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REGULAR ARTICLE

A theoretical approach to molecular single-electron transistors

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Abstract We present theoretical methods and computational strategies of the effects of nanoparticles on linear optical properties of molecules. We present quantum mechanical-molecular mechanics response methods for calculating electromagnetic properties of molecules interacting with nanoparticles and we report strategies for calculating electronic and redox states of molecules sandwiched between gold nanoparticles.

Keywords QM/MM response · Sandwiched molecule · Optical properties

1 Introduction

Our primary focus is to present theoretical methods and computational strategies for investigating the molecular properties related to electron transfer or electron conductance of organic molecules sandwiched between nanoparticles. Our approach only considers the transport of a single-electron and not on two-electron transfer mechanisms. On the basis of these investigations, we wish to understand in detail the mechanisms by which the electronic and redox states of the organic molecules influence the transport behavior of the molecular devices.

The functions of devices and materials are usually through the bulk properties of the materials. Within molecular materials, the functionalities of the materials are based on the molecular properties of the molecular components or units. The properties of the molecular components or units are strongly associated with the nature of the electrons affiliated with the molecular unit. Therefore, the molecular structure, the redox state, electron conjugation, the spin state, localized and delocalized electrons will give for biologists, chemists and physicists a huge number of variables to vary in order to obtain materials having the desired function. Each molecule has its own molecular property and is the smallest building block of the material. All molecular units have their own molecular properties, and the molecular units can perform differently depending on the electronic structure, redox state, nuclear distortions and molecular structure, which relate to different electronic states, oxidation processes, vibrational or rotational excitations and how the molecular units are joined. The molecular units are initially in a specific quantum state at a given time, and the property of the material will be related to the transition of the molecular units from one state to another. For electronic device materials, it is obvious that electron transfer through molecular units is of great interest and seeing how computer chips are getting smaller and smaller it is even more relevant to construct transitors consisting of a single molecule or aggregates of molecules where one could investigate how the electron transport takes place through chemical bonds or vacuum [1]. The present work does not focus on biological systems where the functional unit, the protein, has a most more complex behavior but extending the presented model to proteins and biological systems would be of interest in our future work.

Dedicated to Professor Akira Imamura on the occasion of his 77th birthday and published as part of the Imamura Festschrift Issue.

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One of the most important chemical processes involving molecules is electron transfer, and it occurs in photosynthetic systems of plants, metabolism, electrochemical processes, photography, organic and inorganic chemical reactions along with molecular conductance. For more than 50 years, research groups have investigated the mechanisms of electron transfer and presently electron transfer processes between molecules in solution, in the gas phase and in proteins can be controlled in terms of the free energy differences, distances and relative orientations between the electron donor molecule and the electron acceptor molecule [2–7]. Utilization of spectroscopic methods having high temporal resolution has added another dimension to the understanding of electron transfer reactions since electron transfer reactions do not necessarily occur during equilibrium conditions but in some cases electron transfer occurs faster than solvent motion. Therefore, theoretical descriptions based on the stochastic motion of molecular systems and crossing between the reactant and the product on the multidimensional potential energy surface have been advanced, and they form a solid theoretical foundation for the understanding of electron transfer in the gas phase, in solution and within proteins [8–12].

In recent years, several experimental groups have reported measurements of the current-voltage (I-V) characteristics of individual or small numbers of organic conjugated molecules placed in a metallic junction [13–24]. Thereby, the organic molecular components act as a medium participating in the transport of electrons while being located between the metallic electrodes. This interest is due to the fact that a molecule can act as a conductor, and understanding the properties of the molecular transistors will lead to forming the building blocks for future nanoelectronic devices. Compared to the research concerning electron transfer between molecules in solution, this research field has only been active for about 40 years and it still holds a lot of unanswered questions that need to be addressed in order to achieve material devices of benefit to the human society [25–29].

