rotation operators, respectively

$$\kappa(t) = \sum_{\mu}(\kappa_{\mu}(t)q_{\mu}^{\dagger} + \kappa_{\mu}^{*}(t)q_{\mu}) \tag{421}$$

$$S(t) = \sum_{n}(S_n(t)R_n^{\dagger} + S_n^{*}(t)R_n) \tag{422}$$

Here $\kappa(t)$ is expressed in terms of the orbital-excitation operators $q_{\mu}^{\dagger}$ corresponding to the singlet and triplet excitation operators in eqs 97−100, where μ is a compound MO index for orbital excitations. The state-transfer operator $S(t)$ is expressed in terms of the operators

$$R_n^{\dagger} = |n\rangle\langle\mathrm{MC}| \tag{423}$$

where the $|n\rangle$ states span the orthogonal complement of the MCSCF reference state $|\mathrm{MC}\rangle$. The reference state $|\mathrm{MC}\rangle$ is determined by variationally optimizing the expectation value of the unperturbed Hamiltonian H_0 with respect to the orbital- and state-rotation parameters,[70] yielding the Brillouin conditions

$$\langle\mathrm{MC}|[H_0, q_{\mu}^{\dagger}]|\mathrm{MC}\rangle = 0 \tag{424}$$

$$\langle\mathrm{MC}|[H_0, R_n^{\dagger}]|\mathrm{MC}\rangle = 0 \tag{425}$$

Because of the exponential parametrization in eq 420 the time-dependent MCSCF wave function is normalized by construction and it is not necessary to impose a normalization constraint. In this parametrization we introduce the time-averaged MCSCF quasi-energy

$$\begin{aligned}\mathcal{Q} &= \{\langle\widetilde{\mathrm{MC}}|H - \mathrm{i}\partial_t|\widetilde{\mathrm{MC}}\rangle\}_T \\ &= \{\langle\mathrm{MC}|\mathrm{e}^{-\mathrm{i}S(t)}\mathrm{e}^{-\mathrm{i}\kappa(t)}(H - \mathrm{i}\partial_t)\mathrm{e}^{\mathrm{i}\kappa(t)}\mathrm{e}^{\mathrm{i}S(t)}|\mathrm{MC}\rangle\}_T\end{aligned} \tag{426}$$

where the time-dependent orbital- and state-rotation parameters are determined by optimizing $\mathcal{Q}$ variationally

$$\delta\mathcal{Q} = 0 \tag{427}$$

In the following, we derive the MCSCF linear response function; for higher order response functions, see ref 70.

4.2.2. Second-Order MCSCF Quasi-Energy. The orbital- and state-rotation operators may be expanded in orders of the perturbation

$$\kappa(t) = \kappa^{(1)}(t) + \kappa^{(2)}(t) + ... \tag{428}$$

$$S(t) = S^{(1)}(t) + S^{(2)}(t) + ... \tag{429}$$

where the zero-order parameters vanish because the reference wave function $|\mathrm{MC}\rangle$ is variationally optimized for the unperturbed system. Since the MCSCF quasi-energy is determined variationally, only the first-order response parameters are needed for the linear response function studied here, following the $2n + 1$ rule. The first-order operators may be expanded in terms of their frequency and operator components (similarly to the expansion in eq 218)

$$\kappa^{(1)}(t) = \sum_{B}\varepsilon_B\kappa^{B}\mathrm{e}^{-\mathrm{i}\omega_B t} \tag{430}$$

$$S^{(1)}(t) = \sum_{B}\varepsilon_B S^{B}\mathrm{e}^{-\mathrm{i}\omega_B t} \tag{431}$$

where B is a combined operator−frequency index. The operators κ^B and S^B are written in terms of the parameters κ_{μ}^{B} and S_m^B (equivalently to the expression in the time domain in eqs 421 and 422) as

$$\kappa^{B} = \sum_{\mu}\left(\kappa_{\mu}^{B}q_{\mu}^{\dagger} + \kappa_{\mu}^{-B*}q_{\mu}\right) \tag{432}$$

$$S^{B} = \sum_{n}(S_n^{B}R_n^{\dagger} + S_n^{-B*}R_n) \tag{433}$$

The paired structure of κ^B with respect to the B and $-B$ indices in eq 432 ensures that $\kappa^{-B\dagger} = \kappa^B$ such that $\kappa^{(1)}(t)$ is Hermitian (and likewise for the S operators).

We now expand the MCSCF quasi-energy in orders of the perturbation

$$\mathcal{Q} = \mathcal{Q}^{(0)} + \mathcal{Q}^{(1)} + \mathcal{Q}^{(2)} + ... \tag{434}$$

Limiting ourselves to linear response theory, we need only consider the MCSCF quasi-energy up to second order. The zero-order quasi-energy is simply the MCSCF energy

$$\mathcal{Q}^{(0)} = \langle\mathrm{MC}|H_0|\mathrm{MC}\rangle \tag{435}$$

Because of the $2n + 1$ rule, first-order parameters do not contribute to the first-order quasi-energy, which reduces to a sum of simple expectation values. Furthermore, upon time averaging, only static terms in $V(t)$ contribute to the first-order MCSCF quasi-energy

$$\begin{aligned}\mathcal{Q}^{(1)} &= \left\{\langle\mathrm{MC}|\sum_{B}\varepsilon_B V_B\mathrm{e}^{-\mathrm{i}\omega_B t}|\mathrm{MC}\rangle\right\}_T \\ &= \sum_{B:\omega_B = 0}\varepsilon_B\langle\mathrm{MC}|V_B|\mathrm{MC}\rangle\end{aligned} \tag{436}$$

To determine the second-order MCSCF quasi-energy

$$\mathcal{Q}^{(2)} = \left\{\langle\mathrm{MC}|\mathrm{e}^{-\mathrm{i}S(t)}\mathrm{e}^{-\mathrm{i}\kappa(t)}(H - \mathrm{i}\partial_t)\mathrm{e}^{\mathrm{i}\kappa(t)}\mathrm{e}^{\mathrm{i}S(t)}|\mathrm{MC}\rangle\right\}_T^{(2)} \tag{437}$$

we invoke the Baker–Campbell–Hausdorff (BCH) expansion

$$e^{-A}Be^{A} = B + [B, A] + \frac{1}{2!}[[B, A], A] + \frac{1}{3!}[[[B, A], A], A] + ... \tag{438}$$

to write the part of $\mathcal{Q}^{(2)}$ containing the Hamiltonian $H = H_0 + V(t)$ in the form

$$\begin{aligned}\{\langle\widetilde{\mathrm{MC}}|H|\widetilde{\mathrm{MC}}\rangle\}_{\mathrm{T}}^{(2)} &= \Big\{\langle \mathrm{MC}|\Big(\mathrm{i}\Big[V(t), S^{(1)}(t) + \kappa^{(1)}(t)\Big] \\ &- \Big[\Big[H_0, \kappa^{(1)}(t)\Big], S^{(1)}(t)\Big] - \frac{1}{2}\Big[\Big[H_0, S^{(1)}(t)\Big], S^{(1)}(t)\Big] \\ &- \frac{1}{2}\Big[\Big[H_0, \kappa^{(1)}(t)\Big], \kappa^{(1)}(t)\Big]\Big)|\mathrm{MC}\rangle\Big\}_{T}\end{aligned} \tag{439}$$

where the terms involving second-order rotation parameters vanish by the $2n + 1$ rule. Likewise, using the commutator relation $[\partial_t, X] = \dot{X}$ for a general operator X we find that the time-derivative term in eq 437 becomes

$$\begin{aligned}&\Big\{\langle\widetilde{\mathrm{MC}}| - \mathrm{i}\partial_t|\widetilde{\mathrm{MC}}\rangle\Big\}_{T}^{(2)} \\ &= \Big\{ - \mathrm{i}\langle \mathrm{MC}|\Big(- \frac{1}{2}\Big[\dot{S}^{(1)}, S^{(1)}\Big] - \frac{1}{2}\Big[\dot{\kappa}^{(1)}, \kappa^{(1)}\Big] \\ &- \Big[\dot{\kappa}^{(1)}, S^{(1)}\Big]\Big)|\mathrm{MC}\rangle\Big\}_{T}\end{aligned} \tag{440}$$

The second-order quasi-energy may be written in terms of the different frequencies and perturbations as

$$\mathcal{Q}^{(2)} = \sum_{B_1, B_2} \varepsilon_{B_1}\varepsilon_{B_2}\mathcal{Q}^{B_1B_2}, \omega_{B_1} + \omega_{B_2} = 0 \tag{441}$$

where $\mathcal{Q}^{B_1B_2} = \mathcal{Q}^{B_2B_1}$ and the frequency condition excludes contributions that in any case vanish upon time averaging.

Let us now consider one particular nonvanishing component of the second-order quasi-energy $\mathcal{Q}^{(2)}$

$$\mathcal{Q}^{B_1B_2} = \frac{1}{2}\frac{\mathrm{d}^2\mathcal{Q}^{(2)}}{\mathrm{d}\varepsilon_{B_1}\mathrm{d}\varepsilon_{B_2}} \tag{442}$$

obtained by differentiation of eqs 439 and 440 with respect to ε_{B_1} and ε_{B_2}. From the first term in eq 439 we obtain

$$\begin{aligned}&- \mathrm{i}\frac{\mathrm{d}^2\{\langle \mathrm{MC}|[S^{(1)}(t) + \kappa^{(1)}(t), V(t)]|\mathrm{MC}\rangle\}_{T}}{\mathrm{d}\varepsilon_{B_1}\mathrm{d}\varepsilon_{B_2}} \\ &= - \mathrm{i}\Big\{\Big(\langle \mathrm{MC}|\Big[S^{B_1} + \kappa^{B_1}, V_{B_2}\Big]|\mathrm{MC}\rangle \\ &+ \langle \mathrm{MC}|\Big[S^{B_2} + \kappa^{B_2}, V_{B_1}\Big]|\mathrm{MC}\rangle\Big)e^{-\mathrm{i}(\omega_{B_1} + \omega_{B_2})t}\Big\}_{T} \\ &= - 2\mathrm{i}P_{[1, 2]}\langle \mathrm{MC}|\Big[S^{B_1} + \kappa^{B_1}, V_{B_2}\Big]|\mathrm{MC}\rangle\end{aligned} \tag{443}$$

where $P_{[1,2]}$ averages over permutations, see eq 222. To express eq 443 in a compact manner, we introduce the column vectors $\boldsymbol{\beta}^{B}$ and $\mathbf{T}^{\dagger}$ containing the first-order orbital- and state-rotation parameters and the corresponding operators, respectively

$$\boldsymbol{\beta}^{B} = \begin{pmatrix}\boldsymbol{\eta}^{B} \\ \boldsymbol{\eta}^{-B*}\end{pmatrix} = \begin{pmatrix}\boldsymbol{\kappa}^{B} \\ \mathbf{S}^{B} \\ \boldsymbol{\kappa}^{-B*} \\ \mathbf{S}^{-B*}\end{pmatrix}, \quad \mathbf{T}^{\dagger} = \begin{pmatrix}\mathbf{t} \\ \mathbf{t}^{\dagger}\end{pmatrix} = \begin{pmatrix}\mathbf{q} \\ \mathbf{R} \\ \mathbf{q}^{\dagger} \\ \mathbf{R}^{\dagger}\end{pmatrix} \tag{444}$$

Noting that the conjugate row vectors

$$\boldsymbol{\beta}^{-B\dagger} = \begin{pmatrix}\boldsymbol{\eta}^{-B*} & \boldsymbol{\eta}^{B}\end{pmatrix} = \begin{pmatrix}\boldsymbol{\kappa}^{-B*} & \mathbf{S}^{-B*} & \boldsymbol{\kappa}^{B} & \mathbf{S}^{B}\end{pmatrix} \tag{445}$$

$$\mathbf{T} = \begin{pmatrix}\mathbf{t}^{\dagger} & \mathbf{t}\end{pmatrix} = \begin{pmatrix}\mathbf{q}^{\dagger} & \mathbf{R}^{\dagger} & \mathbf{q} & \mathbf{R}\end{pmatrix} \tag{446}$$

contain the same elements as the column vectors $\boldsymbol{\beta}^{B}$ and $\mathbf{T}^{\dagger}$ (but reordered) we may write $S^{B_1} + \kappa^{B_1}$ of eqs 432 and 433 in the following two equivalent forms

$$S^{B_1} + \kappa^{B_1} = \mathbf{T}\boldsymbol{\beta}^{B_1} = \boldsymbol{\beta}^{-B_1\dagger}\mathbf{T}^{\dagger} \tag{447}$$

Returning to eq 443, we now obtain

$$\begin{aligned}&- 2\mathrm{i}P_{[1, 2]}\langle \mathrm{MC}|\Big[S^{B_1} + \kappa^{B_1}, V_{B_2}\Big]|\mathrm{MC}\rangle \\ &= - 2\mathrm{i}P_{[1, 2]}\boldsymbol{\beta}^{-B_1\dagger}\langle \mathrm{MC}|\Big[\mathbf{T}^{\dagger}, V_{B_2}\Big]|\mathrm{MC}\rangle \\ &= - 2\mathrm{i}P_{[1, 2]}\boldsymbol{\beta}^{-B_1\dagger}\mathbf{V}_{B_2}^{[1]}\end{aligned} \tag{448}$$

where we introduced the column vector

$$\mathbf{V}_{B_2}^{[1]} = \langle \mathrm{MC}|\Big[\mathbf{T}^{\dagger}, V_{B_2}\Big]|\mathrm{MC}\rangle \tag{449}$$

Likewise, we obtain after some algebra the following expression for the remaining terms in eq 439

$$\begin{aligned}&- \frac{\mathrm{d}^2}{\mathrm{d}\varepsilon_{B_1}\mathrm{d}\varepsilon_{B_2}}\Big\{\langle \mathrm{MC}|\Big[\Big[H_0, \kappa^{(1)}(t)\Big], S^{(1)}(t)\Big] + \frac{1}{2}\Big[\Big[H_0, S^{(1)}(t)\Big], S^{(1)}(t)\Big] \\ &+ \frac{1}{2}\Big[\Big[H_0, \kappa^{(1)}(t)\Big], \kappa^{(1)}(t)\Big]|\mathrm{MC}\rangle\Big\}_{T} \\ &= - 2P_{[1, 2]}\langle \mathrm{MC}|\Big[\Big[H_0, \kappa^{B_1}\Big], S^{B_2}\Big] \\ &+ \frac{1}{2}\Big[\Big[H_0, S^{B_1}\Big], S^{B_2}\Big] + \frac{1}{2}\Big[\Big[H_0, \kappa^{B_1}\Big], \kappa^{B_2}\Big]|\mathrm{MC}\rangle \\ &= P_{[1, 2]}\langle \mathrm{MC}|\Big[\Big[\kappa^{B_1}, H_0\Big], S^{B_2}\Big] + \Big[S^{B_1}, \Big[H_0, \kappa^{B_2}\Big]\Big] \\ &+ \Big[S^{B_1}, \Big[H_0, S^{B_2}\Big]\Big] + \Big[\kappa^{B_1}, \Big[H_0, \kappa^{B_2}\Big]\Big]|\mathrm{MC}\rangle \\ &= P_{[1, 2]}\boldsymbol{\beta}^{-B_1\dagger}\mathbf{E}^{[2]}\boldsymbol{\beta}^{B_2}\end{aligned} \tag{450}$$

Here we introduced the electronic Hessian $\mathbf{E}^{[2]}$, which in terms of the matrices

$$\mathbf{A} = \begin{pmatrix}\langle \mathrm{MC}|[\mathbf{q}, [H_0, \mathbf{q}^{\dagger}]]|\mathrm{MC}\rangle & \langle \mathrm{MC}|[[\mathbf{q}, H_0], \mathbf{R}^{\dagger}]]|\mathrm{MC}\rangle \\ \langle \mathrm{MC}|[\mathbf{R}, [H_0, \mathbf{q}^{\dagger}]]|\mathrm{MC}\rangle & \langle \mathrm{MC}|[\mathbf{R}, [H_0, \mathbf{R}^{\dagger}]]|\mathrm{MC}\rangle\end{pmatrix} \tag{451}$$

$$\mathbf{B} = \begin{pmatrix}\langle \mathrm{MC}|[\mathbf{q}, [H_0, \mathbf{q}]]|\mathrm{MC}\rangle & \langle \mathrm{MC}|[[\mathbf{q}, H_0], \mathbf{R}]]|\mathrm{MC}\rangle \\ \langle \mathrm{MC}|[\mathbf{R}, [H_0, \mathbf{q}]]|\mathrm{MC}\rangle & \langle \mathrm{MC}|[\mathbf{R}, [H_0, \mathbf{R}]]|\mathrm{MC}\rangle\end{pmatrix} \tag{452}$$

may be written in block-matrix form[70] (using an asterisk to denote complex conjugation but not transposition)

$$\mathbf{E}^{[2]} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^{*} & \mathbf{A}^{*} \end{pmatrix} \tag{453}$$

The Hessian $\mathbf{E}^{[2]}$ is Hermitian, as follows from the Hermiticity of $\mathbf{A}$ and symmetry of $\mathbf{B}$

$$\mathbf{A} = \mathbf{A}^{\dagger}, \quad \mathbf{B} = \mathbf{B}^{\mathrm{T}} \tag{454}$$

assuming that the Brillouin conditions in eq 425 hold. Combining eqs 448 and 450 we find that the Hamiltonian part of the second-order quasi-energy $\mathcal{Q}^{(2)}$ in eq 439 becomes

$$\frac{\mathrm{d}^2\left\{\langle\widetilde{\mathrm{MC}}|H|\widetilde{\mathrm{MC}}\rangle\right\}_{\mathrm{T}}^{(2)}}{\mathrm{d}\varepsilon_{B_1}\mathrm{d}\varepsilon_{B_2}} = 2P_{[1,\,2]}\left[-\mathrm{i}\boldsymbol{\beta}^{-B_1\dagger}\mathbf{V}_{B_2}^{[1]} + \frac{1}{2}\boldsymbol{\beta}^{-B_1\dagger}\mathbf{E}^{[2]}\boldsymbol{\beta}^{B_2}\right] \tag{455}$$

for a specific set of operator–frequency indices (B_1,B_2).

It remains to consider the part of the second-order quasi-energy that contains the time derivative in eq 440. Noting that the time derivatives of the first-order parameters in eqs 430 and 431 are given by

$$\dot{\kappa}^{(1)}(t) = -\mathrm{i}\sum_{B}\omega_B\varepsilon_B\kappa^{B}\,\mathrm{e}^{-\mathrm{i}\omega_B t} \tag{456}$$

$$\dot{S}^{(1)}(t) = -\mathrm{i}\sum_{B}\omega_B\varepsilon_B S^{B}\,\mathrm{e}^{-\mathrm{i}\omega_B t} \tag{457}$$

we obtain upon time differentiation of eq 440 with respect to ε_{B_1} and ε_{B_2} the expression

$$\begin{aligned}\frac{\mathrm{d}^2\{\langle\widetilde{\mathrm{MC}}|-\mathrm{i}\partial_t|\widetilde{\mathrm{MC}}\rangle\}_T}{\mathrm{d}\varepsilon_{B_1}\mathrm{d}\varepsilon_{B_2}} &= 2P_{[1,\,2]}\omega_{B_1}\langle\mathrm{MC}|\left[\kappa^{B_1} + S^{B_1},\, \kappa^{B_2} + S^{B_2}\right]|\mathrm{MC}\rangle \\ &= -P_{[1,\,2]}\omega_{B_2}\boldsymbol{\beta}^{-B_1\dagger}\mathbf{S}^{[2]}\boldsymbol{\beta}^{B_2}\end{aligned} \tag{458}$$

To obtain the first equality of eq 458 we used the relation

$$\begin{aligned}&2P_{[1,\,2]}\omega_{B_1}\langle\mathrm{MC}|\left[\kappa^{B_1},\, S^{B_2}\right]|\mathrm{MC}\rangle \\ &\quad= 2P_{[1,\,2]}\omega_{B_1}\langle\mathrm{MC}|\left[S^{B_1},\, \kappa^{B_2}\right]|\mathrm{MC}\rangle\end{aligned} \tag{459}$$

while for the second equality we used eq 447, the frequency relation $\omega_{B_1} = -\omega_{B_2}$, and introduced the Hermitian metric matrix

$$\mathbf{S}^{[2]} = \langle\mathrm{MC}|[\mathbf{T}^{\dagger},\, \mathbf{T}]|\mathrm{MC}\rangle = \begin{pmatrix} \boldsymbol{\Sigma} & \boldsymbol{\Delta} \\ -\boldsymbol{\Delta}^{*} & -\boldsymbol{\Sigma}^{*} \end{pmatrix} \tag{460}$$

whose submatrices

$$\boldsymbol{\Sigma} = \begin{pmatrix} \langle\mathrm{MC}|[\mathbf{q},\, \mathbf{q}^{\dagger}]|\mathrm{MC}\rangle & \langle\mathrm{MC}|[\mathbf{q},\, \mathbf{R}^{\dagger}]|\mathrm{MC}\rangle \\ \langle\mathrm{MC}|[\mathbf{R},\, \mathbf{q}^{\dagger}]|\mathrm{MC}\rangle & \langle\mathrm{MC}|[\mathbf{R},\, \mathbf{R}^{\dagger}]|\mathrm{MC}\rangle \end{pmatrix} \tag{461}$$

$$\boldsymbol{\Delta} = \begin{pmatrix} \langle\mathrm{MC}|[\mathbf{q},\, \mathbf{q}]|\mathrm{MC}\rangle & \langle\mathrm{MC}|[\mathbf{q},\, \mathbf{R}]|\mathrm{MC}\rangle \\ \langle\mathrm{MC}|[\mathbf{R},\, \mathbf{q}]|\mathrm{MC}\rangle & \langle\mathrm{MC}|[\mathbf{R},\, \mathbf{R}]|\mathrm{MC}\rangle \end{pmatrix} \tag{462}$$

are Hermitian and antisymmetric, respectively

$$\boldsymbol{\Sigma} = \boldsymbol{\Sigma}^{\dagger}, \quad \boldsymbol{\Delta} = -\boldsymbol{\Delta}^{\mathrm{T}} \tag{463}$$

Combining eqs 455 and 458 we find that the (B_1,B_2) component of the second-order MCSCF quasi-energy of eq 442 becomes

$$\begin{aligned}\mathcal{Q}^{B_1B_2} &= P_{[1,\,2]}\left(-\mathrm{i}\boldsymbol{\beta}^{-B_1\dagger}\mathbf{V}_{B_2}^{[1]} + \frac{1}{2}\boldsymbol{\beta}^{-B_1\dagger}\left(\mathbf{E}^{[2]} - \omega_{B_2}\mathbf{S}^{[2]}\right)\boldsymbol{\beta}^{B_2}\right) \\ &= \frac{1}{2}\left(-\mathrm{i}\boldsymbol{\beta}^{-B_1\dagger}\mathbf{V}_{B_2}^{[1]} - \mathrm{i}\boldsymbol{\beta}^{-B_2\dagger}\mathbf{V}_{B_1}^{[1]} + \boldsymbol{\beta}^{-B_1\dagger}\left(\mathbf{E}^{[2]} - \omega_{B_2}\mathbf{S}^{[2]}\right)\boldsymbol{\beta}^{B_2}\right)\end{aligned} \tag{464}$$

where we used the paired structure of the Hermitian matrices $\mathbf{E}^{[2]}$ and $\mathbf{S}^{[2]}$ in eqs 453 and 460 and the relation $\omega_{B_1} = -\omega_{B_2}$ to arrive at the last expression. In the next subsection we shall use this expression to derive the first-order MCSCF response equation.

4.2.3. First-Order MCSCF Response Equation.

According to the quasi-energy variation principle in eq 427, the quasi-energy must be stationary to all orders with respect to variations in all frequency and operator components. In particular, the second-order quasi-energy component $\mathcal{Q}^{B_1B_2}$ must be stationary with respect to variations in $\boldsymbol{\beta}^{-B_1\dagger}$

$$\frac{\partial\mathcal{Q}^{B_1B_2}}{\partial\boldsymbol{\beta}^{-B_1\dagger}} = \mathbf{0} \tag{465}$$

From eq 464 it then follows that the first-order variations satisfy the set of linear equations

$$\left(\mathbf{E}^{[2]} - \omega_{B_2}\mathbf{S}^{[2]}\right)\boldsymbol{\beta}^{B_2} = \mathrm{i}\mathbf{V}_{B_2}^{[1]} \tag{466}$$

which is our final result for the MCSCF linear response equations. We note that if all matrix blocks involving state-transfer operators are removed then eq 466 reduces to the Hartree–Fock linear response equations in the MO basis, the MO counterpart to the response equations in the AO basis in eq 404.

4.2.4. Linear MCSCF Response Function.

The MCSCF linear response function $\langle\langle A;B\rangle\rangle_{\omega_B}$ is equal to the second derivative of the time-averaged quasi-energy with respect to the perturbation strengths ε_A and ε_B. Using eqs 441 and 464 we thus obtain the following expression for the linear response function

$$\begin{aligned}\langle\langle A;B\rangle\rangle_{\omega_B} &= \frac{\mathrm{d}^2\mathcal{Q}^{(2)}}{\mathrm{d}\varepsilon_A\mathrm{d}\varepsilon_B} = 2\mathcal{Q}^{AB} = -\mathrm{i}\boldsymbol{\beta}^{-A\dagger}\mathbf{V}_{B}^{[1]} - \mathrm{i}\boldsymbol{\beta}^{-B\dagger}\mathbf{V}_{A}^{[1]} \\ &\quad + \boldsymbol{\beta}^{-A\dagger}\left(\mathbf{E}^{[2]} - \omega_B\mathbf{S}^{[2]}\right)\boldsymbol{\beta}^{B}, \quad \omega_A = -\omega_B\end{aligned} \tag{467}$$

By inserting the response equations in eq 466 or in the equivalent equations for perturbation A, the MCSCF linear response function may be written in two alternative forms, in accordance with the general symmetry relations in eq 283

$$\begin{aligned}\langle\langle A;B\rangle\rangle_{\omega_B} &= -\mathrm{i}\boldsymbol{\beta}^{-B\dagger}\mathbf{V}_{B}^{[1]} = -\mathrm{i}\boldsymbol{\beta}^{-A\dagger}\mathbf{V}_{A}^{[1]} \\ &= \langle\langle B;A\rangle\rangle_{\omega_A}, \ \omega_A = -\omega_B\end{aligned} \tag{468}$$

When the matrix blocks involving state-transfer operators are omitted, eq 468 reduces to the Hartree–Fock linear response function in the MO representation, which is the MO counterpart of the AO-based expression in eq 418. The MCSCF quadratic and cubic response functions are obtained by differentiation of the third- and fourth-order quasi-energies, respectively. For a detailed treatment of higher order response functions, see ref 70 as well as the papers describing the implementation of the MCSCF quadratic[99] and cubic[101] response functions.

4.3. Coupled-Cluster Theory

Coupled-cluster theory[30,117] provides the most successful framework so far developed for high-accuracy calculations of the electronic structure and properties of molecules. The theory describes the system in terms of virtual excitations from a reference state, typically taken to be the Hartree–Fock wave function. Using an exponential ansatz for the wave function, a size-extensive description is achieved. The full configuration-interaction (FCI) wave function is approached as increasingly higher order excitations are included in the treatment of the system.

In this section, we present a framework for evaluation of molecular properties in coupled-cluster theory, based on construction of a variational Lagrangian. In the development presented here, we restrict ourselves to the standard formulation of coupled-cluster theory, where the Hartree–Fock state is a good approximation to the reference state. These coupled-cluster models are thus not sufficiently flexible to describe electronic structures characterized by large static correlation effects. Typically, therefore, these models cannot describe bond breaking and molecular dissociation. We do not treat multiconfigurational coupled-cluster theory nor explicitly correlated coupled-cluster theory. Such formulations of coupled-cluster theory are becoming increasingly important but have so far not been extensively developed with respect to calculation of molecular properties.

4.3.1. Coupled-Cluster Model. In coupled-cluster theory the wave function is written in the form

$$|\mathrm{CC}\rangle = \exp(T)|\mathrm{HF}\rangle \tag{469}$$

where $|\mathrm{HF}\rangle$ is the Hartree–Fock reference state and the cluster operator is given by

$$T = \sum_{\mu} t_{\mu}\tau_{\mu} \tag{470}$$

The operator manifold τ_μ constitutes a set of commuting excitation operators

$$[\tau_\mu, \tau_\nu] = 0 \tag{471}$$

which, when working on the Hartree–Fock reference state, generate excited electronic configurations

$$\tau_\mu|\mathrm{HF}\rangle = |\mu\rangle \tag{472}$$

In practice, the cluster operator is partitioned as

$$T = T_1 + T_2 + ... \tag{473}$$

where T_1 produces single excitations, T_2 double excitations, and so on

$$T_1 = \sum_{AI} t_I^A a_A^\dagger a_I \tag{474}$$

$$T_2 = \sum_{A>B}\sum_{I>J} t_{IJ}^{AB} a_A^\dagger a_I a_B^\dagger a_J \tag{475}$$

With each excitation operator τ_μ in eq 470 there is an associated coupled-cluster amplitude t_μ whose squared value is proportional to the probability of the associated virtual excitation occurring.

The amplitudes of the coupled-cluster wave function in eq 469 are not determined variationally. Rather, they are determined by projection, rewriting the Schrödinger equation in the form

$$\exp(-T)H_0\exp(T)|\mathrm{HF}\rangle = E_{\mathrm{CC}}|\mathrm{HF}\rangle \tag{476}$$

This similarity-transformed Schrödinger equation is subsequently projected from the left by the manifold

$$\langle\mu| = \langle\mathrm{HF}|\tau_\mu^\dagger \tag{477}$$

to yield the nonlinear coupled-cluster amplitude equations

$$\langle\mu|\exp(-T)H_0\exp(T)|\mathrm{HF}\rangle = 0 \tag{478}$$

whose solution yields the coupled-cluster amplitudes and wave function. Furthermore, projecting the Schrödinger equation in eq 476 against the Hartree–Fock state we obtain the coupled-cluster energy

$$E_{\mathrm{CC}} = \langle\mathrm{HF}|\exp(-T)H_0\exp(T)|\mathrm{HF}\rangle \tag{479}$$

In coupled-cluster theory, the energy is thus not calculated as an expectation value.

The different models of the coupled-cluster hierarchy differ in the truncation of the coupled-cluster operator T of eq 470. In particular, the coupled-cluster singles–doubles (CCSD) model[118] is obtained by truncating the expansion after the double excitations

$$|\mathrm{CCSD}\rangle = \exp(T_1 + T_2)|\mathrm{HF}\rangle \tag{480}$$

The CCSD amplitude equations are obtained from eq 478 by projecting against the single $\langle\mu_1|$ and double $\langle\mu_2|$ excitation space. Using the BCH expansion in eq 438, we obtain the following equations for the singles and doubles amplitudes

$$\langle\mu_1|H_0^{T_1} + \left[H_0^{T_1}, T_2\right]|\mathrm{HF}\rangle = 0 \tag{481}$$

$$\left\langle\mu_2|H_0^{T_1} + \left[H_0^{T_1}, T_2\right] + \frac{1}{2}\left[\left[H_0^{T_1}, T_2\right], T_2\right]|\mathrm{HF}\right\rangle = 0 \tag{482}$$

where we introduced the T_1-transformed Hamiltonian

$$H_0^{T_1} = \exp(-T_1)H_0\exp(T_1) \tag{483}$$

Alternatively, we may truncate the cluster operator after the triple excitations, giving the coupled-cluster single–double–triple (CCSDT) model.[119,120] Optimization of the CCSD energy scales as n^6 and of the CCSDT energy as n^8, where n is the number of orbitals. The high cost of the optimization makes the coupled-cluster hierarchy applicable only at low levels of theory. On the other hand, the coupled-cluster hierarchy converges rapidly to the FCI electronic energy, at least in the absence of static correlation.

In coupled-cluster theory, the scaling of each model is determined by the scaling of the amplitude equations for the highest excitations, for example, the n^6 scaling of the CCSD model arises from the last two terms of the doubles equations in eq 482. As the contribution to the correlation energy decreases with increasing excitation levels, it makes sense to introduce an intermediate coupled-cluster hierarchy of a lower scaling by making approximations in the highest excitation amplitude equations. For this purpose, we introduce the Møller−Plesset partitioning of the Hamiltonian

$$H_0 = F + U \tag{484}$$

where F is the (zero-order) Fock operator and U the (first-order) fluctuation potential, representing the difference between the true electron−electron interactions and the averaged Fock potential. A hierarchy of intermediate coupled-cluster models is now introduced by approximating the highest excitation amplitude equations by retaining only the leading terms of Møller−Plesset theory, keeping the lower excitation amplitude equations unchanged. In the CC2 model,[121] for example, we keep the CCSD singles equations eq 481, whereas the CCSD doubles equations in eq 482 are approximated by the lowest order Møller−Plesset terms

$$\langle \mu_2 | H_0^{T_1} + [F, T_2] | \mathrm{HF} \rangle = 0 \tag{485}$$

thereby reducing the scaling to n^5. Likewise, by approximating the CCSDT triples equations in the same manner we obtain the CC3 model,[122,123] with an n^7 rather than n^8 scaling. Note that in the resulting coupled-cluster response hierarchy consisting of the models CC2, CCSD, CC3, CCSDT, the cluster amplitudes are determined iteratively by solving nonlinear amplitude equations and the scaling increases by a factor of n at each level in the hierarchy.

A simpler coupled-cluster hierarchy is generated if, for each intermediate model, the contributions from the highest order excitations are calculated from perturbation theory rather than iteratively. The CC2 model then reduces to the second-order Møller−Plesset (MP2) model by setting the t_1 amplitudes to zero, that is, by omitting the singles amplitude equation and determining the doubles amplitudes from eq 485 where the T1-transformed Hamiltonian $H_0^{T_1}$ is replaced by H_0.

In coupled-cluster theory, the triple excitations give contributions to the energy of orders four and higher in the fluctuation potential. In the perturbation-based intermediate model obtained from CCSDT theory, this fourth-order energy contribution is added (in a slightly modified form) to the CCSD energy, yielding the coupled-cluster singles−doubles−perturbative-triples (CCSD(T)) model.[124] Proceeding in this manner, we generate the coupled-cluster energy hierarchy consisting of the models MP2, CCSD, CCSD(T), CCSDT, with the same computational scaling as the coupled-cluster response hierarchy introduced above. Note that, in the energy hierarchy, the highest order contributions of the intermediate models are treated perturbatively rather than iteratively, thereby reducing the cost of the calculations relative to that of the response hierarchy.

In response theory, molecular properties are determined for ground and excited states and for transitions between these states. To apply response theory successfully, we therefore need to have a good zero-order description of these states. As most excited states are dominated by a single excitation from the ground-state configuration, response theory can only be applied confidently for electronic-structure models where single excitations are explicitly treated. In the MP2 model, single excitations do not contribute; consequently, this model does not constitute a useful starting point for determining molecular response functions. Likewise, in the CCSD(T) model, there is no direct interaction between the triple- and single-excitation spaces; the CCSD(T) model therefore also does not constitute a useful starting point for a response treatment. By contrast, in the intermediate models of the coupled-cluster response hierarchy the equation for the single excitations is not truncated, making these models suitable for response-function calculations.

Even though the intermediate models in the coupled-cluster energy hierarchy do not provide a sufficiently flexible description of single excitations for molecular properties, it is possible to improve the description by allowing the orbitals to relax, thereby effectively introducing single excitations. However, when response functions are determined with orbital relaxation included, the orbital-rotation parameters and amplitudes introduce singularities in the response function, rendering the pole and residue analysis problematic. Hence, only static molecular properties can be meaningfully obtained for models with orbital relaxation included. The static molecular properties obtained in this manner may be viewed as an analytic formulation of a finite-field energy determined in the presence of the perturbation, see section 4.4, where we describe how static molecular properties may be determined with orbital relaxation included. In the remainder of this section we consider time-dependent perturbations, thereby restricting ourselves to the coupled-cluster response hierarchy of wave functions.

