ANALYTIC ENERGY DERIVATIVES FOR THE DIRECT ITERATIVE APPROACH TO THE GENERALIZED BLOCH EQUATION

Holger MEISSNER[1] and Josef PALDUS[2,+]

Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1; e-mail: [1] holger.meissner@visualanalysis.com, [2] paldus@theochem.uwaterloo.ca

Received March 21, 2001
Accepted July 9, 2001

A general formalism for the analytic energy derivatives in the context of the recently developed state-selective version of the direct iterative approach to the generalized Bloch equation is presented. An explicit formalism is developed for both the gradients and the Hessian by exploiting the so-called Z-vector method. A procedure for the development of the corresponding algorithm for higher than the second-order properties is also briefly outlined.
Keywords: Quantum chemistry; Bloch equation; Analytic derivatives; Geometry optimization; Property calculations; Multireference approach.

A detailed treatment of reaction dynamics – presently limited to small molecular species – generally requires a rather precise knowledge of the full potential energy (hyper)surface (PES). However, the generation of such surfaces for larger molecular systems, involving more than a few degrees of freedom, is beyond the scope of the present-day computational capabilities. Thus, in order to access the information about the various transition states or intermediate transient species, as well as different paths or channels that characterize reactive processes involving polyatomic molecules, or to examine various stereoisomers of a given molecule, most state-of-the-art *ab initio* quantum chemistry codes rely on the evaluation of gradients and, whenever feasible, of the higher-order energy derivatives. The second derivatives or Hessians are then employed to compute vibrational frequencies or, in the case of imaginary frequencies, to assess the instability of the given intermediate species. Indeed, these facilities are presently available for almost all methods that are commonly exploited to treat the electron correlation

+ Also at: Department of Chemistry and Guelph-Waterloo Center for Graduate Work in Chemistry, Waterloo Campus, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.

doi:10.1135/cccc20011164

effects, notably the many-body perturbation theory (MBPT) up to and including the fourth order[1,2], the coupled cluster (CC) approaches, such as the standard CCSD (refs[3–8]), CCSD(T) (ref.[8]), CCSDT-1 (ref.[2]), and even full CCSDT (ref.[1]), as well as for the configuration interaction (CI) approaches[9–11]. Recently, the analytic derivatives technique was also developed for the equations-of-motion coupled cluster (EOM-CC)[12–14] and similarity transformed (ST) EOM-CC (ref.[15]) methods, as well as for multireference (MR) CC approaches[16].

The facility to compute analytical derivatives enables an efficient search of complex multidimensional PESs, which in turn makes it possible to find the location of various extrema, be they local maxima, minima, or saddle points (gradient method[17]) on the potential energy (hyper)surface of a given polyatomic. Essentially the same codes may then be employed to find the energy derivatives with respect to perturbations due to various external fields and thus be used to calculate various many-electron response properties.

Recently, we have developed a new method for the direct iterative solution of the generalized Bloch equation[18–25], referred to as DGB for the sake of brevity. The generalized Bloch equation lies at the heart of genuine multireference (MR) approaches to the many-electron correlation problem. MR approaches are indispensable for a proper handling of degenerate or quasidegenerate systems. Needless to say that such situations almost always arise when breaking genuine chemical bonds. The DGB method enables a great flexibility in introducing various approximations when truncating the full CI expansion at various levels of excitation, including the complete or partial implementation of the coupled cluster Ansatz. The multitude of possible approximation schemes (*cf.* ref.[18]) was first tested on model systems[22] involving four to sixteen hydrogen atoms (particularly the so-called H4 (ref.[26]) and H8 (ref.[27]) models) and, subsequently, on a number of small molecular species[23–25]. Both ground and excited states of closed- and open-shell type were examined. These preliminary applications yielded very encouraging results.

In this paper we present the analytical energy derivatives for the DGB method. The essence of the method is first briefly summarized in Section I, where we also introduce the necessary nomenclature. Section II is then devoted to the evaluation of the first and second derivatives, and presents a general algorithm for this purpose. The results are summarized in Section III.

I. THE ENERGY

In this section we present a brief summary of the direct iterative approach to the solution of the generalized Bloch equation[18] (DGB approach, see Part II (ref.[18]) for details), in order to introduce the necessary notation.

Reference Space

The general MR approaches employ the concept of the *reference* space $\mathcal{M}_0$, representing a suitable, finite-dimensional subspace of the N-electron space $\mathcal{V}$ which is spanned by all possible N-electron configuration states (or Slater determinants) Φ_α. In all practical calculations, $\mathcal{V}$ is also finite dimensional and is given by the choice of the atomic orbital (AO) basis set defining a given *ab initio* model. An n-dimensional (complete or incomplete) reference space $\mathcal{M}_0$ is defined as a linear span of n orthonormal configurations Φ_α, $\alpha \in I_p \equiv \{1, \cdots, n\}$, the remaining configurations Φ_α, $\alpha \in I_q \equiv \{n + 1, \cdots, n + m\}$ defining its orthogonal complement $\mathcal{M}_0^\perp$ in $\mathcal{V}$. The orthogonal projectors onto $\mathcal{M}_0$ and $\mathcal{M}_0^\perp$ are then designated by $\hat{P}$ and $\hat{Q}$, respectively, so that $\hat{P} + \hat{Q} = \hat{1}$, the identity operator on $\mathcal{V} = \mathcal{M}_0 \oplus \mathcal{M}_0^\perp$.

The basic assumption of any MR approach is that with a suitably chosen set of n exact N-electron eigenstates Ψ_a ($a \in I_p$) of a given Hamiltonian $\hat{H}$,

$$\hat{H}\Psi_a = E_a\Psi_a, \qquad a \in I_p, \tag{1}$$

referred to as the *target states*, we can associate an n-dimensional reference space $\mathcal{M}_0$ providing a reasonable zero-order approximation for Ψ_a in a sense that their projections onto $\mathcal{M}_0$, $\hat{P}\Psi_a = \Psi_a^{(0)}$, $a \in I_p$, span $\mathcal{M}_0$, so that

$$\mathcal{M}_0 = \mathrm{Span}\{\Psi_a^{(0)} | a \in I_p\} = \mathrm{Span}\{\Phi_\alpha | \alpha \in I_p\}. \tag{2}$$

Here E_a ($a \in I_p$) designate the corresponding exact eigenvalues of $\hat{H}$, and the n-dimensional space $\mathcal{M} = \mathrm{Span}\{\Psi_a | a \in I_p\}$ is referred to as the *target space*. In the intermediate normalization,

$$\langle \Psi_a^{(0)} | \Psi_a \rangle = \langle \Psi_a^{(0)} | \Psi_a^{(0)} \rangle = 1, \qquad a \in I_p, \tag{3}$$

the target states Ψ_a ($a \in I_p$) may be represented as follows

$$\Psi_a = \Psi_a^{(0)} + \Psi_a^{(\perp)} = \sum_{\alpha \in I_p} g_\alpha^a \Phi_\alpha + \sum_{\lambda \in I_q} c_\lambda^a \Phi_\lambda \,. \tag{4}$$

With this formulation, the main task is to set up the equations of motion that enable us to determine the energies E_a as well as the coefficients $g_\alpha^a = \langle \Phi_\alpha | \Psi_a \rangle, (a, \alpha \in I_p)$, and the wave function expansion coefficients (WECs) $c_\lambda^a = \langle \Phi_\lambda | \Psi_a \rangle, (a \in I_p, \lambda \in I_q)$, defining the reference space component $\Psi_a^{(0)}$ and the outer space component $\Psi_a^{(\perp)}$ of Ψ_a, respectively. This has been done in our earlier work that is described in Part II (ref.[18], *cf.* also refs[19–25]).

We next recall the matrix notation used in Part II. Clearly, both $\{\Phi_\alpha | \alpha \in I_p\}$ and $\{\Psi_a^{(0)} | a \in I_p\}$ can serve as a basis for $\mathcal{M}_0$. However, since the latter basis is nonorthogonal, we also introduce the corresponding dual basis $\tilde{\Psi}_a^{(0)}$, namely

$$\langle \tilde{\Psi}_a^{(0)} | \Psi_b^{(0)} \rangle = \langle \Psi_a^{(0)} | \tilde{\Psi}_b^{(0)} \rangle = \delta_{ab} \,. \tag{5}$$

We then define row matrices

$$|\mathbf{\Phi}\rangle = (|\mathbf{\Phi}_p\rangle, |\mathbf{\Phi}_q\rangle) \,, \tag{6}$$

with

$$|\mathbf{\Phi}_p\rangle = (|\Phi_1\rangle, |\Phi_2\rangle, \ldots, |\Phi_n\rangle) \,, \quad |\mathbf{\Phi}_q\rangle = (|\Phi_{n+1}\rangle, |\Phi_{n+2}\rangle, \ldots, |\Phi_{n+m}\rangle) \tag{7}$$

and

$$|\mathbf{\Psi}^{(0)}\rangle = (|\Psi_1^{(0)}\rangle, \ldots, \Psi_n^{(0)}\rangle) \,, \quad |\mathbf{\Psi}\rangle = (|\Psi_1\rangle, \ldots, \Psi_n\rangle) \,, \tag{8}$$

so that

$$\langle \mathbf{\Phi} | \mathbf{\Phi} \rangle = \mathbf{1}_{M \times M} = \langle \mathbf{\Phi}_p | \mathbf{\Phi}_p \rangle \oplus \langle \mathbf{\Phi}_q | \mathbf{\Phi}_q \rangle = \mathbf{1}_{n \times n} \oplus \mathbf{1}_{m \times m} \equiv \mathbf{1}_p \oplus \mathbf{1}_q \,, \tag{9}$$

and

$$\langle \mathbf{\Psi}^{(0)} | \mathbf{\Psi} \rangle = \mathbf{1}_{n \times n} = \mathbf{1}_p \,, \quad \langle \mathbf{\Psi}^{(0)} | \mathbf{\Psi}^{(0)} \rangle = \mathbf{S} \,, \tag{10}$$

where $M = n + m$ is the dimension of the N-electron space considered, $M = \dim \mathcal{V} = \dim \mathcal{M}_0 + \dim \mathcal{M}_0^\perp$, and $\mathbf{S}$ is the overlap matrix $\mathbf{S} = ||\langle \Psi_a^{(0)} | \Psi_b^{(0)} \rangle||$. Further

$$\langle \mathbf{\Phi}_p | \mathbf{\Psi}^{(0)} \rangle = \langle \mathbf{\Phi}_p | \mathbf{\Psi} \rangle = \mathbf{G} = || g_\alpha^a ||_{n \times n} , \quad \langle \mathbf{\Phi}_q | \mathbf{\Psi} \rangle = \mathbf{C} = || c_\lambda^a ||_{m \times n} , \tag{11}$$

so that

$$|\mathbf{\Psi}\rangle = |\mathbf{\Psi}^{(0)}\rangle + |\mathbf{\Psi}^{(\perp)}\rangle , \tag{12}$$

with

$$|\mathbf{\Psi}^{(0)}\rangle = |\mathbf{\Phi}_p\rangle \mathbf{G} \quad \text{and} \quad |\mathbf{\Psi}^{(\perp)}\rangle = |\mathbf{\Phi}_q\rangle \mathbf{C} , \tag{13}$$

the latter designating the external component of $|\mathbf{\Psi}\rangle$.