Despite the fast developing field of quantum mechanics, there is still limited correspondence between experimental and theoretical investigations of these conductance junctions but few recent investigations have approached this issue [30]. This is due to the many obstacles arising from both transport theory and the calculation strategies of the desired molecule properties needed for understanding how the sandwiched organic molecule is able to participate in the transport of electrons. Firstly, it is important to propose a proper transport theory that covers the different conductances regimes: the coherent and the Coulomb blockade regimes. Secondly, the effects on the molecule caused by electrodes should also be considered. Thirdly, as the desired transport theory has been established, the quantum mechanic obstacles emerge and one question concerns which molecular geometry should be chosen since the geometry under conduction changes. Often, the molecular geometry is optimized for an isolated molecule. The second question concerns how one should include the molecular response of the molecule while being in a junction. The third question concerns the problems that emerge when several redox states have to be calculated since they contain charged molecules and molecules with unpaired electrons and this has recently been addressed by Saito et al. [31]. This is normally a problem for the conventional methods involving solid-state physics approaches.

In this presentation, we describe the single-molecule junctions in the Coulomb blockade regime, i.e., the single-electron transistor (SET), in the context of the theoretical framework and propose a new strategy connecting the experiments with a recently established theoretical strategy. We have shown [32] how we are able to construct the known Coulomb diamonds based on quantum chemical calculations by considering the combined quantum mechanical and molecular mechanics method (QM/MM), which provides a method that includes the interactions between the electrodes and the molecule [33–44].

In this investigation, we illustrate how to describe molecular and environmental structures using a quantum mechanics/molecular mechanics (QM/MM) model where metal electrodes are given by an atomistic description. We have utilized these approaches at different levels of electronic structure when investigating linear and non-linear optical properties of molecules in solution [45–53].

Our strategy for investigating organic molecules sandwiched between metallic junctions is to treat the organic molecule fully quantum mechanically at the level of density functional theory [54, 55, 60], and the electrodes are treated at a classical level and represented as a structured atomistic environment. The properties of each atom in the metallic junction are given by an isotropic atomic polarizability, and we include the electromagnetic response of the electrodes as a dynamic electric field in the electronic structure calculation. Finally, we solve the entire system self-consistently [43–48, 50–53, 65, 66, 67]. On the basis of calculated molecular properties using the QM/MM response approach, we utilize the non-equilibrium Green's function method to calculate the conductance of the molecular system [14–16, 27, 33–44]. In order to obtain accurate descriptions of the molecular properties using response methods based on density functional theory, we apply the CAM-B3LYP functional that has been shown to provide accurate descriptions of molecular properties [56, 57].

2 The QM/MM method

The complexity, due to many electrons, of large-scale systems provides a substantial computational effort in calculating the property of interest using accurate quantum mechanical methods. Therefore, introducing a QM/MM model combining the more flexible quantum mechanics with the simpler molecular mechanics approaches is advantageous [59]. The two regions are chosen such that the chemical part of interest is treated with quantum mechanic (QM), hence described by a method of higher accuracy, and the less interesting part with molecular mechanics (MM). In this presentation, the gold clusters are treated with MM and the respective molecule with QM, which is due to the fact that the chemical part of interest is the region between the electrodes where the molecular electron transport takes place. For the cases where it is crucial to address the quantum mechanical nature of the interactions between the molecule and the nanoparticles, we include some of the nearby metal atoms in the quantum mechanical part of the system. For modeling the effects of interfaces, it is necessary to include in the interaction operator terms that include dipole- and quadropole interaction terms.

2.1 Outline of the QM/MM method

The system is divided into two regions: (1) a region treated with quantum mechanics and (2) a region treated classically utilizing molecular mechanical force fields. Thereby, we have three contributions to the total energy:

$$E = E_{\mathrm{QM}} + E_{\mathrm{MM}} + E_{\mathrm{QM/MM}} \tag{1}$$

where E_{MM} is the energy of the MM region, E_{QM} is the energy of the QM region and the last term $E_{\mathrm{QM/MM}}$ is the interaction energy of two regions. To obtain this energy, the Hamiltonian is presented in a similar form

$$\hat{H} = \hat{H}_{\mathrm{QM}} + \hat{H}_{\mathrm{MM}} + \hat{H}_{\mathrm{QM/MM}} \tag{2}$$