4.3.2. Coupled-Cluster Quasi-Energy Lagrangian. In section 3 we set up a time-averaged quasi-energy Lagrangian for an intermediately normalized wave function, suitable for coupled-cluster theory. In the following, the optimized coupled-cluster wave function for the unperturbed system in eq 469 is written as

$$|\mathrm{CC}^{(0)}\rangle = \exp(T^{(0)})|\mathrm{HF}\rangle \tag{486}$$

By applying eq 193 with the identifications

$$|\mathrm{R}\rangle = |\mathrm{HF}\rangle \tag{487}$$

$$|\hat{0}^{(0)}\rangle = |\mathrm{CC}^{(0)}\rangle \tag{488}$$

$$|\hat{0}\rangle = |\mathrm{CC}(t)\rangle = \exp(T(t))|\mathrm{HF}\rangle \tag{489}$$

$$\langle \bar{0}| = \sum_{\mu} \bar{t}_{\mu}(t)\langle \bar{\mu}(t)| = \sum_{\mu} \bar{t}_{\mu}(t)\langle \mu | \exp(-T(t)) \tag{490}$$

and noting that $\langle \bar{0}|\hat{0}\rangle = 0$ as assumed in the derivation of eq 193, we obtain the coupled-cluster quasi-energy Lagrangian[66]

$$\mathscr{L} = \mathrm{Re}\left\{ \langle \mathrm{HF}|H|\mathrm{CC}(t)\rangle + \sum_{\mu} \bar{t}_{\mu}(t)\langle \bar{\mu}(t)|H - \mathrm{i}\partial_t|\mathrm{CC}(t)\rangle \right\}_T \tag{491}$$

with $H = H_0 + V(t)$, applicable to the standard hierarchy of coupled-cluster models CCS, CCSD, CCSDT, and so on. We note that the Lagrangian $\mathscr{L}$ is the time-averaged sum of the coupled-cluster quasi-energy $Q(t)$ and the (real part of the) time-dependent coupled-cluster amplitude equations with associated multipliers

$$Q(t) = \mathrm{Re}\langle \mathrm{HF}|H|\mathrm{CC}(t)\rangle \tag{492}$$

$$\langle \bar{\mu}(t)|H - \mathrm{i}\partial_t|\mathrm{CC}(t)\rangle = 0 \tag{493}$$

which are the coupled-cluster analogues of the expressions for exact theory in eqs 183 and 187. For later convenience, we also introduce the time-averaged complex quasi-energy Lagrangian

$$\mathscr{L}^{\mathrm{c}} = \left\{\langle \mathrm{HF}|H|\mathrm{CC}(t)\rangle + \sum_{\mu} \bar{t}_{\mu}(t)\langle\bar{\mu}(t)|H - \mathrm{i}\partial_t|\mathrm{CC}(t)\rangle\right\}_T \tag{494}$$

such that

$$\mathscr{L} = \mathrm{Re}\mathscr{L}^{\mathrm{c}} \tag{495}$$

For the intermediate CCn models, the Lagrangian in eq 491 must be modified as discussed in section 4.3.6.

The cluster amplitudes and multipliers are now expanded in orders of the perturbation

$$T(t) = T^{(0)} + T^{(1)}(t) + T^{(2)}(t) + \ldots \tag{496}$$

$$\bar{t}(t) = \bar{t}^{(0)} + \bar{t}^{(1)}(t) + \bar{t}^{(2)}(t) + \ldots \tag{497}$$

where the zero-order cluster amplitudes are obtained by solving the amplitude equations in eq 478 and the zero-order multipliers are obtained as described in section 4.3.3. Likewise, the real-valued and complex quasi-energy Lagrangians are expanded in orders of the perturbation

$$\mathscr{L} = \mathscr{L}^{(0)} + \mathscr{L}^{(1)} + \mathscr{L}^{(2)} + \ldots \tag{498}$$

$$\mathscr{L}^{\mathrm{c}} = \mathscr{L}^{\mathrm{c}(0)} + \mathscr{L}^{\mathrm{c}(1)} + \mathscr{L}^{\mathrm{c}(2)} + \ldots \tag{499}$$

We here restrict ourselves to determining $\mathscr{L}^{(0)}$, $\mathscr{L}^{(1)}$, and $\mathscr{L}^{(2)}$; the latter will allow us to calculate the coupled-cluster linear response function. By the $2n + 1$ and $2n + 2$ rules we then need to determine the first-order amplitudes and zero-order multipliers. For future reference, we write the first-order amplitude operator in terms of its frequency components

$$T^{(1)}(t) = \sum_{B} \varepsilon_B T_B^{(1)}\, \mathrm{e}^{-\mathrm{i}\omega_B t} \tag{500}$$

where $T_B^{(1)}$ contains the first-order cluster amplitudes

$$T_B^{(1)} = \sum_{B} t_{\mu}^{B}\tau_{\mu} \tag{501}$$

and where B is a combined operator−frequency index.

4.3.3. First-Order Molecular Properties.

By analogy with eq 311, the zero-order coupled-cluster Lagrangian becomes

$$\mathscr{L}^{(0)} = \mathrm{Re}\langle\Lambda^{(0)}|H_0|\mathrm{CC}^{(0)}\rangle = E_{\mathrm{CC}} \tag{502}$$

where we introduced the zero-order coupled-cluster wave function $|\mathrm{CC}^{(0)}\rangle$ of eq 486 and, by analogy with eq 320, the zero-order coupled-cluster lambda state

$$\langle\Lambda^{(0)}| = \langle \mathrm{HF}| + \sum_{\mu} \bar{t}_{\mu}^{(0)}\langle\bar{\mu}|,$$

$$\langle\bar{\mu}| = \langle\mu|\exp(-T^{(0)}) \tag{503}$$

The stationary conditions for the zero-order Lagrange multipliers give the coupled-cluster amplitude equations, while the stationary conditions for the amplitudes determine the zero-order multipliers

$$\frac{\mathrm{d}\mathscr{L}^{\mathrm{c}(0)}}{\mathrm{d}\bar{t}_{\mu}^{(0)}} = \langle\bar{\mu}|H_0|\mathrm{CC}^{(0)}\rangle = 0 \tag{504}$$

$$\frac{\mathrm{d}\mathscr{L}^{\mathrm{c}(0)}}{\mathrm{d}t_{\mu}^{(0)}} = \langle\Lambda^{(0)}|[H_0, \tau_{\mu}]|\mathrm{CC}^{(0)}\rangle = 0 \tag{505}$$

Whereas eq 504 is the cluster amplitude equation in eq 478, the linear equations in eq 505 determine the zero-order multipliers and may be written in the form

$$\bar{\mathbf{t}}^{(0)}\mathbf{A} = -\boldsymbol{\eta} \tag{506}$$

where $\mathbf{A}$ is the nonsymmetric Jacobian matrix and $\boldsymbol{\eta}$ a row vector

$$A_{\mu\nu} = \langle\bar{\mu}|[H_0, \tau_{\nu}]|\mathrm{CC}^{(0)}\rangle \tag{507}$$

$$\eta_{\mu} = \langle \mathrm{HF}|[H_0, \tau_{\mu}]|\mathrm{CC}^{(0)}\rangle \tag{508}$$

According to the $2n + 1$ and $2n + 2$ rules for the wave function parameters and multipliers, respectively, the first-order molecular properties may be written as

$$\mathscr{L}_{B_0}^{(1)} = \frac{1}{2}C^{\pm}\langle\Lambda^{(0)}|V_{B_0}|\mathrm{CC}^{(0)}\rangle, \quad \omega_{B_0} = 0 \tag{509}$$

by analogy with eq 312.

4.3.4. Second-Order Molecular Properties.

According to the $2n + 1$ and $2n + 2$ rules, the second-order coupled-cluster Lagrangian $\mathscr{L}^{(2)}$ may be constructed from the first-order amplitudes and the zero-order multipliers. Using the expansion in eq 302 we now consider the $\mathscr{L}_{B_0,B_1}^{(2)}$ component. To this end, we note that

$$\begin{aligned}|\mathrm{CC}(t)\rangle &= \exp(T(t))|\mathrm{HF}\rangle\\ &= \exp(T(t) - T^{(0)})|\mathrm{CC}^{(0)}\rangle\end{aligned} \tag{510}$$

$$\langle\mu|\exp(T(t)) = \langle\bar{\mu}|\exp(T^{(0)} - T(t)) \tag{511}$$

and apply the BCH expansion in eq 438 to expand the quasi-energy Lagrangian in eq 491, yielding

$$\begin{aligned}\mathscr{L}_{B_0,\,B_1}^{(2)} = \frac{1}{2}C^{\pm}P_{[0,\,1]}\Big(&\langle\Lambda^{(0)}|\left[V_{B_0}, T_{B_1}^{(1)}\right]|\mathrm{CC}^{(0)}\rangle\\ &+ \langle\Lambda^{(0)}|\left[\left[H_0, T_{B_0}^{(1)}\right], T_{B_1}^{(1)}\right]|\mathrm{CC}^{(0)}\rangle\Big)\end{aligned} \tag{512}$$

where we also used eq 471. Next, by inserting the expression for $T_{B_1}^{(1)}$ in eq 501 and introducing the notation

$$\eta_{\mu}^{B_0} = \langle\Lambda^{(0)}|[V_{B_0}, \tau_{\mu}]|\mathrm{CC}^{(0)}\rangle \tag{513}$$

$$F_{\mu\nu} = \langle\Lambda^{(0)}|[[H_0, \tau_{\mu}], \tau_{\nu}]|\mathrm{CC}^{(0)}\rangle \tag{514}$$

(where **F** should not be confused with the Fock matrix), we may express the second-order Lagrangian more compactly as

$$\mathscr{L}^{(2)}_{B_0,\ B_1} = \frac{1}{2} C^{\pm} P_{[0,\ 1]} \left(\sum_{\mu} \eta_{\mu}^{B_0} t_{\mu}^{B_1} + \sum_{\mu\nu} F_{\mu\nu} t_{\mu}^{B_0} t_{\nu}^{B_1} \right) \tag{515}$$

Finally, using eq 307 we arrive at the following expression for the coupled-cluster linear response function

$$\langle\langle A; B\rangle\rangle_{\omega_B} = C^{\pm} P_{[A,\ B]} \left(\sum_{\mu} \eta_{\mu}^{A} t_{\mu}^{B} + \sum_{\mu\nu} F_{\mu\nu} t_{\mu}^{A} t_{\nu}^{B} \right) \tag{516}$$

where we adopted the standard response notation, renaming V_{B_0} and V_{B_1} to A and B, respectively.

In the coupled-cluster response function of eq 516, the zero-order multipliers are obtained from eq 506 while the first-order amplitudes are determined by solving eq 493 to first order. To obtain an explicit expression for the amplitude equations it is convenient to rewrite eq 493 in the form

$$\langle \bar{\mu} | \exp(T^{(0)} - T(t)) \left(H_0 + V(t) - \mathrm{i}\partial_t \right) \exp\left(T(t) - T^{(0)} \right) | \mathrm{CC}^{(0)} \rangle = 0 \tag{517}$$

where we used eqs 510 and 511. By invoking the BCH expansion eq 438 in eq 517 and collecting first-order terms followed by differentiation with respect to a particular perturbation strength ε_{B_0} we obtain an equation for the first-order amplitudes

$$\sum_{\nu} \langle \bar{\mu} | [H_0,\ \tau_{\nu}] | \mathrm{CC}^{(0)} \rangle t_{\nu}^{B_0} + \langle \bar{\mu} | V_{B_0} | \mathrm{CC}^{(0)} \rangle - \omega_{B_0} \sum_{\nu} \langle \bar{\mu} | \tau_{\nu} | \mathrm{CC}^{(0)} \rangle t_{\nu}^{B_0} = 0 \tag{518}$$

By introducing

$$\xi_{\mu}^{B_0} = \langle \bar{\mu} | V_{B_0} | \mathrm{CC}^{(0)} \rangle \tag{519}$$

and noting that

$$\langle \bar{\mu} | \tau_{\nu} | \mathrm{CC}^{(0)} \rangle = \langle \mu | \nu \rangle = \delta_{\mu\nu} \tag{520}$$

we find that eq 518 may be written in the matrix form

$$(\mathbf{A} - \omega_{B_0} \mathbf{I}) \mathbf{t}^{B_0} = -\boldsymbol{\xi}^{B_0} \tag{521}$$

The response function and response equations developed above may be applied to the standard coupled-cluster models (CCS, CCSD, CCSDT, etc.) by introducing the appropriate truncations in the cluster operator and in the projection manifold.

4.3.5. Excitation Energies and Residues.

Excitation energies correspond to the poles of the linear response function and may be determined by solving the Jacobian eigenvalue equation. Since the Jacobian is nonsymmetric, we have left and right eigenvalue equations

$$\mathbf{A}\mathbf{R}^k = \omega_k \mathbf{R}^k, \quad \mathbf{L}^k \mathbf{A} = \mathbf{L}^k \omega_k, \quad \mathbf{L}^k \mathbf{R}^l = \delta_{kl} \tag{522}$$

where $\mathbf{L}^k$ is a left row eigenvector and $\mathbf{R}^k$ is a right column eigenvector. In matrix form we may express the Jacobian eigenvalue problem as

$$\mathbf{L}\mathbf{A}\mathbf{R} = \Omega, \quad \mathbf{L}\mathbf{R} = \mathbf{I} \tag{523}$$

where the diagonal matrix $\boldsymbol{\Omega}$ contains the excitation energies. When all virtual excitations within a given orbital basis are included in T in eq 473, the Jacobian has the same real eigenvalues as the shifted Hamiltonian operator $H_0 - E_{\mathrm{CC}}$. Conversely, when T is truncated, the nonsymmetric Jacobian may have complex eigenvalues or even not be diagonalizable. Complex eigenvalues (and hence complex excitation energies) are unphysical and may occur because the coupled-cluster method is nonvariational. However, such eigenvalues are usually not encountered for electronic systems dominated by a single determinant and may always be removed by extending the excitation manifold.

Assuming that a diagonal representation exists, the linear response function in eq 516 may be expressed as

$$\langle\langle A; B\rangle\rangle_{\omega_B} = C^{\pm} P_{[A,\ B]} \left(\sum_{k} \frac{{}^{\mathrm{d}}\eta_k^A\, {}^{\mathrm{d}}\xi_k^B}{\omega_B - \omega_k} + \sum_{kl} \frac{{}^{\mathrm{d}}\xi_k^A\, {}^{\mathrm{d}}F_{kl}\, {}^{\mathrm{d}}\xi_l^B}{(\omega_B + \omega_k)(\omega_B - \omega_l)} \right) \tag{524}$$

where

$${}^{\mathrm{d}}\eta_k^A = \boldsymbol{\eta}^A \mathbf{R}^k \tag{525}$$

$${}^{\mathrm{d}}\xi_k^A = \mathbf{L}^k \boldsymbol{\xi}^A \tag{526}$$

$${}^{\mathrm{d}}F_{kl} = (\mathbf{R}^k)^{\mathrm{T}} \mathbf{F} \mathbf{R}^l \tag{527}$$

In agreement with the response function for exact states in eq 278 the coupled-cluster linear response function has poles at $\omega_B = \pm\omega_k$. In addition, the coupled-cluster response function has an **F**-dependent term, not present in eq 278. This term vanishes in the limit of a full excitation manifold, as discussed in ref 125.

In coupled-cluster theory, transition strengths may be determined from the residue of the linear response function

$$\lim_{\omega_B \longrightarrow \omega_k} (\omega_B - \omega_k) \langle\langle A; B\rangle\rangle_{\omega_B} = \frac{1}{2} T_{0k}^A T_{k0}^B + \frac{1}{2} \left(T_{0k}^B T_{k0}^A \right)^* \tag{528}$$

where

$$T_{k0}^A = {}^{\mathrm{d}}\xi_k^A, \quad T_{0k}^A = {}^{\mathrm{d}}\left(\boldsymbol{\eta}^A + \mathbf{F}\mathbf{t}^A(-\omega_k) \right)_k \tag{529}$$

Unlike for variational methods, $T_{0k}^A \neq (T_{k0}^A)^*$. However, as for exact states, the transition-strength matrix is Hermitian. The diagonal element of the transition-strength matrix $(1/2)T_{0k}^A T_{k0}^A + (1/2)(T_{0k}^A T_{k0}^A)^*$ is therefore real. However, since the transition strength matrix element is not a squared norm as in exact theory, it is not guaranteed to be positive. Again, this does not give any problems, in practice, when the coupled-cluster wave function is a good representation of the exact wave function.

4.3.6. Response Functions for the CC*n* Models.

The response functions for the intermediate CC*n* models differ from those for the full coupled-cluster models discussed above. To illustrate this, we consider here the CC2 model, for which the time-dependent amplitude equations in eq 493 may be written as[121]

$$\langle \mu_1 | H^{T_1} + [H,\ T_2] | \mathrm{HF} \rangle - \mathrm{i}\dot{t}_{\mu_1} = 0 \tag{530}$$

$$\langle \mu_2 | H^{T_1} + [F + V^{T_1}(t),\ T_2] | \mathrm{HF} \rangle - \mathrm{i}\dot{t}_{\mu_2} = 0 \tag{531}$$

which are the time-dependent analogues of the CCSD singles equation in eq 481 and the CC2 doubles equation in eq 485, respectively. The CC2 version of the quasi-energy Lagrangian in eq 491 may therefore be written in the form

$$\begin{aligned}\mathscr{L} = \mathrm{Re}\Big\{ & \langle \mathrm{HF}|H \exp(T_1 + T_2)|\mathrm{HF}\rangle \\ & + \sum_{\mu_1} \bar{t}_{\mu_1}\left(\langle \mu_1|H^{T_1} + [H, T_2]|\mathrm{HF}\rangle - \mathrm{i}\dot{t}_{\mu_1}\right) \\ & + \sum_{\mu_2} \bar{t}_{\mu_2}\left(\langle \mu_2|H^{T_1} + [F + V^{T_1}(t), T_2]|\mathrm{HF}\rangle - \mathrm{i}\dot{t}_{\mu_2}\right)\Big\}_T \end{aligned} \tag{532}$$

The quasi-energy Lagrangian is stationary with respect to variations in the cluster amplitudes and multipliers. This condition may be used to determine an order expansion of the cluster amplitudes and multipliers, and the CC2 molecular response functions may subsequently be obtained by differentiating the quasi-energy Lagrangian as in eqs 307−309. The CC2 linear response function was first derived in ref 121, whereas the first derivation of the CC3 linear response function was given in ref 122.

4.3.7. Equation of Motion Coupled-Cluster Method.

As an alternative to coupled-cluster response theory, molecular properties may be calculated using the equation of motion coupled-cluster (EOM-CC) method.[126,127] In EOM-CC theory it is assumed that a coupled-cluster ground-state wave function has been determined that satisfies the cluster amplitude equations of eq 478 and has the energy E_{CC} of eq 479. However, unlike in response theory, no time-dependent wave function or equations are introduced. Instead, excitation energies and excited-state wave functions are determined by diagonalization of a shifted Hamiltonian matrix in a biorthonormal basis. Transition moments are subsequently determined directly as matrix elements between these states rather than as residues of response functions, and the response functions are obtained by inserting these matrix elements and excitation energies in the standard sum-over-state expressions for the response functions of an exact (variational) wave function as obtained in the quasi-energy formulation, see eqs 278−280. By comparing the EOM-CC and coupled-cluster response methods for truncated expansions we shall see that the two approaches give identical excitation energies for the standard coupled-cluster models, where the excitation operator is truncated at a given excitation level, whereas other molecular properties in the two approaches differ. For example, transition moments are only size intensive when calculated from the expressions obtained by response theory.

In Figure 2 the different strategies followed in EOM-CC and coupled-cluster response theories are summarized. In the EOM-CC method expressions for the response functions are first obtained using the time-dependent variation principle for the exact wave function. Subsequently, these expressions are used with truncated summations and approximate coupled-cluster wave functions and excitation energies. By contrast, in response theory the wave function is approximated first and the time development of the approximate wave function is subsequently determined from the time-dependent variation principle.

To illustrate the differences between the two approaches, consider a CCSD calculation of a linear-response molecular property such as the frequency-dependent polarizability. In EOM-CC theory electronic states and excitation energies are obtained by solving the EOM-CCSD eigenvalue equation (with a shifted Hamiltonian matrix). The resulting states and excitation energies are then inserted into the expression for the exact linear response function in eq 278. In CCSD response theory the linear response function is determined from eq 516. The main difference between eqs 278 and 516 is that the latter contains a term that is quadratic in the coupled-cluster amplitudes. This term is absent in eq 278, which was obtained using the fact that the exact wave function, unlike an approximate coupled-cluster wave function, is variational. The fact that EOM-CC theory combines equations for variational wave functions with nonvariational coupled-cluster theory thus leads to neglect of the quadratic term. The errors introduced by neglecting the quadratic term in eq 516 are most severe for the simplest coupled-cluster methods, such as the CC2 model. In the limit of no truncation, EOM-CC theory and coupled-cluster response theory become identical.

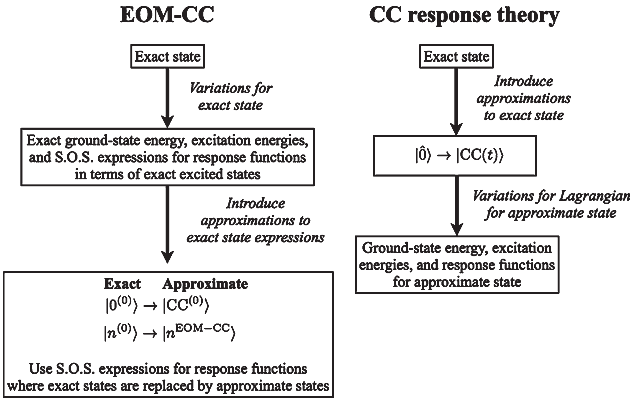

Figure 2. Comparison of EOM-CC and coupled-cluster response theory.

In the coupled-cluster response formulation the response functions and their residues fulfill all relations that follow from the time-dependent variation principle, for example, the equivalence between various response functions and residues discussed for exact states in section 3.4.6 (see also ref 128). In particular, the response functions are size extensive and their residues are size intensive. In truncated EOM-CC theory such relations do not hold, in particular, the EOM-CC response functions are not size extensive[129] and their residues are not size intensive.[125] For example, EOM-CCSD theory gives the exact frequency-dependent polarizability for a two-electron system (the FCI result), while the polarizability for two noninteracting two-electron systems is not equal to the sum of the polarizabilities of the individual systems. Bartlett and co-workers[130,131] proposed to obtain size-extensive EOM-CC models by complete elimination of unlinked terms in the EOM-CC equations. However, for the CCSD model the exact excitation energies (FCI result) are then not obtained for a two-electron system. These problems notwithstanding, calculations of different molecular properties for small molecules indicate that, in practice, the EOM-CC results are close to those obtained with response theory.

We are now ready to examine the EOM-CC model in more detail, limiting ourselves to excitation energies and transition moments. To obtain the EOM-CC excitation energies and states we write the eigenstate $|k\rangle$ of H_0 in the form

$$|k\rangle = s^k|\mathrm{CC}^{(0)}\rangle + \sum_{\mu} R_{\mu}^{k}\tau_{\mu}|\mathrm{CC}^{(0)}\rangle \tag{533}$$

The condition that $|k\rangle$ is an eigenstate of the shifted Hamiltonian $H_0 - E_{CC}$ with excitation energy $\omega_k = E_k - E_{CC}$ may then be expressed as

$$(H_0 - E_{CC})\left(s^k|CC^{(0)}\rangle + \sum_\mu R_\mu^k \tau_\mu |CC^{(0)}\rangle\right) = \omega_k\left(s^k|CC^{(0)}\rangle + \sum_\mu R_\mu^k \tau_\mu |CC^{(0)}\rangle\right) \qquad (534)$$

Projection of eq 534 from the left with the basis $\{\langle HF|, \langle HF|\tau_\mu^\dagger \exp(-T^{(0)})\}$, which is biorthonormal to $\{|CC^{(0)}\rangle, \tau_\mu|CC^{(0)}\rangle\}$, yields

$$\mathbf{H}^b \begin{pmatrix} s^k \\ \mathbf{R}^k \end{pmatrix} = \omega_k \begin{pmatrix} s^k \\ \mathbf{R}^k \end{pmatrix} \qquad (535)$$

where $\mathbf{H}^b$ is the shifted Hamiltonian matrix

$$\mathbf{H}^b = \begin{pmatrix} 0 & -\boldsymbol{\eta} \\ \mathbf{0} & \mathbf{A} \end{pmatrix} \qquad (536)$$

The vector $\boldsymbol{\eta}$ is defined in eq 508, $\mathbf{A}$ is the coupled-cluster Jacobian of eq 507, and the coupled-cluster energy and amplitude equations in eqs 478 and 479 have been used to identify the zero elements of the first column of the Hamiltonian. One solution to eq 535 is $(1,\mathbf{0})^T$ with zero eigenvalue, corresponding to the reference state $|CC^{(0)}\rangle$. The remaining solutions to eq 535 represent excited states, whose eigenvectors from eqs 535 and 536 satisfy the relations

$$s^k = \omega_k^{-1} \boldsymbol{\eta} \mathbf{R}^k \qquad (537)$$

$$\mathbf{A}\mathbf{R}^k = \omega_k \mathbf{R}^k \qquad (538)$$

The vectors $\mathbf{R}^k$ are thus the right eigenvectors of the Jacobian in eq 522, and the coefficient s^k may be obtained from this eigenvector using eq 537.

The left eigenvectors of $\mathbf{H}^b$, which are row vectors of the form (L_{HF}^k, L_μ^k), have the same eigenvalues ω_k as the right eigenvectors and are chosen to satisfy the biorthonormal normalization $\mathbf{L}^k\mathbf{R}^k = 1$. Specifically, the left eigenvector with zero eigenvalue fulfills the equation

$$\begin{pmatrix} L_{HF}^0 & \mathbf{L}^0 \end{pmatrix} \mathbf{H}^b = \mathbf{0} \qquad (539)$$

which, by comparison with eq 506, shows that $(L_{HF}^0, \mathbf{L}^0)$ corresponds to $(1, \bar{\mathbf{t}}^{(0)})$, which contains the zero-order multipliers. The remaining left eigenvectors have nonzero eigenvalues and are from eq 536 seen to have the form $(0, \mathbf{L}^k)$, where $\mathbf{L}^k$ satisfies the condition

$$\mathbf{L}^k \mathbf{A} = \omega_k \mathbf{L}^k \qquad (540)$$

and are therefore identical to the left eigenvectors of the Jacobian in eq 522. We conclude that the excitation energies and eigenvectors of EOM-CC and coupled-cluster response theories are identical.

The first column of the shifted Hamiltonian matrix in eq 536 vanishes since the coupled-cluster state satisfies the amplitude equations in eq 478. For the intermediate CCn models, the amplitudes satisfy modified equations such as the CC2 amplitude equations in eqs 481 and 485; for these models the first column of the Hamiltonian therefore does not vanish. The first decision to be made in developing intermediate EOM-CC models is therefore whether to use a nonvanishing or vanishing first column. By contrast, in the response formulation the variation principle for the quasi-energy Lagrangian may be invoked to obtain the CCn excitation energies as described for the CC2 model in section 4.3.6. With this observation it is not difficult to construct various intermediate EOM-CC models, although we will not discuss this point further here.[132]

We next consider EOM-CC response functions and transition moments, comparing these with their response-theory counterparts. In section 3.4 sum-over-states expressions for linear, quadratic, and cubic response functions of an exact state were given in eqs 278−280 with summations over the eigenstates of the zero-order Hamiltonian. In EOM-CC theory we obtain the expressions for the response functions by replacing these summations over exact states with summations over the biorthonormal eigenstates of the EOM-CC Hamiltonian in eqs 538 and 540 using $|CC^{(0)}\rangle$ and $\langle\Lambda^{(0)}|$ as the right and left reference states, respectively.

When molecular properties are evaluated in EOM-CC theory the exact response functions should be used where it is explicitly imposed that the response functions are real. Consider, for example, the transition-strength matrix elements, which in exact theory are given in eq 290 and in EOM-CC theory become

$$S_{AB}^{0k} = \langle\Lambda^{(0)}|A|k\rangle\langle k|B|CC^{(0)}\rangle \qquad (541)$$

In EOM-CC theory the transition moments are given by

$$\langle k|B|CC^{(0)}\rangle = \sum_\mu \mathbf{L}_\mu^k \langle\mu|\exp(-T^{(0)})B|CC^{(0)}\rangle \qquad (542)$$

$$\langle\Lambda^{(0)}|A|k\rangle = \sum_\mu \left(\langle\Lambda^{(0)}|A\tau_\mu|CC^{(0)}\rangle - \bar{t}_\mu^{(0)}\langle\Lambda^{(0)}|A|CC^{(0)}\rangle\right) R_\mu^k \qquad (543)$$

A comparison of transition moments in EOM-CC and linear-response theories shows that the right transition moments are identical in the two approaches, whereas the left transition moments differ unless the cluster operator contains the full excitation manifold.[125] The EOM-CC left transition moments may be written in the form

$$\langle\Lambda^{(0)}|A|k\rangle = \sum_\mu \Big(\langle\Lambda^{(0)}|[A, \tau_\mu]|CC^{(0)}\rangle R_\mu^k + \langle\Lambda^{(0)}|\tau_\mu A|CC^{(0)}\rangle R_\mu^k - \bar{t}_\mu^{(0)} R_\mu^k \langle\Lambda^{(0)}|A|CC^{(0)}\rangle\Big) \qquad (544)$$

where the first term is identical to the first term in linear response theory. The last two terms become

$$\sum_\mu \left(\langle\Lambda^{(0)}|\tau_\mu A|CC^{(0)}\rangle R_\mu^k - \bar{t}_\mu^{(0)} R_\mu^k \langle\Lambda^{(0)}|A|CC^{(0)}\rangle\right) = \sum_{\mu>\nu} \bar{t}_\mu^{(0)} R_\nu^k \langle\mu|\tau_\nu \exp(-T^{(0)})A|CC^{(0)}\rangle - \sum_\mu \bar{t}_\mu^{(0)} R_\nu^k \sum_\nu \bar{t}_\nu^{(0)} \langle\nu|\exp(-T^{(0)})|CC^{(0)}\rangle \qquad (545)$$

where only the first term is size intensive. Transition moments in EOM-CC theory are therefore not size intensive.

4.4. Orbital-Relaxed Response Functions

As discussed in section 4.3, the intermediate CC*n* models of the coupled-cluster response hierarchy are well suited to the study of frequency-dependent molecular properties; by contrast, the corresponding intermediate models of the coupled-cluster energy hierarchy, for example, the MP2 and CCSD(T) models, provide a poor description of such properties. However, with inclusion of orbital relaxation these models have become the method of choice for determining many static molecular properties at a lower computational cost than their counterparts in the coupled-cluster response hierarchy. In this section we describe the calculation of response properties with orbital relaxation for these perturbation-based intermediate models using the MP2 model as an example.

4.4.1. Orbital-Relaxed Response Functions. For a large class of wave function models the wave function is determined in two consecutive steps. First, a reference state is determined to obtain a qualitatively correct zero-order description of the electronic system; subsequently, dynamical correlation is recovered based on this zero-order description using a correlation method such as perturbation theory or coupled-cluster theory. For systems dominated by a single electronic configuration we may, for example, combine a Hartree–Fock zero-order description with MP2, CCSD, or CCSD(T) treatments of the correlation problem; for systems with several important configurations we may instead combine an MCSCF zero-order reference state with a CASPT2 treatment of the correlation. In both cases the MOs used for the correlation treatment are inherited from the zero-order wave function.

When molecular properties are calculated for such two-step models we must decide whether or not to incorporate the perturbation dependence of the MOs in the calculation of the response functions. In the discussion of the coupled-cluster response functions in section 4.3 the perturbation dependence of the MOs was not considered since orbital relaxation introduces singularities that destroy the pole structure of the response functions, making the calculated frequency-dependent properties unreliable. However, for static molecular properties relaxation of the MOs in the presence of the perturbation may be incorporated without introducing such artifacts; indeed, static molecular properties are typically (but not invariably) calculated from orbital-relaxed response functions. Determination of static molecular properties then becomes equivalent to performing finite-difference energy calculations in the presence of the perturbation.

For static molecular properties, where orbital relaxation is accounted for, the time-averaged quasi-energy Lagrangian in section 3.1.3 reduces to the (time-independent) energy Lagrangian for the two-step model. The orbital-relaxed energy Lagrangian may be expanded in the perturbation strengths as

$$\begin{aligned} L = E_0 &+ \sum_{B_0} \langle (V_{B_0}) \rangle \varepsilon_{B_0} + \frac{1}{2} \sum_{B_0,\, B_1} \langle (V_{B_0}; V_{B_1}) \rangle \varepsilon_{B_0} \varepsilon_{B_1} \\ &+ \frac{1}{6} \sum_{B_0,\, B_1,\, B_2} \langle (V_{B_0}; V_{B_1}, V_{B_2}) \rangle \varepsilon_{B_0} \varepsilon_{B_1} \varepsilon_{B_2} + \ldots \end{aligned} \tag{546}$$

where E_0 is the energy of the two-step model in the absence of the perturbation. No frequency subscript is attached to the response functions since these are always determined at zero frequency, and the notation $\langle (V_{B0};V_{B1}) \rangle$ rather than $\langle\langle V_{B0};V_{B1} \rangle\rangle$ indicates that orbital relaxation of the reference state is included in evaluation of the response function. The orbital-relaxed response functions are thus obtained by simple differentiation of the energy Lagrangian with respect to the relevant perturbation strengths. In section 4.4.2 we describe how orbital-relaxed response functions may be obtained for the MP2 model.

Orbital-relaxed response functions are used for many static molecular properties, for example, for molecular gradients and Hessians (which should be identical to the corresponding finite-difference quantities). A particular difficulty associated with these calculations is the need to take into account the effect of perturbation-dependent basis sets, as described in section 5.1 for geometrical derivatives. Also, when magnetic molecular properties associated with an external magnetic field are evaluated using London orbitals, for example, nuclear shielding constants, orbital-relaxed response functions have to be considered as described in section 5.2. It should be noted that many static molecular properties are best calculated without orbital relaxation. For example, in the calculation of indirect nuclear spin–spin coupling constants the inclusion of orbital relaxation introduces the effects of Hartree–Fock triplet instabilities into the CCSD(T) calculations and should therefore be avoided,[133] as discussed in section 5.2.2.