The dual basis $\{\tilde{\Psi}_a^{(0)}\}$, satisfying Eq. (*5*), is given by

$$|\tilde{\mathbf{\Psi}}^{(0)}\rangle = |\mathbf{\Psi}^{(0)}\rangle \mathbf{S}^{-1} = |\mathbf{\Phi}_p\rangle \mathbf{G} \mathbf{S}^{-1} , \tag{14}$$

since $\langle \mathbf{\Psi}^{(0)} | \mathbf{\Psi}^{(0)} \rangle = \mathbf{G}^\dagger \mathbf{G} = \mathbf{S}$ defines the metric for the basis $\{\Psi_a^{(0)}\}$. The projection operator $\hat{P}$ onto $\mathcal{M}_0$ can take any of the following forms

$$\hat{P} = |\mathbf{\Phi}_p\rangle \langle \mathbf{\Phi}_p| = |\tilde{\mathbf{\Psi}}^{(0)}\rangle \langle \mathbf{\Psi}^{(0)}| = |\mathbf{\Psi}^{(0)}\rangle \langle \tilde{\mathbf{\Psi}}^{(0)}| , \tag{15}$$

while

$$\hat{Q} = \hat{1} - \hat{P} = |\mathbf{\Phi}_q\rangle \langle \mathbf{\Phi}_q| , \tag{16}$$

so that

$$\hat{P} |\mathbf{\Psi}\rangle = |\mathbf{\Phi}_p\rangle \mathbf{G} = |\mathbf{\Psi}^{(0)}\rangle \quad \text{and} \quad \hat{Q} |\mathbf{\Psi}\rangle = |\mathbf{\Phi}_q\rangle \mathbf{C} = |\mathbf{\Psi}^{(\perp)}\rangle . \tag{17}$$

The first task in any MR procedure is thus the choice of a suitable reference space $\mathcal{M}_0$, which contains zero-order reference functions that represent a dominant component of the relevant states and correctly describe the dissociation channel(s) of interest.

Equations of Motion

The key role in the determination of the coefficients g_α^a and c_λ^a is played by the projector $\hat{P}$, Eq. (*15*), and its wave-operator-type counterpart $\hat{U}$ (for precise formulation, see *e.g.* ref.[28]),

$$|\Psi\rangle = \hat{U}|\Psi^{(0)}\rangle = \hat{U}\hat{P}|\Psi\rangle = \hat{U}|\Psi\rangle\,, \qquad \hat{U} = \hat{U}\hat{P}\,, \tag{18}$$

so that

$$\hat{U}|\Phi_q\rangle = 0\,. \tag{19}$$

Using this operator, we define the effective Hamiltonian $\hat{H}^{(\mathrm{eff})}$, acting in $\mathcal{M}_0$, whose eigenvalues E_a are identical with those of $\hat{H}$, Eq. (*1*). Clearly, this is only possible for a *finite* set of states Ψ_a spanning the target space $\mathcal{M}$. Indeed, projecting the Schrödinger equation (*1*) onto $\mathcal{M}_0$ using the projector $\hat{P}$, we obtain using Eq. (*18*) that

$$\hat{P}\hat{H}\hat{U}\hat{P}\,\Psi_a^{(0)} \equiv \hat{H}^{(\mathrm{eff})}\Psi_a^{(0)} = E_a\Psi_a^{(0)}\,. \tag{20}$$

Thus, diagonalizing $\hat{H}^{(\mathrm{eff})}$, represented by an $n \times n$ matrix $\mathbf{H}^{(\mathrm{eff})}$, we find both the exact energies E_a and the *inner space* coefficients $g_\alpha^a = \langle\Phi_\alpha|\hat{U}|\Psi_a^{(0)}\rangle$. The $\mathcal{M}_0$ component $\Psi_a^{(0)}$ of Ψ_a clearly accounts for the static and non-dynamic correlation effects.

In order to determine the outer part of Ψ_a that is responsible for the dynamic correlation, we rely on the generalized Bloch equation $\hat{U}\hat{H}\hat{U}\,\Psi_a^{(0)} = \hat{H}\hat{U}\,\Psi_a^{(0)}$, which is obtained by acting with $\hat{U}$ on the Schrödinger equation (*1*) and using Eq. (*18*). This equation then determines the *outer space* coefficients

$$c_\lambda^a = \langle\Phi_\lambda|\hat{U}|\Psi_a\rangle = \langle\Phi_\lambda|\hat{U}|\Psi_a^{(0)}\rangle\,, \quad a \in I_p\,, \lambda \in I_q\,, \tag{21}$$

as well as $\hat{H}^{(\mathrm{eff})}$. In matrix form, the Bloch equation can be represented as follows

$$\langle\Phi_q|(1-\hat{U})\,\hat{H}\hat{U}|\Psi^{(0)}\rangle = 0\,, \tag{22}$$

while the energies are given by

$$\mathbf{E} = \langle\tilde{\Psi}^{(0)}|\hat{H}\hat{U}|\Psi^{(0)}\rangle = \mathbf{S}^{-1}\mathbf{G}^\dagger\langle\Phi_p|\hat{H}\hat{U}|\Psi^{(0)}\rangle\,. \tag{23}$$

These two equations, Eqs (*22*) and (*23*), thus represent the basic formulas for the derivation of the explicit representation for the derivatives of the energy. In our derivations we shall also rely on the following useful expressions

$$\langle \tilde{\mathbf{\Psi}}^{(0)} | \hat{U} | \mathbf{\Psi}^{(0)} \rangle = \mathbf{1_p} , \quad \langle \mathbf{\Phi}_q | \hat{U} | \mathbf{\Psi}^{(0)} \rangle = \mathbf{C} , \quad \langle \mathbf{\Phi}_q | \hat{U} | \mathbf{\Phi}_q \rangle = 0 . \tag{24}$$

II. DERIVATIVES OF THE ENERGY

In general, the molecular electronic energy depends on parameters appearing in the Hamiltonian. Such parameters represent either the nuclear coordinates, when we are interested in molecular geometry, or characterize the property operator $\hat{O}$ that is added to the standard Hamiltonian $\hat{H}_0$, $\hat{H}(\chi) = \hat{H}_0 + \chi\hat{O}$, when considering properties. The key principle that describes the energy dependence on the parameters characterizing the Hamiltonian is the well-known Hellmann–Feynman theorem[29]

$$\frac{\mathrm{d}E(\chi)}{\mathrm{d}\chi} = \langle \Psi(\chi) | \frac{\partial \hat{\mathrm{H}}(\chi)}{\partial \chi} | \Psi(\chi) \rangle , \tag{25}$$

where the exact eigenstate $\Psi(\chi)$ of $\hat{H}(\chi)$ is assumed to be normalized, *i.e.* $\langle \Psi(\chi) | \Psi(\chi) \rangle = 1$. We note that Eq. (*25*) holds not only for the exact wave function $|\Psi\rangle$, but also for certain classes of (variational) wave functions.

Since the approaches we are interested in are not necessarily variational (*e.g.*, the DGB and CC methods), the Hellmann–Feynman theorem does not generally hold. Nonetheless, Eq. (*25*) represents a useful *approximate formula* when estimating the derivative on the left-hand side (see also ref.[30], pp. 89–104, for an overview of approaches to properties, especially in connection with CC methods).

First Derivatives

The starting point for our considerations is the energy representation, Eq. (*23*), and the generalized Bloch equation, Eq. (*22*), *i.e.*,

$$\mathbf{E}(\chi) = \langle \tilde{\mathbf{\Psi}}^{(0)}(\chi) | \hat{H}(\chi) \hat{U}(\chi) | \mathbf{\Psi}^{(0)}(\chi) \rangle , \tag{26}$$

$$\langle \mathbf{\Phi}_q | (1 - \hat{U}(\chi))\, \hat{H}(\chi)\hat{U}(\chi) | \mathbf{\Psi}^{(0)}(\chi) \rangle = 0 \,. \qquad (27)$$

Here we assume that the system depends on n parameters designated by $\chi = \{\chi_1, \chi_2, ..., \chi_n\}$ – be they nuclear displacements with respect to a given configuration or the parameters defining the perturbed Hamiltonian, $\hat{H}(\chi) = \hat{H}_0 + \chi\hat{O}$.

In addition, we represent the Hamiltonian in its normal product, second-quantized form,

$$\hat{H}(\chi) \equiv \hat{H}_N(\chi) = \hat{F}(\chi) + \hat{V}(\chi) = \sum_{p,q} f_{pq}\, N[\hat{a}_p^\dagger \hat{a}_q] + \frac{1}{4} \sum_{p,q,r,s} v_{pqrs}\, N[\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r] , \quad (28)$$

where f_{pq} and v_{pqrs} designate, respectively, the one-electron (Fock operator) and two-electron integrals, $\hat{a}_p^\dagger$ ($\hat{a}_p$) is the creation (annihilation) operator associated with the spin orbital $|p\rangle$, and N[···] designates the normal product with respect to the Fermi vacuum (for more details, see *e.g.* refs[1,28,30] and references therein). Further, the symbol χ represents either a single parameter (as in the case of single perturbing field $\hat{O}$) or a set of parameters $\chi = \{\chi_1, \chi_2, ..., \chi_n\}$. The dependence of the Hamiltonian on χ is either explicit through f_{pq} and v_{pqrs} due to the external fields or nuclear displacements, or implicit through the orbital basis functions, since the latter vary with molecular displacements or external perturbations (*e.g.* the external field strength). The basis of Slater determinants, $\{|\mathbf{\Phi}_p\rangle, |\mathbf{\Phi}_q\rangle\}$, may then be considered to be independent of the parameters χ.