The QM region is described by the many electronic Hamiltonian of the molecule in vacuum and the MM region, and QM/MM interaction will be treated in the following sections. Through the presentation of the respective parts of the equation above, we introduce the following interaction tensors

$$T = \frac{1}{R} \tag{3}$$

$$T^{\alpha} = -\frac{R_{\alpha}}{R^{3}} \tag{4}$$

$$T^{\alpha\beta} = \frac{3R_{\alpha}R_{\beta} - R^{2}\delta_{\alpha\beta}}{R^{5}} \tag{5}$$

$$T^{\alpha\beta\gamma} = -\frac{15R_{\alpha}R_{\beta}R_{\gamma} - 3R^{2}(R_{\alpha}\delta_{\beta\gamma} + R_{\beta}\delta_{\alpha\gamma} + R_{\gamma}\delta_{\alpha\beta})}{R^{7}} \tag{6}$$

$$\begin{aligned} T^{\alpha\beta\gamma\delta} = \frac{1}{R^{9}}\big(&105R_{\alpha}R_{\beta}R_{\gamma}R_{\delta} - 15R^{2}(R_{\alpha}R_{\beta}\delta_{\gamma\delta} + R_{\alpha}R_{\gamma}\delta_{\beta\delta} \\ &+ R_{\alpha}R_{\delta}\delta_{\beta\gamma} + R_{\beta}R_{\gamma}\delta_{\alpha\delta} + R_{\beta}R_{\delta}\delta_{\alpha\gamma} + R_{\gamma}R_{\delta}\delta_{\alpha\beta}) \\ &+ 3R^{4}(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\big) \end{aligned} \tag{7}$$

where R is the distance between e.g., two sites and will be denoted with a subscript indicating which distance is referred to, hence $T_{ss'} = \frac{1}{|\mathbf{r}_s - \mathbf{r}_{s'}|}$ and R_{α} is the α component of the distance vector. The symbol $\delta_{\alpha\beta}$ denotes the Kronecker delta.

2.1.1 *Molecular mechanics*

In the MM treatment, the Hamiltonian is divided into two main parts: the intermolecular and the intramolecular parts

$$\hat{H}_{\mathrm{MM}} = H^{\mathrm{intra}}_{\mathrm{MM}} + \hat{H}^{\mathrm{inter}}_{\mathrm{MM}} \tag{8}$$

and thereby the energy:

$$E_{\mathrm{MM}} = E^{\mathrm{intra}}_{\mathrm{MM}} + E^{\mathrm{inter}}_{\mathrm{MM}} \tag{9}$$

where the intramolecular contribution is divided into [61]:

$$E^{\mathrm{intra}}_{\mathrm{MM}} = E^{\mathrm{str}}_{\mathrm{MM}} + E^{\mathrm{bend}}_{\mathrm{MM}} + E^{\mathrm{tors}}_{\mathrm{MM}} + E^{\mathrm{cross}}_{\mathrm{MM}} \tag{10}$$

where the term $E^{\mathrm{str}}_{\mathrm{MM}}$ is the energy contribution from the molecules stretching, $E^{\mathrm{bend}}_{\mathrm{MM}}$ is from bending of the molecule, $E^{\mathrm{tors}}_{\mathrm{MM}}$ is from torsional rotation within the molecule and the last term is due to the coupling between stretching, bonding and torsional, because they are not independent of each other. However, the MM region in this presentation, the gold region, is frozen, and hereby, the intraenergy will be constant and hence will be ignored since energy differences and molecular properties of the sandwiched organic molecule are our focus.

The intermolecular energy is also split into different terms:

$$E^{\mathrm{inter}}_{\mathrm{MM}} = E^{\mathrm{el}}_{\mathrm{MM}} + E^{\mathrm{pol}}_{\mathrm{MM}} + E^{\mathrm{vdw}}_{\mathrm{MM}} \tag{11}$$

where $E^{\mathrm{el}}_{\mathrm{MM}}$ is the electrostatic energy, $E^{\mathrm{pol}}_{\mathrm{MM}}$ is the polarization energy also known as the induction energy and last term, $E^{\mathrm{vdw}}_{\mathrm{MM}}$, is the van der Waals energy. The electrostatic energy can be illustrated as a site in the MM region at a position $\mathbf{r}_s$ and a another site at position $\mathbf{r}_{s'}$, where the total electrostatic energy is obtained by summing over all the atomic sites in the MM region [62, 64]