4.4.2. Orbital-Relaxed MP2 Response Functions. In Møller–Plesset perturbation theory the Hamiltonian H_0 is partitioned as in eq 484. The Hartree–Fock wave function is the zero-order eigenfunction of the Fock operator (written here in the canonical representation)

$$F|\mathrm{HF}\rangle = \sum_i \varepsilon_i |\mathrm{HF}\rangle \tag{547}$$

where ε_i are the energies of the occupied canonical orbitals. Applying standard perturbation theory we obtain, to first and second orders in the fluctuation potential, respectively, the Hartree–Fock energy

$$\begin{aligned} E_{\mathrm{HF}} &= \langle \mathrm{HF}|F|\mathrm{HF}\rangle + \langle \mathrm{HF}|U|\mathrm{HF}\rangle + h_{\mathrm{nuc}} \\ &= \sum_i \varepsilon_i + \langle \mathrm{HF}|U|\mathrm{HF}\rangle + h_{\mathrm{nuc}} \end{aligned} \tag{548}$$

and the second-order Møller–Plesset (MP2) correlation energy (given here for a closed-shell system)[30]

$$E_{\mathrm{MP2}} = E_{\mathrm{HF}} - \sum_{aibj} \frac{(2g_{aibj} - g_{ajbi})g_{aibj}}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j} \tag{549}$$

where indices *i*,*j* and *a*,*b* denote occupied and virtual orbitals, respectively. The MP2 model usually recovers a large part of the dynamical correlation energy, providing a useful correction to the Hartree–Fock energy at a cost significantly lower than that of CCSD theory (noniterative n^5 rather than iterative n^6). In this sense MP2 theory represents a highly successful approach to calculation of molecular correlation energies, providing, for many purposes, accurate, size-extensive energy corrections. Higher order energy corrections, such as those provided by third-order Møller–Plesset (MP3) theory and fourth-order Møller–Plesset (MP4) theory, may be derived but are considerably more expensive than the MP2 correction and do not always provide a smooth convergence toward the FCI energy, often oscillating or diverging.[134,135]

For evaluation of the MP2 energy and its derivatives it is convenient to reformulate the theory somewhat. Thus, we write the second-order energy in the form

$$E_{\mathrm{MP2}} = \langle \mathrm{HF}|[U, T_2]|\mathrm{HF}\rangle \tag{550}$$

where T_2 is the double excitation operator in eq 475, whose amplitudes satisfy the equations

$$\sum_{\nu} \langle\mu|[F, \tau_\nu]|\mathrm{HF}\rangle t_\nu = -\langle\mu|U|\mathrm{HF}\rangle \tag{551}$$

where the Fock operator may be written in the form

$$F = \frac{1}{2}\sum_{pq,\ \sigma} \langle\mathrm{HF}|[a_{q\sigma}^\dagger, [a_{p\sigma}, H_0]]_+|\mathrm{HF}\rangle E_{pq} \tag{552}$$

We do not insist on the canonical representation since degeneracies among the occupied or virtual orbitals may lead to instabilities in the derivatives.[136] We therefore only require that the Hartree−Fock state satisfies the Brillouin condition

$$\langle\mathrm{HF}|[E_{ai}, H_0]|\mathrm{HF}\rangle = 0 \tag{553}$$

which is a necessary and sufficient condition for stationarity of the Hartree−Fock energy.

We now introduce a static perturbation V such that the total Hamiltonian can be written as

$$H = H_0 + V = F + U + V \tag{554}$$

The perturbed Hartree−Fock wave function $|\widetilde{\mathrm{HF}}\rangle$, the perturbed excited state $|\tilde{\mu}\rangle$, and the perturbed creation operators $\tilde{a}_{p\sigma}^\dagger$ may then be expressed as[136]

$$|\widetilde{\mathrm{HF}}\rangle = \exp(-\kappa)|\mathrm{HF}\rangle \tag{555}$$

$$|\tilde{\mu}\rangle = \exp(-\kappa)|\mu\rangle \tag{556}$$

$$\tilde{a}_{p\sigma}^\dagger = \exp(-\kappa)a_{p\sigma}^\dagger \exp(\kappa) \tag{557}$$

where κ is an anti-Hermitian orbital-rotation operator

$$\kappa = \sum_{ai} \kappa_{ai}(E_{ai} - E_{ia}) \tag{558}$$

where the excitation operators are given in eq 100, with summation over all pairs of occupied and virtual orbitals.

We may next construct the Møller−Plesset Lagrangian L_{MP2} by introducing the perturbed states and operators in eqs 555−557 into the energy expression in eq 550 and the constraints in eqs 551 and 553 with associated Lagrange multipliers $\bar{t}$ and $\bar{\kappa}$, respectively, yielding

$$\begin{aligned} L_{\mathrm{MP2}} &= \langle\mathrm{HF}|[U_\kappa, T_2]|\mathrm{HF}\rangle + \langle\bar{t}|U_\kappa|\mathrm{HF}\rangle \\ &\quad + \langle\bar{t}|[F\{H_\kappa\}, T_2]|\mathrm{HF}\rangle + \sum_{ai} \bar{\kappa}_{ai}\langle\mathrm{HF}|[E_{ai}, H_\kappa]|\mathrm{HF}\rangle \end{aligned} \tag{559}$$

where we introduced the notation (for a general operator A)

$$A_\kappa = \exp(\kappa)A\exp(-\kappa) \tag{560}$$

$$F\{A\} = \frac{1}{2}\sum_{pq,\ \sigma} \langle\mathrm{HF}|[a_{q\sigma}^\dagger, [a_{p\sigma}, A]]_+|\mathrm{HF}\rangle E_{pq} \tag{561}$$

$$\langle\bar{t}| = \sum_{\mu} \bar{t}_\mu\langle\mu| \tag{562}$$

We note that the orbitals are allowed to relax in the presence of the perturbation, orbital relaxation being described by the κ-transformed Hamiltonian H_κ.[136] From this variational Lagrangian the Møller−Plesset molecular properties are obtained in the usual manner, in accordance with the $2n + 1$ and $2n + 2$ rules

$$L_{\mathrm{MP2}}^{(0)} = \langle\mathrm{HF}|[U^{(0)}, T_2^{(0)}]|\mathrm{HF}\rangle \tag{563}$$

$$\begin{aligned} L_{\mathrm{MP2}}^{(1)} &= \langle\mathrm{HF}|\left[U_\kappa^{(1)}, T_2^{(0)}\right]|\mathrm{HF}\rangle + \langle\bar{t}^{(0)}|U_\kappa^{(1)}|\mathrm{HF}\rangle \\ &\quad + \langle\bar{t}^{(0)}|\left[F\{H^{(1)}\}, T_2^{(0)}\right]|\mathrm{HF}\rangle \\ &\quad + \langle\mathrm{HF}|\left[\bar{\kappa}^{(0)}, H^{(1)}\right]|\mathrm{HF}\rangle \end{aligned} \tag{564}$$

$$\begin{aligned} L_{\mathrm{MP2}}^{(2)} &= \langle\mathrm{HF}|\left[U_\kappa^{(2)}, T_2^{(0)}\right]|\mathrm{HF}\rangle + \langle\bar{t}^{(0)}|U_\kappa^{(2)}|\mathrm{HF}\rangle \\ &\quad + \langle\bar{t}^{(0)}|\left[F\{H^{(2)}\}, T_2^{(0)}\right]|\mathrm{HF}\rangle \\ &\quad + \langle\mathrm{HF}|\left[\bar{\kappa}^{(0)}, H^{(2)}\right]|\mathrm{HF}\rangle \\ &\quad + \langle\mathrm{HF}|\left[U_\kappa^{(1)}, T_2^{(1)}\right]|\mathrm{HF}\rangle \\ &\quad + \langle\bar{t}^{(0)}|\left[F\{H^{(1)}\}, T_2^{(1)}\right]|\mathrm{HF}\rangle \end{aligned} \tag{565}$$

The zero-order equations for the amplitudes and Lagrange multipliers are given by

$$\sum_{\nu} \langle\mu|[F, \tau_\nu]|\mathrm{HF}\rangle t_\nu^{(0)} = -\langle\mu|U^{(0)}|\mathrm{HF}\rangle \tag{566}$$

$$\sum_{\nu} \bar{t}_\nu^{(0)}\langle\nu|[f, \tau_\mu]|\mathrm{HF}\rangle = -\langle\mathrm{HF}|[U^{(0)}, \tau_\mu]|\mathrm{HF}\rangle \tag{567}$$

$$\begin{aligned} &\sum_{j} \langle\mathrm{HF}|\left[\kappa_i, \left[\kappa_j, H^{(0)}\right]\right]|\mathrm{HF}\rangle\bar{\kappa}_j^{(0)} \\ &\quad = -\langle\mathrm{HF}|\left[\left[\kappa_i, U^{(0)}\right], T_2^{(0)}\right]|\mathrm{HF}\rangle - \langle\bar{t}^{(0)}|\left[\kappa_i, U^{(0)}\right]|\mathrm{HF}\rangle \\ &\qquad - \langle\bar{t}^{(0)}|\left[F\left\{\left[\kappa_i, H^{(0)}\right]\right\}, T_2^{(0)}\right]|\mathrm{HF}\rangle \end{aligned} \tag{568}$$

whereas the first-order equations for the orbitals and amplitudes become

$$\sum_{j} \langle\mathrm{HF}|\left[\kappa_i, \left[\kappa_j, H^{(0)}\right]\right]|\mathrm{HF}\rangle\kappa_j^{(1)} = -\langle\mathrm{HF}|\left[\kappa_i, H^{(1)}\right]|\mathrm{HF}\rangle \tag{569}$$

$$\begin{aligned} &\sum_{\nu} \langle\mu|[F, \tau_\nu]|\mathrm{HF}\rangle t_\nu^{(1)} \\ &\quad = -\langle\mu|U_\kappa^{(1)}|\mathrm{HF}\rangle - \langle\mu|\left[F\{H^{(1)}\}, T_2^{(0)}\right]|\mathrm{HF}\rangle \end{aligned} \tag{570}$$

By substituting the solutions to the linear equations in eqs 566−570 into the energy expressions in eqs 563−565 we obtain MP2 static molecular properties up to second order.

4.5. Response Functions with Perturbation-Dependent Basis Sets

When molecular properties that depend on nuclear distortions or external magnetic fields are calculated, perturbation-dependent basis sets are typically used, as discussed in sections 2.4 and 4.4.1. In the present section we discuss the evaluation of response functions for such properties, the most important of which are molecular gradients and Hessians (geometrical distortions) and nuclear shielding constants (magnetic field variations).

For a general perturbation parameter ε (which may represent a nuclear distortion or an applied magnetic field) we expand the energy in orders of the perturbation

$$E(\varepsilon) = E^{(0)} + E^{(1)}\varepsilon + \frac{1}{2}E^{(2)}\varepsilon^2 + ... \tag{571}$$

and are particularly interested in the first- and second-order properties $E^{(1)}$ and $E^{(2)}$. The Hamiltonian is expanded in a similar manner

$$H(\varepsilon) = H_0 + H^{(1)}\varepsilon + \frac{1}{2}H^{(2)}\varepsilon^2 + ... \tag{572}$$

An important difference from the theory discussed before is the appearance of second-order and higher order perturbation operators, all of zero frequency. The appearance of nonlinear terms in the perturbation operator is a generalization of the operator considered in section 3.2, where $V(0) = 2V_0$ of eq 199 contains only a linear term. Expressing the energy in terms of a Lagrangian we then obtain the following expressions for the first- and second-order molecular properties

$$E^{(1)} = \frac{\mathrm{d}\boldsymbol{L}}{\mathrm{d}\varepsilon} = \langle(H^{(1)})\rangle \tag{573}$$

$$E^{(2)} = \frac{\mathrm{d}^2\boldsymbol{L}}{\mathrm{d}\varepsilon^2} = \langle(H^{(2)})\rangle + \langle(H^{(1)}; H^{(1)})\rangle \tag{574}$$

where we used the notation for orbital-relaxed response functions introduced in eq 546, L is the variational Lagrangian, and the linear response function has been evaluated at zero frequency. These expressions are evaluated from the first- and second-order perturbed Hamiltonians

$$H^{(1)} = \sum_{pq} \tilde{h}^{(1)}_{pq} E_{pq} + \frac{1}{2}\sum_{pqrs} \tilde{g}^{(1)}_{pqrs}(E_{pq}E_{rs} - \delta_{qr}E_{ps}) \tag{575}$$

$$H^{(2)} = \sum_{pq} \tilde{h}^{(2)}_{pq} E_{pq} + \frac{1}{2}\sum_{pqrs} \tilde{g}^{(2)}_{pqrs}(E_{pq}E_{rs} - \delta_{qr}E_{ps}) \tag{576}$$

for which explicit expressions are given in section 2.4.4 for the first- and second-order OMO integrals expressed in terms of one-index transformations. Here, we assumed singlet perturbations, which is sufficient for evaluation of molecular gradients and Hessians and also nuclear shielding constants of closed-shell systems. More generally, the first- and second-order operators may also include triplet excitation operators, see eqs 102−108.

Taking the expectation value of the operator in eq 575 we obtain for the first-order property

$$E^{(1)} = \sum_{pq} D_{pq}\tilde{h}^{(1)}_{pq} + \frac{1}{2}\sum_{pqrs} \mathrm{d}_{pqrs}\tilde{g}^{(1)}_{pqrs} + h^{(1)}_{\mathrm{nuc}} \tag{577}$$

where we introduced the one- and two-electron density matrices with elements

$$D_{pq} = \langle(E_{pq})\rangle \tag{578}$$

$$\mathrm{d}_{pqrs} = \langle(E_{pq}E_{rs} - \delta_{qr}E_{ps})\rangle \tag{579}$$

In the simplest cases the density matrices are expectation values of the wave functions, for example, in Hartree−Fock, FCI, and MCSCF theories. For nonvariational methods such as coupled-cluster theory, the density matrices are more complicated, involving contributions from the Lagrange multipliers of the Lagrangian. Inserting the expression for the first-derivative one-electron integrals in eq 134 and the corresponding expression for the two-electron integrals we obtain for all wave function models

$$E^{(1)} = \sum_{pq} D_{pq}h^{(1)}_{pq} + \frac{1}{2}\sum_{pqrs} \mathrm{d}_{pqrs}g^{(1)}_{pqrs} - \sum_{pq} F_{pq}S^{(1)}_{pq} + h^{(1)}_{\mathrm{nuc}} \tag{580}$$

where $\mathbf{S}^{(1)}$ is the derivative of the overlap matrix, and we introduced the generalized Fock matrix

$$F_{pq} = \sum_{o} D_{po}h_{qo} + \sum_{ors} \mathrm{d}_{porsg}g_{qors} \tag{581}$$

For the important special case of molecular gradients the term involving the derivative overlap matrix and the generalized Fock matrix is known as the Pulay force. By re-expressing eq 580 in terms of AO integrals the gradient can be efficiently evaluated from derivative integrals in the AO basis, multiplying these integrals with the density matrices, avoiding storage of the large number of derivative integrals (for example, the Hartree−Fock molecular gradient in the AO basis is given by eq 386 in the time-independent limit).

The second-order property in eq 574 consists of two parts. The expectation value is calculated in the same manner as the molecular gradient in eq 577, replacing first derivatives by second derivatives

$$\langle(H^{(2)})\rangle = \sum_{pq} D_{pq}\tilde{h}^{(2)}_{pq} + \frac{1}{2}\sum_{pqrs} \mathrm{d}_{pqrs}\tilde{g}^{(2)}_{pqrs} + h^{(2)}_{\mathrm{nuc}} \tag{582}$$

The resulting expression is more complicated than that of the first-order property but can be straightforwardly and efficiently evaluated in the same manner. Evaluation of the linear-response part of the second-order property in eq 574 follows the general approach for a frequency-independent perturbation, keeping in mind that $H^{(1)}$ in eq 575 contains two-electron as well as one-electron contributions.

For a concrete example we consider the evaluation of the linear-response contribution in Hartree−Fock theory following the MCSCF formalism developed in section 4.2. Setting the frequency equal to zero in the response equations in eq 466 we obtain $\mathbf{E}^{[2]}\boldsymbol{\beta} = \mathrm{i}\mathbf{V}^{[1]}$, where $\mathbf{E}^{[2]}$ is given in eq 453, $\boldsymbol{\beta}$ in eq 444, and $\mathbf{V}^{[1]}$ in eq 449, yielding

$$\begin{pmatrix} \langle \mathrm{HF}|[\mathbf{q}, [H_0, \mathbf{q}^{\dagger}]]|\mathrm{HF}\rangle & \langle \mathrm{HF}|[\mathbf{q}, [H_0, \mathbf{q}]]|\mathrm{HF}\rangle \\ \langle \mathrm{HF}|[\mathbf{q}^{\dagger}, [H_0, \mathbf{q}^{\dagger}]]|\mathrm{HF}\rangle & \langle \mathrm{HF}|[\mathbf{q}^{\dagger}, [H_0, \mathbf{q}]]|\mathrm{HF}\rangle \end{pmatrix} \begin{pmatrix} \boldsymbol{\kappa} \\ \boldsymbol{\kappa}^* \end{pmatrix} = \mathrm{i}\begin{pmatrix} \langle \mathrm{HF}|[\mathbf{q}, H^{(1)}]|\mathrm{HF}\rangle \\ \langle \mathrm{HF}|[\mathbf{q}^{\dagger}, H^{(1)}]|\mathrm{HF}\rangle \end{pmatrix} \tag{583}$$

where we assumed real matrices $\mathbf{A}$ and $\mathbf{B}$. Expanding the two components and assuming a real perturbation we obtain the following response equations for the real and imaginary components of $\boldsymbol{\kappa}$

$$\langle \mathrm{HF}|[\mathbf{q}^{\dagger} - \mathbf{q}, [\mathbf{q}^{\dagger} - \mathbf{q}, H_0]]|\mathrm{HF}\rangle \mathrm{Im}\boldsymbol{\kappa} = -\langle \mathrm{HF}|[\mathbf{q}^{\dagger} - \mathbf{q}, \mathrm{Re}H^{(1)}]\mathrm{HF}\rangle \tag{584}$$

$$\begin{aligned}&\langle \mathrm{HF}|[\mathbf{q}^{\dagger} + \mathbf{q}, [\mathbf{q}^{\dagger} + \mathbf{q}, H_0]]|\mathrm{HF}\rangle \mathrm{Re}\boldsymbol{\kappa}\\ &\quad = -\langle \mathrm{HF}|[\mathbf{q}^{\dagger} + \mathbf{q}, \mathrm{Im}H^{(1)}]\mathrm{HF}\rangle \end{aligned} \tag{585}$$

Taking into account spin symmetry, these equations may be reduced further, as discussed in ref 6.

4.6. Overview of Developments and Implementations

Having presented a theoretical framework for Hartree−Fock, MCSCF, coupled-cluster, and Møller−Plesset response theory we now review the extensive literature on this subject with emphasis on recent developments and implementations. First, we discuss in section 4.6.1 evaluation of expectation values and first-order properties. Section 4.6.2 is devoted to Hartree−Fock and MCSCF theories, while developments in coupled-cluster theory are described in section 4.6.3, and section 4.6.4 contains a brief discussion of explicitly correlated methods. In section 4.6.5 the second-order polarization-propagator approximation (SOPPA) is discussed, followed by the algebraic-diagrammatic-construction (ADC) method in section 4.6.6. Finally, section 4.6.7 contains a brief discussion of relativistic corrections.

4.6.1. Expectation Values and First-Order Properties.

First-order molecular properties represent the first-order change in the electronic energy upon a perturbation of the system and therefore correspond to the first derivative of the energy with respect to the perturbation strength. For variational electronic-structure models the first derivative of the electronic energy is equal to the expectation value of the operator associated with the perturbation of the system, in accordance with the Hellmann−Feynman theorem,[68,69] see eq 177.

By contrast, nonvariational electronic-structure models do not satisfy the conditions of the Hellmann−Feynman theorem, as discussed in section 3.1.3. For such models, therefore, a molecular property calculated as an energy derivative and as a standard expectation value differ. The first-order property is then usually calculated as an energy derivative from a Lagrangian,[77] where it becomes a generalized expectation value (see eq 198), which, in coupled-cluster theory, for example, includes a contribution from the relaxation of the orbitals to the perturbation.

As an alternative to the Lagrangian method, Korona and Jeziorski presented in 2006 an approach for calculating one-electron density matrices from the explicitly connected commutator expansion of the expectation value at the expectation-value CCSD (XCCSD) level of theory.[137] In their approach the density matrix is obtained at little additional cost beyond calculation of the CCSD energy, making it less demanding than Lagrangian-based CCSD theory by avoiding the multiplier equations, without compromising the quality of the calculated one-electron molecular properties, although we note that the resulting properties are not equivalent to finite-difference results.

Analytic first-order property schemes have a long history, which cannot be covered exhaustively here. Often they are obtained as a byproduct of analytic molecular-gradient implementations by replacing the differentiated Hamiltonian integrals with the integrals for the perturbation operator. Finite-field methods have also been extensively used to compute first-order properties, in particular, for molecular multipole moments, see, for example, ref 138. Thus far we restricted ourselves to considering first-order properties for the electronic ground state, but we note that these properties can also be computed for electronically excited states, as will be discussed in section 5.8.

During the past few years attention has been directed toward reducing the computational scaling of ab initio methods, adapting them to larger molecular systems. As an example of such developments affecting the analytic calculation of first-order properties, Friedrich et al.[139] extended in 2009 their automated implementation of the incremental scheme for CCSD energies to the analytic computation of molecular (unrelaxed) first-order one-electron properties, testing the convergence and accuracy of the incremental scheme for the dipole and quadrupole moments of a variety of chemically interesting systems. An analysis of the influence of local approximations in CCSD theory on electric dipole moments (and static dipole polarizabilities) was presented a few years earlier by Korona et al.[140] utilizing a finite-field approach.

4.6.2. Hartree−Fock and MCSCF Response Theory.

Development of molecular response functions for a Hartree−Fock SCF state has a long history. Time-dependent Hartree−Fock equations were first derived by Dirac in 1930.[141] Derivations and applications in the context of determining atomic and molecular properties were presented by McLachlan and Ball,[142] Dalgarno and Victor,[143] and Dunning and McKoy[144] without explicitly setting up response functions. In this review we concentrate on modern developments, where the time evolution of the approximate state is used to set up response functions, from which molecular properties are determined. For Hartree−Fock theory this development was initiated by Dalgaard,[145] who determined the linear and quadratic response functions for Hartree−Fock states. The more general framework for carrying out response theory at the Hartree−Fock and MCSCF levels of theory was formulated by Olsen and Jørgensen in 1985,[70] who developed tractable expressions for Hartree−Fock and MCSCF linear and quadratic response functions, their poles and residues. Subsequently, efficient implementations of linear,[98] quadratic,[99] and cubic[100,101] response functions were presented.

In the formulation by Olsen and Jørgensen, response functions were obtained by applying the Ehrenfest theorem to determine the time evolution of an expectation value for the Hartree−Fock and MCSCF states. An alternative approach is the quasi-energy formalism, defining response functions as derivatives of the quasi-energy, as done in our discussion of response functions in Hartree−Fock (section 4.1) and MCSCF (section 4.2) theories. An advantage of this approach is that it allows computational expressions for frequency-dependent properties to be obtained by differentiation, thereby facilitating derivation of the working equations for computer implementations. This approach became popular with the work of Aiga, Sasagane, and Itoh[64,65] and Christiansen, Hättig, and Jørgensen.[66] Frequency-dependent polarizabilities obtained as quasi-energy derivatives had been considered earlier by Rice and Handy.[146]

The first open-ended approach for higher order molecular properties was that of Dykstra and Jasien[147] based on energy-derivative theory for static (time-independent) perturbations. Shortly thereafter Sekino and Bartlett presented an open-ended analytic approach for frequency-dependent Hartree−Fock (hyper)-polarizabilities[148] based on Frenkel's variation principle for the Schrödinger equation.[67] A similar scheme for time-dependent Hartree−Fock theory was later presented by Karna and Dupuis.[149]

Hartree−Fock response methods have continued to evolve in recent years, in particular, toward reducing the scaling of the computational cost, ideally to become of linear complexity. These developments have often been connected to those for Kohn−Sham theory, which is not discussed in this review. An essential step has been to abandon the MO basis, working instead directly in the AO basis and in terms of the AO density matrix.[13,14,102−106] The approach by Thorvaldsen et al.[106] is described in section 4.1 and is particularly convenient for calculations with perturbation-dependent basis sets, which are an integral part of this formulation. A historical account of response theory and quasi-energy approaches to the calculation of frequency-dependent magnetic properties is found in ref 150.

4.6.3. Coupled-Cluster Response Theory. Coupled-cluster response theory was first developed by Monkhorst,[151] Dalgaard and Monkhorst,[152] and Mukherjee and Mukherjee[153] in the late 1970s. However, development of coupled-cluster theory into the most accurate black-box approach for calculation of molecular properties took place in the 1990s, initiated by the derivation of the linear and quadratic response functions and their residues for the standard coupled-cluster models where the cluster operator is truncated at a given excitation level.[154] Response functions were obtained by examining the time evolution of a generalized coupled-cluster averaged value $\langle\Lambda|A|\mathrm{CC}\rangle$, where the coupled-cluster state and the associated lambda state are required to satisfy the time-dependent Schrödinger equation. In ref 154 it was not imposed that $\langle\Lambda|A|\mathrm{CC}\rangle$ is real. This requirement was later imposed by Pedersen and Koch,[155] thereby ensuring that the resulting response functions satisfy the symmetry relations of section 3.4.4 also for complex Hamiltonians. The quasi-energy Lagrangian approach was subsequently developed[64,66,121] following the introduction a few years earlier of the Lagrangian technique.[77,156] The quasi-energy Lagrangian approach simplified the derivation of the response functions, in particular, for intermediate coupled-cluster models such as the CC2 and CC3 models.

The first CCSD linear response implementation of excitation energies was reported in ref 157. Implementations of the CCSD linear,[129,158,159] quadratic,[160] and cubic[75] response functions were subsequently presented. Introduction of the intermediate CC*n* hierarchy for frequency-dependent properties was an important development in the 1990s, including the CC2[121] and CC3[122,123] models as approximate CCSD and CCSDT models, respectively, see the discussion in section 4.3. Implementations of the CC3 model were first reported by Christiansen et al. for the linear response function,[161] by Gauss et al. for the quadratic response function,[162] and by Pawlowski et al. for the cubic response function.[163] More recently, Kállay and co-workers derived and implemented linear[164] and quadratic[165] response functions for general coupled-cluster models with arbitrary excitation levels in the cluster operator.

Whereas the CC3 and higher order coupled-cluster models are still mostly used for small systems and benchmarking, the CC2 model, especially in combination with Cholesky decomposition[166,167] and resolution of the identity[168−170] techniques for the two-electron integrals, constitutes the only practical alternative to Kohn−Sham theory for computing response properties of larger systems (mainly excitation energies and other linear-response properties),[171−177] although ongoing work on linear-scaling formulations of coupled-cluster theory appear promising with respect to future extensions to more accurate coupled-cluster models.

Very recently, Korona[178] proposed a noniterative correction to the (X)CCSD polarization propagator/linear response function, correct to third order in Møller−Plesset theory and of only n^6 complexity (compared with n^7 for the CC3 model). The same author also presented a variant of the CC2 linear response approach,[179] denoted XCC2, where the time-independent coupled-cluster polarization propagator of Moszynski et al.[180] is combined with CC2 excitation operators. For molecular properties the XCC2 model appears to be a practical alternative to the CC2 model.

Within the framework of coupled-cluster theory, molecular properties may also be calculated using the EOM-CC model discussed in section 4.3.7, developed primarily by Bartlett and co-workers, see refs 181 and 182, and the contribution from other authors to the present volume, for recent reviews. For the standard coupled-cluster hierarchy, EOM-CC theory yields the same excitation energies as those obtained with linear response theory, but there are differences for other properties such as the lack of size intensitivity of EOM-CC transition moments discussed in section 4.3.7.[125,129]

Extensions of the EOM-CC model to higher order response properties have been proposed by Rozyczko and Bartlett.[183,184] Importantly, the EOM-CC model provides an excellent framework for calculation of ionization potentials and electron-attachment energies, see, for example, refs 181, 185, and 186. Approximate triples models for excitation energies were introduced by Watts and Bartlett based on the CCSDT-1a model.[187,188] The CCSDT-1a calculations showed that excitation energies dominated by a double excitation were significantly improved relative to the CCSD results, while excitation energies dominated by a single excitation did not show any improvement. Christiansen et al.[189] demonstrated that when the dominant triples contribution in the triples equation is considered, and importantly, no approximations are made in the singles and doubles amplitude equations; then excitation energies dominated by a single excitation are correct to third order in Møller−Plesset perturbation theory and are thus improved compared to the CCSD excitations (which are correct to second order). The CCSDT-1a model and most other proposed approximate triples models[190,191] introduce approximations in the singles and doubles equations and therefore do not improve upon excitations dominated by a single excitation. By contrast, improvements are observed for the CC3[192,193] and CCSDT-3[194] models, where no approximations are made in the singles and doubles equations.

Most of the development of coupled-cluster response theory has been concerned with the properties of singlet states, although extensions to properties of states of other spins have been made. The EOM-CC method in the spin−orbital basis as presented by Stanton and Bartlett allows evaluation of properties of states with general spin[127] within the limits of this approach. Hald et al.[195] presented an extension of the CC2 method to triplet excitation energies of closed-shell molecules using an integral-direct approach and explicitly spin-coupled triplet excitations in the orbital basis and with an implementation which has roughly the same operation count as for singlet excitations. The approach was subsequently extended to the CCSD[196] and CC3[197,198] models. Several important implementations of the coupled-cluster hierarchies to open-shell references have appeared over the years, and we refer to the review by Stanton and Gauss[199] for an account of earlier contributions on this subject up to 2003. In addition (limiting ourself to some of the most recent work) we mention here the spin-flip EOM-CC approach of Krylov and co-workers,[181,200−203] and the open-shell variant of the CC3 method by Crawford and co-workers.[204]

Concerning local coupled-cluster response methods we mention here the work of Russ and Crawford,[205] which extends the local coupled-cluster approach of Pulay and Saebø[206,207] to dipole polarizabilities[208] and the optical rotation tensor,[208] and the already mentioned analysis of Korona et al.[140] We also note the local multistate CC2 response method of Schütz and coworkers for calculating excitation energies and first-order properties of excited singlet[209−212] and triplet[213] states in extended molecular systems.

4.6.4. Explicit Correlation. In recent years, explicitly correlated electronic-structure theory has established itself as an efficient and accurate alternative to the traditional treatment of correlation energies in quantum chemistry. In particular, explicitly correlated techniques are now being applied not just to calculation of electronic energies but also to calculation of molecular properties. The first analytic implementation of the calculation of first-order properties was presented in 2005 by Kordel et al. at the MP2-R12 level of theory[214] using an auxiliary basis for the resolution of the identity approximation with and without a frozen core. Two years later their approach was generalized to calculation of the full geometrical gradient.[215] Recently, Höfener et al. presented an analytical scheme for first-order properties in MP2-F12 theory.[216] Smooth and rapid convergence toward the basis-set limit was observed for the dipole moments of small closed- and open-shell molecules in augmented correlation-consistent polarized-valence basis sets optimized for MP2-F12 theory. Finally, regarding response theory for explicitly correlated methods we refer to refs 217−219, noting here its recent extension to higher order response functions by Hanauer and Köhn.[220]

4.6.5. Second-Order Polarization-Propagator Approximation. A well-established framework for calculation of molecular response properties is the second-order polarization-propagator approximation (SOPPA).[221−223] The SOPPA linear response function (the polarization propagator) was proposed as an extension to Hartree−Fock theory with the response function and its pole structure correct to second order in perturbation theory. It may be derived using a superoperator formalism;[221] alternatively, it may be obtained by an exponential parametrization of the time evolution, consisting of products of exponentials for orbital rotations and higher order excitations, truncated such that the response function and its poles are correct to second order in Møller−Plesset perturbation theory.[223] The second strategy is particularly convenient for extension of SOPPA to quadratic and higher order response functions, making calculation of molecular properties such as hyperpolarizabilities, TPA cross sections, and excited-state properties possible within the SOPPA model, see ref 223 for details.

A few variants of the SOPPA approach have been proposed over the years, like the CCSDPPA (coupled-cluster polarization-propagator approximation with single and double excitations) of Geertsen and Oddershede[224,225] and the more recent SOPPA(CCSD)[226,227] and SOPPA(CC2)[228] models, which have the same excitation orders as the SOPPA model but employ CCSD or CC2 amplitudes instead of the Møller−Plesset correlation coefficients. The idea is to retain as much as possible the n^5 computational scaling of the SOPPA model in the propagator calculation (even though generation of the CCSD amplitudes in SOPPA(CCSD) theory still scales as n^6). The performance of both the traditional SOPPA approach and of its coupled-cluster-modified variants for calculation of various properties, including excitation energies, dipole oscillator strengths, shielding constants, indirect nuclear spin−spin coupling constants, C_6 dispersion coefficients, and rotational g tensors, has been the subject of several benchmark studies during the last 5 years.[229−232]

4.6.6. Algebraic-Diagrammatic-Construction Method. Another popular polarization-propagator method is the algebraic-diagrammatic-construction (ADC) approach of Schirmer.[233] The second-order ADC(2) model[233−237] allows for a theoretical description of single and double excitations consistently to second and first order, respectively, in perturbation theory. The computational scheme is essentially an eigenvalue problem of a Hermitian secular matrix defined with respect to the space of singly and doubly excited configurations. The configuration space is smaller (more compact) than that of comparable CI expansions, and the method leads to size-extensive results. As discussed by Hättig,[238] the ADC(2) method is closely related to the CIS(D_∞)[239] and CC2 approximations. In the same paper the author reports an implementation of the analytic excited-state gradients for the ADC(2) and CIS(D_∞) models. A modified ADC(2) method,[234,237] with an implemented core−valence separation approximation, has been extensively applied to evaluation of excitation energies and transition moments in the X-ray region, see, for example, refs 237 and 240−242.

The third-order ADC(3) model, for direct computation of electronic excitation energies and transition moments, has been presented by Trofimov et al.[236] based on a specific reformulation of the diagrammatic perturbation expansion for the polarization propagator. The computational scheme combines diagonalization of a Hermitian secular matrix and perturbation theory for the matrix elements. The relationship of the ADC(3) scheme to coupled-cluster theory, in particular, with respect to treatment of transition moments, was also discussed. Recently, calculation of linear and quadratic response functions using the ADC(2) and ADC(3) models has been presented, based on a Lanczos procedure.[243]

4.6.7. Relativistic Corrections. Over the years many approaches have been proposed and implemented to compute relativistic first-order and higher order properties. Referring to the excellent monograph of Dyall and Fægri Jr.[27] for details, we note that relativistic methods may be divided into perturbative and nonperturbative approaches. In the first group a nonrelativistic calculation of energies and properties is followed by a perturbation treatment with the squared fine-structure constant α^2 as perturbation strength. In the second group a relativistic Hamiltonian is used as the starting point. The distinction between the two groups is blurred by the fact that perturbation theory is used to determine the relativistic Hamiltonian and that, even in perturbative approaches, scalar relativistic terms, often using scalar-relativistic Hamiltonians, such as the Douglas−Kroll−Hess Hamiltonian[244−247] or relativistic effective core potentials,[248,249] may be included in a nonperturbative fashion, treating only the more complicated nonscalar relativistic terms such as spin−orbit terms perturbatively.

With respect to the perturbative approaches, direct perturbation theory (DPT) to second order (DPT2) has been applied by Stopkowicz et al. to compute corrections to electrical first-order properties for coupled-cluster methods.[250] Very recently, also energy gradients were implemented using DPT to fourth order (DPT4), allowing for calculation of fourth-order relativistic corrections of the Hartree−Fock energy.[251] Combining the fourth-order gradients with numerical differentiation, these authors also determined relativistic corrections to various first-order electrical properties at the Hartree−Fock level of theory for selected systems.[252] We also mention the general second-quantization formalism presented by Helgaker et al.[253] for calculation of relativistic corrections to molecular electronic energies and properties; in their formalism a Hamiltonian valid for all values of the fine-structure constant α is used to set up a perturbation expansion in orders of α^2 using the general framework of time-independent response theory in the same manner as for geometrical and magnetic perturbations. Cheng and Gauss[254] proposed an analytical scheme for calculation of first-order electrical properties using the spin-free Dirac—Coulomb Hamiltonian, which thus exploits density-matrix formulations in nonrelativistic coupled-cluster derivative theory, with benchmark calculations for first-order electrical properties of the hydrogen halides up to HAt and of a few selected iodo(fluoro)methanes.