For practical calculations of molecular gradients or one-electron properties, we have to evaluate the derivatives at $\chi = 0$ and, in the former case, we also have to add the analytic derivatives of the nuclear repulsion energy and the derivatives of the energy of the reference determinat at $\chi = 0$ in order to obtain the derivatives of the total energy. Therefore, all the following expressions for the derivatives are considered to be evaluated at $\chi = 0$. For the wave operator $\hat{U}$, the Hamiltonian $\hat{H}$, and the energy **E**, as well as for their first derivatives, we thus write

$$\hat{U} = \hat{U}(\chi)|_{\chi=0} \,, \quad \partial_i \hat{U} = \partial_i \hat{U}(\chi)|_{\chi=0} \,, \qquad (29)$$

$$\hat{H} = \left(\hat{F}(\chi) + \hat{V}(\chi)\right)|_{\chi=0} \,, \quad \partial_i \hat{H} = \left(\partial_i \hat{F}(\chi) + \partial_i \hat{V}(\chi)\right)|_{\chi=0} \,, \qquad (30)$$

$$\mathbf{E} = \mathbf{E}(\chi)|_{\chi=0} , \quad \partial_i \mathbf{E} = \partial_i \mathbf{E}(\chi)|_{\chi=0} . \tag{31}$$

In Eqs (*29*)–(*31*) and in the following text, we use the ubiquitous shorthand notation for partial differentiation, $\partial/\partial\chi_i \equiv \partial_i$, $\partial^2/\partial\chi_i\partial\chi_j \equiv \partial_{ij}$, *etc.*

In order to calculate the energy gradient, we have to differentiate Eq. (*26*) with respect to the parameters χ. Applying the partial differentiation operator ∂_i to Eq. (*26*) or Eq. (*23*), we obtain the components of the gradient of the energy, namely

$$\begin{aligned} \partial_i \mathbf{E} = {} & \partial_i(\mathbf{S}^{-1}\mathbf{G}^{\dagger})\langle \mathbf{\Phi}_p | \hat{H}\hat{U} | \mathbf{\Psi}^{(0)} \rangle \\ & + \langle \tilde{\mathbf{\Psi}}^{(0)} | \hat{H}\hat{U} | \mathbf{\Phi}_p \rangle \partial_i(\mathbf{G}) \\ & + \langle \tilde{\mathbf{\Psi}}^{(0)} | (\partial_i \hat{H})\hat{U} + \hat{H}(\partial_i \hat{U}) | \mathbf{\Psi}^{(0)} \rangle . \end{aligned} \tag{32}$$

On the right-hand side of Eq. (*32*), all the terms are known, in principle, from the energy calculations, except $\partial_i(\mathbf{GS}^{-1})$ or $\partial_i(\mathbf{G})$, and $\partial_i\hat{U}$. Thus, when using the MR formalism, we must rely not only on the generalized Bloch equation in order to determine $\partial_i\hat{U}$, but also on the effective Hamiltonian in order to obtain equations for $\partial_i(\mathbf{G})$. To avoid this procedure, which leads to coupled algebraic equations as in the case of the energy calculation, we consider a simpler case, assuming that the coefficients of the reference functions **G** are fixed, *i.e.* $\mathbf{G}(\chi) = \mathbf{G}(0)$, so that $\partial_i(\mathbf{G}) = 0$. This requirement is realized in the so-called *state-selective* (SS) version of the DGB method, in which case the Hamiltonian is first diagonalized within the model space $\mathcal{M}_0$ and the resulting eigenstates are then handled one at a time. Clearly, the biorthogonal basis then simply becomes $\langle \mathbf{\Psi}^{(0)}|$ by construction (so that $\mathbf{S} = \mathbf{1_p}$). We can thus drop the first two terms on the right-hand side of Eq. (*32*) and set $\langle \tilde{\mathbf{\Psi}}^{(0)}| = \langle \mathbf{\Psi}^{(0)}|$.

In the spirit of the SS approach, we thus consider a single reference state, *e.g.* $|\Psi_a^{(0)}\rangle$. This implies that the basis set $\{|\mathbf{\Phi}_q\rangle\}$, $q \in I'_q = I_q \cup (I_p \backslash \{a\})$, now contains $|\Phi_q\rangle \in \mathcal{M}_0^{\perp}$ when $q \in I_q$ as well as $|\Phi_q\rangle \equiv |\Psi_b^{(0)}\rangle \in \mathcal{M}_0$ when $q = b \in I_p \backslash \{a\}$. With this new notation, the energy derivative becomes

$$\partial_i E_a = \langle \Psi_a^{(0)} | (\partial_i \hat{H})(\hat{P} + \hat{Q})\hat{U} + \hat{H}(\hat{P} + \hat{Q})(\partial_i \hat{U}) | \Psi_a^{(0)} \rangle$$

$$= \langle \Psi_a^{(0)} | (\partial_i \hat{H}) | \Psi_a \rangle + \langle \Psi_a^{(0)} | \hat{H} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | \partial_i \hat{U} | \Psi_a^{(0)} \rangle \tag{33}$$

$$= \langle \Psi_a^{(0)} | \partial_i \hat{H} | \Psi_a^{(0)} \rangle + \langle \Psi_a^{(0)} | \partial_i \hat{H} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | \hat{U} | \Psi_a^{(0)} \rangle$$

$$+ \langle \Psi_a^{(0)} | \hat{H} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | \partial_i \hat{U} | \Psi_a^{(0)} \rangle .$$

Here, we used the fact that $\langle \Psi_a^{(0)} | \partial_i \hat{U} | \Psi_a^{(0)} \rangle = \partial_i \langle \Psi_a^{(0)} | \hat{U} | \Psi_a^{(0)} \rangle = 0$ (*cf.* the first Eq. (*24*)). Since $\hat{H}(\chi)$, $\hat{U}(\chi)$, and therefore $\partial_i \hat{H}(\chi)$, are known at $\chi = 0$, only $\partial_i \hat{U}$ must be found. Specifically, we have to determine $\langle \mathbf{\Phi}_q | \partial_i \hat{U} | \Psi_a^{(0)} \rangle$. Note that the first term on the right-hand side of the last Eq. (*33*) restates the Hellmann–Feynman theorem, Eq. (*25*), for the case of the "unperturbed" reference state $|\Psi_a^{(0)}\rangle$.

In the subsequent development, leading to the determination of the first derivatives of the WECs, we follow a more or less standard strategy (*cf.* refs[8,30], and references therein), except that we rely on the generalized Bloch equation rather than, *e.g.*, the standard SR CC equations. Thus, differentiating Eq. (*27*), we find

$$\partial_i \langle \mathbf{\Phi}_q | (1 - \hat{U}) \hat{H} \hat{U} | \Psi_a^{(0)} \rangle = \tag{34}$$

$$\langle \mathbf{\Phi}_q | (-(\partial_i \hat{U}) \hat{H} \hat{U} + (1 - \hat{U})(\partial_i \hat{H}) \hat{U} + (1 - \hat{U}) \hat{H} (\partial_i \hat{U})) | \Psi_a^{(0)} \rangle = 0 ,$$

and inserting the identity $1 = \hat{P} + \hat{Q}$ between $\partial_i \hat{U}$ and $\hat{H}$ in the first term, and between $\hat{H}$ and $\partial_i \hat{U}$ in the last term, we obtain after some manipulations (recall that $\hat{U} = \hat{U}\hat{P}$) the following matrix representation for the derivatives of the wave operator,

$$\langle \mathbf{\Phi}_q | \partial_i \hat{U} | \Psi_a^{(0)} \rangle \langle \Psi_a^{(0)} | \hat{H} \hat{U} | \Psi_a^{(0)} \rangle - \langle \mathbf{\Phi}_q | (1 - \hat{U}) \hat{H} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | \partial_i \hat{U} | \Psi_a^{(0)} \rangle = \tag{35}$$

$$\langle \mathbf{\Phi}_q | \hat{\Pi}^{(i)} | \Psi_a^{(0)} \rangle ,$$

where $\hat{\Pi}^{(i)}$ is the Bloch-transformed derivative of the Hamiltonian:

$$\hat{\Pi}^{(i)} \equiv (1 - \hat{U})(\partial_i \hat{H}) \hat{U} . \tag{36}$$

Since $\langle \Psi_a^{(0)} | \hat{H} \hat{U} | \Psi_a^{(0)} \rangle$ represents the energy E_a (*cf.* Eq. (*26*)), we can simplify Eq. (*35*) as follows

$$\langle \mathbf{\Phi}_q | \partial_i \hat{U} | \Psi_a^{(0)} \rangle E_a - \langle \mathbf{\Phi}_q | (1 - \hat{U}) \hat{H} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | \partial_i \hat{U} | \Psi_a^{(0)} \rangle = \langle \mathbf{\Phi}_q | \hat{\Pi}^{(i)} | \Psi_a^{(0)} \rangle , \quad (37)$$

yielding an ordinary linear algebraic system of equations for the derivatives $\langle \mathbf{\Phi}_q | \partial_i \hat{U} | \Psi_a^{(0)} \rangle$, namely

$$\{ \langle \mathbf{\Phi}_q | E_a \mathbf{1}_\mathbf{q} - (1 - \hat{U}) \hat{H} | \mathbf{\Phi}_q \rangle \} \langle \mathbf{\Phi}_q | \partial_i \hat{U} | \Psi_a^{(0)} \rangle = \langle \mathbf{\Phi}_q | \hat{\Pi}^{(i)} | \Psi_a^{(0)} \rangle . \quad (38)$$

Solving formally Eq. (*38*) for $\langle \mathbf{\Phi}_q | \partial_i \hat{U} | \Psi_a^{(0)} \rangle$ and inserting into the gradient component of the energy, Eq. (*33*), we obtain

$$\partial_i E_a = \langle \Psi_a^{(0)} | \partial_i \hat{H} | \Psi_a \rangle + \langle \Psi_a^{(0)} | \hat{H} | \mathbf{\Phi}_q \rangle [\langle \mathbf{\Phi}_q | E_a \mathbf{1}_\mathbf{q} - \hat{\mathcal{H}} | \mathbf{\Phi}_q \rangle]^{-1} \langle \mathbf{\Phi}_q | \hat{\Pi}^{(i)} | \Psi_a^{(0)} \rangle \quad (39)$$

$$= \langle \Psi_a^{(0)} | \partial_i \hat{H} | \Psi_a \rangle + \langle \Psi_a^{(0)} | \hat{\Lambda} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | \hat{\Pi}^{(i)} | \Psi_a^{(0)} \rangle ,$$

where $\hat{\mathcal{H}} \equiv (1 - \hat{U}) \hat{H}$. Following the so-called "Z-vector" or "interchange" method[9,31,32] (see also refs[8,30]), we introduced in the last step the operator $\hat{\Lambda}$, which is independent of χ, and whose vector components in $\{|\mathbf{\Phi}_q\rangle\}$ are given by the solution of the system of linear equations

$$\langle \Psi_a^{(0)} | \hat{\Lambda} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | (E_a \mathbf{1}_\mathbf{q} - \hat{\mathcal{H}}) | \mathbf{\Phi}_q \rangle = \langle \Psi_a^{(0)} | \hat{H} | \mathbf{\Phi}_q \rangle . \quad (40)$$

Defining the elements of column matrices $\boldsymbol{\lambda}^a$ and $\mathbf{h}^a$ as follows

$$\lambda_\mu^a = \langle \Psi_a^{(0)} | \hat{\Lambda} | \Phi_\mu \rangle , \qquad h_\mu^a = \langle \Psi_a^{(0)} | \hat{H} | \Phi_\mu \rangle , \quad (41)$$

as well as the matrix elements

$$A_{\mu\nu} = E_a \delta_{\mu\nu} - \mathcal{H}_{\mu\nu} , \quad (42)$$

$$\mathcal{H}_{\mu\nu} = \langle \Phi_\mu | (1 - \hat{U}) \hat{H} | \Phi_\nu \rangle = \langle \Phi_\mu | \hat{H} | \Phi_\nu \rangle - c_\mu^a \langle \Psi_a^{(0)} | \hat{H} | \Phi_\nu \rangle ,$$

we can rewrite Eq. (*40*) in the following standard matrix form

$$\hat{\mathbf{A}}^T \boldsymbol{\lambda}^a = \mathbf{h}^a \,. \tag{43}$$

At this point we should recall the fact that in the case that μ and/or $\nu \in I_p \backslash \{a\}$, we have that $\langle \Psi_b^{(0)} | \hat{H} | \Psi_c^{(0)} \rangle = E_b^{(0)} \delta_{bc}$, where $E_b^{(0)}$ is the energy expectation value of $|\Psi_b^{(0)}\rangle$. We must also stress that this "interchange" method completely eliminates the dependence on the first derivatives of WECs.