$$E^{\mathrm{el}}_{\mathrm{MM}} = \sum_{s}\sum_{s'>s}\sum_{\alpha\beta\gamma\delta}\begin{pmatrix} q^{s}T_{ss'}q^{s'} + q^{s}T^{\alpha}_{ss'}\mu^{s'}_{\alpha} - \mu^{s}_{\alpha}T^{\alpha}_{ss'}q^{s'} + \frac{1}{3}q^{s}T^{\alpha}_{ss'}\Theta^{s'}_{\alpha\beta} \\ -\mu^{s}_{\alpha}T^{\alpha\beta}_{ss'}\mu^{s'}_{\beta} + \frac{1}{3}\Theta^{s}_{\alpha\beta}T^{\alpha\beta}_{ss'}q^{s'} + \frac{1}{3}\Theta^{s}_{\alpha\beta}T^{\alpha\beta\gamma}_{ss'}\mu^{s'}_{\gamma} \\ -\frac{1}{3}\mu^{s}_{\alpha}T^{\alpha\beta\gamma}_{ss'}\Theta^{s'}_{\beta\gamma} + \frac{1}{9}\Theta^{s}_{\alpha\beta}T^{\alpha\beta\gamma\delta}_{ss'}\Theta^{s'}_{\gamma\delta} \end{pmatrix} \tag{12}$$

Here, the tensor notation has been used to give the interaction distance between two sites s and s'. The charge at site s is given by q^{s}, μ^{s}_{α} is the α component of the dipole moment at site s and $\Theta^{s}_{\alpha\beta}$ is the quadrupole moment at the same site. It is clear that Eq. 12 gives the possible interaction between two sites with the first term representing the point charge–point charge interaction and second term the point charge–dipole interaction. Since the above equation comes from an expansion of Taylor series [62, 64], it could be continued to obtain expressions for higher-order multipoles, which is the case for many of the following expressions in this section; however, we have in this presentation chosen to stop at the quadrupole moments.

The induction describes the changes in the charge distribution arising from the existence of an external electric field. The linear dipole approximation is then used to describe the induced dipole as a linear function of the total applied electric field [62, 64]

$$\mu_{\alpha}^{\mathrm{ind},s} = \sum_{\beta} \alpha_{\alpha\beta}^{s} \mathbf{F}_{\beta}^{\mathrm{tot}}(\mathbf{r}_s) \tag{13}$$

where $\mathbf{F}_{\beta}^{\mathrm{tot}}(\mathbf{r}_s)$ is the β component of the total electric field at the polarizable site s and α is the polarizability tensor. The polarization/induction energy is then given by [62, 64]

$$E_{\mathrm{MM}}^{\mathrm{pol}} = \frac{1}{2}\sum_{s}\sum_{s'>s}\sum_{\alpha\beta\gamma}\Big(\mu_{\alpha}^{\mathrm{ind},s}T_{ss'}^{\alpha}q^{s'} - \mu_{\alpha}^{\mathrm{ind},s}T_{ss'}^{\alpha\beta}\Big(\mu_{\beta}^{s'} + \mu_{\beta}^{\mathrm{ind},s'}\Big) + \frac{1}{3}\mu_{\alpha}^{\mathrm{ind},s}T_{ss'}^{\alpha\beta\gamma}\Theta_{\beta\gamma}^{s'}\Big) \tag{14}$$

where q^s is the point charge on site s, $\mu_{\beta}^{s'}$ is the dipole on site s', $\mu_{\alpha}^{\mathrm{ind},s}$ is the induced dipole on site s' and $\Theta_{\beta\gamma}^{s'}$ is the quadrupole moment on site s' just like in the electrostatic expression.