For the nonperturbative approaches a method to calculate properties to arbitrary order within the framework of Douglas—Kroll—Hess theory has been suggested by Wolf and Reiher.[255] By consistent use of unitary transformations of both wave functions and property operators the picture-change error is eliminated. This method has been applied to calculate expectation values of powers of $1/r$.[256] Regarding fully relativistic treatments we note that van Stralen et al. in 2005 presented the first implementation of analytical first-order one-electron molecular properties at the Dirac—Coulomb MP2 level of theory using a formalism that allows use of inactive spinors.[257]

Second-order and higher order electric and magnetic properties may also be calculated using the perturbative or nonperturbative relativistic approaches. Norman et al.[258] compared Douglas—Kroll—Hess, effective core potentials, and Dirac—Coulomb Hartree—Fock calculations for the study of nonlinear optical processes. Klopper et al.[259] presented an implementation of first-order relativistic corrections to electrical response properties (with applications to the static and frequency-dependent dipole polarizability and second dipole hyperpolarizability of Ne) at the level of closed-shell coupled-cluster theory within the DPT framework. Perturbative studies of spin—orbit effects have been presented in a number of works, in particular, in connection to nuclear magnetic shielding constants.[43,260] Examples of nonperturbative approaches to calculation of molecular properties is the no-pair four-component linear response theory and implementation of Visscher et al.,[261] the four-component Hartree—Fock linear response theory and implementation by Saue and Jensen,[262] and the quadratic response theory and implementation of Norman and Jensen.[263] More recently, the open-ended response theory of Thorvaldsen et al.[106] was extended to the two- and four-component levels of theory for calculation of arbitrary one-electron properties to any order,[109] including London atomic orbitals to first order.[264]

5. SURVEY OF MOLECULAR PROPERTIES

The present section contains a survey of molecular properties with emphasis on correlated electronic-structure methods and recent computational advances. The section is divided into eight subsections, covering molecular geometrical properties in section 5.1, NMR and EPR parameters in sections 5.2 and 5.3, respectively, electric multipole moments in section 5.4, linear and nonlinear response properties in sections 5.5 and 5.6, respectively, intermolecular interactions in section 5.7, and excitation energies and excited-state properties in section 5.8. Our survey is necessarily incomplete but should be sufficiently exhaustive and representative to illustrate the enormous impact that the ab initio evaluation of molecular properties now has in many areas of chemistry.

5.1. Geometrical Derivatives

Since the pioneering work of Bratož,[265] Gerratt and Mills,[266] Pulay,[110] Moccia,[267] and Thomsen and Swanstrøm[268] the analytic calculation of geometrical derivatives such as molecular gradients and Hessians has revolutionized quantum chemistry by enabling efficient and automated calculation of molecular structure, spectroscopic constants, reaction paths, and classical trajectories. Indeed, there is still a vigorous activity in this field, new techniques and implementations being developed at all levels of ab initio theory, from linear-scaling techniques for large molecular systems to highly accurate force-field calculations on small systems with explicitly correlated wave functions. We do not discuss here the evaluation of specific spectroscopic constants related to geometrical derivatives and distortions but note that the combined development of advanced analytic derivative procedures and high-accuracy quantum-chemistry methods has had a great impact on, for example, rotational spectroscopy. A thorough account of the theory and application of state-of-the-art quantum-chemical methods for accurate determination of the spectroscopic parameters relevant to rotational spectroscopy has very recently been reported by Puzzarini, Stanton, and Gauss;[3] we refer the interested reader to this work for more information on the ab initio study of these molecular properties.

5.1.1. Molecular Gradients and Hessians.

Geometrical derivatives may be calculated using the general methods of response theory, for example, denoting nuclear coordinates by $\mathbf{R}_K$, we obtain for the molecular gradient and Hessian, respectively

$$\frac{\mathrm{d}E}{\mathrm{d}\mathbf{R}_K} = \left\langle \left(\frac{\mathrm{d}H}{\mathrm{d}\mathbf{R}_K} \right) \right\rangle \tag{586}$$

$$\frac{\mathrm{d}^2E}{\mathrm{d}\mathbf{R}_K\mathrm{d}\mathbf{R}_L} = \left\langle \left(\frac{\mathrm{d}^2H}{\mathrm{d}\mathbf{R}_K\mathrm{d}\mathbf{R}_L} \right) \right\rangle + \left\langle \left(\frac{\mathrm{d}H}{\mathrm{d}\mathbf{R}_K}; \left(\frac{\mathrm{d}H}{\mathrm{d}\mathbf{R}_L} \right)^{\mathrm{T}} \right) \right\rangle \tag{587}$$

Evaluation of these expressions was discussed in some detail in section 4.5 and is also discussed in many specialist reviews. In particular, we here refer to the review of Stanton and Gauss,[269] who thoroughly reviewed the field up to the year 2000. In the following, we focus on developments during the past decade. Moreover, in the present section we restrict ourselves to calculation of forces, force constants, and property gradients, postponing discussion of excited-state gradients to section 5.8.5.

Coupled-cluster theory is today recognized as the method of choice for providing ab initio results of high accuracy, the CCSD(T) method being considered the gold standard of ab initio theory.[30,270] In 2003, an integral-density direct implementation of the analytic CCSD(T) molecular gradient based on a Lagrangian formulation was presented. This implementation circumvented the bottleneck of storing either $O(N^4)$ two-electron integrals or $O(N^4)$ density matrix elements on disk and included a frozen-core variant.[271] However, for molecules with difficult electronic structures, more elaborate methods are needed for high accuracy, based on a multiconfigurational reference wave function or on inclusion of higher order excitations. Thus, Gauss and Stanton[272] implemented in 2000 analytic first and second derivatives for the CCSDT-n (n = 1, 2, 3) models,[273,274] CCSDT-1 first derivatives having been implemented already in 1998 by Scuseria and Schaefer.[275] In ref 272 analytic derivatives were also presented for the CC3 model,[122] later extended to include full triples corrections

CCSDT.[276] Using the string-based many-body formalism of Kállay and co-workers,[277−279] Kállay et al. implemented first and second analytic derivatives for these general coupled-cluster methods.[280,281]

For molecules with a strong multireference character, correlated methods based on the dominance of a single reference determinant are insufficient for high-accuracy calculations. In recent years there has been increasing interest in the development of analytical derivatives for multireference wave functions. Lischka, Dallos, and Shepard developed analytic gradients for multistate MRCI wave functions for excited electronic states,[282,283] whereas Khait, Theis, and Hoffmann recently presented an implementation of MRCI single−doubles (MRCISD) gradients[284] based on the Lagrangian formulation of Helgaker and Jørgensen,[77,156] allowing them to calculate state-averaged MCSCF wave functions with varying weights on the electronic states, a restriction in the approach of Lischka et al.[283] Celani and Werner, on the other hand, implemented analytic gradients for multireference perturbation theory,[285] providing an efficient route to dynamic correlation for multireference wave functions.[115,286,287] More recently, Gauss and co-workers[288,289] implemented analytic gradients for two-determinant reference wave functions in Mukherjee's state-specific multireference coupled-cluster theory,[290] later including orbital relaxation at the MCSCF rather than Hartree−Fock level of theory.[289]

A well-known difficulty with determinantal wave function expansions is their slow convergence with respect to the size of the orbital basis.[30,291] This problem is solved by introducing an explicit dependence on interelectronic distances into the wave function in R12 theory,[292,293] later generalized to F12 theory.[294,295] For an overview of recent developments in this field, see also the review by Helgaker, Klopper, and Tew.[270] The added complications of explicit correlation on top of the difficulties associated with nonvariational wave functions make it difficult to develop analytic techniques for geometrical derivatives and other properties. Still, an analytic gradient for the MP2-R12 method has been implemented by Kordel, Villani, and Klopper.[215]

During the past decade, several approaches have been proposed to reduce the computational cost of correlated wave function methods, making them applicable to large molecular systems. One successful approach is the resolution of the identity approximation,[168−170] in which one of the overlap distributions of the two-electron integrals is fitted in an auxiliary basis, reducing cost by avoiding calculation of four-center integrals. Distasio, Steele, and Head-Gordon implemented analytic gradients for this technique,[296] in which the number of orbital responses required for gradients in their dual-basis resolution of the identity MP2 (DB-RI-MP2) method has been reduced to the product of the number of occupied and virtual orbitals determined by the rank of the small AO basis, leading to an efficient code for systems up to about 100 atoms. Kossmann and Neese recently presented an efficient implementation of gradients for the RI-J chain of spheres-exchange RI-MP2 (RIJCOSX-MP2) approach.[297,298] We also note the RI implementation of gradients for the spin-component-scaled (SCS) methods by Hellweg, Grün, and Hättig.[299]

A related technique for reducing the cost of two-electron integral evaluation is Cholesky decomposition, recently applied to gradient integrals, but only in Kohn−Sham theory.[300] Likewise, an efficient linear-scaling method for molecular forces has recently been presented in Kohn−Sham theory,[301] based on the combined use of density fitting, the continuous fast-multipole method,[302] and expansion of solid-harmonic Gaussians in Hermite rather than Cartesian Gaussians;[303] we also note the Kohn−Sham molecular gradient of Dominguez-Soria et al.[304] for use in calculations on large molecules. For these molecular-gradient techniques to be useful in a wave function context more efficient methods must be developed for evaluation of exact-exchange integrals.

An important approach for reducing the computational scaling for large molecules is the use of local orbitals and local correlation methods.[206,207] Schutz et al. presented a local-correlation implementation of analytic gradients utilizing the resolution of the identity approximation,[305] demonstrating that the approach yields quadratic scaling with respect to molecule size and cubic scaling with respect to basis-set size. A local coupled-cluster gradient has been presented by Rauhut and Werner but appears not to be used in practical calculations.[306] Regarding orbital localization, we also mention the work of Leininger et al.[307] on preserving orbital locality during CASSCF geometry optimizations.

The frozen natural-orbital coupled-cluster (FNO-CC) approach[308,309] allows for faster coupled-cluster calculations by reducing the size of the virtual space, see also related work by Klopper et al.[310] Taube and Bartlett presented an implementation of analytic gradients for the FNO-CC approach,[311] including orbital relaxation for noncanonical and semicanonical perturbed orbitals. Although the method was successful in reproducing benchmark data for energies, geometries, and vibrational frequencies, it requires substantial disk storage, making it less attractive for larger systems. These authors also presented analytic derivatives for the variational ΛCCSD(T) method[312−316] (also known as the a-CCSD(T) method[313]), demonstrating the improvements in the potential-energy surfaces with this method due to its better performance in bond-breaking situations.[316] Analytical ΛCCSD(T) derivatives were also discussed, but not implemented, by Crawford and Stanton in 1998.[313]

In recent years, Gauss and co-workers developed highly correlated methods for relativistic corrections based on a perturbative treatment of the leading order relativistic corrections.[317−320] Michauk and Gauss presented analytic gradients for such an approach, including relativistic corrections from the mass−velocity and (one- and two-electron) Darwin terms,[317] see eqs 39 and 40. More recently, Wang and Gauss presented analytic gradients[318] and Hessians[319] for two-component CCSD(T) wave functions including spin−orbit corrections,[320] providing a cost-effective and highly accurate alternative to four-component coupled-cluster calculations.[321,322] Also very recently, Zou et al.[323] derived and implemented the analytical energy gradient of the normalized elimination of the small component (NESC) method,[324] which allows calculation of NESC geometries and other first-order molecular properties in combination with Hartree−Fock theory, Kohn−Sham theory, coupled-cluster theory, or any electron correlation-corrected quantum-chemical method, provided the NESC Hamiltonian is determined in an efficient, yet accurate, way. Another interesting recent development in coupled-cluster theory has been the appearance of several parallel implementations, also for molecular gradients and Hessians.[325−327] Analytic derivatives are beginning to appear for nonstandard wave function models such as multiwavelets[328] and the contracted anti-Hermitian Schrödinger equation.[329] Finally, we note recent work on quantum algorithms for molecular properties and geometries.[330,331]

5.1.2. Molecular Higher Order Derivatives. Analytic calculations of cubic and higher order contributions to molecular force fields are very limited. Handy and co-workers developed an analytic approach for cubic[332] and quartic[333] force fields as well as first and second geometric derivatives of the dipole moment and the electric polarizability.[334] Despite the obvious advantages of such an analytic approach, the code has not been much used after the initial applications but we note a study of the anharmonic force field of benzene.[335] To the best of our knowledge, higher order geometrical derivatives have not been explored by analytical techniques since these pioneering works. Instead, such derivatives have been obtained in a mixed numerical−analytical manner in which higher order derivatives are obtained by finite differences of analytically calculated gradients and Hessians, see, for example, refs 336−338.

5.1.3. Property Geometrical Derivatives. Besides energy derivatives, significant efforts have been directed toward development of analytical procedures for computing the geometric (and magnetic) derivatives of molecular response properties, which are important for (accurate) determination of various observables and spectroscopic constants. For instance, analytic computation of the gradient of the dipole moment, required for calculating infrared intensities in the double-harmonic approximation, was pioneered by Bratož in 1958 with efficient wave function implementations appearing from the mid-1980s.[339,340] Likewise, the gradient of the electric dipole polarizability is needed for vibrational Raman intensities[334] and for description of the related coherent anti-Stokes Raman (CARS)[80,150,341] and vibrational Raman optical activity ROA[2,342] techniques. Geometric derivatives of second-order and higher order response functions are needed to evaluate their vibrational corrections within the Born−Oppenheimer approximation, as discussed in more detail in section 6. The first geometric derivative of the transition dipole strength yields information on how the motion of the nuclei affects the UV spectrum (or the one-photon absorption) of a molecule through the Herzberg−Teller contribution—that is, the linear dependence of the transition dipole moment on the nuclear coordinates, which must be taken into account to describe how forbidden transitions become allowed by vibronic effects.[343−345] Finally, the first geometric derivative of the excited-state energy can be used to determine and characterize the equilibrium geometry of a system in an excited electronic state, as discussed in section 5.8.5.

At present, most implementations of polarizabilities, hyperpolarizabilities, and transition-moment geometric gradients have been presented at the Hartree−Fock and Kohn−Sham levels of theory,[79,80,334,345−347] with the notable exception of the coupled-cluster implementation of the polarizability gradient presented by O'Neill et al. in 2007,[348] which includes a general string-based program for calculation of Raman intensities for arbitrary coupled-cluster and CI methods.

5.2. Nuclear Magnetic Resonance

Evaluation of NMR parameters has become an important application of quantum chemistry over the last two decades. In the present subsection we consider the ab initio evaluation of the two basic parameters of high-resolution NMR: nuclear shielding constants and indirect nuclear spin−spin constants; in addition, we consider here the nuclear spin−rotation constants of microwave spectroscopy, which conceptually and computationally are closely related to the nuclear shielding constants.

Consider a closed-shell molecule in the presence of an external field B along the z axis, with nuclear spins $\mathbf{I}_K$ related to the nuclear magnetic moments $\mathbf{M}_K$ as in eq 55. Assuming free molecular rotation, the nuclear-magnetic energy levels can be reproduced by the following high-resolution NMR spin Hamiltonian

$$\begin{aligned} H^{\mathrm{NMR}} &= -\sum_K \gamma_K \hbar (1-\sigma_K) B I_{K,z} \\ &\quad + \sum_{K>L} \gamma_K \gamma_L \hbar^2 K_{KL} \mathbf{I}_K \cdot \mathbf{I}_L \end{aligned} \tag{588}$$

where we introduced the nuclear shielding constants σ_K and the (reduced) indirect nuclear spin−spin coupling constants K_{KL}. Whereas the first term represents the Zeeman interaction of the nuclei with the external magnetic field, the second term represents the interactions between the nuclear moments. This is an effective nuclear spin Hamiltonian: it reproduces NMR spectra without considering the electrons explicitly. In experimental work the parameters σ_K and K_{KL} are adjusted to fit the observed spectra; here, we consider their evaluation using molecular electronic-structure theory. For specialized reviews, see refs 6 and 349.

5.2.1. Nuclear Shielding Constants. From a consideration of the NMR spin Hamiltonian in eq 588 we find that the shielding tensor of nucleus K is related to the second derivative of the molecular energy with respect to the applied field $\mathbf{B}$ and the nuclear magnetic moment $\mathbf{M}_K$ as

$$\frac{\mathrm{d}^2 E}{\mathrm{d}\mathbf{B}\mathrm{d}\mathbf{M}_K} = -\mathbf{I}_3 + \boldsymbol{\sigma}_K \tag{589}$$

The first term, which represents the coupling of the nucleus to the magnetic field in the absence of electrons, arises from the nuclear part of the Zeeman Hamiltonian H_z of eq 65. The second part of eq 589 is the nuclear shielding tensor $\boldsymbol{\sigma}_K$ and describes the modification to the Zeeman interaction introduced by the electrons. From an inspection of the molecular electronic Breit−Pauli Hamiltonian in eq 57 we note that there is a second-order diamagnetic coupling from H_{BM} in eq 72 and first-order couplings of the electrons with the field in the Zeeman operator H_z of eq 65 and with the nuclei in the paramagnetic spin−orbit operator H_{so} of eq 67, yielding (with the gauge origin at $\mathbf{O}$ and omitting summation over electrons for clarity)

$$\begin{aligned} \sigma_K &= \left\langle \left(\frac{\mathrm{d}^2 H_{\mathrm{BM}}}{\mathrm{d}\mathbf{B}\mathrm{d}\mathbf{M}_K} \right) \right\rangle + \left\langle \left(\frac{\mathrm{d}H_{\mathrm{z}}}{\mathrm{d}\mathbf{B}}; \left(\frac{\mathrm{d}H_{\mathrm{so}}}{\mathrm{d}\mathbf{M}_K} \right)^{\mathrm{T}} \right) \right\rangle \\ &= \frac{\alpha^2}{2} \left\langle 0 \left| \frac{\mathbf{r}_{\mathbf{O}}^{\mathrm{T}} \mathbf{r}_K \mathbf{I}_3 - \mathbf{r}_{\mathbf{O}} \mathbf{r}_K^{\mathrm{T}}}{r_K^3} \right| 0 \right\rangle - \alpha^2 \sum_{n_{\mathrm{S}}} \frac{\langle 0 | \mathbf{l}_{\mathbf{O}} | n_{\mathrm{S}} \rangle \langle n_{\mathrm{S}} | r_K^{-3} \mathbf{l}_K^{\mathrm{T}} | 0 \rangle}{E_{n_{\mathrm{S}}} - E_0} \end{aligned} \tag{590}$$

where the Rayleigh−Schrödinger expression, valid for closed-shell states only, was derived by Ramsey in 1950.[350] By symmetry there are no spin contributions from H_z and H_{so} for closed shells. The summations are therefore only over singlet excited states, as indicated by the summation indices n_{S}.

The first term in eq 590 is the diamagnetic contribution to the shielding. With the gauge origin at the nucleus in question its isotropic component is positive and represents the shielding arising from induced currents in the unperturbed electron density according to Lenz's law, opposing the applied field. The second, paramagnetic contribution in eq 590 arises from the induced electronic magnetic moment (wave function relaxation), which typically aligns with the field and hence opposes the diamagnetic term. Since the nuclear shielding constants arise from a hyperfine interaction between the electrons and the nuclei it is proportional to $\alpha^2 \approx 5 \times 10^{-5}$ and is measured in ppm. For

^{1}S systems (closed-shell atoms) the paramagnetic term vanishes completely and the shielding is given by the Lamb formula: $\sigma_K = \alpha^2\langle 0|r_K^{-1}|0\rangle/3$.

In practice, the shielding constants are not evaluated from the sum-over-states expressions in eq 590 but from the response-theory expression, taking the derivative of the energy with respect to the external magnetic field $\mathbf{B}$ and the nuclear magnetic moments $\mathbf{M}_K$. According to the $2n + 1$ rule only first-order responses are needed; to reduce costs we evaluate these for the three magnetic field directions; for very large molecules other strategies may be important when only a few shielding constants are of interest.[351] To avoid gauge-origin problems, London orbitals[44,61,352] (or some equivalent scheme[353−359]) must be used for all but the smallest systems.

In the following we review recent computational advances in the study of shielding constants. Although this field is dominated by Kohn−Sham theory,[360,361] MP2 theory with London orbitals[362] remains a standard method for shielding calculations, providing accurate results at a reasonable cost; moreover, as in many other areas of computational chemistry, the most accurate results are obtained using coupled-cluster theory. For developments up to 2002, see refs 6, 249, and 363; we also note the more recent perspective article by Vaara.[364] In the following we restrict ourselves to the most recent developments in wave function theory for calculation of shielding constants.

During the past decade most developments in high-level calculations of NMR shielding constants have been carried out at the coupled-cluster level of theory. In particular, Kállay and Gauss implemented the calculation of NMR shieldings at arbitrary excitation levels for coupled-cluster and CI wave functions.[281] The quality of the results that can be obtained can be seen from Tables 1 and 2. Although higher order excitation levels give significant corrections to the shielding constants, these tables highlight the excellent performance of the CCSD(T) method for shielding constants.

For highly accurate calculations of nuclear shielding constants inclusion of zero-point vibrational corrections is important.[366−368] These corrections can be on the order of 3−5% and larger than errors arising from approximations in the CCSD(T) model. Ruud et al.[369] noted that the zero-point vibrational corrections for functional protons are transferable between molecules since the protons vibrate almost independently of the molecular skeleton. Both harmonic and anharmonic corrections to the zero-point vibrational corrections can be important. An approach such as the vibration mode following (VMF) method,[370] which only includes harmonic contributions, often gives an incorrect description of the vibrational effects, both their sign and magnitude. An alternative to perturbation theory for zero-point vibrational corrections is the Feynman-path integral Monte Carlo method, but the large number of configurations needed to perform an accurate vibrational averaging have prevented the use of methods more accurate than Hartree−Fock theory for the vibrationally averaged shielding constants.[371,372]

A number of CCSD(T) benchmark studies with perturbational zero-point vibrational corrections have been presented,[373−379] yielding an agreement with experiment within 1−2 ppm. By parallelizing the CCSD(T) calculation of shielding constants,[326] Harding et al. showed that only by combining highly accurate equilibrium geometries with CCSD(T) calculations in quadruple-ζ basis sets were the shielding constants of the 1-adamantyl cation obtained in good agreement with experimental observations.[326]

Table 1. Isotropic (σ) and Anisotropic ($\Delta\sigma$) NMR Shielding Constants (in ppm) of the BH Molecule Calculated at Different Levels of Electronic-Structure Theory at a Bond Distance of 123.24 pm in the TZP+ Basis with All Electrons Correlated[281,365]

	$\sigma(^{11}B)$	$\Delta\sigma(^{11}B)$	$\sigma(^{1}H)$	$\Delta\sigma(^{1}H)$
HF	−261.3	690.1	24.21	14.15
MP2	−220.7	629.9	24.12	14.24
CCSD	−166.6	549.4	24.74	13.53
CCSD(T)	−171.5	555.2	24.62	13.69
CCSDT	−171.8	557.3	24.59	13.72
CCSDTQ	−170.1	554.7	24.60	13.70
CISD	−182.4	572.9	24.49	13.87
CISDT	−191.7	587.0	24.35	14.06
CISDTQ	−170.2	554.9	24.60	13.70
FCI	−170.1	554.7	24.60	13.70

Table 2. Coupled-Cluster Convergence of Isotropic (σ) and Anisotropic ($\Delta\sigma$) NMR Shielding Constants (in ppm) in CO Calculated in the cc-pVDZ Basis with a Frozen Core[281]

	CCSD	CCSD(T)	CCSDT	CCSDTQ	CCSDTQ5	FCI
$\sigma(^{13}C)$	32.23	35.91	35.66	36.10	36.14	36.15
$\Delta\sigma(^{13}C)$	361.30	356.10	356.47	355.85	355.80	355.79
$\Delta\sigma(^{17}O)$	−13.93	−13.03	−13.16	−12.81	−12.91	−12.91
$\Delta\sigma(^{17}O)$	636.01	634.55	634.75	634.22	634.52	634.35

Although London orbitals are today the most popular method for ensuring gauge-origin-independent calculations of magnetic properties, a number of different schemes have also been proposed.[353−359] Among these the method of continuous transformation of the gauge origin of the current density by setting the diamagnetic contribution to zero (CTOCD-DZ)[357,358] has gained popularity for correlated calculations since it ensures, for properties linear in the external magnetic field, gauge-origin independence without introducing field-dependent two-electron integrals. Sauer and co-workers implemented the CTOCD-DZ approach at various correlated levels, including the MCSCF and SOPPA[381] and CCSD[382] levels of theory. Garcia et al.[383] compared the effect of coupled-cluster truncation on nuclear shieldings with an orbitally unrelaxed scheme using the CTOCD-DZ method, different from the energy-derivative approach used by Kállay and Gauss,[281] in which orbital relaxation is included in the calculation.

For high accuracy in the calculated shielding constants a carefully selected basis set that properly describes the outer-core−inner-valence region is necessary; at the same time, it must be constructed in a manner that allows for a systematic improvement in the description of the correlation energy. Manninen and Vaara developed a technique for designing basis sets for molecular properties with special requirements in the core or valence regions[384] based on the use of completeness profiles for measuring basis-set saturation in selected exponent ranges.[385] The authors applied the developed basis sets to calculation of molecular magnetizabilities, nuclear magnetic shieldings, and indirect spin−spin coupling constants.[384] We also note that several studies of basis-set extrapolation schemes for NMR shielding constants have been presented,[386−390] but these have not gained the same popularity as for energetics.[270,391]

A novel application of the highly accurate methods that have been developed for nuclear magnetic shielding constants is the combination of measurement and theory to revisit and reassign values of nuclear magnetic moments. The tabulated magnetic moments have usually been derived from magnetic resonance measurements of atomic or molecular species with an assumed value for the diamagnetic shielding of the atomic species. As many of these values are from the 1950s, their accuracy is often low. Jackowski, Jaszuński, and co-workers performed important, pioneering work in revising and proposing new values for the nuclear magnetic moments of ^{13}C, ^{14}N, ^{15}N, ^{17}O, ^{19}F, ^{31}P, and ^{33}S,[392] ^{29}Si and ^{73}Ge,[393] and ^{10}B and ^{11}B.[394]

With the development of accurate methods for calculating NMR shielding constants there has been increased interest in smaller corrections to these constants. Whereas shielding polarizabilities (the derivatives of the shielding constants with respect to external electric fields) previously attracted interest as a means of rationalizing intermolecular and solvent effects on shielding constants, these effects are now calculated explicitly and we are aware of only one recent correlated study of shielding polarizabilities.[395] To complement this study, Vaara, Manninen, and Lounila investigated the magnetic-field dependence of atomic systems to explore potential consequences for high-field NMR spectrometers.[396] Recently, Kjær et al.[397] explored the validity of the multipole shielding polarizabilities in combination with a reaction-field approach against the solvent effect induced by a polarizable molecular force field, showing that, by a fortuitous error cancellation, the best results are obtained by including only the linear electric-field effects.

Despite its smallness the effect of parity violation on nuclear magnetic shielding constants has been investigated to establish whether NMR spectroscopy is suitable for observing the effects of parity violation in chiral molecules.[398,399] Both perturbation theory based on a nonrelativistic reference frame[398] and four-component theory have been used to investigate these effects.[399]

Following the proposal of Buckingham and Parlett,[400] Jaszuński and Rizzo, on the other hand, investigated the effect of circularly polarized light on nuclear magnetic moments (a magnetic moment-induced Faraday effect) using MCSCF quadratic response functions.[401]

For heavier elements, relativistic effects are important, not only for the shielding of the heavy atoms but also for light elements in close proximity to a heavy element. This heavy-atom effect arises because spin−orbit coupling at the heavy atom induces a spin polarization of the electrons that couples (by the Fermi-contact and spin−dipole mechanisms) to the nuclear magnetic moment of the nearby light atom in the same way that this nuclear moment couples to the spin polarization induced by other nuclei; indeed, Kaupp et al.[43] demonstrated the close connection between the spin−spin coupling constants and the spin−orbit corrections to the shielding constant of light elements in the vicinity of heavy atoms.

Vaara and co-workers performed a complete perturbation analysis of the relativistic corrections to order α^4 to the shielding constants and presented calculations at the MCSCF level of theory.[260,402−404] Nakatsuji and co-workers developed a generalized unrestricted quasirelativistic approach based on a mixed analytic and numerical scheme for calculation of relativistic nuclear magnetic shielding constants[405,406] and extended it to the inclusion of electron correlation at the MP2 level of theory.[407]

The past decade has seen the emergence of two- and four-component methods for calculation of nuclear magnetic shielding constants. Much of this development has taken place using Kohn−Sham theory, but we focus here on the wave function-based developments. In the relativistic domain the Dirac operator is linear in the momentum operator; consequently, the shielding constant is fully described by a linear response function, without an apparent diamagnetic contribution. However, as discussed by Aucar et al.,[408] the diamagnetic term arises from a redressing of the electrons in the presence of the magnetic field, being described by the electron−positron rotations in the linear response equations. However, the basis-set convergence of these rotations is very slow. It may therefore be advantageous to ignore these rotations and instead calculate the diamagnetic contribution through the Sternheim approximation.[409]

An important issue in four-component calculations is the balanced treatment of the large and small components. In the absence of magnetic fields it is useful to enforce that the small and large components are related through the restricted-kinetic balance condition,[410,411] often enforced in the calculation and design of dual family basis sets[412] or explicitly in the integral evaluation.[413] Given that the small and large components are related by the momentum operator, application of an external magnetic field extends this condition to what is known as the restricted magnetic balance condition. Because it is difficult to design basis sets that fulfill this extended condition, unrestricted kinetic balance is instead often used to ensure accurate shielding constants,[408] leading to the need for using much larger basis sets. An elegant solution to this problem was recently proposed by Komorovsky et al.,[413] who enforced relativistic kinetic balance in calculations at the integral level, extending the approach to include contributions from London orbitals.[414−416] We here also note that Ilias et al.[417] presented gauge-origin-independent calculations of nuclear shielding constants at the four-component Dirac−Coulomb Hartree−Fock level of theory using London atomic orbitals.

Kudo et al.[418,419] presented calculations of shielding constants using the method of NESC tensors by Filatov and Cremer,[324] giving results in the zero-order regular approximation (ZORA)[420,421] and in the second-order regular approximation (SORA) very similar to those obtained using the infinite-order two-component coupled Hartree−Fock method.[422] Kato et al.[423] presented four-component relativistic calculations of nuclear shielding constants at the CISD and CCSD levels of theory but without strictly enforcing gauge-origin invariance. We also note that Aucar and co-workers presented relativistic four-component calculations of nuclear shielding constants at the Dirac−Coulomb Hartree−Fock level of theory.[424,425]

Calculation of current densities arising from application of an external magnetic field to a molecular electron density has been extended to the correlated levels of theory using London atomic orbitals, both for closed-[426] and for open-shell species.[427] It is noteworthy that London orbitals are not sufficient to ensure current conservation,[60] but they do lead to a significantly reduced current nonconservation.[426] Bast et al.[428] extended the scheme for calculating induced magnetic currents to the relativistic four-component Kohn−Sham level of theory but using a common gauge-origin approach. Jusélius and Sundholm advocated the use of calculated current densities to define the aromatic character of molecules[429] as an alternative to the nucleus-independent chemical shift.[430]

We end the discussion of computational models for NMR shielding constants by considering developments aimed at large molecules based on Hartree–Fock and Kohn–Sham theories. Gauss and Werner presented in 2000 a local GIAO-MP2 approach for calculation of NMR shielding constants.[431] Although promising results were obtained, there does not appear to be many applications of the formalism. Ochsenfeld and co-workers developed linear-scaling methods for Hartree–Fock calculations of shielding constants using London atomic orbitals.[12,432] Recently, Beer, Kussmann, and Ochsenfeld[351] extended this approach to achieve sublinear scaling by utilizing the locality of the perturbed density arising from the nuclear magnetic moment of interest. Loibl, Manby, and Schütz recently presented a density-fitting Hartree–Fock code for calculation of NMR shielding constants using London orbitals.[433] We also note that Morokuma and co-workers extended their “our own *n*-layer integrated molecular orbital and molecular mechanics” (ONIOM) multilevel method to the two-level GIAO-MP2:GIAO-HF approach for shielding constants.[434,435]

5.2.2. Nuclear Spin–Spin Couplings.

To determine the coupling between the nuclear magnetic moments $\mathbf{M}_K$ and $\mathbf{M}_L$ we differentiate the molecular electronic energy with respect to these magnetic moments yielding

$$\frac{\mathrm{d}^2E}{\mathrm{d}\mathbf{M}_K\mathrm{d}\mathbf{M}_L} = \mathbf{D}_{KL} + \mathbf{K}_{KL} \tag{591}$$

where $\mathbf{D}_{KL}$ and $\mathbf{K}_{KL}$ are the direct and indirect nuclear spin–spin coupling tensors, respectively. The direct coupling, which arises from the purely nuclear part of the spin–spin operator H_{ss} in eq 68, occurs by a classical dipole mechanism

$$\mathbf{D}_{KL} = \alpha^2 R_{KL}^{-5}(R_{KL}^2\mathbf{I}_3 - 3\mathbf{R}_{KL}\mathbf{R}_{KL}^{\mathrm{T}}) \approx 10^{-12}\ \mathrm{au} \tag{592}$$

However, since this coupling is anisotropic it vanishes in isotropic media such as gases and liquids and does not contribute to the high-resolution NMR spin Hamiltonian of eq 588. Instead, the spin–spin coupling in the NMR spin Hamiltonian is mediated by the electrons and is fully described by the indirect coupling tensor in eq 591.

From inspection of the Breit–Pauli Hamiltonian in eq 57 we find that the nuclear moments couple quadratically to the electrons in the diamagnetic operator H_{MM} of eq 73 and linearly to the electrons in the spin–orbit operator H_{so} of eq 67 and in the spin–spin operator H_{ss} of eq 68, yielding the following expression for the indirect nuclear spin–spin coupling constant[436]

$$\begin{aligned}\mathbf{K}_{KL} &= \left\langle\left(\frac{\mathrm{d}^2H_{\mathrm{MM}}}{\mathrm{d}\mathbf{M}_K\mathrm{d}\mathbf{M}_L}\right)\right\rangle + \left\langle\left(\frac{\mathrm{d}H_{\mathrm{so}}}{\mathrm{d}\mathbf{M}_K};\left(\frac{\mathrm{d}H_{\mathrm{so}}}{\mathrm{d}\mathbf{M}_L}\right)^{\mathrm{T}}\right)\right\rangle \\ &\quad + \left\langle\left(\frac{\mathrm{d}H_{\mathrm{ss}}}{\mathrm{d}\mathbf{M}_K};\left(\frac{\mathrm{d}H_{\mathrm{ss}}}{\mathrm{d}\mathbf{M}_L}\right)^{\mathrm{T}}\right)\right\rangle = \frac{\alpha^4}{2}\left\langle 0\left|\frac{\mathbf{r}_K^{\mathrm{T}}\mathbf{r}_L\mathbf{I}_3 - \mathbf{r}_K\mathbf{r}_L^{\mathrm{T}}}{r_K^3r_L^3}\right|0\right\rangle \\ &\quad - 2\alpha^4\sum_{n_{\mathrm{S}}}\frac{\langle 0|r_K^{-3}\mathbf{l}_K|n_{\mathrm{S}}\rangle\langle n_{\mathrm{S}}|r_L^{-3}\mathbf{l}_L^{\mathrm{T}}|0\rangle}{E_{n_{\mathrm{S}}} - E_0} \\ &\quad - 2\alpha^4\sum_{n_{\mathrm{T}}}\frac{\left\langle 0\left|\frac{8\pi}{3}\delta(\mathbf{r}_K)\mathbf{s} + \frac{3\mathbf{r}_K\mathbf{r}_K^{\mathrm{T}} - r_K^2\mathbf{I}_3}{r_K^5}\mathbf{s}\right|n_{\mathrm{T}}\right\rangle\left\langle n_{\mathrm{T}}\left|\frac{8\pi}{3}\delta(\mathbf{r}_L)\mathbf{s}^{\mathrm{T}} + \frac{3\mathbf{r}_L\mathbf{r}_L^{\mathrm{T}} - r_L^2\mathbf{I}_3}{r_L^5}\mathbf{s}^{\mathrm{T}}\right|0\right\rangle}{E_{n_{\mathrm{T}}} - E_0}\end{aligned} \tag{593}$$

where we omitted summations over electrons for clarity and where n_{S} and n_{T} denote singlet and triplet excited states, respectively. The first term is the diamagnetic spin–orbit contribution to the spin–spin coupling constant, which arises from the diamagnetic H_{MM} operator in eq 73. The second term in eq 593 is the paramagnetic spin–orbit contribution and arises from the part of the spin–orbit operator H_{so} in eq 67 that represents the coupling of the nuclear spins with the orbital motion of the electrons $\alpha^2\mathbf{M}_K\cdot\mathbf{l}_{iK}/r_{iK}^3$. As this operator does not contain electron spin, the first summation in eq 593 is only over singlet states. The paramagnetic and especially diamagnetic orbital contributions are usually but not invariably small; for large internuclear separations they cancel.[437] The second summation in eq 593 arises from the hyperfine part of the spin–spin operator H_{ss} in eq 68, with summation over triplet states only. With a large prefactor $(8\pi/3)^2 \approx 70.2$, the isotropic Fermi-contact–Fermi-contact mechanism often dominates short-range spin–spin coupling constants, whereas the mixed Fermi-contact–-spin-dipolar mechanism dominates the anisotropic part of the coupling tensor.[349] However, there are many exceptions to these rules, and none of the contributions to the spin–spin coupling constants can be a priori neglected. Since the indirect nuclear spin–spin coupling constant arises from hyperfine interactions it is exceedingly small: $\mathbf{K}_{KL} \approx 10^{-16}$ au. Experimentalists usually work in terms of the isotope-dependent indirect nuclear spin–spin coupling constants $\mathbf{J}_{KL} = h\gamma_K\gamma_L\mathbf{K}_{KL}/4\pi^2 \approx 1$ Hz, see eq 588.