Solving now Eq. (*43*) for $\boldsymbol{\lambda}^a$, and substituting into Eq. (*39*), we can write for the components of the energy gradient

$$\partial_i E_a = \langle \mathbf{g}^a | \hat{\mathbf{H}}_p^{(i)} \mathbf{g}^a \rangle + \langle \mathbf{g}^a | \hat{\mathbf{H}}_q^{(i)} \mathbf{c}^a \rangle + \langle \boldsymbol{\lambda}^a | \mathbf{b}^{(i,a)} \rangle \,, \tag{44}$$

where the components of $\mathbf{b}^{(i,a)}$ are given by

$$\begin{aligned} b_\mu^{(i,a)} = \Pi_{\mu a}^{(i)} &= \langle \Phi_\mu | (1 - \hat{U})(\partial_i \hat{H}) \hat{U} | \Psi_a^{(0)} \rangle \\ &= \langle \Phi_\mu | \partial_i \hat{H} | \Psi_a^{(0)} \rangle + \sum_\nu \langle \Phi_\mu | \partial_i \hat{H} | \Phi_\nu \rangle c_\nu^a \\ &\quad - c_\mu^a \{ \langle \Psi_a^{(0)} | \partial_i \hat{H} | \Psi_a^{(0)} \rangle + \sum_\nu \langle \Psi_a^{(0)} | \partial_i \hat{H} | \Phi_\nu \rangle c_\nu^a \} \,, \end{aligned} \tag{45}$$

while $\mathbf{g}^a = || g_\alpha^a ||$ are the coefficients of the reference function (*cf.* Eq. (*4*)), and $\mathbf{c}^a = || c_\mu^a || = || \langle \Phi_\mu | \hat{U} | \Psi_a^{(0)} \rangle ||$ are WECs associated either with outer space basis states $|\Phi_\mu\rangle \in \mathcal{M}_0^\perp$ when $\mu = q \in I_q$ or with the remainder of $\mathcal{M}_0$ relative to $|\Psi_a^{(0)}\rangle$ when $\mu = b \in I_p \backslash \{a\}$ and $|\Phi_b\rangle \equiv |\Psi_b^{(0)}\rangle$. Further, we define

$$(\hat{\mathbf{H}}_p^{(i)})_{\alpha\beta} = (\langle \Phi_\alpha | \partial_i \hat{H} | \Phi_\beta \rangle) = \mathcal{G}_{\alpha\beta}^i \,, \quad \alpha, \beta \in I_p \,, \tag{46}$$

$$(\hat{\mathbf{H}}_q^{(i)})_{\alpha\mu} = (\langle \Phi_\alpha | \partial_i \hat{H} | \Phi_\mu \rangle) = \mathcal{G}_{\alpha\mu}^i \,, \quad \alpha \in I_p \,, \ \mu \in I_q' \,, \tag{47}$$

where in the case that $\mu \in I_p \backslash \{a\}$ we have that

$$\mathcal{G}_{\alpha b}^i = \sum_{\beta \in I_p} \mathcal{G}_{\alpha\beta}^i \, g_\beta^b \,. \tag{48}$$

Explicitly, Eq. (*45*) takes the form

$$\partial_i E_a = \sum_{\alpha,\beta \in I_p} g^a_\alpha \mathcal{G}^i_{\alpha\beta} g^a_\beta + \sum_{\substack{\alpha \in I_p \\ \mu \in I'_q}} g^a_\alpha \mathcal{G}^i_{\alpha\mu} c^a_\mu + \sum_{\mu \in I'_q} \lambda^a_\mu \{\gamma^i_{\mu a} - c^a_\mu \sum_{\beta \in I_p} g^a_\beta \gamma^i_{\beta a}\}, \qquad (49)$$

where

$$\gamma^i_{\zeta a} = \sum_{\alpha \in I_p} \mathcal{G}^i_{\zeta\alpha} g^a_\alpha + \sum_{\gamma \in I'_q} \mathcal{G}^i_{\zeta\gamma} c^a_\gamma . \qquad (50)$$

An important feature of this result is the fact that Eq. (*49*) is completely independent of the derivatives of the WECs c^a_μ. This will no longer be the case when we consider higher derivatives of the energy.

Since the g^a_α, c^a_μ, and λ^a_μ are either available or easily generated once the DGB calculation is carried out, the only quantities that remain to be evaluated are the matrix elements $\mathcal{G}^i_{\mu\nu}$ of the derivatives of the Hamiltonian (*cf.* also Eq. (*30*)), which depend both on the basis functions and the MO coefficients (and, eventually, on the external field, as already mentioned), and thus on the parameters χ. The explicit expressions for the derivatives of the Hamiltonian, $\partial_i \hat{F}(\chi)$ and $\partial_i \hat{V}(\chi)$ at $\chi = 0$ can be found, for example, in Section III.B of ref.[1] (*cf.* also the Appendix).

Second Derivatives

Besides the first derivatives, the second derivatives are essential when evaluating higher-order properties, *e.g.*, polarizabilities and susceptibilities, and in the case of nuclear displacements, when determining the force constants and vibrational frequencies. Following the same procedure as for the first derivative, we thus next present the required formalism enabling the computation of the second derivatives.

Formally, we first apply the partial derivative ∂_j to Eq. (*33*), yielding the second derivatives of the energy

$$\begin{aligned}
\partial_{ij} E_a(\chi)\big|_{\chi=0} &= \partial_j \{\langle \Psi^{(0)}_a | \partial_i \hat{H} | \Psi^{(0)}_a \rangle + \langle \Psi^{(0)}_a | \partial_i \hat{H} | \Phi_q \rangle \langle \Phi_q | \hat{U} | \Psi^{(0)}_a \rangle \qquad (51) \\
&\quad + \langle \Psi^{(0)}_a | \hat{H} | \Phi_q \rangle \langle \Phi_q | \partial_i \hat{U} | \Psi^{(0)}_a \rangle\} \\
&= \langle \Psi^{(0)}_a | \partial_{ij} \hat{H} | \Psi^{(0)}_a \rangle + \langle \Psi^{(0)}_a | \partial_{ij} \hat{H} | \Phi_q \rangle \langle \Phi_q | \hat{U} | \Psi^{(0)}_a \rangle \\
&\quad + \langle \Psi^{(0)}_a | \partial_i \hat{H} | \Phi_q \rangle \langle \Phi_q | \partial_j \hat{U} | \Psi^{(0)}_a \rangle + \langle \Psi^{(0)}_a | \partial_j \hat{H} | \Phi_q \rangle \langle \Phi_q | \partial_i \hat{U} | \Psi^{(0)}_a \rangle \\
&\quad + \langle \Psi^{(0)}_a | \hat{H} | \Phi_q \rangle \langle \Phi_q | \partial_{ij} \hat{U} | \Psi^{(0)}_a \rangle .
\end{aligned}$$

The only new quantities that have to be determined are the second partial derivatives of the wave operator and of the Hamiltonian. Again, the latter derivatives can be calculated directly (for the pertinent explicit expressions, we refer the reader to Section II.B of ref.[2]). Further, we use analogous notation to that of Eqs (*29*)–(*31*), implying that all quantities are evaluated at $\chi = 0$.

We can thus proceed in the same way as in the case of the first derivatives, namely, we determine the second derivatives of the wave operator $\hat{U}$ by relying on the generalized Bloch equation, or its first derivative, Eq. (*34*), yielding

$$\partial_j\{\langle \mathbf{\Phi}_q| - (\partial_i \hat{U})\,\hat{H}\hat{U} + (1-\hat{U})(\partial_i \hat{H})\,\hat{U} + (1-\hat{U})\,\hat{H}(\partial_i \hat{U})|\Psi_a^{(0)}\rangle\} = 0\ . \qquad (52)$$

To find the matrix elements for $\langle \mathbf{\Phi}_q|\partial_{ij}\hat{U}|\Psi_a^{(0)}\rangle$, we follow the above outlined procedure for $\langle \mathbf{\Phi}_q\,|\partial_i \hat{U}|\Psi_a^{(0)}\rangle$. Thus, in complete analogy to Eq. (*35*), we find

$$\langle \mathbf{\Phi}_q\,|\partial_{ij}\hat{U}|\Psi_a^{(0)}\rangle\langle\Psi_a^{(0)}|\hat{H}\hat{U}|\Psi_a^{(0)}\rangle - \langle \mathbf{\Phi}_q|\hat{\mathcal{H}}|\,\mathbf{\Phi}_q\rangle\langle \mathbf{\Phi}_q\,|\,\partial_{ij}\hat{U}\,|\Psi_a^{(0)}\rangle = \langle \mathbf{\Phi}_q|\hat{\Pi}^{(ij)}|\,\Psi_a^{(0)}\rangle, \qquad (53)$$

where we defined

$$\begin{aligned}\hat{\Pi}^{(ij)} \equiv\ & -(\partial_i\hat{U})\partial_j(\hat{H}\hat{U}) + \partial_j[(1-\hat{U})\,(\partial_i\hat{H})\hat{U}] + \partial_j[(1-\hat{U})\,\hat{H}](\partial_i\hat{U}) \qquad (54)\\ =\ & -\{(\partial_i\hat{U})(\partial_j\hat{H}) + (\partial_j\hat{U})(\partial_i\hat{H}) - (1-\hat{U})(\partial_{ij}\hat{H})\}\hat{U}\\ & -\{(\partial_i\hat{U})\hat{H} - (1-\hat{U})\,(\partial_i\hat{H})\}\,(\partial_j\hat{U})\\ & -\{(\partial_j\hat{U})\hat{H} - (1-\hat{U})\,(\partial_j\hat{H})\}\,(\partial_i\hat{U})\ .\end{aligned}$$

Replacing $\langle\Psi_a^{(0)}|\hat{H}\hat{U}|\Psi_a^{(0)}\rangle$ by the energy E_a, we can write Eq. (*53*) as follows

$$\langle \mathbf{\Phi}_q\,|\partial_{ij}\hat{U}|\Psi_a^{(0)}\rangle E_a - \langle \mathbf{\Phi}_q|\hat{\mathcal{H}}|\,\mathbf{\Phi}_q\rangle\,\langle \mathbf{\Phi}_q\,|\partial_{ij}\hat{U}|\Psi_a^{(0)}\rangle = \langle \mathbf{\Phi}_q\,|\hat{\Pi}^{(i)}|\,\Psi_a^{(0)}\rangle, \qquad (55)$$

yielding again a linear system

$$\{\langle \mathbf{\Phi}_q\,|E_a\mathbf{1}_\mathbf{q} - \hat{\mathcal{H}}\,|\mathbf{\Phi}_q\rangle\}\,\langle \mathbf{\Phi}_q\,|\,\partial_{ij}\hat{U}|\Psi_a^{(0)}\rangle = \langle \mathbf{\Phi}_q\,|\hat{\Pi}^{(ij)}|\,\Psi_a^{(0)}\rangle. \qquad (56)$$