The van der Waals energy $E_{\mathrm{MM}}^{\mathrm{vdw}}$ is the term that describes the repulsion or attraction between non-bonded atoms. As the distance increases between two atoms, the van der Waals energy should become smaller, hence zero within large interatomic distances. For short distances, it should be very repulsive, due to the overlap of negative electron clouds; however, there is a slightly attraction due to the induced dipole—dipole interactions [61], even for a molecule without a permanent dipole. This is due to the fact that motion of electrons will create a small uneven distribution at some point; this is often referred to as dispersions forces.

Several functionals are known, which obey these requirements but one of the most popular is the *Lennard–Jones* potential [63]

$$E_{\mathrm{MM}}^{\mathrm{vdw}} = \sum_{s}\sum_{s'>s}\left[\frac{A_{ss'}}{|\mathbf{R}_s - \mathbf{R}_{s'}|^{12}} - \frac{B_{ss'}}{|\mathbf{R}_s - \mathbf{R}_{s'}|^{6}}\right] \tag{15}$$

where $A_{ss'}$ and $B_{ss'}$ are the interaction coefficients, and the summations cover the van der Waals interaction between the classical sites. The first term is the repulsive part, and the second term is the attraction part. For the cases where chemical bonds are formed between the nanoparticles, we include the nearby metal atoms in the QM part of the system in order to describe properly the chemical bond between the metal atoms and the molecular subsystem.

2.1.2 *The model for the QM/MM interactions*

Like in the MM Hamiltonian, the QM/MM Hamiltonian is separated into severals terms

$$\hat{H}_{\mathrm{QM/MM}} = \hat{H}_{\mathrm{QM/MM}}^{\mathrm{el}} + \hat{H}_{\mathrm{QM/MM}}^{\mathrm{pol}} + \hat{H}_{\mathrm{QM/MM}}^{\mathrm{vdw}} \tag{16}$$

The $\hat{H}_{\mathrm{QM/MM}}^{\mathrm{el}}$ term describes the electrostatic interactions, $\hat{H}_{\mathrm{QM/MM}}^{\mathrm{pol}}$ the polarization energy and $\hat{H}_{\mathrm{QM/MM}}^{\mathrm{vdw}}$ the van der Waals interactions between the MM region and the QM region.

The Hamiltonian for the electrostatic interactions is separated into two parts, which is convenient when the energy has to be evaluated.

$$\hat{H}_{\mathrm{QM/MM}}^{\mathrm{el}} = \hat{H}_{\mathrm{QM/MM}}^{\mathrm{el},m} + \hat{H}_{\mathrm{QM/MM}}^{\mathrm{el},i} \tag{17}$$

The first term represents the contribution from the QM nuclei and the second term the contribution involving the electrons of the QM system. The first term is given as [62, 64]

$$\hat{H}_{\mathrm{QM/MM}}^{\mathrm{el},m} = \sum_{ms}\left(Z_m\hat{T}_{ms}q^s + \sum_{\alpha}Z_m\hat{T}_{ms}^{\alpha}\mu_{\alpha}^{s} + \frac{1}{3}\sum_{\alpha\beta}Z_m\hat{T}_{ms}^{\alpha\beta}\Theta_{\alpha\beta}^{s}\right) \tag{18}$$

here the convenience becomes obvious because of the evaluated energy; hence, the expectation value is the exact same expression as the Hamiltonian because the Hamiltonian does not depend on the electronic coordinates. On the other hand, we have the contribution involving the electrons of the QM subsystem

$$\hat{H}_{\mathrm{QM/MM}}^{\mathrm{el},i} = -\sum_{is}\left(\hat{T}_{is}q^s + \sum_{\alpha}\hat{T}_{is}^{\alpha}\mu_{\alpha}^{s} + \frac{1}{3}\sum_{\alpha\beta}\hat{T}_{is}^{\alpha\beta}\Theta_{\alpha\beta}^{s}\right) \tag{19}$$

and to obtain the energy we evaluate the expectation value as [64]

$$E_{\mathrm{QM/MM}}^{\mathrm{el},i} = -\int \rho(\mathbf{r})\sum_{s}\left(T_{is}q^s + \sum_{\alpha}\left(T_{is}^{\alpha}\mu_{\alpha}^{s} + \frac{1}{3}\sum_{\alpha\beta}T_{is}^{\alpha\beta}\Theta_{\alpha\beta}^{s}\right)\right)\mathrm{d}\mathbf{r} \tag{20}$$

where the point charge and the multipoles at the sites in the MM region are given and the electron density is $\rho(\mathbf{r})$.