The indirect nuclear spin–spin coupling constants are evaluated using response theory, calculating the second derivative of the electronic energy with respect to the nuclear magnetic moments. According to the 2*n* + 1 and 2*n* + 2 rules, only first-order responses are needed. Thus, for a molecule containing N_{M} magnetic nuclei, $3N_{\mathrm{M}}$ response equations must be solved. However, to take advantage of spin symmetry, the Wigner–Eckart theorem is usually invoked, yielding three singlet and six triplet response equations for each nucleus, each of smaller dimension (the same as for a magnetic field perturbation, for example).[6] Unlike for calculations of nuclear shielding constants, London orbitals are not needed for spin–spin calculations since no external magnetic field is involved.

Apart from requiring the solution of a large number of response equations, evaluation of indirect nuclear spin–spin coupling constants poses several challenges. First, nuclear spin–spin coupling constants are extremely sensitive to an inadequate description of static electron correlation.[6] As a result, the restricted Hartree–Fock model is unsuitable for spin–spin calculations, producing erratic results. Therefore, only correlated wave function models give reliable spin–spin constants, adding to the cost of such calculations. With the emergence of DFT as a computational model in quantum chemistry,[438−441] it became possible to perform spin–spin calculations reliably, at low cost, by providing a description less affected by triplet instabilities than Hartree–Fock theory; for a recent discussion of this point, see ref 442. In the present review we concentrate on high-accuracy calculations of nuclear spin–spin coupling constants by wave function theory. In Table 3 we listed calculated spin–spin coupling constants for a set of small molecules.

The first accurate calculations of indirect spin–spin coupling constants were the CI calculations on HD by Kowalewski et al.[443] in 1974. More recently, the FCI model has been applied to evaluate the coupling constant of the helium dimer[444] and the BH molecule.[445] To study larger molecules, MCSCF theory has been widely used following the first implementation by Vahtras et al. in 1992.[446] For small molecules such as C_2H_2 highly accurate results may be obtained with MCSCF theory;[447] for larger systems it becomes difficult to choose an adequate active orbital space.[448] Indeed, after introduction of Kohn–Sham

Table 3. Calculated Spin−Spin Coupling Constants (in Hertz) Compared with Experimental Values[a]

		RHF	CAS	RAS	SOPPA	CCSD	CC3	exp*	vib
HF	$^1J_{\mathrm{HF}}$	59.2	48.0	48.1	46.8	46.1	46.1	47.6	−3.4
CO	$^1J_{\mathrm{CO}}$	13.4	−28.1	−39.3	−45.4	−38.3	−37.3	−38.3	−1.7
N_2	$^1J_{\mathrm{NN}}$	175.0	−5.7	−9.1	−23.9	−20.4	−20.4	−19.3	−1.1
H_2O	$^1J_{\mathrm{OH}}$	63.7	51.5	47.1	49.5	48.4	48.2	52.8	−3.3
	$^2J_{\mathrm{HH}}$	−1.9	−0.8	−0.6	−0.7	−0.6	−0.6	−0.7	0.1
NH_3	$^1J_{\mathrm{NH}}$	61.4	48.7	50.2	51.0	48.1		50.8	−0.3
	$^2J_{\mathrm{HH}}$	−1.9	−0.8	−0.9	−0.9	−1.0		−0.9	0.1
C_2H_4	$^1J_{\mathrm{CC}}$	1672.0	99.6	90.5	92.5	92.3		87.8	1.2
	$^1J_{\mathrm{CH}}$	249.7	51.5	50.2	52.0	50.7		50.0	1.7
	$^2J_{\mathrm{CH}}$	−189.3	−1.9	−0.5	−1.0	−1.0		−0.4	−0.4
	$^2J_{\mathrm{HH}}$	−28.7	−0.2	0.1	0.1	0.0		0.2	0.0
	$^3J_{\mathrm{cis}}$	30.0	1.0	1.0	1.0	1.0		0.9	0.1
	$^3J_{\mathrm{tn}}$	33.3	1.5	1.5	1.5	1.5		1.4	0.2
$\lvert\bar{\Delta}\rvert$	abs	180.3	3.3	1.6	1.8	1.2	1.6	*at *Re*	
	%	5709	60	14	24	23	6		

[a] For references to calculated and experimental values, see ref 349.

theory for calculation of spin−spin coupling constants in the 1990s[438−441] MCSCF theory has played a less prominent role in this area.

For high-accuracy calculations of spin−spin coupling constants, coupled-cluster theory is the preferred method. At the basic CCSD level of theory there are two implementations for spin−spin calculations: the EOM-CCSD implementation by Perera, Sekino, and Bartlett[449] and the analytic second-derivative implementation by Stanton and Gauss.[269,326] To avoid problems associated with triplet instabilities, derivative-based coupled-cluster calculations of spin−spin coupling constants should be performed in an orbital-unrelaxed manner, without relaxing the orbitals in response to the triplet perturbations; the effects of orbital relaxation are instead described by means of the coupled-cluster singles amplitudes.[133] Beyond the CCSD model the first implementations of coupled-cluster theory for calculation of spin−spin coupling constants are the CCSDT, CCSD(T), and CC3 implementations of Auer and Gauss.[133] Being suited to an unrelaxed orbital treatment, the CC3 model is more appropriate than the CCSD(T) model for spin−spin coupling constants.

The SOPPA model has played an important role in the study of indirect spin−spin coupling constants, being first applied by Geertsen and Oddershede already in 1984.[450] In the related SOPPA(CCSD) model the MP2 amplitudes are replaced by CCSD amplitudes, yielding more accurate coupling constants.[226,227] The MP2 model has also been used for spin−spin coupling constants but with much less success.[451,452]

Indirect nuclear spin−spin coupling constants depend sensitively on the molecular geometry and often have large vibrational corrections. Indeed, with the quality of today's electronic-structure calculations the differences between the calculated and the experimental coupling constants are often smaller than the vibrational corrections. For example, in calculations of the C≡C coupling constant in acetylene it was estimated that the residual error does not exceed 2−3 Hz,[447] whereas the vibrational correction is greater than 10 Hz.[453] We also note the work by Åstrand et al.[454] who found a large zero-point vibrational correction of −25 Hz using MCSCF theory in the HF molecule. In similar studies, Wigglesworth et al.[453] applied SOPPA(CCSD) theory to C_2H_2 while Jordan et al.[455] used EOM-CCSD theory to study the NH···N coupling in CNH:NCH. Because of the high cost of such calculations, DFT provides an attractive alternative to wave function methods for vibrational corrections.[456,457] Indeed, an attractive approach is to calculate the equilibrium spin−spin coupling constants using high-level wave function theory but to generate their rovibrational corrections using Kohn−Sham theory.

5.2.3. Nuclear Spin−Rotation Constants.

The spin $\mathbf{I}_K$ of nucleus K can also interact with the magnetic moment generated by the rotation of the molecule. This rotationally induced magnetic moment is a non-Born−Oppenheimer effect, arising from a slight decoupling of the electronic and nuclear rotation moments.[458] The resulting interaction is one of the mechanisms responsible (together with the nuclear quadrupole coupling) for the hyperfine structure (i.e., splitting or shift of the spectral lines) of molecular rotational spectra. To describe this splitting quantum mechanically the following effective Hamiltonian was introduced by Flygare[458]

$$H_{\mathrm{NSR}} = \sum_K \mathbf{I}_K^{\mathrm{T}} \mathbf{C}_K \mathbf{J} \tag{594}$$

where $\mathbf{J}$ is the total rotational angular momentum of the molecule and $\mathbf{C}_K$ is the nuclear spin−rotation (NSR) tensor of nucleus K, which contains both a nuclear and an electronic contribution

$$\mathbf{C}_K = \mathbf{C}_K^{\mathrm{nuc}} + \mathbf{C}_K^{\mathrm{el}} \tag{595}$$

Whereas the nuclear contribution depends only on the nuclear framework

$$\mathbf{C}_K^{\mathrm{nuc}} = \alpha \gamma_K \mathbf{I}^{-1} \sum_{L \neq K} \frac{R_{LK}^2 \mathbf{I}_3 - \mathbf{R}_{LK} \mathbf{R}_{LK}^{\mathrm{T}}}{R_{LK}^3} \tag{596}$$

where $\mathbf{I}$ is the inertia tensor, the electronic contribution can be expressed as a second derivative of the electronic energy

$$\mathbf{C}_K^{\mathrm{el}} = \left(\frac{\mathrm{d}^2 E}{\mathrm{d}\mathbf{I}_K \mathrm{d}\mathbf{J}} \right)_{\mathbf{I}_K,\, \mathbf{J} = \mathbf{0}} \tag{597}$$

It is most efficiently calculated using analytic derivative techniques, although, in their early work, Oddershede and co-workers calculated NSR constants using the polarization propagator approach.[459−461] Use of perturbation-dependent basis functions, known as rotational London orbitals and defined as

$$\chi_\mu(\mathbf{r}, \mathbf{B}, \mathbf{J}) = \exp[-\mathrm{i}(\mathbf{A}_\mu^{\mathbf{B}} + \mathbf{A}_\mu^{\mathbf{J}}) \cdot \mathbf{r}] \chi_\mu(\mathbf{r}) \tag{598}$$

where $\chi_\mu(\mathbf{r})$ is a standard Gaussian and where

$$\mathbf{A}_\mu^{\mathbf{B}} = \frac{1}{2} \mathbf{B} \times (\mathbf{R}_\mu - \mathbf{O}), \quad \mathbf{A}_\mu^{\mathbf{J}} = -\mathbf{I}^{-1} \mathbf{J} \times \mathbf{R}_\mu \tag{599}$$

is recommended to improve basis-set convergence. Note, however, that there is no gauge-origin problem in calculations of NSR constants as the origin for the orbital magnetic dipole operator is dictated by the point about which the molecule rotates, that is, the center of mass of the molecule. Use of rotational London orbitals in calculations of NSR tensors and rotational *g* tensors (vide infra) was proposed in 1996 by Gauss et al.[462] at the Hartree−Fock level of theory, later extended to the coupled-cluster[463] and MCSCF[464,465] methods.

The recent review by Puzzarini et al. contains a detailed discussion of the computational requirements for NSR tensors.[3] In short, the CCSD(T) approach is the method of choice for accurate NSR-tensor calculations; moreover, despite the use of rotational London orbitals, large basis sets may still be needed for high accuracy. Accurate calculations of NSR tensors have proven important in assisting in the assignment of experimental rotational lines in various systems; in ref 466, for instance, such calculations have guided the revision of the experimental result for CF_2.[467] Other examples are reviewed in ref 3.

The NSR tensor is used to determine an absolute NMR scale. The need for an absolute NMR scale stems from the fact that, experimentally, only the chemical shift, that is, the difference in the magnetic shielding for a nucleus in two different chemical environments, is measured, preventing a direct comparison of experimental and computational results, see refs 468 and 469. An absolute shielding scale is established based on the following relation between the paramagnetic part of the shielding constant for a given nucleus and the electronic part of the NSR tensor

$$\boldsymbol{\sigma}^{K}_{\text{para}} = -\frac{m_{\text{p}}}{3m_{\text{e}}g_{K}}\mathbf{I}\mathbf{C}^{\text{el}}_{K} \tag{600}$$

Experimental determination of the absolute chemical-shielding constant thus consists of several steps, where the only purely experimental one is measurement of the molecular rotational spectrum and extraction of the NSR tensor, $\mathbf{C}_K$, for each nucleus K from its hyperfine structure.[469] By subtracting rovibrational contributions from $\mathbf{C}_K$, the purely electronic part $\mathbf{C}^{\text{el}}_K$ is obtained, which in turn can be converted to the paramagnetic shielding $\boldsymbol{\sigma}^{K}_{\text{para}}$. Adding the diamagnetic contribution $\boldsymbol{\sigma}^{K}_{\text{dia}}$ from accurate quantum-chemical calculations and correcting for rovibrational and temperature effects, the experimental absolute shielding constant for each nucleus can be determined and compared with the corresponding purely computational results, see, for instance, refs 366 and 470−473.

5.3. Electron Paramagnetic Resonance

The EPR effective spin Hamiltonian including contributions from the nuclear spins and ignoring contributions from the nuclear quadrupole moments may be written as[474]

$$H^{\text{EPR}} = H^{\text{ex}} + H^{\text{sZ}} + H^{\text{ZFS}} + H^{\text{hf}} + H^{\text{nZ}} \tag{601}$$

Like the NMR effective Hamiltonian in eq 588 the EPR Hamiltonian contains no reference to the electronic structure of the molecule. The different contributions to the EPR Hamiltonian thus describe phenomenologically the interactions present in the molecule.

The first term H^{ex} in eq 601, the exchange contribution, accounts for the difference in energy between electronic states of different multiplicity, and the Hamiltonian

$$H^{\text{ex}} = -2J\mathbf{s}_1\cdot\mathbf{s}_2 \tag{602}$$

is often referred to as the Heisenberg Hamiltonian. The study of spin states in molecular complexes is an active research field in which correlated wave function methods play an important role because of the strong multireference character of intermediate-spin complexes. Although such spin states can be determined with the spin-flip coupled-cluster method of Krylov,[200] most ab initio calculations are performed by calculating the energy differences between explicitly optimized states using multireference methods.[475−478] As this review focuses on quasi-energy response methods we do not consider this contribution to the EPR effective spin Hamiltonian any further, referring instead to the review by Neese.[7]

The second contribution to the Hamiltonian in eq 601 is the electron spin-Zeeman interaction, describing the interaction between the magnetic moment of the electron with the external magnetic induction

$$H^{\text{sZ}} = \mu_{\text{B}}\mathbf{S}^{\text{T}}\mathbf{g}\mathbf{B} \tag{603}$$

where $\mathbf{g}$ is the electron g tensor and $\mathbf{S}$ the total effective spin of the system. For a free electron the strength of this interaction is determined by the free-electron g factor of eq 65, yielding $\mathbf{g} = g_{\text{e}}\mathbf{I}_3 = 2\mathbf{I}_3$, see eq 28. However, electrons in a molecule experience a local magnetic field, arising from a partial shielding (or deshielding) by the other electrons in the molecule, which leads to a shift relative to g_{e}

$$\mathbf{g} = g_{\text{e}}\mathbf{I}_3 + \Delta\mathbf{g} \tag{604}$$

We note that $\mathbf{g}$ in general is a nonsymmetric matrix.

The third contribution to the EPR spin Hamiltonian in eq 601 is the spin−spin-interaction operator

$$H^{\text{ZFS}} = \mathbf{S}^{\text{T}}\mathbf{D}\mathbf{S} \tag{605}$$

which gives rise to the zero-field splitting of the EPR spectrum, describing the dipole interaction between the spin magnetic moments of unpaired electrons. This contribution is thus only present in states with more than one unpaired electron, leading to a splitting of the spin sublevels of a given spin state.

The interactions of the spin magnetic moments of the electrons with the nuclear magnetic moments give rise to hyperfine structure in the EPR spectrum described by the operator

$$H^{\text{hf}} = \sum_{K}(A^{\text{fc}}_{K}\mathbf{S}^{\text{T}}\mathbf{I}_K + \mathbf{S}^{\text{T}}\mathbf{A}^{\text{sd}}_{K}\mathbf{I}_K) \tag{606}$$

The isotropic first part has the form of a contact interaction and measures the spin density at a given nucleus, whereas the anisotropic second part corresponds to the dipolar interaction of the electron spin magnetic moment and the nuclear magnetic moment. The last term in eq 601 is in general not observable in EPR spectroscopy because of the increased line widths due to the presence of the unpaired electrons. The nuclear Zeeman interaction H^{nZ} corresponds to the last term in eq 65. It is analogous to the interaction included in the NMR effective Hamiltonian eq 588, where instead the shift is thought of as arising with respect to the bare nuclear g factor as described by the shielding constant.

5.3.1. Electronic *g* Tensors. For molecules with a single open-shell electronic doublet state and high-spin radicals in the strong-field limit the energy difference between the eigenvalues of the effective EPR Hamiltonian can be written as[474]

$$\Delta E = \mu_{\text{B}}\sqrt{\mathbf{B}^{\text{T}}\mathbf{G}\mathbf{B}} \tag{607}$$

where we introduced the symmetric g tensor $\mathbf{G} = \mathbf{g}\mathbf{g}^{\text{T}}$, which contains both the orbital and the electron spin contributions that contribute to the effective spin and thus correspond to the quantity measured in experiment. Because the unperturbed state is degenerate, degenerate perturbation theory needs to be employed for calculation of the electronic g tensor.[479,480]

In a nonrelativistic treatment the electronic g tensor reduces to the free-electron g value. All corrections to the electronic g tensor are therefore relativistic in origin. Furthermore, in a relativistic two- or four-component framework the electronic g tensor can be calculated as an expectation value of the electronic spin density, making its calculation fairly straightforward.[481−483] By contrast, for calculations that start from a nonrelativistic reference wave function the leading order relativistic corrections are accounted for by perturbation theory. To order α^2 in the perturbation we obtain the following correction to the free-electron g tensor

$$\Delta\mathbf{g} = \Delta\mathbf{g}^{\mathrm{SO}} + \Delta\mathbf{g}^{\mathrm{RMC}} + \Delta\mathbf{g}^{\mathrm{GC}} + O(\alpha^4) \tag{608}$$

where the spin−orbit, relativistic mass-correction, and gauge-correction contributions are given by

$$\Delta g_{\alpha\beta}^{\mathrm{SO}} = \frac{2}{\langle S_z(\max)\rangle} \langle\langle (\mathrm{d}H_z^{\mathrm{orb}}/\mathrm{d}\mathbf{B})_\alpha ; H_{\mathrm{so},\,\beta}\rangle\rangle \tag{609}$$

$$\Delta g_{\alpha\beta}^{\mathrm{RMC}} = \frac{2}{\langle S_z(\max)\rangle} \langle 0|(\mathrm{d}H_{\mathrm{MVBs}}/\mathrm{d}\mathbf{B})_{\alpha\beta}|0\rangle \tag{610}$$

$$\Delta g_{\alpha\beta}^{\mathrm{GC}} = \frac{2}{\langle S_z(\max)\rangle} \langle 0|(\mathrm{d}H_{\mathrm{Bs}}/\mathrm{d}\mathbf{B})_{\alpha\beta}|0\rangle \tag{611}$$

where H_z^{orb} is the orbital part of the Zeeman operator in eq 65, H_{MVBs} is the diamagnetic part of the mass−velocity operator in eq 74, and H_{Bs} is the diamagnetic part of the spin−orbit operator in eq 75. $\langle S_z(\max)\rangle$ corresponds to the maximum spin projection on the z axis for the given spin state. The spin−orbit contribution $\Delta\mathbf{g}^{\mathrm{SO}}$ usually dominates, representing the interaction of the spin−orbit operator H_{so} with the orbital part H^{B} of the Zeeman Hamiltonian H_z in eq 65. For more details, see refs 40 and 484−486. Higher order relativistic corrections have also been derived[480] and shown to be important in oxo-molybdenium(V) and oxo-tungsten(V) complexes.[482]

Most calculations of electronic g tensors employ spin-unrestricted models for which conventional response theory can be used to calculate the relevant quantities from a nonrelativistic wave function, see refs 487 and 488. Spin-restricted models have also been applied, but it is then important to ensure that the triplet operators acting on the open-shell reference state properly take all possible excitations into account.[480]

Multireference CI and MCSCF wave functions have been used to calculate the g tensor of small molecules, see, for example, refs 489−495. In recent years there has been increasing interest in the calculation of electronic g tensors at the ab initio level of theory. Neese introduced spectroscopy-oriented multireference CI (SORCI) theory[496,497] using a sum-over-states approach. A sum-over-states approach based on the spin−orbit-restricted active space−state interaction (SO-RASSI) model[498] was introduced by Bolvin,[479,499,500] who showed that the invariance of the Zeeman Hamiltonian under symmetry transformations and its continuous change with the variations of the parameters of the system (geometry and crystal field) lead to a unique determination of the elements of the g tensor, in contrast to previous assumptions.[501] The approach of Bolvin, in which the spin−orbit interaction has been applied to the electronic states prior to evaluation of the electronic g tensor, was compared at the multistate CASPT2 level[502,503] to the approach of Neese and Solomon, where an effective Hamiltonian approach is used to include spin−orbit effects to second order.[504]

Very recently, Gauss, Kállay, and Neese presented a coupled-cluster linear-response approach for calculating electronic g factors for arbitrary excitation levels, based on an unrestricted Hartree−Fock reference wave function.[505] This development allows for a critical assessment of the ability of various Kohn−Sham exchange-correlation kernels to model the effect of correlation on electronic g tensors.

In approximate theories the computed electronic g tensor will in general be origin dependent, since it depends on the external magnetic field. In exact theory the origin dependence of the orbital magnetic dipole operator is canceled by the origin dependence of the gauge-correction term. This means that in approximate calculations care should be exercised to ensure gauge-origin independence, for instance, using London orbitals.[481,483,505,506] In general, however, electronic g tensors appear to be less sensitive than other properties involving magnetic-field perturbations to the choice of gauge origin (see, for instance, ref 507).

5.3.2. Zero-Field Splittings. In degenerate perturbation theory the zero-field splitting of a spin-degenerate energy level $^{2S+1}E_0$ is evaluated from the eigenvalues of the matrix

$$\begin{aligned} H_{ij}^{\mathrm{ZFS}} &= \langle {}^{2S+1}\Psi_0^i | H_{\mathrm{ss}} | {}^{2S+1}\Psi_0^j \rangle \\ &\quad - \sum_{n\lambda} \sum_k \frac{\langle {}^{2S+1}\Psi_0^i | H_{\mathrm{so}} | {}^{\lambda}\Psi_n^k \rangle \langle {}^{\lambda}\Psi_n^k | H_{\mathrm{so}} | {}^{2S+1}\Psi_0^j \rangle}{{}^{\lambda}E_n - {}^{2S+1}E_0} \end{aligned} \tag{612}$$

where ${}^{\lambda}\Psi_n^k$ is a zero-order wave function of spin multiplicity λ and spin projection k. The zero-field splitting, which occurs only in molecules with two or more unpaired electrons, has two distinct contributions. The first contribution in eq 612 is an expectation value of the two-electron spin−spin dipole−dipole coupling operator of eq 68, whereas the other term is the indirect interaction between the spin−magnetic moments of two electrons, mediated by the one- and two-electron contributions of the spin−orbit operator in eq 67. In most cases the spin−orbit contribution dominates the zero-field splitting, in particular, if heavier elements are involved. For transition-metal complexes the spin−orbit effect, often dominated by a few close-lying electronic states, can be included in a limited sum-over-states expansion or using ligand-field theory.[508] For molecules with weak spin−orbit interactions such as triplet-spin organic molecules, the electron spin−spin interaction may dominate the zero-field splitting.[38] However, in transition-metal complexes the indirect spin−spin coupling has also been shown to be important in some cases.[509]

The perturbation-theory approach of Neese and Solomon has also been applied to the calculation of zero-field splittings using a sum-over-states methodology to calculate the linear-response contribution to the zero-field splitting from CI-like wave functions.[504] A linear-response approach for calculating zero-field splittings, also including the contributions from the direct spin−spin dipolar interaction was presented by Vahtras et al.,[38] later extended to include solvent effects.[510,511] Ganyushin et al. demonstrated that the resolution of the identity approximation could be efficiently used to reduce the four-index spin−spin interaction integrals to three-index integrals, facilitating highly correlated calculations on large systems.[512]

The group of Neese has been active both in developing efficient methodology for calculating zero-field splittings for multireference wave functions[39,513] and in providing benchmarks for DFT approaches.[509,514,515] Benchmark studies using CASPT2/NEVPT2 methods[516,517] and multireference wave functions[518] have been presented in recent years. We note that the calculation of zero-field splittings in DFT has been controversial, with different expressions for the zero-field splitting constants having been proposed;[509,513,519] this controversy was recently resolved by Schmitt et al.[520]

5.3.3. Hyperfine Coupling Tensors. The EPR hyperfine splitting constants

$$\mathbf{A}_K = A_K^{\mathrm{fc}}\mathbf{I}_3 + \mathbf{A}_K^{\mathrm{sd}} \tag{613}$$

of H^{hf} in eq 606 couple the electron and nuclear spins, providing detailed information about the structure of radicals, in much the same manner as shielding constants do in NMR spectroscopy. The isotropic contribution to the hyperfine interaction A_K^{fc} and the anisotropic contribution $\mathbf{A}_K^{\mathrm{sd}}$[40] in eq 613 arise from the electron–nuclear Fermi-contact and the spin–dipole operators in H_{ss} of eq 68, respectively. Both contributions are simple expectation values of the respective operators

$$A_K^{\mathrm{fc}} = -\frac{4\pi}{3} g_K g_{\mathrm{e}} \mu_{\mathrm{B}} \mu_{\mathrm{N}} \alpha^2 \frac{1}{\langle S_z(\max)\rangle} \sum_{pq} \langle \phi_p | \delta(\mathbf{r}_K) | \phi_q \rangle \langle 0 | T_{pq}^{1,\,0} | 0 \rangle \tag{614}$$

$$\mathbf{A}_K^{\mathrm{sd}} = -\frac{1}{2} g_K g_{\mathrm{e}} \mu_{\mathrm{B}} \mu_{\mathrm{N}} \alpha^2 \frac{1}{\langle S_z(\max)\rangle} \sum_{pq} \langle \phi_p | \frac{3\mathbf{r}_K \mathbf{r}_K^{\mathrm{T}} - r_K^2 \mathbf{I}_3}{r_K^5} | \phi_q \rangle \langle 0 | \mathbf{T}_{pq} | 0 \rangle \tag{615}$$

where the expectation values of the triplet excitation operators in eqs 98 and 101 are elements of the triplet density matrix. There are also relativistic corrections to the hyperfine coupling from the diamagnetic operator H_{Ms} in eq 76; we refer to refs 521 and 522 for more details.

The EPR hyperfine coupling is governed by triplet perturbations. Thus, as for the g tensor, it is common to use unrestricted wave functions for describing the reference state, in which case the hyperfine interactions can be calculated as regular expectation values, for example, from coupled-cluster wave functions in an orbital-relaxed formulation.[523,524]

Correlated methods were presented early for the study of hyperfine interactions using, for instance, symmetry-adapted-cluster CI (SAC-CI) theory[525,526] and MRCISD theory.[527−529] Kossmann and Neese recently presented a correlated approach for calculating hyperfine coupling constants in larger molecules based on the orbital-optimized SCS-MP2 method.[530] Orbital optimization significantly reduces spin contamination, whereas spin-component scaling[531] improves the dipolar hyperfine coupling constants relative to the orbital-optimized MP2 method.

Hyperfine coupling constants can also be calculated from spin-restricted wave functions, letting the system respond in an unrestricted manner to the triplet perturbation.[532] Within such a restricted–unrestricted approach first-order properties are calculated as a restricted expectation value but with an unrestricted correction for the response to the triplet perturbation. First implemented at the SCF and MCSCF levels of theory it has recently been extended to Kohn–Sham theory.[533]

In general, the most severe basis-set requirements in calculations of hyperfine coupling constants come from the isotropic hyperfine contribution, the anisotropic contribution being less demanding. We mention, in particular, that there are basis sets specifically designed for DFT calculations of hyperfine coupling constants (EPR-III).[534] Alternatively, the Hiller–Sucher–Feinberg identity can be applied to the Fermi-contact operator to reduce basis-set requirements.[535] This approach and its extensions have been explored by Rassolov and Chipman[536−538] and by Sundholm.[539] There is a large computational activity on the study of hyperfine couplings, especially using DFT; see the review by Improta and Barone.[540]

5.4. Electric Multipole Moments

As discussed in section 2.2.5 the most important electric multipole moments are the electric dipole moment $\boldsymbol{\mu}$ and the (traceless) quadrupole moment $\boldsymbol{\Theta}$. The molecular dipole moment is the first nonvanishing electric moment for neutral systems with an asymmetric charge distribution, whereas the quadrupole moment is the first nonvanishing moment of nonpolar systems. In the gas phase permanent dipole moments are usually determined from the shift in the rotational energy levels caused by an applied electric field in high-resolution microwave spectroscopy (the Stark effect[541,542]) or from measurements of the dielectric constant.[543] Electric quadrupole moments are typically obtained from measurements of an electric-field-gradient-induced-birefringence (EFGB) effect (anisotropy of the refractive index) known as the Buckingham effect.[544] Alternatively, they can be deduced from the deflection of a molecular beam by an electric or inhomogeneous magnetic field or in an indirect manner from microwave Zeeman experiments.[458]

5.4.1. Electric Dipole Moments. Several benchmark studies of the dipole moment of small- and medium-sized molecules using high-accuracy methods, in particular, coupled-cluster theory, have appeared over the last 15 years, examining the basis-set and excitation-level requirements and the requirements for vibrational corrections.[545−549] We also note a study of the divergence of Møller–Plesset theory of the dipole moments of BH and HF.[550,551] The accuracy of the computed dipole moments with state-of-the-art coupled-cluster methods is comparable to the experimental accuracy, in a few instances, even superior to experiment, prompting a revision of experimental results.[548]

In a very recent benchmark study by Hellweg[552] the accuracy of dipole moments calculated from wave function methods based on second-order perturbation theory was investigated for ground and excited states, focusing on large systems, for which highly accurate methods were still out of reach.[552] The MP2, CC2, and ADC(2) methods were discussed, together with their SCS and scaled-opposite-spin (SOS) variants. It was concluded that an accuracy of about 0.2−0.1 D in the ground state (and about 0.3−0.2 D in the excited states) can be achieved with these approaches.

As reviewed in ref 3, dipole moments govern the intensity of rotational transitions in microwave spectroscopy. Theory can therefore help to predict rotational transitions and intensities. In general, reliable but not necessarily very accurate values are sufficient for such purposes. An interesting application of computed dipole moments is that presented in ref 553, where the theoretical values were used to determine the relative stability and abundance of the cis and trans forms of trisulfane and 1-oxatrisulfane, see also ref 3.

Accurate dipole moments are used in the investigation of interaction-induced properties, see section 5.7.2. For instance, the key role of the accuracy of the dipole-moment surface for prediction of the infrared transition intensities in the Ar−HF complex has been investigated by Jankowski and Ziolkowski.[554]

5.4.2. Electric Quadrupole Moments. Over the last two decades development of more accurate electronic-structure methods and advances in experimental techniques have rekindled interest in the ab initio determination of molecular quadrupole moments.[555−565] As an example, the quadrupole moment of N_2 determined by Graham and co-workers[566] in 1998 was in noticeable disagreement with existing theoretical and experimental values. Taking advantage of newly developed high-accuracy methods for first-order molecular properties, Halkier et al.[567] performed a thorough investigation of the quadrupole moment of N_2, proposing a new reference value, $\Theta = (-4.93 \pm 0.03) \times 10^{-40}$ C m^2. Simultaneously, Coriani et al. identified the use of erroneous correction terms for the temperature-independent contribution in the experimental values as the main source of discrepancy between the theoretical and experimental values, and proposed a revised experimental dipole moment based on their CCSD value of the temperature-independent contribution to the EFGB.[555] In 2003, a reinvestigation of the Buckingham effect in gaseous N_2 over a range of temperatures confirmed that the temperature-independent contribution to the effect is not negligible, yielding a new experimental value, $\Theta = -(4.97 \pm 0.16) \times 10^{-40}$ Cm^2,[562] in excellent agreement with the ab initio value of Halkier et al. from 1998.[567]

5.5. Linear Response Properties

Many of the microscopic properties obtained from linear response theory are in the theory of electromagnetism defined by multipole expansions, that is, from the perturbative expansion of the real induced oscillating electric and magnetic multipole moments[2,569,568] (in the Einstein summation convention)

$$\mu_\alpha = \alpha_{\alpha\beta} E_\beta + \frac{1}{\omega} \alpha'_{\alpha\beta} \dot{E}_\beta + \frac{1}{3} A_{\alpha,\,\beta\gamma} \nabla_\beta E_\gamma + \ldots \tag{616}$$

$$\Theta_{\alpha\beta} = A_{\gamma,\,\alpha\beta} E_\gamma - \frac{1}{\omega} A'_{\gamma,\,\alpha\beta} \dot{E}_\gamma + C_{\alpha\beta,\,\gamma\delta} \nabla_\gamma E_\delta + \ldots \tag{617}$$

$$m'_\alpha = \xi_{\alpha\beta} B_\beta + \frac{1}{\omega} \xi'_{\alpha\beta} \dot{B}_\beta + G_{\beta\alpha} E_\beta - \frac{1}{\omega} G'_{\beta\alpha} \dot{E}_\beta + \ldots \tag{618}$$

In the following a few of the tensors entering the above expansions are discussed, due to the fundamental role they play in rationalizing a variety of physical and chemical phenomena. Because of its relation with the magnetizability $\xi_{\alpha\beta}$, the rotational g tensor will also be discussed below, even if it originates from a different mechanism, namely, the interaction of the rotationally induced magnetic moment with an external magnetic field.

5.5.1. Dipole Polarizabilities. Among the expansion coefficients introduced above, the electric dipole polarizability tensor

$$\alpha_{\alpha\beta}(-\omega, \omega) = -\langle\langle \mu_\alpha; \mu_\beta \rangle\rangle_\omega \tag{619}$$

is probably the best-known second-order property, being the leading term in the perturbative expansion of the (induced) dipole moment μ_α in the presence of a radiation field. The polarizability is used to rationalize, at the microscopic level, macroscopic observables such as the refractive index and the dielectric constant of a medium. It plays an important role in Raman spectroscopy and enters the temperature-dependent part of various birefringence effects (vide infra). The dipole polarizability gives information about molecular shape and charge complementary to that provided by the dipole moment and is important for characterization and elucidation of the molecular structure of various substances. Like the dipole moment, the dipole polarizability is a popular benchmark property for the many linear response methods that have been presented over the years. The numerous studies that have been carried out for the dipole polarizability have clarified the performance of the various computational approaches, see, for instance, refs 570 and 571. Moreover, high-accuracy ab initio dipole polarizabilities have been used to benchmark the performance of approximate Kohn−Sham exchange-correlation functionals.[572]

Owing to the importance of the polarizability itself through its connection to the refractive index and of the many observables derived from the polarizability, the literature on theoretical studies of polarizabilities is vast and would require a review of its own. For an up-to-date critical review of relevant literature of theoretical calculations of polarizabilities, we refer the reader to ref 573.

Apart from ground-state polarizabilities, excited-state polarizabilities can also be determined from response theory, for instance, as second residues of the cubic response function of the ground state, as done by Jonsson and co-workers at the Hartree−Fock[574,575] and MCSCF[101] levels of theory. For CCSD wave functions excited-state first-order properties were derived by Koch and Jørgensen[154] and by Stanton and Gauss,[576,577] who also discussed the theory for static excited-state second-order properties. Alternatively, Hättig et al.[578] presented an implementation based on an excited-state Lagrangian,[579] which yields excited-state properties equivalent to those identified from ground-state double residues but with the artificial secular divergent terms removed, thereby remaining numerically stable in the limit of static external fields; the approach was applied to compute the dipole polarizabilities of the S_1 states of s-tetrazine and pyrimidine.