The vector components of $\langle \mathbf{\Phi}_q | \hat{\Pi}^{(ij)} | \Psi_a^{(0)} \rangle$ may be transformed as follows

$$\begin{aligned}
\langle \Phi_\mu | \Pi^{(ij)} | \Psi_a^{(0)} \rangle = & - \langle \Phi_\mu | \partial_i \hat{U} | \Psi_a^{(0)} \rangle \{ \langle \Psi_a^{(0)} | \partial_j \hat{H} | \Psi_a^{(0)} \rangle \\
& + \sum_\nu \langle \Psi_a^{(0)} | \partial_j \hat{H} | \Phi_\nu \rangle \langle \Phi_\nu | \hat{U} | \Psi_a^{(0)} \rangle \\
& + \sum_\nu \langle \Psi_a^{(0)} | \hat{H} | \Phi_\nu \rangle \langle \Phi_\nu | \partial_j \hat{U} | \Psi_a^{(0)} \rangle \} \\
& - \langle \Phi_\mu | \partial_j \hat{U} | \Psi_a^{(0)} \rangle \{ \langle \Psi_a^{(0)} | \partial_i \hat{H} | \Psi_a^{(0)} \rangle \\
& + \sum_\nu \langle \Psi_a^{(0)} | \partial_i \hat{H} | \Phi_\nu \rangle \langle \Phi_\nu | \hat{U} | \Psi_a^{(0)} \rangle \\
& + \sum_\nu \langle \Psi_a^{(0)} | \hat{H} | \Phi_\nu \rangle \langle \Phi_\nu | \partial_i \hat{U} | \Psi_a^{(0)} \rangle \} \\
& + \langle \Phi_\mu | (1 - \hat{U}) \partial_{ij} \hat{H} | \Psi_a^{(0)} \rangle \\
& + \sum_\nu \{ \langle \Phi_\mu | (1 - \hat{U}) \partial_i \hat{H} | \Phi_\nu \rangle \langle \Phi_\nu | \partial_j \hat{U} | \Psi_a^{(0)} \rangle \\
& + \langle \Phi_\mu | (1 - \hat{U}) \partial_j \hat{H} | \Phi_\nu \rangle \langle \Phi_\nu | \partial_i \hat{U} | \Psi_a^{(0)} \rangle \\
& + \langle \Phi_\mu | (1 - \hat{U}) \partial_{ij} \hat{H} | \Phi_\nu \rangle \langle \Phi_\nu | \hat{U} | \Psi_a^{(0)} \rangle \} \\
= & - \langle \Phi_\mu | \partial_i \hat{U} | \Psi_a^{(0)} \rangle \cdot \partial_j E_a - \langle \Phi_\mu | \partial_j \hat{U} | \Psi_a^{(0)} \rangle \cdot \partial_i E_a \\
& + \langle \Phi_\mu | (1 - \hat{U}) \partial_{ij} \hat{H} | \Psi_a^{(0)} \rangle \\
& + \sum_\nu \{ \langle \Phi_\mu | (1 - \hat{U}) \partial_i \hat{H} | \Phi_\nu \rangle \langle \Phi_\nu | \partial_j \hat{U} | \Psi_a^{(0)} \rangle \\
& + \langle \Phi_\mu | (1 - \hat{U}) \partial_j \hat{H} | \Phi_\nu \rangle \langle \Phi_\nu | \partial_i \hat{U} | \Psi_a^{(0)} \rangle \\
& + \langle \Phi_\mu | (1 - \hat{U}) \partial_{ij} \hat{H} | \Phi_\nu \rangle \langle \Phi_\nu | \hat{U} | \Psi_a^{(0)} \rangle \} .
\end{aligned} \tag{57}$$

Finally, the second energy derivatives are given by the expression

$$\begin{aligned}
\partial_{ij} E = & \langle \Psi_a^{(0)} | \partial_{ij} \hat{H} | \Psi_a \rangle \\
& + \langle \Psi_a^{(0)} | \hat{\Lambda}^{(i)} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | \hat{\Pi}^{(j)} | \Psi_a^{(0)} \rangle
\end{aligned}$$

$$+ \langle \Psi_a^{(0)} | \hat{\Lambda}^{(j)} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | \hat{\Pi}^{(i)} | \Psi_a^{(0)} \rangle \tag{58}$$

$$+ \langle \Psi_a^{(0)} | \hat{\Lambda} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | \hat{\Pi}^{(ij)} | \Psi_a^{(0)} \rangle,$$

where $\langle \mathbf{\Phi}_q | \hat{\Pi}^{(i)} | \Psi_a^{(0)} \rangle$ or $\langle \mathbf{\Phi}_q | \hat{\Pi}^{(j)} | \Psi_a^{(0)} \rangle$ are defined by Eqs (*36*) and (*45*), $\langle \mathbf{\Phi}_q | \hat{\Pi}^{(ij)} | \Psi_a^{(0)} \rangle$ are given by Eq. (*57*), $\langle \Psi_a^{(0)} | \hat{\Lambda} | \mathbf{\Phi}_q \rangle$ are obtained by solving Eq. (*40*) or (*43*), and, similarly, $\langle \Psi_a^{(0)} | \hat{\Lambda}^{(i)} | \mathbf{\Phi}_q \rangle$ are obtained from

$$\langle \Psi_a^{(0)} | \hat{\Lambda}^{(i)} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | (E_a \mathbf{1}_\mathbf{q} - \hat{\mathcal{H}}) | \mathbf{\Phi}_q \rangle = \langle \Psi_a^{(0)} | \partial_i \hat{H} | \mathbf{\Phi}_q \rangle , \tag{59}$$

or, respectively,

$$\hat{\mathbf{A}}^T \boldsymbol{\lambda}^{(i,a)} = \mathbf{h}^{(i,a)} , \tag{60}$$

where

$$\lambda_\mu^{(i,a)} = \langle \Psi_a^{(0)} | \hat{\Lambda}^{(i)} | \Phi_\mu \rangle, \quad h_\mu^{(i,a)} = \langle \Psi_a^{(0)} | \partial_i \hat{H} | \Phi_\mu \rangle = \sum_{\alpha \in I_p} g_\alpha^a \mathcal{G}_{\alpha\mu}^i . \tag{61}$$

Here, we also use the definition of $\hat{\mathbf{A}}$ from Eq. (*42*). With regard to Eq. (*41*), $\boldsymbol{\lambda}^{(i,a)}$ can be interpreted as the first derivative of $\hat{\Lambda}$ and $\mathbf{h}^{(i,a)}$ as the first derivative of a "dressed" Hamiltonian, so that $\boldsymbol{\lambda}^a \equiv \boldsymbol{\lambda}^{(0,a)}$ as well as $\mathbf{h}^a \equiv \mathbf{h}^{(0,a)}$. Then, Eq. (*57*) is explicitly given by the following representation:

$$\begin{aligned} \langle \Phi_\mu | \hat{\Pi}^{(ij)} | \Psi_a^{(0)} \rangle = & -c_\mu^{(i,a)} \cdot \partial_j E_a - c_\mu^{(j,a)} \cdot \partial_i E_a \\ & + \sum_{\alpha \in I_p} \{ \mathcal{G}_{\mu\alpha}^{ij} - c_\mu^a \sum_{\beta \in I_p} g_\beta^a \mathcal{G}_{\beta\alpha}^{ij} \} g_\alpha^a \\ & + \sum_{\nu \in I'_q} \{ (\mathcal{G}_{\mu\nu}^i - c_\mu^a h_\nu^{(i,a)}) c_\nu^{(j,a)} \\ & + (\mathcal{G}_{\mu\nu}^j - c_\mu^a h_\nu^{(j,a)}) c_\nu^{(i,a)} \\ & + (\mathcal{G}_{\mu\nu}^{ij} - c_\mu^a h_\nu^{(ij,a)}) c_\nu^{(a)} \} , \end{aligned} \tag{62}$$

where c_μ^a ($\equiv c_\mu^{(0,a)}$) are the WECs, and further

$$c_\nu^{(j,a)} \equiv \langle \Phi_\nu | \partial_j \hat{U} | \Psi_a^{(0)} \rangle , \quad \mathcal{G}_{\mu\nu}^{ij} \equiv \langle \Phi_\mu | \partial_{ij} \hat{H} | \Phi_\nu \rangle \tag{63}$$

$$h_{\nu}^{(ij,a)} \equiv \langle \Psi_a^{(0)} | \partial_{ij} \hat{H} | \Phi_{\nu} \rangle = \sum_{\alpha \in I_p} g_{\alpha}^{a} \mathcal{G}_{\alpha\nu}^{ij} \,. \tag{64}$$

The matrix elements $\mathcal{G}_{\mu\nu}^{j}$ are defined by Eqs (*46*) and (*47*), and analogous formulas hold for $\mathcal{G}_{\mu\nu}^{ij}$ with respect to the indices μ and ν.

In contrast to the first energy derivatives, Eq. (*49*), where no first derivatives of the WECs ($c_{\nu}^{(j,a)}$) are needed, in the case of the second derivatives of the energy, the $c_{\nu}^{(j,a)}$ quantities are required. Therefore, besides determining $\boldsymbol{\lambda}^{(i,a)}$ (*cf.* Eq. (*59*) or (*60*)), we have to solve the linear algebraic equations for $c_{\nu}^{(j,a)}$ (*cf.* Eq. (*38*)), in which case the matrix $\hat{\mathbf{A}}$ is also required. Obviously, by applying the interchange method, we can formulate the second derivatives without requiring the second derivatives of WECs. Yet, we have to calculate and/or store the first derivatives of WECs and the energy in order to obtain the second derivatives of the energy.

Instead of using Eq. (*51*) to define the second derivatives of the energy, we can exploit the first derivatives given by Eq. (*49*). As expected, Eq. (*58*) shows an explicit symmetric structure of the second derivatives, *i.e.*, the symmetry with respect to the transposition of the parameters or indices, respectively. On the other hand, the direct differentiation of the expression for the first derivatives, Eq. (*49*), with respect to parameters, *e.g.* χ_j, leads to an asymmetric representation of the second derivatives, namely

$$\begin{aligned}
\partial_{ij} E_a = & \sum_{\alpha,\beta \in I_p} g_{\alpha}^{a} \mathcal{G}_{\alpha\beta}^{ij} g_{\beta}^{a} + \sum_{\substack{\alpha \in I_p \\ \mu \in I'_q}} g_{\alpha}^{a} \mathcal{G}_{\alpha\mu}^{ij} c_{\mu}^{a} + \sum_{\substack{\alpha \in I_p \\ \mu \in I'_q}} g_{\alpha}^{a} \mathcal{G}_{\alpha\mu}^{i} c_{\mu}^{(j,a)} \\
& + \sum_{\mu \in I'_q} (\partial_j \lambda_{\mu}^{a}) \{ \gamma_{\mu a}^{i} - c_{\mu}^{a} \sum_{\beta \in I_p} g_{\beta}^{a} \gamma_{\beta a}^{i} \} \\
& + \sum_{\mu \in I'_q} \lambda_{\mu}^{a} \{ (\partial_j \gamma_{\mu a}^{i}) - c_{\mu}^{(j,a)} \sum_{\beta \in I_p} g_{\beta}^{a} \gamma_{\beta a}^{i} - c_{\mu}^{a} \sum_{\beta \in I_p} g_{\beta}^{a} (\partial_j \gamma_{\beta a}^{i}) \} \,,
\end{aligned} \tag{65}$$

where

$$\partial_j \gamma_{\zeta a}^{i} = \sum_{\alpha \in I_p} \mathcal{G}_{\zeta\alpha}^{ij} g_{\alpha}^{a} + \sum_{\gamma \in I'_q} \{ \mathcal{G}_{\zeta\gamma}^{ij} c_{\gamma}^{a} + \mathcal{G}_{\zeta\gamma}^{i} c_{\gamma}^{(j,a)} \} . \tag{66}$$

As already mentioned, this representation is not only asymmetric with respect to the interchange of the indices, but it also depends on the first derivatives of Λ. Therefore, this formulation requires an additional system of equations for the Λ derivatives. To generate this system of equations, we simply differentiate Eq. (*43*), obtaining

$$\hat{\mathbf{A}}^T(\partial_j \mathbf{\Lambda}^a) = \partial_j \mathbf{h}^a - (\partial_j \hat{\mathbf{A}}^T)\boldsymbol{\lambda}^a \,. \tag{67}$$

The asymmetric form is more advantageous than the symmetric one when, for instance, two different kinds of physical parameters are at play. If n_1 components are related to one parameter set and n_2 components to the parameters of the second kind and, *e.g.* $n_1 > n_2$, we have to determine $n_1 + n_2 = n$ perturbed WECs in the symmetric variant, while in the asymmetric case we first exploit a smaller set of n_2 χ_j components, so that this formulation requires only n_2 components for both the perturbed WECs and perturbed Λ amplitudes. For more details, especially those pertaining to the energy derivatives for various coupled cluster approximations, we refer the reader to ref.[8] and references therein.

Higher Derivatives

When we are interested in hyperpolarizabilities or, generally, in higher-order properties, we must evaluate higher derivatives of the energy. Guided by the above given examples, we can write the general expression for the $\binom{n+r-1}{r}$ derivatives of the r-th order of the energy as a function of n parameters $\chi = (\chi_1, \chi_2, \ldots, \chi_n)$ as follows

$$\begin{aligned} \partial_{i_1 i_2 \ldots i_r} E_a(\chi)|_{\chi=0} = \partial_{[r]} E_a &= \langle \Psi_a^{(0)} | \partial_{[r]} \hat{H} | \Psi_a \rangle \\ &+ \sum_{k=1}^{r-1} \sum_{m \in P_r(k)} \langle \Psi_a^{(0)} | \hat{\Lambda}^{[m]} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | \hat{\Pi}^{[\{m\}]} | \Psi_a^{(0)} \rangle \\ &+ \langle \Psi_a^{(0)} | \hat{\Lambda} | \mathbf{\Phi}_q \rangle \langle \mathbf{\Phi}_q | \hat{\Pi}^{[r]} | \Psi_a^{(0)} \rangle \,. \end{aligned} \tag{68}$$

Without restricting the generality, we assume that a multi-index $[r] \equiv (i_1, i_2, \ldots, i_r)$ with $i_1 \le i_2 \le \ldots \le i_r$ defines a selection of r, not necessarily distinct, parameters from the parameter set χ. Then $m \in P_r(k)$ runs over the set $P_r(k)$ of k-th order multi-indices $[m] \equiv (j_1, \ldots, j_k)$, characterizing k-th order partial derivatives $\partial_{[m]} \equiv \partial^k / \partial\chi_{j1} \ldots \partial\chi_{jk}$, while $[\{m\}] \in \{P_r(k)\}$ designates the complementary set of multi-indices with respect to $[r]$. Note that for $r = 1$ (the gradient case), when $[r] = (i)$, the second term on the right-hand side of Eq. (*68*) is absent (the upper limit $k = r - 1$ is smaller than the lower limit $k = 1$) and we recover Eq. (*39*). For the second derivative case, when $r = 2$ and $[r] = (i, j)$, we have that $P_2(1) = (i, j)$ and $\{P_2(1)\} = (j, i)$, recovering Eq. (*58*).

For the derivatives of higher order than 2 we proceed in a similar way. Thus, for example, with $n = r = 3$ and [3] = (1, 2, 3), we have that $P_3(1)$ = (1, 2, 3), $\{P_3(1)\}$ = (23, 13, 12) and $P_3(2) = \{P_3(1)\}$, $\{P_3(2)\} = P_3(1)$, while for [3] = (1, 1, 2), $P_3(1)$ = (1, 1, 2), $\{P_3(1)\}$ = (12, 12, 11), and again $P_3(2) = \{P_3(1)\}$, $\{P_3(2)\} = P_3(1)$. Note that when some of the indices in [r] are identical, we get correspondingly identical terms on the right-hand side of Eq. (*68*).

As in the preceding cases, $\langle \Psi_a^{(0)} | \Lambda | \Phi_q \rangle$ is given by Eq. (*40*) or (*43*) and $\langle \Phi_q | \hat{\Pi}^{[m]} | \Psi_a^{(0)} \rangle$ is defined as follows

$$\hat{\Pi}^{[m]} \equiv \partial_{[m]}\{(1-\hat{U})\,\hat{H}\hat{U}\} + \partial_{[m]}\{\hat{U}\}\,\hat{H}\hat{U} - (1-\hat{U})\,\hat{H}\,\partial_{[m]}\{\hat{U}\}. \qquad (69)$$

Since $\hat{\Pi}^{[m]}$ contains k-th order derivatives of WECs $c_\mu^{(k,a)}$, ($0 \le k \le \#m - 1$, where $\#m$ designated the number of indices in [m]), (*cf.* Eq. (*62*)), we must store these derivatives from the preceding calculations of the lower-order derivatives. Otherwise we have to calculate them by solving an analogous system of equations to that of Eq. (*56*), namely

$$\{\langle \Phi_q | E_a \mathbf{1}_\mathbf{q} - \hat{\mathcal{H}} | \Phi_q \rangle\} \langle \Phi_q | \partial_{[l]} \hat{U} | \Psi_a^{(0)} \rangle = \langle \Phi_q | \hat{\Pi}^{[l]} | \Psi_a^{(0)} \rangle\,, \qquad (70)$$

or, respectively,

$$\hat{\mathbf{A}}\mathbf{c}^{(l,a)} = \boldsymbol{\pi}^{(l,a)}, \quad \boldsymbol{\pi}^{(l,a)} \equiv \langle \Phi_q | \hat{\Pi}^{[l]} | \Psi_a^{(0)} \rangle \qquad (71)$$

Finally, $\langle \Psi_a^{(0)} | \hat{\Lambda}^{[m]} | \Phi_q \rangle$ are obtained by solving the linear equations (*cf.* Eqs (*40*) and (*59*))

$$\langle \Psi_a^{(0)} | \hat{\Lambda}^{[m]} | \Phi_q \rangle \langle \Phi_q | (E_a \mathbf{1}_\mathbf{q} - \hat{\mathcal{H}}) | \Phi_q \rangle = \langle \Psi_a^{(0)} | \partial_{[m]} \hat{H} | \Phi_q \rangle\,. \qquad (72)$$

Needless to say that the first term on the right-hand side of Eq. (*68*), involving Ψ_a, is approximated according to the DGB scheme employed, so that the projector $|\Phi_q\rangle\langle\Phi_q|$ involves the singly, doubly, triply, and/or up to quadruply excited determinants or configurations, depending on the scheme employed. (The same holds for the representations of the first and second derivatives.) We also note that the derivatives of the Hamiltonian, as given in refs[1,2] for the first and second derivatives, are (unfortunately)

not available in standard packages for higher derivatives. Finally, although Eq. (*68*) can be exploited to calculate required higher-order derivatives, the most efficient way to generate the derivatives or properties of very high orders seems to be that based on the linear response approaches, as first suggested by Monkhorst[33] for the standard CC methods, and as first implemented by Kondo, Piecuch and Paldus[34] (for applications, see refs[35–37]).

III. SUMMARY

In this paper we describe a general procedure for the calculation of the energy derivatives with respect to a set of parameters χ in the framework of the recently introduced DGB method. To determine the required expressions, we have exploited the generalized Bloch equation in the context of the direct iterative approach that constitutes the basis of the DGB method. Our considerations were restricted to the so-called state-selective approach (SS-DGB).

For the most important first and second derivatives of the energy, we give explicit expressions in Section II. We also briefly outline an extension of this formalism to the derivatives of higher than the second order (last part of Section II).

APPENDIX: EXPLICIT GRADIENT FORMULAS

In this appendix we address the derivation of explicit formulas that are required for the actual implementation of the analytic energy derivatives within the DGB formalism. For simplicity's sake, we shall focus on gradients, Eq. (*49*). Since we shall employ Hartree–Fock (HF) orbitals, we can exploit many of the details of both the variational and perturbative (including coupled cluster) approaches to the evaluation of the energy derivatives that have been developed in the past, starting with the pioneering work by Gerratt and Mills[38] and coupled perturbed HF (CPHF) theory by Caves and Karplus[39] (going back to Dalgarno[40] and Stevens *et al.*[41]). We thus concentrate on the distinctions brought about by the DGB formalism, while relying on the perturbation theory approach of Handy *et al.*[42] and the coupled cluster formalism for gradients of Salter *et al.*[1], wherever appropriate.

To simplify our notation, we drop the state labels and write $E_a \equiv E$, $g_\alpha^a \equiv g_\alpha$, *etc.*, and set $\chi_i \equiv \chi$. We also introduce the replacement operator notation (*cf.*, *e.g.* refs[28,30,43]) and use the letters from the middle of the Latin alphabet (*i, j, k, l, ...*) as generic labels for the HF molecular orbitals (MOs),

while those from the beginning (*a*, *b*, *c*, *d*, ...) and the end (*r*, *s*, *t*, *u*, ...) of this alphabet we reserve to designate, respectively, the occupied and the unoccupied MOs in the HF reference $|\Phi_0\rangle$. Consequently, we have that the matrix elements of the Fock operator in the HF MO basis between the occupied and virtual orbitals vanish, *i.e.*, $f_{qr} = 0$ for any *q* and *r*, so that our normal product Hamiltonian $\hat{H}_N \equiv \hat{H} \equiv H(\lambda)$, Eq. (*28*), takes the form

$$\hat{H} = \sum_{a,b} f_{ab} \tilde{e}^{a}_{b} + \sum_{r,s} f_{rs} \tilde{e}^{r}_{s} + \tfrac{1}{4} \sum_{i,j,k,l} v_{ijkl} \tilde{e}^{ij}_{kl} , \tag{73}$$

where $\tilde{e}^{i}_{j} \equiv \mathrm{N}[a_i^\dagger a_j]$, $\tilde{e}^{ij}_{kl} \equiv \mathrm{N}[a_i^\dagger a_j^\dagger a_l a_k]$, *etc.*