5.5.2. Magnetizabilities. The molecular magnetizability describes the magnetic moment induced in a molecule by an external magnetic field induction and how this induced moment may interact with the external field to yield an energy correction. It is computed as the second derivative of the electronic energy with respect to the components of an external magnetic field

$$\xi = -\left.\frac{\mathrm{d}^2 E}{\mathrm{d}\mathbf{B}^2}\right|_{\mathbf{B}=\mathbf{0}} \tag{620}$$

In the response-theory formalism this expression is equivalent to

$$\xi = -\left\langle \left(\frac{\mathrm{d}^2 H_{\mathrm{BB}}}{\mathrm{d}\mathbf{B}^2} \right) \right\rangle - \langle\langle \mathbf{m}; \mathbf{m}^{\mathrm{T}} \rangle\rangle_0 = \xi^{\mathrm{dia}} + \xi^{\mathrm{para}} \tag{621}$$

where the first contribution, known as the diamagnetic contribution, is the expectation value of the diamagnetic magnetizability operator in eq 71, differentiated twice with respect to the magnetic field. The second, paramagnetic contribution arises from the interaction of the magnetic dipole operator with itself. In closed-shell systems, due to quenching of the magnetic moment, see eq 66, the magnetizability yields the first nonvanishing contribution to the energy in the presence of a static magnetic field

$$\Delta E(\mathbf{B}) = -\frac{1}{2} \mathbf{B}^{\mathrm{T}} \xi \mathbf{B} \tag{622}$$

For closed-shell molecular systems the diamagnetic contribution usually dominates the magnetizability, making the molecule diamagnetic. For some closed-shell molecules with low-lying excited states it is the paramagnetic contribution that dominates, making the molecule paramagnetic. However, as discussed by Tellgren, Helgaker, and Soncini,[580] all closed-shell molecules become diamagnetic in sufficiently strong magnetic fields.

As for other magnetic properties, calculation of the magnetizability is hampered by gauge-origin dependence. The most successful solution to this problem is the use of London orbitals.[581] When London orbitals are employed the paramagnetic contribution to the magnetizability is best defined as[462]

$$\xi^{\mathrm{para,\ LAO}}(\mathbf{O}) = \xi^{\mathrm{LAO}} - \xi^{\mathrm{dia}}(\mathbf{O}) \tag{623}$$

which is equivalent to the definition in eq 621 in the limit of a complete basis set.

In addition to ensuring gauge-origin independence, use of London orbitals ensures fast basis-set convergence in calculations of magnetizabilities, as shown, for instance, in the study of the magnetizability anisotropy of PF_3 in ref 582. Even in the relatively large aug-cc-pVQZ basis the magnetizability anisotropy computed without London orbitals has the wrong sign.

Magnetizabilities have been extensively studied at the Hartree–Fock and MCSCF levels of theory.[52,581,583–589]An implementation of the gauge-origin-independent calculation of magnetizabilities (and rotational *g* tensors) at the general coupled-cluster level with London orbitals has been presented by Gauss et al.[590] An implementation of the polarizable-continuum model (PCM) in its integral-equation formulation for calculation of the magnetizabilities of solvated molecules at the Hartree–Fock, MCSCF, and (hybrid) Kohn–Sham levels of theory with London orbitals was reported in ref 591. The theory of a hybrid quantum-mechanics/molecular-mechanics (QM/MM) approach for gauge-origin-independent calculations of the molecular magnetizability using Hartree–Fock and Kohn–Sham theories was presented in ref 592.

These studies have shown that the isotropic magnetizability is not particularly sensitive to electron correlation[464] (which contributes less than 3% in most cases) nor to nonelectronic effects such as zero-point vibrational corrections (with aromatic and antiaromatic ring systems as exceptions)[593,594] or medium effects. By contrast, for the anisotropic magnetizability these effects may be sizable.[591,594] Despite the insensitivity to correlation and other effects for the isotropic magnetizability, the agreement between experimental and theoretical results is quite poor. Since most of the experimental results are relative to some reference compound it has been suggested that inaccurate reference magnetizabilities in the experimental determination is the reason for the disagreement and that, for small molecules at least, calibration of measurements should be based on accurate computed values.[595]

Recently, Lutnæs et al.[596] established an accurate benchmark data set of magnetizabilities (and rotational *g* tensors) of 28 molecules using the CCSD and CCSD(T) models with extrapolation techniques to obtain estimates of the basis-set-limit quantities and used this set to examine the performance of Kohn–Sham theory for a wide variety of exchange-correlation functionals. None of the functionals examined proved competitive with the CCSD or CCSD(T) methods. The coupled-cluster results were also compared with the results of density-functional calculations constrained to give the same density, and the importance of current dependence in exchange-correlation functionals was discussed in light of this comparison.

The theory for the frequency-dependent magnetizability remains unresolved. A gauge-origin-independent theory for the frequency-dependent magnetizability for exact states has been proposed by Raab and de Lange.[597] Although origin independent, the derivation of the frequency-dependent magnetizability is based on ad hoc (but physically reasonable) conditions to be fulfilled rather than on exact conditions. An apparently very similar expression can be obtained by considering the constitutive relations for the material constants,[598] although we note that the definition of the inverse permeability in this case is not unique.[599] Independent of the formalism, for approximate calculations also the frequency-dependent magnetizabilities require the use of London atomic orbitals. Krykunov et al. started from the expressions of Raab and de Lange[597] and calculated static and dynamic linear magnetic responses in approximate time-dependent DFT (TDDFT).[600]

5.5.3. Rotational *g* Tensors.

We already noted that molecular rotation leads to an induced magnetic moment, as described in section 5.2.3. The rotational *g* tensor arises from the interaction of this rotationally induced magnetic moment with an external magnetic field and is often referred to as the rotational Zeeman effect.[458] The rotational *g* tensor is closely related to the molecular magnetizability in the nonrelativistic description of magnetic interactions,[458] being governed by the paramagnetic part of the magnetizability

$$\mathbf{g} = -4m_{\mathrm{p}}\xi^{\mathrm{para}}(\mathbf{R}_{\mathrm{CM}})\mathbf{I}^{-1} + \mathbf{g}^{\mathrm{nuc}} \tag{624}$$

where we used the definition of the paramagnetic magnetizability in eq 623 with the center of mass as gauge origin. The nuclear contribution to the rotational *g* tensor is given by

$$\mathbf{g}^{\mathrm{nuc}} = \frac{1}{2\mu_{\mathrm{N}}}\sum_{K} Z_K[R_K^2\mathbf{I}_3 - \mathbf{R}_K\mathbf{R}_K^{\mathrm{T}}]\mathbf{I}^{-1} \tag{625}$$

where the nuclear positions $\mathbf{R}_K$ are given relative to the center of mass of the molecule.

Because of its close connection to the magnetizability the rotational *g* tensor inherits many of the computational characteristics of the magnetizability, including its gauge-origin dependence and sensitivity to the choice of basis set. Gauss et al.[462] demonstrated that, by introducing rotational London orbitals, a computationally efficient scheme for calculation of rotational *g* tensors is obtained, where basis-set and gauge-origin problems are largely removed. An extreme case of the strong basis-set dependence observed for the rotational *g* tensor was provided by Ruud and Helgaker[582] for PF_3, for which the $g_\perp$ values obtained with and without rotational London AOs in the aug-cc-pVDZ basis are of the same magnitude but of opposite sign. The results obtained in this basis with London AOs are within 4% of the basis-set limit for this molecule, in marked contrast to the non-London results.

Unlike the magnetizability, rotational *g* tensors can be determined with high accuracy in molecular-beam[601] and microwave Zeeman experiments.[458] These experiments thus serve as an important source of high-quality data against which accurate ab initio methods can be benchmarked. Cybulski and Bishop presented two early studies of correlated calculations of rotational *g* tensors of diatomic molecules at the MP2 and the linearized-CCD levels of theory.[471,602] Large (but non-London) basis sets were used to ensure convergence and vibrational corrections were applied to get results within the narrow experimental error bars.

Sauer and co-workers presented a number of studies of the rotational *g* tensor of small molecules using the SOPPA method[603–605] and more recently the SOPPA(CCSD) method.[606–609] In many of these studies special attention has been given to the vibrational and temperature dependence of the rotational *g* tensors.[461] Enevoldsen et al.[610] presented calculations of the rotational *g* tensor at the relativistic four-component Dirac–Coulomb Hartree–Fock level of theory using the same definition of the rotational *g* tensor at the relativistic and nonrelativistic levels of theory. We note, however, that a relativistic treatment of the induced rotational magnetic moments has not yet been presented, and it is unclear whether the direct connection between the magnetizability and the rotational *g* tensor also holds in a relativistic framework.

With introduction of rotational London AOs[462] larger molecules came within the reach of wave function-based calculations, and highly accurate MCSCF studies of rotational *g* tensors have been presented by Ruud and co-workers,[454,464,587,593,611,612] including studies of the rotational *g* tensor of electronically excited states.[613,614] Gauss et al.[590] implemented the calculation of rotational *g* tensors at the coupled-cluster level of theory for arbitrary excitation levels using the string-based approach of Kállay and Surjan.[278] This implementation has been used to provide high-level theoretical data for rotational *g* tensors (and magnetizabilities) that have served as a benchmark set for exploring the suitability of different exchange-correlation functionals in calculations of magnetic properties.[596,615]

An important application of rotational *g* tensors is for determination of molecular structures. It can be shown[3,458,616] that the leading order electronic correction $\Delta\mathbf{B}_{\mathrm{el}}$ to the rotational tensor $\mathbf{B}_{\mathrm{e}}$ of a molecule is proportional to the rotational *g* tensor

$$\Delta\mathbf{B}_{\mathrm{el}} = \frac{m_{\mathrm{e}}}{m_{\mathrm{p}}}\mathbf{g}\mathbf{B}_{\mathrm{e}} \tag{626}$$

The importance of this correction varies from molecule to molecule. For HF, N_2, and HOF it is 1−2 orders of magnitude smaller than the vibrational correction, whereas it is sizable and nonnegligible for BH, CH^+, and SiC_3.[3,617] We refer to the recent review by Puzzarini et al.[3] for a detailed discussion of this correction to rotational constants.

5.5.4. Optical Rotation Tensors. The trace of the mixed magnetic−electric G' tensor is proportional to the magnitude of the specific optical rotation $[\alpha]_\omega$ in (isotropic) chiral systems[618−620]

$$G'_{\alpha\beta} = \mathrm{i}\langle\langle m_\alpha, \mu_\beta\rangle\rangle_\omega, \quad [\alpha]_\omega \propto \sum_\alpha G'_{\alpha\alpha} \tag{627}$$

Calculations of the G' tensor are routinely used to help in the assignment of the absolute configuration of chiral species, see, for instance, refs 619 and 621−623. Owing to the presence of the magnetic dipole operator, determination of optical rotation is hampered by the problem of gauge-origin dependence. Thus, even if this tensor is easily accessible from the linear response function by replacing one electric dipole operator in the electric dipole polarizability with the magnetic dipole operator special care must be exercised to remove the unphysical gauge-origin dependence. For the variational Hartree−Fock, Kohn−Sham, and MCSCF models, translational invariance of the optical rotation (i.e., the trace of G' but not of the individual tensor components) can be achieved using London orbitals.[54,107,624,625] London orbitals are therefore routinely employed for optical-rotation calculations at the Hartree−Fock and Kohn−Sham levels of theory. Alternatively, the velocity gauge can be used in such calculations.[626]

The first CCSD calculations of optical rotation were performed by Ruud and Helgaker[627] as part of a benchmark study of Kohn−Sham exchange-correlation functionals. However, a fundamental problem remains concerning gauge-origin independence of optical rotation for the truncated coupled-cluster model and other models that do not satisfy the hypervirial relation; for such models, use of London orbitals does not ensure invariance of the optical rotation.[155,619,628] As a solution, Pedersen et al. proposed to compute the optical rotation instead from the velocity-gauge expression, subtracting its static limit from the G' tensor.[629] Their approach avoids use of London orbitals and allows use of the same velocity-gauge formula for variational and nonvariational electronic-structure models. Moreover, the basis-set convergence in their formulation is similar to that of the conventional length-gauge method with London orbitals.

Crawford and co-workers have been particularly active in the area of determination of chiroptical properties using coupled-cluster (and Kohn−Sham) linear response methods.[208,619,630−636] In a study similar to that of Ruud et al.,[637] Crawford and Stephens compared the performance of the CCSD and Becke-3-parameter−Lee−Yang−Parr[638,639] (B3LYP) models (at the sodium D line) for 13 molecules, observing a good agreement (in sign) except for norbornanone.[635] At lower frequencies the B3LYP and CCSD models often differ substantially owing to the more accurate prediction of excitation energies and rotatory strengths by the latter.

Russ and Crawford[208] presented a new scheme for constructing localized correlation domains for reducing the scaling of coupled-cluster response calculations for optical rotation. The approach exploits an atom-based decomposition of the coupled-perturbed Hartree−Fock response to both external electric and magnetic fields to select the correlation domain of each occupied orbital, as an extension of their earlier work on calculations of dipole polarizabilities using local coupled-cluster approaches.[205] Applying their domain-selection scheme to a series of chiral molecules (including pseudolinear structures, cage-like structures, and aromatic rings) the authors found that the crossover points between the canonical- and the local-correlation approaches are larger than for the conventional scheme of Boughton−Pulay domains,[640] in agreement with their earlier analysis for dipole polarizabilities. Localization errors are reasonably small (a few percent) for pseudolinear structures with domain sizes of 6−8 atoms, whereas cage-like molecules are significantly more problematic, requiring natural domain sizes of 10 or more atoms to obtain the most reliable localization errors.

For the reliable prediction of optical rotation, inclusion of vibrational, conformational, and solvent corrections is often crucial.[620,641−648] An extreme case is methyloxirane,[633,649−651] where vibrational effects must be taken into account to reproduce the experimental gas-phase optical rotation to within a few degrees and for which the vibrational corrections may even lead to a change in the sign of the optical rotation. In ref 633 Pedersen et al. presented gas-phase optical rotations calculated from coupled-cluster theory with zero-point vibrational corrections calculated using Kohn−Sham theory, concluding that it is more important to use high-level electronic-structure methods than to include zero-point vibrational corrections. For the importance of conformational flexibility, see, for example, refs 645, 652, and 653.

For optical rotation of nonisotropic (oriented) systems an additional tensor quantity must be accounted for in calculations of the optical rotation, namely, the dipole, quadrupole polarizability tensor[2]

$$A_{\alpha,\,\beta\gamma} = -\langle\langle \mu_\alpha, \Theta_{\beta\gamma}\rangle\rangle_\omega \tag{628}$$

obtained by replacing one dipole operator with the quadrupole operator in the linear response function for the dipole polarizability. The $A_{\alpha,\beta\gamma}$ and $G'_{\alpha\beta}$ tensors are also important for other

Table 4. Frequency Matching for Various NLO Processes

tensor	frequency matching	NLO process	acronym
$\beta_{\alpha\beta\gamma}(\omega_\alpha;\omega_\beta,\omega_\gamma)$	$\omega_\beta = \omega_\gamma = \omega$	second-harmonic generation	SHG
	$\omega_\beta = \omega$, $\omega_\gamma = 0$	electro-optic Pockels effect	EOPE
	$\omega_\beta = -\omega_\gamma = \omega$	optical rectification	OR
$\gamma_{\alpha\beta\gamma\delta}(\omega_\alpha;\omega_\beta,\omega_\gamma,\omega_\delta)$	$\omega_\beta = \omega_\gamma = \omega_\delta$	third-harmonic generation	THG
	$\omega_\beta = \omega$, $\omega_\gamma = \omega_\delta = 0$	electro-optical Kerr effect	dc-Kerr
	$\omega_\beta = \omega_\gamma = \omega$, $\omega_\delta = -\omega$	intensity-dependent refractive index	IDRI
		degenerate four-wave mixing	DFWM
	$\omega_\beta = \omega_\gamma = \omega$, $\omega_\delta = 0$	electric-field induced SHG	ESHG
	$\omega_\beta = 0$, $\omega_\gamma = \omega$, $\omega_\delta = -\omega$	dc-optical rectification	dc-OR

optical effects, for instance, the Buckingham birefringence[560,654] and for ROA.[2,342]

5.6. Nonlinear Response Properties

Interest in molecular nonlinear properties has increased enormously in the last few decades, reflecting the growing importance of nonlinear optics in several fields of advanced technology.[655−657] One example is the design of new optical materials and optical devices for data storage, since many nonlinear optical processes are mediated by the third-order nonlinear susceptibility, which corresponds to the second electric dipole hyperpolarizability. These properties have therefore always attracted much attention from theoreticians as well as experimentalists. On the one hand, when (accurate) experimental results are available they are often used as a test bed for benchmarking new computational approaches and approximations. On the other hand, given that their experimental determination is often difficult, theoretical predictions, in particular, when made with methods whose accuracy can be assessed with confidence, often help in the calibration of experimental measurements, sometimes even prompting the design of novel experimental set-ups.

5.6.1. Hyperpolarizabilities and Nonlinear Optics. The first and second dipole hyperpolarizabilities

$$\beta_{\alpha\beta\gamma}(\omega_\alpha;\omega_\beta,\omega_\gamma) = \langle\langle\mu_\alpha;\mu_\beta,\mu_\gamma\rangle\rangle_{\omega_\beta,\,\omega_\gamma}, \qquad \omega_\alpha = -\omega_\beta - \omega_\gamma \tag{629}$$

$$\gamma_{\alpha\beta\gamma\delta}(\omega_\alpha;\omega_\beta,\omega_\gamma,\omega_\delta) = -\langle\langle\mu_\alpha;\mu_\beta,\mu_\gamma,\mu_\delta\rangle\rangle_{\omega_\beta,\,\omega_\gamma,\,\omega_\delta}, \qquad \omega_\alpha = -\omega_\beta - \omega_\gamma - \omega_\delta \tag{630}$$

are the best known examples of molecular properties obtained from the quadratic and cubic response functions, respectively. Depending on the choice of frequencies ω_i associated with the perturbations, a wealth of nonlinear optical (NLO) phenomena[655−657] may be addressed, see Table 4.

For NLO properties, highly accurate ab initio methods such as coupled-cluster theory have been applied primarily to small molecules, where there has been a significant interplay between theory and experiment, see ref 74 for a detailed review. This interplay has been essential for illuminating the role of various mechanisms in NLO processes and for identification and design of molecules, chromophores, and functional groups with specific properties. Indeed, as for the polarizability, the literature on theoretical (and experimental) studies of hyperpolarizabilities is vast, with several dedicated collective contributions. We refer the interested reader to the book edited by Papadopoulos, Leszczynski, and Sadlej[10] for contributions covering various aspects related to NLO properties: current advances in the computation of the NLO properties of molecules, crystalline solids, and nanoparticles, methods employed to compute the properties of both microscopic and macroscopic forms of matter, studies of NLO properties of organometallic compounds, rotaxanes, glasses, Langmuir−Blodget films, gold, and silver nanoparticles, and more. Strategies for developing new NLO materials are discussed in connection with the hyper-Rayleigh scattering technique.

We here note that the four-component Hartree−Fock quadratic-response code of Norman and Jensen[263] has been applied to compute the second-harmonic generation (SHG) hyperpolarizabilities of CsAg and CsAu. Kussman and Ochsenfeld extended their linear-scaling Hartree−Fock and Kohn−Sham code to calculation of first hyperpolarizabilities for molecules with a nonvanishing band gap, presenting calculations of the first hyperpolarizability of α-D-glucose polymers with up to 48 monomer units.[13]

5.6.2. Mixed Hyperpolarizabilities and Birefringences. Response theory has played an important role in the study of birefringences, that is, the optical anisotropy of the refractive index Δn for two different directions, often induced when the probing light (either polarized or unpolarized) passes through the sample in the presence of additional fields in specific geometrical setups with respect to the direction of propagation of the probing beam. Interest in these birefringences (and their absorptive counterparts, the dichroisms) has steadily increased during the last two decades, reflecting the steady progress in optics and detection techniques from the experimental side and rapid advances of methods and computational power from the theoretical side.[658] Among the birefringences studied computationally in recent years are the linear birefringences induced by an externally applied magnetic induction field (Cotton−Mouton effect),[658−662] by an electric field gradient (the Buckingham effect or EFGB),[544] and by mixed electric and magnetic induction fields (Jones and magneto-electric birefringences),[663] axial magnetochiral birefringence,[664,665] and circular birefringence (Faraday rotation).[666−669]

At a fixed pressure the general form of an optical anisotropy is[658]

$$\Delta n \propto A_0 + \frac{1}{T}A_1 + \ldots \tag{631}$$

The temperature-dependent contribution A_1 arises from different mechanisms of molecular reorientation and involves the interaction of the fields with permanent electric or magnetic moments. The temperature-independent contribution A_0 arises from electronic reorganization and involves different higher order tensors (hyperpolarizabilities and hypermagnetizabilities). Terms with more than a linear inverse temperature dependence are possible and usually connected to the presence of permanent magnetic dipole moments or higher order processes involving more complicated interactions between fields and multipoles. The temperature-independent terms are the only nonzero terms for systems of spherical symmetry.

At the molecular level the terms A_0, A_1, ... contain isotropic averages of molecular, both static and frequency-dependent, tensor properties such as permanent multipole moments, polarizabilities, and hyperpolarizabilities. In particular, we find for the Faraday rotation ϕ, usually discussed in terms of the Verdet constant $V(\omega)$[669−672]

$$\phi = V(\omega)B_z \propto B_z\varepsilon_{\alpha\beta\gamma}\left(\alpha'^{(m)}_{\alpha\beta,\,\gamma} + \frac{1}{kT}m^n_\gamma\alpha'_{\alpha\beta}\right) \tag{632}$$

$$\alpha'^{(m)}_{\alpha\beta,\,\gamma} = \mathrm{i}\langle\langle\mu_\alpha;\mu_\beta,\, m_\gamma\rangle\rangle_{\omega,\,0} \tag{633}$$

$$\alpha'_{\alpha\beta} = -\mathrm{i}\langle\langle\mu_\alpha;\mu_\beta\rangle\rangle_\omega \tag{634}$$

for the Buckingham effect[544,555,557,673]

$${}_mQ \propto b(\omega) + \frac{1}{kT}\left[\Theta_{\alpha\beta}\alpha_{\alpha\beta} - \mu_\alpha\left(A_{\beta,\,\alpha\beta} + \frac{5}{\omega}\varepsilon_{\alpha\beta\gamma}G'_{\beta\gamma}\right)\right] \tag{635}$$

$$b(\omega) = \frac{1}{15}\left(B_{\alpha\beta,\,\alpha\beta} - \mathscr{B}_{\alpha,\,\alpha\beta,\,\beta} - \frac{5}{\omega}\varepsilon_{\alpha\beta\gamma}J'_{\alpha,\,\beta,\gamma}\right) \tag{636}$$

$$B_{\alpha\beta,\,\gamma\delta} = \langle\langle\mu_\alpha;\mu_\beta,\,\Theta_{\gamma\delta}\rangle\rangle_{\omega,\,0} \tag{637}$$

$$\begin{aligned}\mathscr{B}_{\alpha,\,\beta\gamma,\,\delta} &= \langle\langle\mu_\alpha;\Theta_{\beta\gamma},\,\mu_\delta\rangle\rangle_{\omega,\,0}\\ &= \langle\langle\mu_\alpha;\mu_\delta,\,\Theta_{\beta\gamma}\rangle\rangle_{0,\,\omega}\end{aligned} \tag{638}$$

$$J'_{\alpha,\,\beta,\,\gamma} = \mathrm{i}\langle\langle\mu_\alpha;m_\beta,\,\mu_\gamma\rangle\rangle_{\omega,\,0} \tag{639}$$

for the Cotton−Mouton effect[659−662]

$${}_mC \propto \Delta\eta + \frac{1}{15kT}(3\alpha_{\alpha\beta}\xi_{\alpha\beta} - \alpha_{\alpha\beta}\xi_{\alpha\beta}) \tag{640}$$

$$\eta_{\alpha\beta\gamma\delta} = -\langle\langle\mu_\alpha;\mu_\beta,\,m_\gamma,\,m_\delta\rangle\rangle_{\omega,\,0,\,0} + \langle\langle\mu_\alpha;\mu_\beta,\,\xi_{\gamma\delta}\rangle\rangle_{\omega,\,0} \tag{641}$$

and for the magnetoelectric Jones effect[663]

$$\begin{aligned}n_{-45^\circ} - n_{+45^\circ} \propto\ & 3G_{\alpha\beta\alpha\beta}\\ &+ 3G_{\alpha\beta\beta\alpha} - 2G_{\alpha\alpha\beta\beta} - \frac{\omega}{2}\varepsilon_{\alpha\beta\gamma}\left(a'_{\alpha\beta\delta\delta\gamma} + a'_{\alpha\beta\delta\gamma\delta}\right)\\ &+ \frac{1}{kT}\Big[\mu_\alpha(3G_{\alpha\beta\beta} + 3G_{\beta\alpha\beta} - 2G_{\beta\beta\alpha})\\ &- \frac{\omega}{2}\varepsilon_{\alpha\beta\gamma}\left(\mu_\gamma a'_{\alpha\beta\delta\delta} + \mu_\delta a'_{\alpha\beta\delta\gamma}\right)\Big]\end{aligned} \tag{642}$$

$$G_{\alpha\beta\gamma} = \langle\langle\mu_\alpha;m_\beta,\,m_\gamma\rangle\rangle_{\omega,\,0} - \langle\langle\mu_\alpha;\xi^{\mathrm{dia}}_{\beta\gamma}\rangle\rangle_\omega \tag{643}$$

$$G_{\alpha\beta\gamma\delta} = -\langle\langle\mu_\alpha;m_\beta,\,m_\gamma,\,\mu_\delta\rangle\rangle_{\omega,\,0,\,0} + \langle\langle\mu_\alpha;\xi^{\mathrm{dia}}_{\beta\gamma},\,\mu_\delta\rangle\rangle_{\omega,\,0} \tag{644}$$

$$a'_{\alpha\beta\gamma\delta} = \mathrm{i}\langle\langle\mu_\alpha;Q_{\beta\gamma},\,m_\delta\rangle\rangle_{\omega,\,0} \tag{645}$$

$$a'_{\alpha\beta\gamma\delta\varepsilon} = -\mathrm{i}\langle\langle\mu_\alpha;Q_{\beta\gamma},\,m_\delta,\,\mu_\varepsilon\rangle\rangle_{\omega,\,0,\,0} \tag{646}$$

Accurate theoretical investigations of birefringences have proven important in several instances, both in relation to the interplay between experiment and theory and in clarification of the fundamental theories of the effects. For instance, calculations of the Cotton−Mouton effect may be used for calibration of the experiment,[659,674] whose accuracy needs to be assessed with great precision if one hopes to be able to detect the magnetic birefringence of vacuum.[674−678] State-of-the-art computations of the Buckingham birefringence have been used to revise the experimentally derived quadrupole moments of various molecules from single-temperature measurements and, in particular, identify inconsistencies in the experimentally derived quadrupole moment of N_2.[555,567] Calculations on CO[557,560] and other species helped settle a discrepancy between the Buckingham−Longuet-Higgins[654] and the Imrie−Raab[679] theories of the linear birefringence induced in a gas of dipolar molecules by an electric-field gradient in favor of the former theory. A later revision brought the theories into agreement, confirming the validity of the original result obtained by Buckingham and Longuet-Higgins.[680,681]

Among the recent methodological advances that affect the ability to compute birefringences is the gauge-origin-independent formulation and implementation of the Verdet constant at the CCSD level of theory using London orbitals,[668] where the Verdet constant was reformulated as a magnetic-field derivative of the dipole polarizability. A similar formulation was used in the AO-based Hartree−Fock (and Kohn−Sham) implementation by Kjærgaard et al.[669] A quasi-energy formulation of Hartree−Fock and Kohn−Sham response theories enabled the temperature-independent term of the Buckingham effect[682] and the Cotton−Mouton effect at nonzero frequencies[106] to be determined in a gauge-origin-independent manner. A relativistic extension of the latter formulation has recently been used to investigate the importance of relativity for the Buckingham effect of carbon dichalcogenides.[264]

5.6.3. Dispersion Coefficients.

The dispersion (i.e., frequency dependence) of response functions in the nonabsorptive region is often accounted for by an expansion in powers of the frequency. For instance, the electric dipole polarizability is expanded according to the Cauchy series

$$\alpha(\omega) = \sum_{k=0}^{\infty}\omega^2 S(-2k-2) \tag{647}$$

where the dispersion coefficients $S(-2k-2)$ are known as Cauchy moments

$$S(-k) = \sum_{n\neq 0}\frac{f^{\alpha\beta}_{0n}}{\omega^k_{0n}},\quad f^{\alpha\beta}_{0n} = 2\omega_{0n}\langle 0|\mu_\alpha|n\rangle\langle n|\mu_\beta|0\rangle \tag{648}$$

with $S(-2) = \alpha(0)$. Similar expansions can be introduced for the hyperpolarizabilities.

Hättig and co-workers[683−685] derived analytic expressions for the dispersion coefficients of linear, quadratic, and cubic response functions using the time-averaged quasi-energy Lagrangian technique within coupled-cluster response theory for the CCS, CC2, and CCSD models, demonstrating that the dispersion coefficients are sensitive to basis-set effects and correlation treatment in a manner similar to that of static (hyper)-polarizabilities. The analytic dispersion coefficients for frequency-dependent properties are calculated from the derivatives of the properties with respect to their frequency arguments using Padé approximants to improve the results. A derivation and implementation of the analytic expressions for the second-order dispersion coefficients of second-, third-, and fourth-order properties in FCI linear, quadratic, and cubic response theory have been presented by Larsen et al.[686]

5.7. Interaction Properties

Many molecular properties are related to intermolecular interactions and can be evaluated using the general techniques of response theory. In the following we consider first evaluation of dispersion-interaction coefficients and next evaluation of interaction-induced properties of van der Waals complexes.

5.7.1. Weak Interactions and Long-Range Dispersion-Interaction Coefficients. At large separations the forces between two neutral systems are dispersive, arising from a weak correlation of the motion of the electrons in the two systems. The dispersion energy, the dominant contribution to the interaction energy at large intermolecular distances, can be computed from response functions. Denoting two closed-shell atoms by A and B the dispersion energy has the form

$$E^{\mathrm{AB}} = \sum_{n}\sum_{m} \frac{|\langle 0_{\mathrm{A}}0_{\mathrm{B}}|V^{\mathrm{AB}}|n_{\mathrm{A}}m_{\mathrm{B}}\rangle|^{2}}{\omega_{n0}^{\mathrm{A}} + \omega_{m0}^{\mathrm{B}}} \tag{649}$$

which may be expanded in terms of dispersion coefficients as

$$E^{\mathrm{AB}} = -\frac{C_{6}^{\mathrm{AB}}}{R^{6}} - \frac{C_{8}^{\mathrm{AB}}}{R^{8}} - \frac{C_{10}^{\mathrm{AB}}}{R^{10}} + \ldots \tag{650}$$

According to the Casimir−Polder formula,[687] the C_6 coefficient, for which accurate experimental results are available, can be computed from the integral

$$C_{6}^{\mathrm{AB}} = \frac{3}{\pi}\int_{0}^{\infty} \alpha^{\mathrm{A}}(-\mathrm{i}\omega;\mathrm{i}\omega)\alpha^{\mathrm{B}}(-\mathrm{i}\omega;\mathrm{i}\omega)\mathrm{d}\omega \tag{651}$$

which involves the dipole polarizability (linear response function) at imaginary frequencies (iω). Higher order coefficients are similarly obtained from expressions involving higher order multipole polarizabilities.

Direct evaluation of the polarizability at imaginary frequencies in eq 651 by regular response theory may be cumbersome since it involves complex arithmetics, standard nonrelativistic quantum-chemical codes being based on real arithmetics. One typical solution is to exploit the expansion formula for the polarizability in terms of the real Cauchy moments in eq 647, which has a radius of convergence in the complex plane equal to the lowest dipole excitation frequency. Evaluation of the C_6 dispersion coefficients in MCSCF linear response theory was presented by Fowler, Jørgensen, and Olsen in 1990.[87] An alternative strategy, proposed by Norman and co-workers,[88] is based on the complex polarization propagator, where the dynamical polarizabilities at imaginary frequencies are obtained directly from the complex polarization propagator and the C_6 coefficients are determined from the Casimir−Polder relation, see also refs 688 and 689 for Hartree−Fock and Kohn−Sham applications to C_{60}, sodium clusters, and *n*-alkanes.

In ref 231 Paidarova and Sauer used the SOPPA, SOPPA-(CCSD), CC2, and CCSD models to determine the dipole oscillator strength sum rules of the hydrogen halides HX (with X = F, Cl, Br, and I) and the C_6 dispersion coefficient for all pairs of interacting HX molecules by numerical integration of the Casimir−Polder formula. The dependence of the polarizabilities, their dispersion, and C_6 coefficients on the level of correlation and the dependence of the C_6 coefficients on the two intramolecular bond lengths were studied.

5.7.2. Interaction-Induced Properties. Coupled-cluster (response) methods have been extensively employed to determine intermolecular potential energies, interaction-induced first-order properties, and polarizability and hyperpolarizability surfaces of van der Waals complexes (dimers).[690−694] Indeed, van der Waals dimers have received much attention during the last two decades, both experimentally and theoretically. One of the most important research objectives of the many studies that have appeared is to obtain a better understanding of the nature of pair interactions. Interaction-induced polarizabilities are an important source of information on intermolecular forces; therefore, much work has been carried out over recent years aimed at their accurate experimental determination.[695−700]

From a theoretical point of view, evaluation of interaction-induced properties in van der Waals complexes is difficult, given that dispersion places substantial demands on the level of electron-correlation treatment and on the choice of basis set.[661,690,692,701−703] Interaction-induced properties are usually computed according to

$$\Delta P(\mathbf{R}) = P_{\mathrm{AB}}(S_{\mathrm{AB}}|\mathbf{R}) - P_{\mathrm{A}}(S_{\mathrm{AB}}|\mathbf{R}) - P_{\mathrm{B}}(S_{\mathrm{AB}}|\mathbf{R}) \tag{652}$$

where $P_{\mathrm{AB}}(S_{\mathrm{AB}}|\mathbf{R})$ is the property of the A−B dimer (at geometry $\mathbf{R}$) and $P_{\mathrm{A}}(S_{\mathrm{AB}}|\mathbf{R})$ and $P_{\mathrm{B}}(S_{\mathrm{AB}}|\mathbf{R})$ are the properties of monomers A and B at the same geometry. All quantities are calculated in the dimer basis S_{AB} to reduce basis-set superposition errors.

A typical study of interaction-induced properties is determination of the effect of many-body collisions or, in macroscopic terms, of the density on some property P such as the refractive index or the EFGB of a real gas. To this end, the property is expressed in terms of virial expansions[704,705]

$$P = A_{P} + B_{P}\rho + C_{P}\rho^{2} + \ldots \tag{653}$$

where ρ is the density and A_P, B_P, C_P, ..., are the first, second, third, ... virial coefficients. Usually only the first and second virial coefficients are considered; for the latter, a semiclassical expression of the form[706,707]

$$B_{P} \propto 4\pi N^{2}\int \Delta P(R_{\mathrm{AB}})R_{\mathrm{AB}}^{2}\mathrm{e}^{-V(R_{\mathrm{AB}})/kT}\,\mathrm{d}R_{\mathrm{AB}} \tag{654}$$

is often adopted,[706,707] where R_{AB} is the distance from A to B, $V(R_{\mathrm{AB}})$ is the interaction potential, and $\Delta P(R_{\mathrm{AB}})$ the relevant interaction-induced property.