With this notation, the matrix elements $G^{\chi}_{\mu\nu}$, Eqs (*46*) and (*47*), become

$$G^{\chi}_{\mu\nu} \equiv \langle \Phi_\mu | \partial_\chi \hat{H} | \Phi_\nu \rangle \equiv \langle \Phi_\mu | \hat{H}^{\chi} | \Phi_\nu \rangle \tag{74}$$

$$= \sum_{a,b} f^{\chi}_{ab} M^{\mu\nu}_{a,b} + \sum_{r,s} f^{\chi}_{rs} M^{\mu\nu}_{r,s} + \sum_{i,j,k,l} \tilde{v}^{\chi}_{ijkl} M^{\mu\nu}_{ij,kl} ,$$

where

$$f^{\chi}_{ij} \equiv \partial_\chi f_{ij}|_{\chi=0} = \langle i|\hat{h}|j\rangle^{\chi} + \sum_a \langle ia||ja\rangle^{\chi}, \quad \tilde{v}^{\chi}_{ijkl} = \tfrac{1}{4}\langle ij||kl\rangle^{\chi} , \tag{75}$$

with $\langle\cdots\rangle^{\chi} = \partial_\chi \langle\cdots\rangle|_{\chi=0}$ and $\langle i|\hat{h}|j\rangle$ designating the one-electron component of the Hamiltonian. Further,

$$M^{\mu\nu}_{i,j} = \langle \Phi_\mu | \tilde{e}^{i}_{j} | \Phi_\nu \rangle, \quad M^{\mu\nu}_{ij,kl} = \langle \Phi_\mu | \tilde{e}^{ij}_{kl} | \Phi_\nu \rangle , \tag{76}$$

with μν designating αβ, α*b* or αμ. Using now Eq. (*74*) in Eq. (*49*), and sorting the terms with respect to one- and two-electron derivative terms f^{χ}_{ij} and $\tilde{v}^{\chi}_{ijkl}$, we get

$$E^{\chi} = \sum_{a,b} D_{a,b} f^{\chi}_{ab} + \sum_{r,s} D_{r,s} f^{\chi}_{rs} + \sum_{i,j,k,l} D_{ij,kl} \tilde{v}^{\chi}_{ijkl} , \tag{77}$$

where

$$D_{x,y} = \sum_{\alpha \in I_p} g_\alpha \Gamma^{\alpha}_{x,y} + \sum_{\mu \in I'_q} \lambda_\mu \{\Gamma^{\mu}_{x,y} - c_\mu \sum_{\beta \in I_p} g_\beta \Gamma^{\beta}_{x,y}\}, \tag{78}$$

with *x*,*y* = *a*,*b*; *r*,*s* or *ij*,*kl*, and

$$\Gamma^{\zeta}_{x,y} = \sum_{\alpha \in I_p} g_\alpha M^{\zeta\alpha}_{x,y} + \sum_{\gamma \in I'_q} c_\gamma M^{\zeta\gamma}_{x,y} \,. \tag{79}$$

In order to evaluate the derivative terms f^{χ}_{ij} and $\tilde{v}^{\chi}_{ijkl}$, we rely on the CPHF formalism[1,42], as well as on the procedure eliminating the singularities due to the vanishing denominators when solving for the CPHF coefficients U^{χ}_{ab} and U^{χ}_{rs} (*cf.* ref.[1]). This is done by setting $U^{\chi}_{ij} = -\frac{1}{2} S^{\chi}_{ij}$ ($i,j = a,b$ or r,s), where S^{χ}_{ij} designates the derivative of the pertinent overlap integral,

$$S^{\chi}_{ij} = \sum_{\bar{\mu},\bar{\nu}} b^{*}_{\bar{\mu}i} b_{\bar{\nu}j} \langle \bar{\mu} \,|\, \bar{\nu} \rangle^{\chi} \,, \tag{80}$$

the barred indices labeling AOs and $b_{\bar{\mu}i}$ designating the LCAO coefficients defining the i-th MO. (Note that these terms will be absent in property calculations when the AO positions are fixed). This enables us to bring the expression for the components of the gradient of energy, Eq. (*77*), to the form (*cf.* Eq. (*34*) of ref.[1])

$$\begin{aligned} E^{\chi} = & \sum_{a,b} D_{a,b} Q^{\chi}_{ab} + \sum_{r,s} D_{r,s} Q^{\chi}_{rs} + 2 \sum_{r,a} D_{r,a} Q^{\chi}_{ra} \\ & + \sum_{a,b} I_{a,b} S^{\chi}_{ab} + \sum_{r,s} I_{r,s} S^{\chi}_{rs} + 2 \sum_{a,r} I_{a,r} S^{\chi}_{ar} \\ & + \sum_{i,j,k,l} D_{ij,kl} \langle ij \,||\, kl \rangle^{\chi} \,, \end{aligned} \tag{81}$$

where

$$I_{i,j} = -\tfrac{1}{2} K_{i,j} \quad (i,j = a,b \text{ or } r,s), \qquad I_{a,r} = -\tfrac{1}{4} K_{a,r} \,, \tag{82}$$

and ($i,j = a,b$; r,s; or a,r),

$$K_{i,j} = \sum_{klm} [D_{jk,lm} \langle ik \,||\, lm \rangle + D_{kj,lm} \langle ki \,||\, lm \rangle + D_{kl,im} \langle kl \,||\, jm \rangle + D_{kl,mi} \langle kl \,||\, mj \rangle]. \tag{83}$$

Now, the "off-diagonal" matrix elements $D_{r,a}$ are obtained by solving the linear system of equations that arises by the application of the Z-vector method (*cf.* refs[42,1])

$$\sum_{r,a} D_{r,a}(\varepsilon_a - \varepsilon_r)A_{ra,sb} = X_{s,b}\,, \tag{84}$$

where

$$2X_{s,b} = K_{s,b} + \sum_{c,d} D_{c,d}[\langle cb||ds\rangle + \langle cs||db\rangle] + \sum_{t,u} D_{t,u}[\langle tb||us\rangle + \langle ts||ub\rangle] \tag{85}$$

and[1]

$$A_{ra,sb} = 1 + \frac{\langle rs||ab\rangle + \langle rb||as\rangle}{(\varepsilon_r - \varepsilon_a)}\,, \tag{86}$$

while Q^{χ}_{ij} ($ij = ab, rs$) are given by (assuming real MO's, *cf.* Eq. (*25*) of ref.[1])

$$Q^{\chi}_{ij} = h^{\chi}_{ij} - \tfrac{1}{2}S^{\chi}_{ij}(\varepsilon_i + \varepsilon_j) - \sum_{a,b} S^{\chi}_{ab}\langle ia||jb\rangle + \sum_{\bar{\mu}\bar{\nu}\bar{\lambda}\bar{\sigma}} b_{\bar{\mu}i}b_{\bar{\nu}j}\,P_{\bar{\sigma}\bar{\lambda}}\langle\bar{\mu}\bar{\lambda}||\bar{\nu}\bar{\sigma}\rangle^{\chi} \tag{87}$$

with $h^{\chi}_{ij} = \sum_{\bar{\mu}\bar{\nu}} b_{\bar{\mu}i}b_{\bar{\nu}j}\langle\bar{\mu}|\hat{h}|\bar{\nu}\rangle^{\chi}$, $P_{\bar{\sigma}\bar{\lambda}} = \sum_a b_{\bar{\sigma}a}b_{\bar{\lambda}a}$, the first order density matrix elements, and ε_i the i-th orbital energy. Note also that

$$f^{\chi}_{ij} = Q^{\chi}_{ij} + \sum_{r,a} U^{\chi}_{ra}\big(\langle ir||ja\rangle + \langle ia||jr\rangle\big). \tag{88}$$

It thus remains to work out the explicit form of the matrix elements $D_{x,y}$ with $x,y = a,b;\ r,s$ and ij, kl, which in our case are given by (*cf.* Eq. (*78*))

$$D_{x,y} = \sum_{\alpha\in I_p} g_{\alpha}\Gamma^{\alpha}_{x,y}\{1 - \sum_{\mu\in I'_q}\lambda_{\mu}c_{\mu}\} + \sum_{\mu\in I'_q}\lambda_{\mu}\Gamma^{\mu}_{x,y}\,, \tag{89}$$

with $\Gamma^{\zeta}_{x,y}$ given by Eq. (*79*) with $x,y = a,b$; r,s or ij, kl.

Clearly, at this stage, we have to specify the approximation scheme used in the DGB approach in order to proceed. As an illustration, let us briefly consider the 2D-SS case, taking into account singles and doubles. We thus write the wave function for the state $|\Psi_a\rangle$ as follows

$$|\Psi_a\rangle = |\overline{\Psi}^{(0)}_a\rangle + C_R|\overline{\Psi}^{(0)}_R\rangle + \sum_{a,r} C^r_a\big|\Phi_0\binom{r}{a}\big\rangle + \sum_{\substack{a<b\\ r<s}} C^{rs}_{ab}\big|\Phi_0\binom{rs}{ab}\big\rangle\,, \tag{90}$$

where $|\Phi_R^{(0)}\rangle$ designates the residue state of $I_p\backslash\{a\}$. The two states spanning the model space are then

$$|\overline{\Psi}_a^{(0)}\rangle \equiv |0\rangle = g_{00}|\Phi_0\rangle + g_{01}|\Phi_1\rangle \,, \tag{91}$$

$$|\overline{\Psi}_R^{(0)}\rangle \equiv |R\rangle = g_{10}|\Phi_0\rangle + g_{11}|\Phi_1\rangle \,.$$

Note that the coefficients C_a^r and C_{ab}^{rs} are available to us once we carry out the DGB calculation, regardless whether we employ the B0, BD2, or BQ_2 approximation (recall that we are neglecting higher than doubles for the sake of simplicity).

With the restrictions just pointed out, we thus have that

$$\begin{aligned} D_{x,y} &= (g_{00}\Gamma_{x,y}^0 + g_{01}\Gamma_{x,y}^1)[1 - \lambda_R C_R - \sum_{a,r}\lambda_a^r C_a^r - \sum_{\substack{a<b\\ r<s}}\lambda_{ab}^{rs} C_{ab}^{rs}] \\ &+ \lambda_R \Gamma_{x,y}^R + \sum_{a,r}\lambda_a^r \Gamma_{x,y}(_a^r) + \sum_{\substack{a<b\\ r<s}}\lambda_{ab}^{rs}\Gamma_{x,y}(_{ab}^{rs}) . \end{aligned} \tag{92}$$

Recall, that λ_R, λ_a^r, and λ_{ab}^{rs} are determined from Eq. (*43*). The various Γ-terms in Eq. (*92*) are then given by Eq. (*79*). Specifically, in the case considered, we get

$$\Gamma_{x,y}^0 = g_{00}M_{x,y}^{00} + g_{01}M_{x,y}^{01} + C_R M_{x,y}^{0R} + \sum_{a,r} C_a^r M_{x,y}^{0(_a^r)} + \sum_{\substack{a<b\\ r<s}} C_{ab}^{rs} M_{x,y}^{0(_{ab}^{rs})} \,, \tag{93}$$

and similarly for $\Gamma_{x,y}^1, \Gamma_{x,y}^R, \Gamma_{x,y}(_a^r)$, and $\Gamma_{x,y}(_{ab}^{rs})$. The matrix elements $M_{x,y}^{\mu\nu}$ then represent the matrix elements of the replacement operator e_y^x relative to the states μ and ν. Clearly, many of these matrix elements vanish or equal to ±1. Thus, for example

$$M_{ij}^{00} = \langle\Phi_0|\tilde{e}_j^i|\Phi_0\rangle = \delta_{ij} \,, \tag{94}$$

when *i* and *j* are occupied while zero otherwise,

$$M_{ij,kl}^{0(_{ab}^{rs})} = \langle\Phi_0|\tilde{e}_{kl}^{ij}|\Phi_0(_{ab}^{rs})\rangle = \langle\Phi_0|\tilde{e}_{kl}^{ij}e_{ab}^{rs}|\Phi_0\rangle = \Delta_{kl}^{rs}\Delta_{ab}^{ij} \,, \textit{ etc.} \tag{95}$$

Here Δ_{mn}^{pq} designates the generalized antisymmetric Kronecker delta (*cf.* the second ref.[28]), *i.e.*,

$$\Delta_{mn}^{pq} = \delta_m^p \delta_n^q - \delta_n^p \delta_m^q \,. \qquad (96)$$

Obviously, these *M*-matrix elements represent simple numerical factors that can be best generated automatically using similar codes as in the case of the unitary-group-approach coupled-cluster (UGA-CC) method[44], since they can always be expressed as the Fermi (*i.e.*, HF) vacuum mean value of a string of unitary group generators. This is indeed the best way to proceed in order to avoid error prone *ad hoc* derivation by hand.