During the past decade, several coupled-cluster studies have been performed of the second dielectric and second refractivity virial coefficients, the Kerr and hyperpolarizability second virial coefficients, as well as the second virial coefficients for the Cotton−Mouton and Buckingham birefringences in various systems, see, for example, refs 661, 690, 691, 694, and 708.

5.8. Excited-State Energies, Properties, and Transition Properties

An attractive feature of response theory is the fact that excited-state molecular properties, for example, excitation energies from the ground state and between excited states, (multiphoton) transition strengths, excited-state first-order properties, and excited-state structure parameters, may be calculated without the explicit optimization of the excited-state wave function. Vertical excitation energies are obtained as poles of the linear response function by solving a generalized eigenvalue problem, one-photon transition strengths such as UV oscillator strengths and ECD rotational strengths are obtained from the residues of the linear response function, while multiphoton strengths and excited-state (hyper)polarizabilities are accessible from residues of higher order response functions. Excited-state polarizabilities were briefly discussed in section 5.5.1; in the following, some more excited-state properties (including transition properties) are discussed.

5.8.1. Excitation Energies and One-Photon Transition Strengths. Implementations of response theory for (vertical) excitation energies have been reported at many levels of wave function theory: Hartree−Fock theory or the random-phase approximation (RPA), CI-singles (CIS) theory or the Tamm−Dancoff approximation (TDA), MCSCF theory, coupled-cluster theory (CC2,[121] CCSD,[157] CC3,[122,123] and CCSDR(3)[189]), EOM-CC theory,[126,181,182,203] propagator theories such as ADC(2), ADC(3),[233,236,709] SOPPA and SOPPA(CCSD),[226] second-order RPA (RPA(D)) theory,[710] and CIS(D) theory. The corresponding dipole transition strengths can be obtained from the residues of the linear response function (the dipole polarizability), available for most of these methods. The choice of the electronic-structure method for excitation energies and transition strengths depends on the problem at hand and the preferences of the user; we do not discuss these aspects here, referring instead to recent benchmark studies.[230,711−713] We also refer to refs 714 and 715 for a discussion of the relation between the ADC approach, coupled-cluster linear response theory, EOM-CC theory, multireference coupled-cluster MRCC schemes, and the SAC-CI approach.

As an illustration we mention here a recent coupled-cluster study of the electronic gas-phase spectrum of glycine, alanine, related amines, and carboxylic acids by Osted et al.[716] The systems were chosen in order to investigate the origin of the common electronic excitations in amino acids, paying special attention to the valence excitation from the nonbonding lone pair on the CO oxygen atom to the antibonding π orbital ($n(\mathrm{O}) \rightarrow \pi^*(\mathrm{CO})$) and to the first Rydberg excitation from the nonbonding lone pair on the nitrogen atom ($n(\mathrm{N}) \rightarrow 3s$). Excellent agreement with all reliable experimental values was achieved. Predictions for vertical excitation energies were given for all molecules, including glycine and alanine, for which no gas-phase experimental results are available. Finally, calculations on protonated amino acids were presented, showing an isolation of the $n(\mathrm{O}) \rightarrow \pi^*$ (CO) transition from higher lying states by as much as 1.9 eV for alanine. As another example of excitation energy studies, vertical excitation energies and transition dipole moments between excited electronic states were in ref 717 calculated for the *trans*-polyene series C_4H_6 to $C_{12}H_{14}$ to study formation of excited-state absorption spectra of these species, applying quadratic response theory in conjunction with Hartree−Fock and coupled-cluster theories. As a final example, Åstrand et al. performed an ab initio SOPPA investigation of the electronic spectra of azobenzene dyes, suggesting that the information obtained about spectra in this nonempirical manner may be useful for identifying promising diazo components for development of data-storage devices.[718]

5.8.2. Electronic Circular Dichroism. Residues of the optical rotation tensor G' give access to electronic circular dichroism (ECD). The key molecular quantity is in this case the ECD rotational strength, which in the length gauge is given by

$$R_{n0} = \mathrm{Im}\langle 0|\boldsymbol{\mu}|n\rangle \cdot \langle n|\mathbf{m}|0\rangle \tag{655}$$

ECD studies based on wave function methods are still somewhat limited, the field being dominated by TDDFT. The status of the ab initio determination of ECD (and optical rotation) was reviewed a few years ago by Pecul and Ruud,[620] and by Crawford and coworkers.[619,636]

The use of London orbitals for gauge-origin-independent ECD calculations was proposed by Bak et al. in 1995 for the variational Hartree−Fock and MCSCF methods, later extended to TDDFT by Pecul et al.[719] Alternatively, as for optical rotation, origin invariance of the ECD rotational strengths may be achieved using a velocity-gauge representation for the electric-dipole operator

$$R_{n0} = \frac{1}{\omega_{n0}} \mathrm{Re}\langle 0|\mathbf{p}|n\rangle \cdot \langle n|\mathbf{m}|0\rangle \tag{656}$$

Several modern ECD implementations utilize the velocity-gauge formulation, which, for variational models, becomes equivalent to its length-gauge counterpart in the complete-basis-set limit.

The lack of gauge invariance of the truncated coupled-cluster model affects calculation of ECD in the same manner as that of optical rotation discussed earlier.[720] In particular, London orbitals do not suffice to ensure invariance. Pedersen and Koch proposed a reformulation of coupled-cluster theory that would allow gauge-invariant results to be obtained in coupled-cluster theory,[721,722] although this proposal has not yet been implemented. The work of Pedersen et al. in ref 720 is the first ECD implementation and calculation at the CCSD level of theory. The authors considered gauge and origin invariance in the scalar rotational strength and rotational-strength tensor, the latter which provides the ECD intensity of oriented samples. Subsequently, EOM-CC (and DFT) studies of ECD have been carried out by Crawford and co-workers.[636,723,724] Moreover, Diedrich and Grimme[725] systematically investigated the ability of different quantum-chemical methods, TDDFT, CC2, MRMP2, and DFT/MRCI, to predict experimental ECD on a test suite of seven molecules containing a range of difficult chromophores and to three model systems for which accurate ab initio MRCI reference data were used for comparison.

5.8.3. Multiphoton Absorption and Dichroism. Two-photon absorption (TPA) and two-photon circular dichroism (TPCD)[726] are further examples of optical phenomena accessible by response theory. We mention here a coupled-cluster study of formaldehyde, diacetylene, and water by Paterson et al.,[727] in which the effect of triple excitations on TPA cross sections was determined for the first time. This study presented a detailed comparison of the coupled-cluster results with those obtained using Kohn−Sham theory with a variety of exchange-correlation functionals. Best results were obtained with the Coulomb attenuating method B3LYP (CAM-B3LYP) functional,[728] although it was noted that care must be exercised with diffuse Rydberg states. Nielsen et al.[729] presented a detailed investigation of TPA cross sections of water, employing different series of correlation-consistent basis sets in combination with several coupled-cluster, CI, and Kohn−Sham models, finding it difficult to reach convergence. TPCD has so far only been investigated at the Hartree−Fock and TDDFT levels of theory, see, for example, refs 730−733. Calculation of three-photon absorption cross-sessions using response theory have been reported at the Hartree−Fock level in refs 734−736.

On the basis of an analysis of the first residues of coupled-cluster response functions, Hättig et al.[737] devised variational functionals from which the transition moments for *n*-photon excitations can be calculated as *n*th-order derivatives. Combining these functionals with variational perturbation theory, these authors developed a new approach for derivation of multiphoton transition moments, allowing them to utilize the full strength of variational perturbation theory directly rather than through residues. Coupled-cluster multiphoton transition moments derived by this approach were shown to be formally equivalent to those identified from the first residues of the ground-state response functions. The strength of the new approach was demonstrated by derivation of three- and four-photon transition moments.[737]

A similar approach, based on an analysis of the second residues of the coupled-cluster ground-state response functions, yielded general expressions for multiphoton transition moments between two excited states and for excited-state response functions in ref 579. The second residues were rewritten as derivatives of variational functionals, and computational efficient expressions were obtained in accordance with the $2n + 1$ and $2n + 2$ rules. For the excited-state response functions, secular divergencies were removed by reformulating the expressions identified from the second residues of the ground-state response functions as derivatives of an excited-state quasi-energy Lagrangian. Explicit expressions were given for coupled-cluster one-, two-, and three-photon transition moments between two excited states and for excited-state first-order properties and linear and quadratic response functions.

5.8.4. Magnetic Circular Dichroism. The single and double residues of the mixed dipole−dipole−magnetic-dipole quadratic response function have been shown to correspond to, respectively, the $\mathcal{B}$ and $\mathcal{A}$ terms of magnetic circular dichorism (MCD), the absorption counterpart of Faraday rotation discussed in section 5.6.2.[96,669,738] The $\mathcal{A}$ and $\mathcal{B}$ terms can also be formulated as derivatives with respect to the strength of an external magnetic field of, respectively, the excitation energy[96,739] and the dipole oscillator strength,[668,669] that is, as derivatives of the pole and residues of the magnetic-field-dependent dipole polarizability. In this way, the field-dependent contributions from London orbitals are more easily incorporated and gauge-origin independence ensured, even for the nonvariational coupled-cluster method.[668,669] Most MCD methodological developments (in a response-function theory context) have taken place within TDDFT, except for the original MCSCF implementation of the $\mathcal{B}$ term[738] and a CCSD London-orbital implementation,[668,740] both by Coriani and co-workers.

5.8.5. Excited-State Molecular Gradients and First-Order Properties. By combining analytic gradient techniques with response theory, excited-state molecular gradients can be calculated and hence excited-state potential-energy surfaces efficiently explored without explicitly calculating the excited-state wave function.

Analytic derivative techniques for the gradient and other properties of excited-state energy surfaces began to appear in the early 1990s, with the CIS implementation of Foresman et al. in 1992.[741] Formulas for the EOM-CCSD excited-state gradient were presented by Stanton in 1993[742] and subsequently implemented by Stanton and Gauss,[576,577] whereas an alternative derivation and implementation were presented by Szalay.[743] An extension to general coupled-cluster and CI models using string-based methods was given by Kállay and Gauss in 2004.[744] Spin-flip EOM-CCSD gradients were presented by Levchenko et al.[745] and molecular gradients for the similarity-transformed EOM-CC method by Gwaltney et al.[746] The automated algebraic derivation of excited-state gradients for EOM-CC and similarity-transformed EOM-CC techniques was also discussed by Wladyslawski and Noojien in 2005.[747]

The CIS model has for a long time been considered the standard approach for excited-state optimizations of large systems.[748,749] However, Köhn and Hättig[174] presented in 2003 a derivation and implementation of excited-state molecular gradients at the CC2 level of theory, employing the resolution of the identity approximation for the electron repulsion integrals. Adiabatic excitation energies, excited-state-structure constants, and vibrational frequencies could be calculated. Generalizations of the SCS and SOS modifications of MP2 perturbation theory to the CC2 model (termed SCS-CC2 and SOS-CC2) were discussed, and a preliminary implementation was presented in ref 299. In ref 750 a quartic-scaling algorithm for evaluating the analytical gradient of quasidegenerate SOS second-order perturbation corrections to the CIS energy method (SOS-CIS(D_0)) was presented, where the low-order scaling was attained using the resolution-of-the-identity approximation and the Laplace transform. The efficiency of the method was demonstrated by calculating the excited-state gradients of molecules of varying sizes. An implementation of the analytic excited-state gradients for the ADC(2) and CIS(D_∞) models was presented in 2005 by Hättig.[238] Owing to the non-Hermiticity of its Jacobian, the CC2 method appears to give a physically incorrect description of conical intersections between states of the same symmetry. This problem does not arise in ADC(2) theory, where a Hermitian secular matrix is used. An AO-based Lagrangian Hartree−Fock (and Kohn−Sham) implementation was recently presented by Coriani et al.[345]

Regarding excited-state first-order properties other than molecular gradients, Devarajan et al.[751] reported an investigation of the dipole moments of low-lying singlet and triplet excited states of ozone and the ozone cation radical, obtained using the Fock-space multireference-coupled-cluster (FS-MRCC) analytical linear response approach. A benchmark study of the accuracy of excited-state dipole moments of furan and pyrrole calculated in coupled-cluster theory has been presented by King[752] and compared with TDDFT results by Burcl et al.[753]

Kats et al.[210] presented a method for calculating transition strengths and first-order properties of singlet ground and excited states of extended molecular systems based on the CC2 model, with local approximations in the doubles part of the wave function and density fitting for the electron repulsion integrals. The Boughton−Pulay domains[640] for local correlation were found to be inadequate for excited-state properties and a new scheme proposed.

Tellgren et al.[754] reported an implementation of the second-order residue of the quadratic response function in the four-component Hartree−Fock approximation, from which first-order properties of electronically excited states can be obtained. The scheme was used to compute the excited-state electric dipole moments of the valence excited states in CsAg and CsAu, for which nonscalar relativistic effects were found to be substantial.

5.8.6. Phosphorescence. Whereas transition moments between singlet and triplet states are obtained directly from the residue of the linear response function when relativistic two- or four-component wave functions are used,[262,755] we must in the nonrelativistic case consider the spin−orbit-perturbed ground- and excited-state wave functions to make these dipole transitions allowed

$$|^3 0^{(1)}\rangle = -\sum_{^3n} \omega_n^{-1} |^3n^{(0)}\rangle\langle ^3n^{(0)}|H_{so}|^1 0^{(0)}\rangle \qquad (657)$$

$$|^1 f^{(1)}\rangle = \sum_{^1n} (\omega_f - \omega_n)^{-1} |^1n^{(0)}\rangle\langle ^1n^{(0)}|H_{so}|^3 f^{(0)}\rangle \qquad (658)$$

Including these first-order corrections in the expression for the transition moments we find that the first-order contribution to the dipole transition moment between singlet and triplet states may be written as a residue of a quadratic response function[70,756]

$$\langle ^1 0|\mu|^3 f\rangle^{(1)} = \lim_{\omega \longrightarrow \omega_f} (\omega - \omega_f)\langle\langle \mu; H_{so}, V^{\omega}\rangle\rangle_{0,\ \omega} \qquad (659)$$

where V^{ω} is an arbitrary triplet operator (that determines the excitation vector) and ω matches the singlet−triplet excitation energy. The phosphorescent radiative lifetime τ_k of the kth component of $|^3 f\rangle$ can be obtained from the relation

$$\frac{1}{\tau_k} = \frac{4\omega_f^3 \alpha^3}{3} \sum_{\nu} |\langle ^1 0|r_{\nu}|^3 f_k\rangle|^2 \qquad (660)$$

and depends not only on the transition moment but also on the excitation energy. The transition moment may vary for different polarizations of the light. The average phosphorescent lifetime is dominated by the shortest lifetime, corresponding to the polarization with the largest partial transition rate. Implementations of single residues of the triplet quadratic response function have been presented by Vahtras et al.[756] for MCSCF theory and Christiansen and Gauss for coupled-cluster theory.[757] A number of studies of phosphorescent lifetimes, including heavy-atom effects on these lifetimes, have been presented by Minaev and coworkers using MCSCF wave functions.[510,511,755,758]

5.8.7. Spin−Orbit Coupling Constants. Spin−orbit coupling constants describe the coupling between singlet and triplet states and correspond to the residue of the triplet linear response function[759]

$$\lim_{\omega \longrightarrow \omega_f} (\omega - \omega_f)\langle\langle H_{so}; V^{\omega_f}\rangle\rangle_{\omega} \qquad (661)$$

Although the spin−orbit operator in eq 67 has both one- and two-electron parts, the one-electron mean-field[760] or scaled[761] spin−orbit operators are commonly used; the differences in these approximate spin−orbit operators have been analyzed by Neese.[762] Most calculations of spin−orbit coupling constants involve the variational CI optimization of the relevant states using multireference theory.[763−767] However, spin−orbit matrix elements have also been calculated using MCSCF and coupled-cluster linear response theory.[759,768] Within a relativistic framework, the spin−orbit interaction arises naturally and is included in the optimization of the wave function. Fedorov and Gordon have given an extensive overview of the different methods used for calculating spin−orbit coupling constants up to 2003.[769] An interesting recent development is the extension of the Columbus spin−orbit graphical unitary group approach (GUGA) for multireference wave functions[282,770] to a hybrid MRCI/DFT level[771] in the spirit of the DFT/MRCI approach of Grimme and Waletzke.[772]

The spin−orbit coupling is the main intramolecular interaction mechanism responsible for intersystem crossings. Moreover, spin−orbit effects often differ substantially in their behavior from the scalar relativistic effects, leading, for instance, to an interesting correlation between spin−orbit effects on nuclear shielding constants and indirect spin−spin coupling constants for molecules with heavy nuclei.[43] By enabling singlet−triplet transitions it provides a very different pole structure for relativistic linear response functions than for nonrelativistic ones.[262] It is therefore important to consider spin−orbit effects separately from other relativistic effects, even in four-component calculations. A scheme for removing spin−orbit effects in relativistic calculations has been proposed by Dyall[773] and applied at the four-component level of theory by Visscher and Saue.[774] More recently, Cheng and Gauss applied a spin-free Dirac−Coulomb Hamiltonian to calculate the electric properties at the coupled-cluster level of theory.[254]

5.8.8. Finite Lifetimes. As discussed in section 3.7, an important methodological development within response theory in the past decade is the implementation of damped response approaches. Even though the idea of introducing a phenomenological damping factor in the perturbative expressions for the (hyper)polarizability to account for the finite lifetime of the excited states is not new,[71,775] its most successful formulation and implementation in the context of response theory is probably the complex polarization propagator method presented about 10 years ago by Norman et al. for the linear response function at the Hartree−Fock and MCSCF levels of theory.[93] Extension of the method to the quadratic response function along with a more rigorous justification of the methodology appeared a few years later.[89] In the same year a damped response approach was presented by Jensen et al.[91] within DFT. A different but equivalent formulation of the complex polarization propagator based on the quasi-energy formulation, called damped response theory, was recently proposed by Kristensen et al.[90] Damped response formulations are now available at the Hartree−Fock, MCSCF, and Kohn−Sham levels of theory. Similar approaches have also been proposed in the context of vibrational CI,[776,777] based on a Lanczos method, to evaluate the pure vibrational contributions to the polarizabilities and first hyperpolarizabilities of molecules and to compute infrared spectra from the imaginary part of the damped vibrational linear response function.

The phenomenological introduction of empirical lifetimes for the excited states in the response functions is useful for several reasons. It allows us, for instance, to study properties and spectra in resonant regions without the need to compute individual excitation energies and transition strengths and the subsequent convolution with line-shape functions. Thus, absorption, ECD, and MCD are computed directly from the imaginary or real part of the relevant response functions over the entire frequency range, including the highly energetic region of X-ray absorption.[83,84,91,95,778−780] Applications, mainly at the TDDFT level, include, for instance, the first calculations of the complete optical-rotation dispersion curves using origin-independent DFT by Norman et al.[85] Another application, already mentioned in section 5.7.1, is the direct evaluation of the polarization propagator (linear response function) on the whole imaginary frequency axis, avoiding the expansion of the polarizability in a series of the Cauchy moments. In this manner, Casimir−Polder interaction potentials (C_6 coefficients) can be determined.[88,688,781]

6. PURE VIBRATIONAL CORRECTIONS

In this section we consider an additional, nonelectronic contribution to molecular properties that, in principle, appears for any response function, namely, pure vibrational contributions, arising from excitations within the vibrational domain of the electronic ground state. The corresponding pure rotational contributions are usually assumed to be small and neglected.[782] In the sum-over-states expressions for the response functions in section 3.4 the summations are, in principle, over the vibronic rather than electronic states of the molecule. For the polarizability, for example, these summations may be written in the form (following the notation in ref 783)

$$\alpha_{\alpha\beta}(-\omega_\sigma;\omega_1) = \sum P_{-\sigma,\,1} \sum_{k,\,K\neq 0,\,0} \frac{\langle 0,\,0|\mu_\alpha|k,\,K\rangle\langle k,\,K|\mu_\beta|0,\,0\rangle}{\omega_{kK,\,00}-\omega_\sigma} \tag{662}$$

where k and K denote electronic and vibrational states, respectively. In the Born–Oppenheimer approximation[784,785] the vibronic wave function is written as a product of a nuclear wave function C_K^{N} and an electronic wave function ψ_k^{el} that depends parametrically on the nuclear positions

$$\Psi_{k,\,K}(\mathbf{R},\,\mathbf{r}) = C_K^{\mathrm{N}}(\mathbf{R})\psi_k^{\mathrm{el}}(\mathbf{r},\,\mathbf{R}) \tag{663}$$

Separating the sum in eq 662 into a sum over the vibrational manifold of the electronic ground state and a sum over all the electronic excited states we obtain the expression

$$\begin{aligned}\alpha_{\alpha\beta}&(-\omega_\sigma;\omega_1)\\ &= \sum P_{-\sigma,\,1}\left(\sum_{K\neq 0}\frac{\langle 0,\,0|\mu_\alpha|0,\,K\rangle\langle 0,\,K|\mu_\beta|0,\,0\rangle}{\omega_{0K,\,00}-\omega_\sigma}\right.\\ &\qquad\left.+\sum_{k\neq 0}\frac{\langle 0,\,0|\mu_\alpha|k,\,0\rangle\langle k,\,0|\mu_\beta|0,\,0\rangle}{\omega_{k,\,0}-\omega_\sigma}\right)\end{aligned} \tag{664}$$

where the first term is the pure vibrational contribution to the polarizability whereas the second term corresponds to the zero-point vibrationally averaged electronic polarizability, simplified by application of the closure approximation for the vibrations. In Table 5 we collected the pure vibrational contributions to polarizabilities and hyperpolarizabilities for exact nuclear–electronic wave functions in the Born–Oppenheimer approximation.[783,786]

For diatomic molecules we may evaluate the pure vibrational corrections in Table 5 using the vibrational sum-over-states expressions.[570,787−789] The literature on pure vibrational contributions to diatomic molecules has been surveyed by Bishop and Norman.[783] For polyatomic molecules a number of approximate schemes have been introduced, the most popular being the perturbation-theory approach of Bishop and Kirtman,[783,790] whose accuracy was investigated for diatomic molecules by Bishop and Norman[789] and for polyatomic molecules by Torrent-Sucarrat et al.[791] Bishop et al. introduced an alternative scheme, where the molecular geometry relaxes in the presence of applied static electric fields;[792] subsequently, Luis et al. proposed a scheme involving electric-field-relaxed coordinates, significantly reducing the computational cost.[793] An advantage of the latter two approaches is the implicit inclusion of the leading order anharmonic corrections, whose inclusion otherwise requires expensive calculation of cubic force constants (for mechanical anharmonicity) or geometric second derivatives of the (hyper)polarizabilities.

A very different approach has been taken by Christiansen et al.,[776,794] who calculated the pure vibrational contributions from vibrational linear response theory using the vibrational CI method.[795,796] Unlike for the perturbation-based methods, the potential-energy and property surfaces are calculated on a grid. Their approach has been extended to the quadratic response theory level to recover anharmonic effects.[797] An interesting analysis of the vibrational pole structure has been published.[776]

The theory and calculation of pure vibrational corrections have been reviewed several times.[782,798,799] In this review, with its focus on molecular electronic response theory, we restrict ourselves to the perturbative treatment of pure vibrational contributions. Representing the zero-order vibrational wave function as a product of harmonic-oscillator wave functions, one for each vibrational normal mode, the molecular properties are expanded around the equilibrium geometry in the nuclear displacements. Evaluation of the pure vibrational corrections thus requires calculation of geometric derivatives of the (hyper)polarizabilities. In Table 6, we list the expressions for the contributions to the pure vibrational (hyper)polarizabilities.[783]

Although a Hartree–Fock implementation of analytic derivatives for cubic and quartic force fields[332,333] and dipole moment and polarizability derivatives[334] was presented by Handy and coworkers in the early 1990s, it is only with the recent Hartree–Fock implementation of Champagne and co-workers[346,800−804] that analytic calculations of pure vibrational contributions have appeared; recently, an AO-based Kohn–Sham implementation was presented by Thorvaldsen et al.[79] and later extended to two- and four-component relativistic theory.[109] In post-Hartree–Fock theory, calculations of pure vibrational contributions involves taking finite differences along normal coordinates of analytically calculated hyperpolarizabilities. Following an early correlated study by Hättig and Jørgensen,[805] Norman et al. considered the combined effect of electron correlation and solvation on the electronic and vibrational hyperpolarizabilities in methanol.[806] Using CCSD(T) theory, Sadlej and Papadopoulos examined the effects of electron correlation and relativity on electronic and vibrational hyperpolarizabilities, demonstrating that these are not always additive.[807−809]

Pure vibrational contributions to nonlinear properties involving magnetic fields are typically less important than their electric analogues, often vanishing by symmetry as illustrated in eq 66. Indeed, only properties with a quadratic dependence on the magnetic field exhibit pure vibrational corrections, such as the hypermagnetizability that determines the Cotton–Mouton effect.[810,811] Correlated calculations of pure vibrational contributions to hypermagnetizabilities have been presented.[812] Rizzo and Cappelli also recently presented CCSD investigations of the pure vibrational contributions to EFGB and Jones birefringence.[813]

Whereas pure vibrational contributions are negligible for processes at optical frequencies, they may be significant and even dominate for static hyperpolarizabilities, see, for example, ref 814. Considering the known difficulties of Kohn–Sham theory in treating electric properties of extended systems[815] and the importance of electron correlation for electronic and vibrational hyperpolarizabilities,[816,817] the lack of analytic correlated wave function-based methods for calculating geometrical derivatives of electric properties beyond the dipole gradient is unfortunate; with the recent implementation of CCSD(T) polarizability gradients,[348] this situation is beginning to change.

7. MOLECULAR PROPERTIES IN THE LIQUID AND SOLID PHASES

The changes observed in a molecule when going from the gas phase to the liquid or solid phase are conveniently divided into

Table 5. Pure Vibrational Contributions to the Polarizability $\boldsymbol{\alpha}^{\mathrm{pv}} = [\boldsymbol{\mu}^2]$, First Hyperpolarizability $\boldsymbol{\beta}^{\mathrm{pv}} = [\boldsymbol{\mu\alpha}] + [\boldsymbol{\mu}^3]$, and Second Hyperpolarizability $\boldsymbol{\gamma}^{\mathrm{pv}} = [\boldsymbol{\mu\beta}] + [\boldsymbol{\alpha}^2] + [\boldsymbol{\mu}^2\boldsymbol{\alpha}] + [\boldsymbol{\mu}^4]$ for Exact Nuclear−Electronic Wave Functions in the Born−Oppenheimer Approximation in the Notation $(P)_{MN} = \langle M|P|N \rangle$[a]

type	vibrational contribution
$[\mu^2]$	$\sum P_{-\sigma,\ \sigma} \sum_K{}'(\mu_\alpha)_{0K}(\mu_\beta)_{K0}(\omega_{K0} - \omega_\sigma)^{-1}$
$[\mu\alpha]$	$\frac{1}{2}\sum P_{-\sigma;1,\ 2} \sum_K{}'(\mu_\alpha)_{0K}(\alpha_{\beta\gamma})_{K0}(\omega_{K0} \pm \omega_\sigma)^{-1}$
$[\mu^3]$	$\sum P_{-\omega;1,\ 2} \sum_{KL}{}'(\mu_\alpha)_{0K}(\bar{\mu}_\beta)_{KL}(\mu_\gamma)_{L0}(\omega_{K0} - \omega_\sigma)^{-1}(\omega_1 - \omega_2)^{-1}$
$[\mu\beta]$	$\frac{1}{6}\sum P_{-\sigma,\ 1,\ 2,\ 3} \sum_K{}'(\mu_\alpha)_{0K}(\beta_{\beta\gamma\delta})_{K0}(\omega_{K0} \pm \omega_\sigma)^{-1}$
$[\alpha^2]$	$\frac{1}{4}\sum P_{-\sigma,\ 1,\ 2,\ 3} \sum_K{}'(\alpha_{\alpha\beta})_{0K}(\alpha_{\gamma\delta})_{K0}(\omega_{K0} - \omega_2 - \omega_3)^{-1}$
$[\mu^2\alpha]$	$\frac{1}{2}\sum P_{-\sigma,\ 1,\ 2,\ 3} \sum_{KL}{}'[(\mu_\alpha)_{0K}(\bar{\mu}_\beta)_{KL}(\alpha_{\gamma\delta})_{L0}(\omega_{K0} \pm \omega_\sigma)^{-1}\{\omega_{L0} \pm (\omega_2 + \omega_3)\}^{-1} + (\mu_\alpha)_{0K}(\bar{\alpha}_{\beta\gamma})_{KL}(\mu_\delta)_{L0}(\omega_{K0} - \omega_\sigma)^{-1}(\omega_{L0} - \omega_3)^{-1}]$
$[\mu^4]$	$\sum P_{-\sigma,\ 1,\ 2,\ 3}[\sum_{KLM}{}'(\mu_\alpha)_{0K}(\bar{\mu}_\beta)_{KL}(\bar{\mu})_{LM}(\mu_\delta)_{M0}(\omega_{K0} - \omega_\sigma)^{-1}(\omega_{L0} - \omega_2 - \omega_3)^{-1}(\omega_M - \omega_3)^{-1}$ $- \sum_{KL}{}'(\mu_\alpha)_{0K}(\mu_\beta)_{K0}(\mu_\gamma)_{0L}(\mu_\delta)_{L0}(\omega_{K0} - \omega_\sigma)^{-1}(\omega_{L0} - \omega_3)^{-1}(\omega_{L0} + \omega_2)^{-1}]$

[a] The notation $\Sigma_K{}'$ indicates that the summations are over excited states only.

direct and indirect effects.[818] The direct effects arise from the polarization of the solute's electron density by the surrounding solvent molecules or by the surrounding crystal molecules; the indirect effects arise from relaxation of the solute's geometry induced by this polarization. We here focus on the direct solvent effects, noting that the indirect effects are straightforwardly accounted for by allowing the molecular structure to relax in the presence of the solvent.

Solvent effects are usually treated by one of the following solvation models: the supermolecule model, the multilevel model, or the implicit model. In the following these models are discussed briefly; for more detailed discussions we refer to the review by Tomasi, Mennucci, and Cammi,[818] where calculation of molecular properties of solvated molecules is also treated. As an illustration of the accuracy of explicit, discrete, and continuum approaches for calculation of the excitation energies, we refer to the recent study on camphor by Kongsted et al.[819]

7.1. Supermolecular Models

The supermolecular model is conceptually the simplest solvation model. The properties of the solute are calculated in the presence of the neighboring solvent molecules, which are treated at the same theoretical level as the solute. For correlated wave function methods this approach has severe limitations with respect to the size of the systems that can be treated, although recent advances in linear-scaling techniques, local correlation methods, and incremental schemes have made this approach more practical.[139,208,209,211,820−822] A contributing factor to the high cost of such studies is the need to perform a statistical averaging over solute−solvent configurations, a procedure that may require sampling over 100−500 configurations depending on the property of interest.[823]

In discussing supermolecular property calculations it is important to distinguish between intensive and extensive properties. Asymptotically, intensive molecular properties are independent of the size of the system, whereas extensive properties are proportional to the system size. Intensive properties are easily extracted from supermolecular calculations, as the solvent molecules only act as perturbers on the property of interest. Extensive properties, by contrast, depend on the response of all molecules present in the system; a polarizability calculation, for example, provides the polarizability of all molecules in the system rather than that of the solute alone. Indeed, the response may actually be dominated by the solvent molecules and by surface effects.