The authors are indebted to Dr X. Li for fruitful discussions and help. One of us (H. M.) also wishes to thank his co-author and the Department of Applied Mathematics of the University of Waterloo for their hospitality. The continued support by the National Sciences and Engineering Research Council of Canada (J. P.) that enabled this collaboration is also gratefully acknowledged.

REFERENCES

1. Salter E. A., Trucks G. W., Bartlett R. J.: *J. Chem. Phys.* **1989**, *90*, 1752.
2. Salter E. A., Bartlett R. J.: *J. Chem. Phys.* **1989**, *90*, 1767.
3. Adamowicz L., Laidig W. D., Bartlett R. J.: *Int. J. Quantum Chem., Quantum Chem. Symp.* **1984**, *18*, 245.
4. Schreiner A. C., Scuseria G. E., Rice J. E., Lee T. J., Schaefer III H. F.: *J. Chem. Phys.* **1987**, *87*, 5361.
5. Koch H., Jensen H. J. A., Jørgensen P., Helgaker T., Scuseria G. E., Schaefer III H. F.: *J. Chem. Phys.* **1990**, *92*, 4924.
6. Gauss J., Stanton J. F., Bartlett R. J.: *J. Chem. Phys.* **1991**, *95*, 2623.
7. Gauss J., Stanton J. F., Bartlett R. J.: *J. Chem. Phys.* **1991**, *95*, 2639.
8. Stanton J. F., Gauss J. in: *Recent Advances in Computational Chemistry*, Vol. 3, *Recent Advances in Coupled Cluster Methods* (R. J. Bartlett, Ed.), p. 49. World Scientific, Singapore 1997.
9. Handy N. C., Schaefer III H. F.: *J. Chem. Phys.* **1984**, *81*, 5031.
10. Rice J. E., Amos R. D.: *Chem. Phys. Lett.* **1985**, *122*, 585.
11. Handy N. C., Lee T. J., Schaefer III H. F.: *J. Chem. Phys.* **1986**, *85*, 963.
12. Stanton J. F.: *J. Chem. Phys.* **1993**, *99*, 8840.
13. Stanton J. F., Gauss J.: *J. Chem. Phys.* **1994**, *100*, 4695.
14. Stanton J. F., Gauss J.: *J. Chem. Phys.* **1995**, *103*, 8931.
15. Gwaltney S. R., Bartlett R. J., Nooijen M.: *J. Chem. Phys.* **1999**, *111*, 58.
16. a) Piecuch P., Paldus J.: *J. Chem. Phys.* **1995**, *99*, 15354; b) Ajitha D., Pal S.: *J. Chem. Phys.* **1999**, *111*, 3832.

17. Helgaker T. in: *Lecture Notes in Chemistry* (B. O. Roos, Ed.), Vol. 58, p. 295. Springer-Verlag, Berlin 1992.
18. Meissner H., Paldus J.: *J. Chem. Phys.* **2000**, *113*, 2594; referred to as Part II.
19. Meissner H.: *Ph.D. Thesis*. Universität Regensburg, Regensburg 1995. Compressed .dvi and .ps files can be obtained *via* URL: http://www.chemie.uni-regensburg.de/preprint.html.
20. Meissner H., Steinborn E. O.: *Int. J. Quantum Chem.* **1997**, *61*, 777; referred to as Part I.
21. Meissner H., Steinborn E. O.: *J. Mol. Struct. (Theochem)* **1998**, *433*, 119.
22. Meissner H., Paldus J.: *J. Chem. Phys.* **2000**, *113*, 2612; referred to as Part III.
23. Meissner H., Paldus J.: *J. Chem. Phys.* **2000**, *113*, 2622; referred to as Part IV.
24. Meissner H., Paldus J.: *Int. J. Quantum Chem.* **2000**, *80*, 782; referred to as Part V.
25. Meissner H., Ema I.: *J. Mol. Struct. (Theochem)* **2001**, *547*, 171.
26. Jankowski K., Paldus J.: *Int. J. Quantum Chem.* **1980**, *18*, 1243.
27. a) Jankowski K., Meissner L., Wasilewski J.: *Int. J. Quantum Chem.* **1985**, *28*, 931; b) Meissner L., Jankowski K., Wasilewski J.: *Int. J. Quantum Chem.* **1988**, *34*, 535.
28. Paldus J. in: *Methods in Computational Molecular Physics; NATO Advanced Study Institute, Series B: Physics* (S. Wilson and G. H. F. Diercksen, Eds), Vol. 293, p. 99. Plenum Press, New York 1992; *idem* in: *Relativistic and Electron Correlation Effects in Molecules and Solids; NATO Advanced Study Institute, Series B: Physics* (G. L. Malli, Ed.), Vol. 318, p. 207. Plenum Press, New York 1994.
29. a) Hellmann H.: *Einführung in die Quantenchemie*, p. 285. Franz Deuticke, Vienna 1937; b) Feynman R.: *Phys. Rev.* **1939**, *56*, 340.
30. Paldus J., Li X.: *Adv. Chem. Phys.* **1999**, *110*, 1.
31. a) Dalgarno A., Lewis J. T.: *Proc. R. Soc. London, Ser. A* **1955**, *233*, 70; b) Dalgarno A., Stewart A. L.: *Proc. R. Soc. London, Ser. A* **1956**, *238*, 269 and 276; c) Dalgarno A., Stewart A. L.: *Proc. R. Soc. London, Ser. A* **1958**, *247*, 245.
32. Sternheimer R. M., Foley H. M.: *Phys. Rev.* **1952**, *92*, 1460.
33. a) Monkhorst H. J.: *Int. J. Quantum Chem., Quantum Chem. Symp.* **1977**, *11*, 421; b) Dalgaard E., Monkhorst H. J.: *Phys. Rev. A: At., Mol., Opt. Phys.* **1983**, *28*, 1217.
34. a) Kondo A. E., Piecuch P., Paldus J.: *J. Chem. Phys.* **1995**, *102*, 6511; *J. Chem. Phys.* **1996**, *104*, 8566.
35. a) Piecuch P., Kondo A. E., Špirko V., Paldus J.: *J. Chem. Phys.* **1996**, *104*, 4699; b) Špirko V., Piecuch P., Kondo A. E., Paldus J.: *J. Chem. Phys.* **1996**, *104*, 4716; c) Piecuch P., Špirko V., Paldus J.: *J. Chem. Phys.* **1996**, *105*, 11068; d) Piecuch P., Špirko V., Paldus J.: *Polish J. Chem.* **1998**, *72*, 1635.
36. Piecuch P., Paldus J.: *J. Math. Chem.* **1997**, *21*, 51.
37. Piecuch P., Špirko V., Kondo A. E., Paldus J.: *Mol. Phys.* **1998**, *94*, 55.
38. Gerratt J., Mills I. M.: *J. Chem. Phys.* **1968**, *49*, 1719.
39. Caves T. C., Karplus M.: *J. Chem. Phys.* **1969**, *50*, 3649.
40. Dalgarno A.: *Adv. Phys.* **1962**, *11*, 281; and references therein.
41. Stevens R. M., Pitzer R. M., Lipscomb W. N.: *J. Chem. Phys.* **1963**, *38*, 550.
42. Handy N. C., Amos R. D., Gaw J. F., Rice J. E., Simandiras E. D.: *Chem. Phys. Lett.* **1985**, *120*, 151.
43. Paldus J., Jeziorski B.: *Theor. Chim. Acta* **1988**, *73*, 81.
44. Li X., Paldus J.: *J. Chem. Phys.* **1994**, *101*, 8812.

Josef Paldus, RNDr, CSc., DrSc., FRSC was born in 1935 in Bzí, near Železný Brod in Northern Bohemia. In 1953, he entered the Faculty of Mathematics and Physics of the Charles University in Prague, where he later wrote his Master's dissertation under the supervision of Drs. V. Hanuš and J. Koutecký. In 1958 he started a CSc. (Ph.D.) program at the Institute of Physical Chemistry of the Czechoslovak Academy of Sciences (presently the J. Heyrovský Institute) under the supervision of Dr. J. Koutecký. He was his first student to tackle the newly developing field of quantum chemistry and, subsequently, became one of the founders of the Prague theoretical school. In 1962 he was awarded a National Research Council of Canada Postdoctoral Fellowship in the Division of Pure Physics (presently the Herzberg Institute for Astrophysics) and worked under the supervision of Dr. D. A. Ramsay, FRS in the field of high-resolution spectroscopy. In 1968, following the Russian invasion of Czechoslovakia, he decided to settle permanently in Canada and accepted the offer of an Associate Professorship in the Department of Applied Mathematics at the University of Waterloo. He was cross-appointed to the Department of Chemistry in 1973 and to the Guelph-Waterloo Center for Graduate Work in Chemistry in 1974, promoted to Professor in 1975, and served as an Associate Dean for Graduate Studies (Mathematics) from 1978 to 1980. In the meantime, he held several visiting Professorships at various European institutions: University of Rheims, France (1973), University of Louis Pasteur, Strasbourg, France (1975–1976, 1982–1983), University of Nijmegen, The Netherlands (1981), Free University, Berlin (1981), and Technion, Haifa, Israel (1983). He also spent a year as a Fellow of the Institute for Advanced Study in Berlin (1986–1987) and was awarded a Killam Research Fellowship (1987–1989). Since 1984 he is an Adjunct Professor of Chemistry at the University of Florida in Gainesville, FL and he also acted as one of the Associate Directors of the newly founded Fields Institute for Research in Mathematical Sciences during its stay in Waterloo. Dr. Paldus was elected a Corresponding Member of the European Academy of Sciences, Arts and Letters in Paris in 1981, a Fellow of the Royal Society of Canada in 1983, and a Member of the International Academy of Quantum Molecular Science in 1984. He also serves on the Board of Directors of the International Society for Theoretical Chemical Physics. In 1992 he received a J. Heyrovský Gold Medal of the Czechoslovak Academy of Sciences, a Gold Medal of the Comenius University in 1994 and, most recently, was honoured by an Alexander von Humboldt Senior Scientist Award (1996). He also served and continues to serve on a number of Editorial Boards or Advisory Editorial Boards (Int. J. Quantum Chem., Comtex Sci. Co., Adv. Quantum Chem., J. Chem. Phys., Theor. Chim. Acta, J. Math. Chem., and Can. J. Chem.) During his time at Waterloo, he supervised or co-supervised ten Master's and ten Doctoral theses, as well as worked with an almost two dozen Postdoctoral Fellows and Visiting Scientists. This work resulted in over 250 scientific papers.