For extensive properties a differential-shell approach has been proposed,[824] where the molecular property of interest is calculated as the difference between the property of the full system (solute and solvent) and the property of the system with the solute removed. The approach has been used with some success, reproducing experimental solvent shifts[824] for the first hyperpolarizability, for which it reproduces the experimentally observed sign change for water going from the gas to the liquid phase; it has also been applied to the magnetizability[588] and the Cotton−Mouton effect.[825] In some cases the solute itself may produce an imprint on the solvent configuration, for instance, for a chiral molecule in an achiral solvent. In these cases a supermolecular calculation is necessary to recover these effects. Perhaps the most striking example of such an effect was provided by Zuber, Beratan, and co-workers, who showed that the largest effect on the optical rotation of methyloxirane solvated in water or benzene arises from the response of the solute's imprint on the solvent structure.[826,827] This observation also explained the strong solvent dependence observed for methyloxirane and, in particular, the change of sign of its optical rotation when changing the solvent from benzene to water.[827]

From a methodological point of view, supermolecular models do not require special computational technology beyond those methods developed for studying isolated molecules in the gas phase. We therefore do not discuss these models further here but note that, because of the large systems considered, DFT is the method of choice for such calculations. Furthermore, given the

Table 6. Contributions to Dynamic Vibrational Polarizabilities and Hyperpolarizabilities[a]

term formula
$[\mu^2]^{0,\ 0} = \frac{1}{2}\sum P_{\alpha,\ \beta} \sum_{a} \frac{\partial \mu_\alpha}{\partial Q_a} \frac{\partial \mu_\beta}{\partial Q_a} \lambda_a^{\pm\sigma}$
$[\mu^2]^{2,\ 0} = \frac{1}{8}\sum P_{\alpha,\ \beta} \sum_{a,\ b} \left[\frac{\partial^2 \mu_\alpha}{\partial Q_a \partial Q_b} \frac{\partial^2 \mu_\beta}{\partial Q_a \partial Q_b} \left(\frac{1}{\omega_a} + \frac{1}{\omega_b} \right) \lambda_{ab}^{\pm\sigma} + \frac{\partial^3 \mu_\alpha}{\partial Q_a \partial Q_a \partial Q_b} \frac{\partial \mu_\beta}{\partial Q_b} \frac{\lambda_b^{\pm\sigma}}{\omega_a} + \frac{\partial \mu_\alpha}{\partial Q_b} \frac{\partial^3 \mu_\beta}{\partial Q_a \partial Q_a \partial Q_b} \frac{\lambda_b^{\pm\sigma}}{\omega_a} \right]$
$[\mu^2]^{1,\ 1} = -\frac{1}{4}\sum P_{\alpha,\ \beta} \sum_{a,\ b,\ c} \left[F_{abc} \frac{\partial^2 \mu_\alpha}{\partial Q_a \partial Q_b} \frac{\partial \mu_\beta}{\partial Q_c} \left(\frac{1}{\omega_a} + \frac{1}{\omega_b} \right) \lambda_{ab}^{\pm\sigma} \lambda_c^{\pm\sigma} + F_{bcc} \frac{\partial^2 \mu_\alpha}{\partial Q_a \partial Q_b} \frac{\partial \mu_\beta}{\partial Q_a} \frac{\lambda_a^{\pm\sigma}}{\omega_b^2 \omega_c} \right]$
$[\mu^2]^{0,\ 2} = -\frac{1}{8}\sum P_{\alpha,\ \beta} \sum_{a,\ b,\ c} \frac{1}{\omega_a} \left[F_{aabc} \frac{\partial \mu_\alpha}{\partial Q_b} \frac{\partial \mu_\beta}{\partial Q_c} \lambda_b^{\pm\sigma} \lambda_c^{\pm\sigma} - \sum_{\mathrm{d}} \left\{ F_{aab} F_{bc\mathrm{d}} \frac{\partial \mu_\alpha}{\partial Q_c} \frac{\partial \mu_\beta}{\partial Q_{\mathrm{d}}} \frac{\lambda_c^{\pm\sigma} \lambda_{\mathrm{d}}^{\pm\sigma}}{\omega_b^2} + 2 F_{abc} F_{ab\mathrm{d}} \frac{\partial \mu_\alpha}{\partial Q_c} \frac{\partial \mu_\beta}{\partial Q_{\mathrm{d}}} \lambda_{ab}^{\pm\sigma} \lambda_c^{\pm\sigma} \lambda_{\mathrm{d}}^{\pm\sigma} \right\} \right]$
$[\mu^3]^{1,\ 0} = \frac{1}{2}\sum P_{\alpha,\ \beta,\ \gamma} \sum_{a,\ b} \frac{\partial \mu_\alpha}{\partial Q_a} \frac{\partial^2 \mu_\beta}{\partial Q_a \partial Q_b} \frac{\partial \mu_\gamma}{\partial Q_b} \lambda_a^{\pm\sigma} \lambda_b^{\pm 2}$
$[\mu^3]^{0,\ 1} = -\frac{1}{6}\sum P_{\alpha,\ \beta,\ \gamma} \sum_{a,\ b,\ c} F_{abc} \frac{\partial \mu_\alpha}{\partial Q_a} \frac{\partial \mu_\beta}{\partial Q_b} \frac{\partial \mu_\gamma}{\partial Q_c} \lambda_a^{\pm\sigma} \lambda_b^{\pm 1} \lambda_c^{\pm 2}$
$[\mu^2\alpha]^{1,\ 0} = \frac{1}{4}\sum P_{\alpha,\ \beta,\ \gamma,\ \delta} \sum_{a,\ b} \left[\frac{\partial \mu_\alpha}{\partial Q_a} \frac{\partial^2 \alpha_{\beta\gamma}}{\partial Q_a \partial Q_b} \frac{\partial \mu_\delta}{\partial Q_b} \lambda_a^{\pm\sigma} \lambda_b^{\pm 3} + 2 \frac{\partial \mu_\alpha}{\partial Q_a} \frac{\partial^2 \mu_\beta}{\partial Q_a \partial Q_b} \frac{\partial \alpha_{\gamma\delta}}{\partial Q_b} \lambda_a^{\pm\sigma} \lambda_b^{\pm 23} \right]$
$[\mu^2\alpha]^{0,\ 1} = -\frac{1}{4}\sum P_{\alpha,\ \beta,\ \gamma,\ \delta} \sum_{a,\ b,\ c} F_{abc} \frac{\partial \mu_\alpha}{\partial Q_a} \frac{\partial \mu_\beta}{\partial Q_b} \frac{\partial \alpha_{\gamma\delta}}{\partial Q_c} \lambda_a^{\pm\sigma} \lambda_b^{\pm 1} \lambda_c^{\pm 23}$
$[\mu^4]^{2,\ 0} = \frac{1}{6}\sum P_{\alpha,\ \beta,\ \gamma,\ \delta} \sum_{a,\ b,\ c} \left[3 \frac{\partial \mu_\alpha}{\partial Q_a} \frac{\partial^2 \mu_\beta}{\partial Q_a \partial Q_b} \frac{\partial^2 \mu_\gamma}{\partial Q_b \partial Q_c} \frac{\partial \mu_\delta}{\partial Q_c} \lambda_a^{\pm\sigma} \lambda_b^{\pm 23} \lambda_c^{\pm 3} + \frac{\partial^3 \mu_\alpha}{\partial Q_a \partial Q_b \partial Q_c} \frac{\partial \mu_\beta}{\partial Q_a} \frac{\partial \mu_\gamma}{\partial Q_b} \frac{\partial \mu_\delta}{\partial Q_c} \lambda_a^{\pm 1} \lambda_b^{\pm 2} \lambda_c^{\pm 3} \right]$
$[\mu^4]^{1,\ 1} = -\frac{1}{2}\sum P_{\alpha,\ \beta,\ \gamma,\ \delta} \sum_{a,\ b,\ c,\ \mathrm{d}} F_{abc} \frac{\partial \mu_\alpha}{\partial Q_a} \frac{\partial \mu_\beta}{\partial Q_b} \frac{\partial^2 \mu_\gamma}{\partial Q_c \partial Q_{\mathrm{d}}} \frac{\partial \mu_\delta}{\partial Q_{\mathrm{d}}} \lambda_a^{\pm\sigma} \lambda_b^{\pm 1} \lambda_c^{\pm 23} \lambda_{\mathrm{d}}^{\pm 3}$
$[\mu^4]^{0,\ 2} = -\frac{1}{24}\sum P_{\alpha,\ \beta,\ \gamma,\ \delta} \sum_{a,\ b,\ c,\ \mathrm{d}} \left[F_{abc\mathrm{d}} \frac{\partial \mu_\alpha}{\partial Q_a} \frac{\partial \mu_\beta}{\partial Q_b} \frac{\partial \mu_\gamma}{\partial Q_c} \frac{\partial \mu_\delta}{\partial Q_{\mathrm{d}}} \lambda_a^{\pm\sigma} \lambda_b^{\pm 1} \lambda_c^{\pm 2} \lambda_{\mathrm{d}}^{\pm 3} - 3 \sum_{e} F_{abc} F_{c\mathrm{d}e} \frac{\partial \mu_\alpha}{\partial Q_a} \frac{\partial \mu_\beta}{\partial Q_b} \frac{\partial \mu_\gamma}{\partial Q_{\mathrm{d}}} \frac{\partial \mu_\delta}{\partial Q_e} \lambda_a^{\pm\sigma} \lambda_b^{\pm 1} \lambda_c^{\pm 23} \lambda_{\mathrm{d}}^{\pm 2} \lambda_e^{\pm 3} \right]$

[a] (i) For the $[\mu^2]$ terms, $\omega_\sigma = \omega_1$; for the $[\mu^3]$ and $[\mu^2\alpha]$ terms, $\omega_\sigma = \omega_1 + \omega_2$; for the $[\mu^4]$ terms, $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$. (ii) $\Sigma P_{\alpha,\beta}$ indicates the sum over terms generated by the permutation of the pairs of optical frequencies and indices: $(-\omega_\sigma,\alpha)$ and $(-\omega_1,\beta)$; $\Sigma P_{\alpha,\beta,\gamma}$ indicates the permutations of $(-\omega_\sigma,\alpha)$ and (ω_1,β); and (ω_2,γ); $\Sigma P_{\alpha,\beta,\gamma,\delta}$ indicates the permutations of $(-\omega_\sigma,\alpha)$ and (ω_1,β), and (ω_2,γ), and (ω_3,δ). (iii) $\lambda_{\mathrm{x}}^{\pm\mathrm{i}} = (\omega_{\mathrm{x}}^2 - \omega_{\mathrm{i}}^2)^{-1}$; $\lambda_{\mathrm{xy}}^{\pm\mathrm{i}} = [(\omega_{\mathrm{x}} + \omega_{\mathrm{y}})^2 - \omega_{\mathrm{i}}{}^2]^{-1}$; $\lambda_x^{\pm ij} = [\omega_x^2 - (\omega_i + \omega_j)^2]^{-1}$.

dynamic nature of the liquid system, a conformational averaging is in general needed. This can be achieved either by a Boltzmann averaging over energetically accessible equilibrium structures or by a sampling of instantaneous solute−solvent configurations generated by Car−Parrinello[828] or molecular-dynamics[829] simulations.

7.2. Multilevel Models

In the quantum-mechanics/molecular-mechanics (QM/MM) approach[830−832] the solute is treated quantum mechanically by a suitable electronic-structure method whereas the solvent is treated by molecular mechanics. Phenomenologically, we may write the energy of the QM/MM system as

$$E^{\mathrm{QM/MM}} = E^{\mathrm{QM}} + E^{\mathrm{MM}} + E^{\mathrm{QM/MM}} \tag{665}$$

where E^{QM} is the energy of the quantum-mechanical part of the system, E^{MM} the classical energy of the solvent described by molecular mechanics, and $E^{\mathrm{QM/MM}}$ the energy arising from the interaction between the solute and the solvent. The molecular-mechanics energy E^{MM} contains contributions from parametrized force fields involving bond stretching and bending motions, and van der Waals interactions are typically modeled using a Lennard−Jones potential.[833]

The coupling term $E^{\mathrm{QM/MM}}$ requires special attention. In the simplest case the MM surroundings may be represented by (distributed) multipoles (charges, dipoles, quadrupoles, etc.)[834,835]

$$\begin{aligned} E^{\mathrm{QM/MM(unpol)}} &= E^{\mathrm{nuc/mul}} + E^{\mathrm{el/mul}} \\ &= E^{\mathrm{nuc/mul}} + \langle 0 | G^{\mathrm{es}} | 0 \rangle \end{aligned} \tag{666}$$

where $E^{\mathrm{nuc/mul}}$ is the interaction energy between the nuclear charges of the solute and the distributed multipoles used to describe the surrounding nuclei while G^{es} describes the electrostatic (Coulomb) interaction between the electrons of the solute with the MM multipoles. In practice, the QM/MM calculations are performed in the same manner as conventional quantum-chemical calculations but with a modified one-electron part due to the additional Coulomb interactions, see, for example refs 592, 835, and 836.

Although the multipolar description of the solvent often works well for energies, it is in most cases inadequate for molecular properties, where the perturbation associated with the property of interest polarizes both solvent and solute, thereby affecting the solute−solvent interaction. Such polarization effects can be accounted for by introducing induced dipoles, in addition to the static multipole moments, at the MM sites. In a compact notation

$$\boldsymbol{\mu}^{\mathrm{ind}} = \boldsymbol{\alpha}\mathbf{F}^{\mathrm{tot}} \tag{667}$$

where the induced dipole moment $\boldsymbol{\mu}^{\mathrm{ind}}$ and the polarizability $\boldsymbol{\alpha}$ collect all dipole vectors and polarizability tensors at the MM sites and where $\mathbf{F}^{\mathrm{tot}} = \mathbf{F}^{\mathrm{sta}} + \mathbf{F}^{\mathrm{ind}}$ represents the total electric field (at the MM sites) as composed of a static component (due to the QM nuclei, QM electrons, and the MM multipoles) and an induced component (due to the induced dipoles themselves).

At the correlated level of electronic-structure theory, Kongsted and co-workers developed a coupled-cluster/molecular-mechanics (CC/MM) method for accurate studies of molecular properties in solution, within the framework of a polarizable molecular-mechanics force field. Expectation values and dipole moments were first studied,[837] followed shortly by implementation of the linear response function at the CC/MM level of theory.[838−840] Although polarizabilities have been studied, the main focus in these studies is the excitation energies and transition moments, for which a detailed comparison with experiment is possible. We note, however, that the CC/MM methodology was able to reproduce the sign change of the optical rotation of (R)-methyloxirane when going from the gas phase to solution.[647]

Kongsted and co-workers later extended their CC/MM approach to quadratic response theory, presenting calculations of first hyperpolarizabilities[841] and TPA cross sections[842] of solvated molecules. Given the high cost of coupled-cluster theory, in particular, with triples included, it becomes important to reduce the number of solute−solvent configurations that need to be averaged. Osted et al.[843] performed an investigation on liquid water, paying particular attention to how the computational cost can be reduced while maintaining accuracy.

Recently, the polarizable QM/MM method was significantly extended by incorporating self-consistent polarization effects in a more efficient fashion, appropriate for systems with thousands of MM sites. The new strategy is referred to as the polarizable embedding (PE) model.[834] Sneskov et al.[835] extended the PE method to linear and quadratic response functions at the CC2 and CCSD levels of theory, including also an approximate treatment of triple excitations through the CCSDR(3)/MM model.[844] In the PE approach the environmental effects are conveniently incorporated into a coupled-cluster QM/MM quasi-energy Lagrangian

$$\mathscr{L}_{\mathrm{QM/MM}} = \mathscr{L} + \langle \Lambda^{(0)}|G^{\mathrm{es}}|\mathrm{CC}^{(0)}\rangle - \frac{1}{2}\left(\boldsymbol{\mu}^{\mathrm{ind}}\right)^{\mathrm{T}}\mathbf{F}^{\mathrm{sta}} + U \tag{668}$$

where $\mathscr{L}$ is the standard QM part defined in eq 491 whereas U represents the remaining contributions to the total energy, which do not have an explicit dependence on the electronic parameters and thus are of minor importance from a coupled-cluster response point of view. Employing the same strategy as in the vacuum case (see section 4.3), we obtain modified amplitude and multiplier equations

$$0 = \langle \mu|\exp(-T)(H + G)\exp(T)|\mathrm{HF}\rangle \tag{669}$$

$$0 = \langle \Lambda^{(0)}|[H + G, \tau_{\nu_j}]|\mathrm{CC}^{(0)}\rangle \tag{670}$$

The only difference compared with the vacuum equations is the presence of an effective solvent operator

$$G = G^{\mathrm{es}} - \sum_{a,\ \nu} \mu_{\nu}^{a,\ \mathrm{ind}} \varepsilon_{\nu}^{a} \tag{671}$$

which couples the amplitude and multiplier equations. Here, ε_{ν}^{a} is a second-quantized operator representing the field at an MM site due to the QM electrons, the summation running over all Cartesian components (index ν) of all MM sites (index a). It is important to note the prominent role of the Lagrangian in this solvent model. In conventional vacuum coupled-cluster theory the Lagrangian is not needed for calculating energies but convenient for calculating other properties. In coupled-cluster QM/MM theory it is the cornerstone of the model: it is only the evaluation of the energy Lagrangian itself that guarantees convergence to the FCI limit. A related difference to vacuum theory is the coupled nature of eqs 669 and 670, arising from the self-consistent inclusion of polarization. For details, see ref 835.

Recently, Steindal et al.[845] presented a fully polarizable three-level model in which the polarizable QM/MM approach was combined with the PCM of Tomasi and Mennucci.[846−848] The method was used to study excitation energies in solution, exploring the convergence of the excitation energies with the radius of the cutoff sphere used to define the solute−solvent clusters. An alternative three-level model is based on the use of the effective fragment potential (EFP) model in combination with the PCM.[849,850] Both these methodologies thus allow for fully polarizable multiscale models. However, only gradients have so far been implemented for the EFP/PCM model.

In the reference-interaction-site model (RISM) the liquid is represented by a set of atoms where chemical bonds are described by strong intramolecular correlations. The approach was first proposed by Chandler and Anderson[851] and applied to molecules by inclusion of charge distributions and molecular structure by Hirata and Rossky.[852,853] The methodology was put in a quantum-mechanical framework by Hirata, Kato, and Ten-No,[854,855] referred to as the RISM-SCF method. The statistical nature of the solute−solvent interactions are included through correlation functions, and the interactions between the solute and the solvent are expressed in the form of an integral equation. A comparison of the performance of the RISM-SCF and PCM approaches has been presented by Sato and Sakaki.[856] The RISM-SCF method has been extended to treatment of nondynamical solvation of excited states (vide infra) by Ishida et al.[857]

An early application of the RISM-SCF approach was calculation of NMR chemical shieldings and the gas-to-liquid solvation shift of water[858] using London orbitals for gauge-origin independence. An interesting property of the statistical nature of the RISM approach is the possibility to study temperature and density effects; however, the results reported in ref 858 were in poor agreement with experiment, and the method has since not been used for such purposes. This is unfortunate as the poor agreement may have arisen from a need to include the nearest-neighbor solvent molecules in the quantum-mechanical description of the shielding constants.[588,859,860] The RISM-SCF method has been extended to calculation of molecular gradients, including CCSD(T) gradients, allowing for an automated optimization of molecular structures in solution.[861,862]

In the EFP method of Gordon and Jensen[863] exchange-repulsion effects are included in the ground state in addition to

Table 7. Electrostatic Contributions to the n → π^* Transition Energies (cm^{-1}) in Acetone in Various Solvents, Comparing Equilibrium and Nonequilibrium Solvation[a]

	transition energies		excitation-energy shift relative to cyclohexane		
	equilibrium	nonequilibrium	equilibrium	nonequilibrium	exp.
cyclohexane	37 386	37 386	0	0	0
CH_2Cl_2	37 529	37 611	143	225	570
ethanol	37 919	38 256	524	870	1360
water	37 960	38 342	574	956	2000

[a] Results taken from ref 883 and obtained at the CAS(4,3)/6-31G(d) level of theory.

the electrostatic and polarization contributions included in the QM/MM methods. As such, for the ground-state energy the EFP approach is somewhat more complicated to implement than the polarized QM/MM approach but includes effects that are important, in particular, for description of surfaces and interfaces and for the solvation process itself. As for the RISM-SCF method, one of the first applications of the EFP method was to model NMR shielding constants.[864] In the most recent EFP formulations molecular gradients have been implemented at the Hartree−Fock and Kohn−Sham levels of theory;[850,865,866] Kohn−Sham linear response functions[867] and excited-state gradients have also been implemented.[862] In the Kohn−Sham implementation, exchange repulsion is treated by a set of fitting parameters, in contrast to the Hartree−Fock implementations where the exchange contribution is treated more rigorously, allowing for a simpler theoretical framework and application to response properties.

An emerging technique that may prove important for property calculations is the density embedding of wave function models of Carter et al.,[868,869] recently extended by Gomes et al. to calculation of solvatochromic shifts.[870] The method is based on the embedding scheme of Wesolowski and Warshel[871] for weakly interacting systems, where the solvent is described by DFT. This technique is useful in that it enables us to study the solute with high-level quantum-chemistry methods while retaining a quantum-mechanical description of the solvent. The approach has been generalized to coupled chromophores within a fully DFT-in-DFT model;[872] it would be interesting to see an extension of this method to a wave function treatment of the solute.

We finally note that the three-level multiscale ONIOM approach[873,874] may also be used for solvation studies. As for all methods involving specific solvent molecules, dynamical averaging must be taken into account. The ONIOM approach is a difference approach, where the result for the solute or molecule of interest is obtained by a set of energy differences between different model calculations. It is therefore straightforward to calculate molecular properties for any computational model that allows for calculation of molecular properties. As such, the developments discussed in earlier sections for calculation of gas-phase molecular properties can be straightforwardly applied in the ONIOM approach.

7.3. Continuum Models

A different approach to solvation is to assume that because of dynamical averaging the solvent can be represented as a structureless, homogeneous, polarizable dielectric medium, with the solute contained inside a cavity in the medium. This assumption forms the basis for the continuum models.[818] In this way we do not have to consider the internal degrees of freedom of the solvent and the Hamiltonian becomes

$$H^{\mathrm{eff}} = H + H^{\mathrm{int}} \tag{672}$$

where H is the isolated solute Hamiltonian and H^{int} describes the interaction between the solute and the solvent. The solvent is represented by a dielectric constant, which may be tensorial for nonisotropic media such as liquid crystals[875] or position dependent for inhomogeneous systems such as surfaces or interfaces.[876−879] Given that the Hamiltonian H^{eff} describes the interaction between the solute and a polarizable dielectric medium it depends on the solute density. Therefore, as for the polarizable QM/MM models, the Schrödinger equation must be solved in a self-consistent manner. Special care needs to be given to methods that are nonvariational.[880,881] However, the framework presented in section 3 can straightforwardly be extended to include the effects of a dielectric continuum by addition of a contribution from the interaction Hamiltonian, whose form depends on the description of the solute−solvent interactions (in terms of, for instance, boundary-element methods or multipole expansions).[818]

In continuum calculations the properties of the solvent are described by a dielectric constant that has both a static and an optical component. Whereas the static dielectric constant describes both nuclear and electronic polarization of the dielectric medium, the optical dielectric constant describes only the electronic polarization. The optical dielectric constant is appropriate for processes involving dynamic electromagnetic fields, where only the electronic degrees of freedom are able to respond to the applied perturbation (with the nuclear degrees of freedom remaining in their unperturbed state), resulting in nonequilibrium solvation.[882] While there is a large variation in the static dielectric constant for different compounds (from about 2 for nonpolar molecules to about 80 for highly polar solvents such as water), the variation in the optical dielectric constant is small (between 1.5 and 2.5 depending on the electronic polarizability of the solvent). Nonequilibrium solvation is of little concern for nonpolar solvents (because of the small differences between the static and optical dielectric constants) but can be significant for polar solvents. This is illustrated for the excitation energies of acetone in Table 7, where large shifts in the excitation energies also arise from nonelectrostatic interactions, which can be accounted for by including the neighboring solvent molecules in the quantum-mechanical system.[883,884]

The origin of nonequilibrium solvation is illustrated in Figure 3. From an equilibrated ground-state electronic structure the molecule is excited into a solvated structure where only the electronic degrees of freedom of the solvent are able to adjust

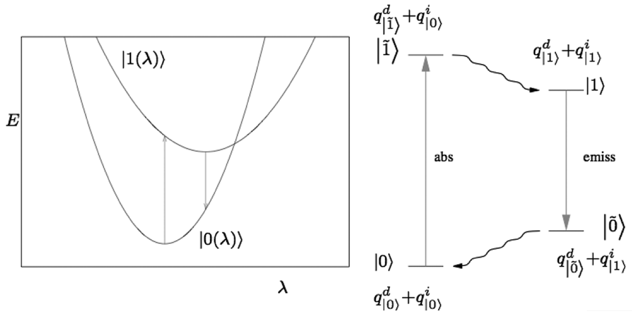

Figure 3. Schematic representation of nondynamical solvation effects in absorption and emission processes. Reprinted with permission of Luca Frediani (University of Tromsø), 2011.

instantaneously to the solute excitation. Given sufficient time the solvent molecules readjust to the excited-state electron density of the solute, leading to a new excited-state equilibrated structure, from which the molecule may be de-excited into a nonequilibrated ground-state electronic structure. Because of the induced restructuring of the solute in the excited state, absorption and emission energies are no longer identical. Note that during the equilibration time for the excited state, the solute geometry may relax, giving rise to an additional indirect solvation effect on the difference between the absorption and the emission spectra of the solute. Even without considering nuclear relaxation the separation of the solvent response into static and dynamic parts means that there is no longer a one-to-one correspondence between excitation energies obtained by an explicit optimization of the excited state and by linear response theory, as demonstrated by Cammi.[885]

Over the years a variety of continuum models, differing in the choice of H^{int}, have been proposed; for a recent review, see ref 818. We consider here continuum models that have been extended to calculation of molecular properties and comment on their suitability for studies of solvation effects, the main difference between these being the shape of the cavity in which the solute is placed.

Mikkelsen and co-workers developed a continuum model with a spherical cavity.[886] Because of the simple cavity structure the solute−solvent interactions can be represented by a multipole expansion of the solute density. This model has been adapted to MCSCF cubic response theory with nonequilibrium solvation,[887−893] to gauge-origin-independent calculations of NMR shielding constants and magnetizabilities with London orbitals,[588,894] to mixed electric−magnetic properties,[825,895] to nonequilibrium solvation with triplet perturbations,[891] and to inhomogeneous solvation (e.g., from a metal surface) up to cubic response functions.[876,877] The spherical-continuum model has recently been extended to linear and quadratic coupled-cluster response theory[841,896,897] with applications to optical rotation.[647] A review of the field has been provided by Mikkelsen.[898]

The cavity shape and distance between the nuclear positions and the cavity boundary are nearly always empirical factors in continuum calculations. An interesting exception to this rule was presented by Luo et al.[899] By combining the classical Maxwell field theory with quantum-chemical reaction-field theory using spherical cavities these authors showed that the cavity radius is uniquely determined by the calculated polarizability and dielectric constant of the neat liquid. The radius for a spherical cavity of a neat liquid is therefore uniquely defined and no longer a parameter in the calculation.

Use of a spherical cavity leads to a simple interaction Hamiltonian, requiring only calculation of multipole integrals (and their derivatives for perturbation-dependent basis sets). However, accurate results can only be expected for molecules of a nearly spherical shape or for properties that depend on the response along the longest molecular axis, for example, nonlinear optical properties of conjugated push−pull molecules.[900] In general, a more realistic, molecule-shaped cavity must be used, as provided by the polarizable-continuum model (PCM) in its various flavors[846,848,901−905] and by the conductor-screening model (COSMO).[906−910] In these models the cavity surface is partitioned into small surface elements, onto which charges are attached to describe the induced polarization. For calculations of properties with wave function methods, the PCM is used more often than the COSMO model; given the focus on wave function methods in this review our discussion of solvent calculations with molecule-shaped cavities is therefore biased toward PCM calculations.

The PCM has been extended to the calculation of linear, quadratic, and cubic response functions using MCSCF wave functions,[911−914] including nonequilibrium solvation and local-field effects.[915] Ferrighi et al. implemented the calculation of magnetizabilities using London orbitals.[591] Also, zero-field splittings have been studied using continuum models within the framework of a spherical-cavity approach and using MCSCF wave functions.[510,511] However, solvent effects on magnetic properties are in general poorly reproduced both by continuum[588,860,916] and by QM/MM[917−921] models. It appears mandatory to include the nearest solvent molecules in the quantum system, indicating the presence of quantum effects that cannot be recovered by the simple electrostatic PCM and QM/MM models. It would be of interest to investigate whether visualization of ring currents[426] in weakly interacting systems would reveal effects of ring-current interactions in solvated complexes.

Finally, we note that Caricato et al. combined the EOM-CC method with PCM[922] as an alternative to the coupled-cluster linear-response approach of Christiansen and Mikkelsen.[881,896] Cammi also described evaluation of molecular gradients for excited states using the EOM-CC method.[923]

7.4. Molecular Properties with Periodic Boundary Conditions

Restricting ourselves to wave function methods, the number of studies of molecular properties in the solid state are limited, mainly because few codes have been developed for calculations subject to periodic boundary conditions, although we note the recently presented projected-augmented wave code by Marsman et al.[924] More fundamentally, the representation of the electric dipole operator is nontrivial for periodic systems, noting that the form given in eq 62 breaks the periodicity of the sample.[925,926]

Hartree−Fock codes for treating one-dimensional systems were presented independently by Champagne and Andre[927] and Otto[928] in 1992. Otto applied the code to the calculation of polarizabilities and hyperpolarizabilities of linear chains of hydrogen, water, and lithium hydride molecules, whereas Champagne and Andre focused on the polarizabilities of polyethene and polysilane.[927] An alternative formulation was later presented by Kirtman et al.[929] On the basis of the approaches for one- and two-dimensional systems by Del Re et al.[930] and by André et al.,[931,932] Hirata and Iwata implemented analytic molecular gradients at the MP2 level of theory[933] and force fields at the Hartree−Fock level of theory.[934] An implementation of time-dependent Hartree−Fock theory for one-dimensional periodic systems has also been developed.[935]

For two- and three-dimensional systems Kudin and Scuseria first presented a finite-field approach to the calculation of polarizabilities of periodic systems at the Hartree−Fock level of theory,[936] later extended to the analytic calculation of Hartree−Fock and Kohn−Sham frequency-dependent polarizabilities by Izmaylov et al.[937] The group of Scuseria also developed analytic approaches for calculation of forces,[938] force fields,[939] and dipole gradients.[940] A geometry optimization method based on internal coordinates has also been presented by the same group.[941] In a parallel development, Dovesi and Orlando reported similar extensions in the CRYSTAL code for molecular gradients,[942] static polarizabilities,[943] and first hyperpolarizabilities[944,945] at the Hartree−Fock and Kohn−Sham levels of theory. Maschio et al. furthermore presented the first optimized structures at the local-MP2 level of theory for periodic systems using a mixed analytic and numerical scheme.[946]

8. CONCLUDING REMARKS

Molecular properties can nowadays be calculated for all important wave function models using the sophisticated methods developed in quantum chemistry over the last decades. The underlying framework for such calculations is molecular response theory. In the present review we have given a uniform treatment of this theory, applicable to time-dependent and time-independent perturbations, to variational and nonvariational wave function models, for perturbation-dependent and perturbation-independent basis sets. This general framework will undergo further developments and adaptations in the future, for example, to the linear-scaling calculation of molecular properties of large molecular systems at the correlated and uncorrelated levels of theory, to calculation of molecular properties using explicitly correlated methods, and to calculation of properties using multiconfigurational coupled-cluster techniques. The future will also see a stronger merging of wave function and density-functional methods, for example, through development of range-separated and orbital-dependent functionals for exchange and correlation; such developments will necessitate a merging of property techniques for wave function and density-functional methods. We believe the property techniques presented and reviewed here are sufficiently flexible to be adapted to all these developments of quantum chemistry, although the increasing accuracy of quantum-chemical calculations may lead to development of techniques that go beyond the regular perturbation-theory approach within the minimal-coupling scheme discussed by us.[947]

As demonstrated in the present review, molecular response theory has been applied to a vast range of systems and perturbations. Apart from calculation of molecular forces and force constants, essential to explore chemistry, molecular response theory is today applied to all forms of molecular spectroscopy for interpretation and prediction of molecular spectra and spectroscopic constants. Important theoretical developments over the last two decades have been application of quantum chemistry to magnetic resonance spectroscopies, optical activity and birefringence, nonlinear optics, and excited-state properties. In the future, the range of molecular properties routinely studied theoretically will broaden further to reflect new experimental developments in nonlinear and multidimensional electronic and vibrational spectroscopies. Although these and related applications of quantum chemistry have not all been fully reviewed here, we believe that our review is sufficiently exhaustive to direct the reader to the most important developments in wave function-based molecular response theory over the last two decades.

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BIOGRAPHIES

Trygve Helgaker is a professor of theoretical chemistry at the University of Oslo (Norway). He received his Ph.D. degree from the University of Oslo in 1986 (supervisor Jan Almlöf) and spent 1 year as a postdoctoral fellow at the University of Minneapolis and 2 years at the University of Aarhus (Denmark), before taking a position as Lecturer at the University of Oslo in 1989, where he became Full Professor in 1993. His research interests are in the area of high-accuracy quantum chemistry, density-functional theory, molecular properties, and linear-scaling techniques. He has spent sabbatical years at the University of Cambridge and University of Durham, United Kingdom. He is an author of the Dalton and Dirac programs.

Sonia Coriani is a researcher in physical chemistry at the University of Trieste (Italy). She graduated from the University of Modena (Italy) in 1993 and received her Ph.D. degree from the University of Aarhus (Denmark) in 2000. She was a research fellow at the ICQEM in Pisa in 1995, associate professor II at the Centre for Theoretical and Computation Chemistry (Norway) in 2007−2011, and Marie-Curie IEF fellow at the University of Aarhus in 2010−2011. Her research focuses on the development and application of wave-function- and density-functional-based methods for accurate determination of molecular properties, with emphasis on structural properties, nonlinear optics, birefringence, and dichroism effects, and, more recently, X-ray related phenomena. She is an author of the Dalton program.

Poul Jørgensen is Professor at Aarhus University (Denmark), where he received his doctoral degree in 1976. He is coauthor of more than 300 papers and 3 monographs. His major interest is electronic structure theory, in particular, determination of molecular properties using response function theory. Recently, his interest has turned toward a description of large molecular systems using linear-scaling algorithms.

Kasper Kristensen is a postdoctoral fellow at the Lundbeck Foundation Center for Theoretical Chemistry, Aarhus University (Denmark), where he also received his Ph.D. degree (2011). His research topics are response theory for self-consistent field models and local coupled-cluster theory.

Jeppe Olsen is a professor of chemistry at Aarhus University (Denmark). He received his Ph.D degree in Chemistry from University of Aarhus and was a postdoctoral fellow at Texas A&M University with Danny L. Yeager and the University of Utah with Jack Simons. From 1986 to 1998 he was employed at Lund University and returned to Aarhus University in 1998. His main research interests are development of ab initio methods for the study of molecular structure and properties, including high-accuracy methods for small molecules, methods for large molecules, and relativistic contributions. He is an author of the Dalton, Dirac, MOLCAS, and LUCIA programs.

Kenneth Ruud is a professor of theoretical chemistry at the University of Tromsø (Norway). He received his Ph.D. degree from the University of Oslo in 1998 (supervisor Trygve Helgaker) and spent 2 years as a postdoctoral fellow in San Diego with Peter Taylor before moving to Tromsø in 2001. His main research interests are development of new ab initio methods for the study of molecular properties. Additional interests include solvent effects (continuum and QM/MM methods) and vibronic and relativistic effects. He is an author of the Dalton and Dirac programs.

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ACRONYMS

ADC	algebraic diagrammatic construction [model]
ADC(*n*)	*n*th-order ADC [model]
AO	atomic orbital
BCH	Baker–Campbell–Hausdorff [expansion]
B3LYP	Becke-3-parameter–Lee–Yang–Parr [functional]
CAM-B3LYP	Coulomb-attenuating-method B3LYP [functional]
CARS	coherent anti-Stokes Raman scattering
CAS	complete active space
CASPT2	second-order CAS perturbation theory
CC	coupled cluster [model]

CC*n*	CC [rank] *n* [hybrid model]
CCS	CC singles [model]
CCSD	CC singles—doubles [model]
CCSDPPA	CCSD polarization-propagator approximation
CCSDR(3)	CC singles—doubles—response-triples [model]
CCSDT	CC singles—doubles—triples [model]
CCSD(T)	CC singles—doubles—perturbative-triples [model]
CCSDTQ	CC singles—doubles—triples—quadruples [model]
CCSDTQ5	CC singles—doubles—triples—quadruples—quintuples [model]
CD	circular dichroism
CI	configuration interaction [model]
CIS	CI singles [model]
CISD	CI singles—doubles [model]
CIS(D)	CI singles—perturbative-doubles [model]
CISDT	CI singles—doubles—triples [model]
CISDTQ	CI singles—doubles—triples—quadruples [model]
CIS(D_∞)	iterative CIS(D) [model]
COSMO	conductor-screening model
CTOCD-DZ	continuous transformation of the origin of the current density by setting diamagnetic contribution to zero [model]
DB-RI-MP2	dual-basis-RI-MP2 [model]
DFT	density-functional theory
DFWM	degenerate four-wave mixing
DPT	direct perturbation theory
DPT*n*	*n*-order DPT
ECD	electronic CD [spectroscopy]
EFGB	electric-field-gradient-induced birefringence
EFP	effective fragment potential [model]
EOM-CC	equation of motion CC [model]
EOPE	electro-optic Pockels effect
EPR	electron paramagnetic resonance
ESHG	electric-field-induced SHG
FCI	full-CI [model]
FNO-CC	frozen-natural-orbital-CC
GIAO	gauge-origin-including AO
GUGA	graphical unitary group approach
HF	Hartree—Fock [model]
IDRI	intensity-dependent refractive index
ΛCCSD(T)	λ-based CCSD(T) [model]
MCD	magnetic CD [spectroscopy]
MCSCF	multiconfigurational SCF [model]
MM	molecular mechanics
MO	molecular orbital
MP*n*	*n*-order Møller—Plesset [model]
MRCI	multireference CI [model]
MRCISD	multireference CISD [model]
MRMP2	multireference MP2 [model]
NESC	normalized elimination of the small component [model]
NEVPT2	second-order *n*-electron valence-state perturbation theory
NLO	nonlinear optics
NMR	nuclear magnetic resonance
NQR	nuclear quadrupole resonance
NSR	nuclear spin rotation
OMO	orthonormalized MO
ONIOM	our own *n*-layer integrated molecular orbital and molecular mechanics [model]
OR	optical rectification
PCM	polarizable-continuum model
RISM	reference-interaction-site model
QM	quantum mechanics
RAS	restricted active space
RHF	restricted HF [model]
RI	resolution of the identity
RIJCOSX-MP2	RI-J chain of spheres exchange MP2 [model]
ROA	Raman optical activity
SAC-CI	symmetry-adapted-cluster CI [model]
SCF	self-consistent field
SCS	spin-component-scaled [model]
SHG	second-harmonic generation
SOPPA	second-order polarization-propagator approximation
SOPPA(CCSD)	SOPPA with CCSD amplitudes
SOPPA(CC2)	SOPPA with CC2 amplitudes
SORA	second-order regular approximation
SO-RASSI	spin—orbit RAS state interaction [model]
SORCI	spectroscopy-oriented MRCI [model]
SOS	scaled opposite spin [model]; sum-over-states [expression]
TDDFT	time-dependent DFT
TDSCF	time-dependent self-consistent field [method]
THG	third-harmonic generation
TPA	two-photon absorption
TPCD	two-photon CD
UMO	unmodified MO
UV	ultraviolet
VCD	vibrational CD
VMF	vibration-mode-following [model]
XCC*n*	expectation-value CC*n* [model]
XCCSD	expectation-value CCSD [model]
(X)CCSD	noniterative XCCSD [model]
ZORA	zero-order regular approximation

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NOTE ADDED IN PROOF

Reference to relatively recent work of Kowalski and coworkers on coupled-cluster response properties (see, e.g., refs 948−950 and references therein) and on the completely-renormalized EOM-CC formalism for excited-state energies (see, e.g., ref 951 and references therein) was inadvertently omitted in sections 4.6.3, 5.5, and 5.8.