The polarization energy is obtained from the expectation value of the polarization Hamiltonian, which is for the convenience split into the nuclei part and the electron part, just like the Hamiltonian for the electrostatic interactions, giving

$$E^{\mathrm{pol}}_{\mathrm{QM/MM}} = \frac{1}{2}\sum_{sm}\sum_{\alpha}\mu^{\mathrm{ind},s}_{\alpha}T^{\alpha}_{sm}Z^{m} - \frac{1}{2}\sum_{s}\sum_{\alpha}\mu^{\mathrm{ind},s}_{\alpha}\int T^{\alpha}_{is}\rho(\mathbf{r})\mathrm{d}\mathbf{r} \tag{21}$$

where Z^m is the nuclear charge on the atom in the QM region and the remaining parts have already been defined earlier.

The van der Waals interactions are given within the *Lennard–Jones* potential as in the MM treatment, although the summations are slightly different.

$$E^{\mathrm{vdw}}_{\mathrm{QM/MM}} = \sum_{s=1}^{S}\sum_{m:\mathrm{center}}\left[\frac{A_{ms}}{|\mathbf{R}_m - \mathbf{R}_s|^{12}} - \frac{B_{ms}}{|\mathbf{R}_m - \mathbf{R}_s|^{6}}\right] \tag{22}$$

where A_{ms} and B_{ms} are the interaction coefficients, and the summations cover the van der Waals interaction between the nuclei m and the classical sites s.

2.2 DFT/MM

Finally, the combined method of DFT and MM can be introduced as the total energy divided into three terms, where the energy is written as a function of the electron density.

$$E[\rho] = E_{\mathrm{MM}}[\rho] + E_{\mathrm{DFT}}[\rho] + E_{\mathrm{DFT/MM}}[\rho] \tag{23}$$

The second term depends on the chosen functional, and the first term can be divided into

$$E_{\mathrm{MM}}[\rho] = E^{\mathrm{el}}_{\mathrm{MM}} + E^{\mathrm{pol}}_{\mathrm{MM}}[\rho] + E^{\mathrm{vdw}}_{\mathrm{MM}} \tag{24}$$

and we found that only the polarization energy depends on the electron density, which is due to Eq. 14 with the induced dipole moment defined as [64]

$$\mu^{\mathrm{ind},s}_{\alpha} = \sum_{\beta}\alpha^{s}_{\alpha\beta}\mathbf{F}^{\mathrm{tot}}_{\beta}(\mathbf{r}_s) = \sum_{\beta}\alpha^{s}_{\alpha\beta}\left(F^{i}_{\beta}(\mathbf{r}_s) + F^{m}_{\beta}(\mathbf{r}_s) + F^{s}_{\beta}(\mathbf{r}_s) + F^{\mathrm{ind}}_{\beta}(\mathbf{r}_s)\right) \tag{25}$$

where the electric fields are defined as

$$F^{i}_{\beta}(\mathbf{r}_s) = \int T^{\beta}_{is}\rho(\mathbf{r})\mathrm{d}\mathbf{r} \tag{26}$$

$$F^{m}_{\beta}(\mathbf{r}_s) = -\sum_{m}T^{\beta}_{sm}Z_{m} \tag{27}$$

$$F^{s}_{\beta}(\mathbf{r}_s) = \sum_{s\neq s'}\left(-T^{\beta}_{ss'}q^{s'} + \sum_{\gamma}T^{\beta\gamma}_{ss'}\mu^{s'}_{\gamma} - \frac{1}{3}\sum_{\gamma\delta}T^{\beta\gamma\delta}_{ss'}\Theta^{s'}_{\gamma\delta}\right) \tag{28}$$

$$F^{\mathrm{ind}}_{\beta}(\mathbf{r}_s) = \sum_{s'\neq s}\sum_{\gamma}T^{\beta\gamma}_{ss'}\mu^{\mathrm{ind},s'}_{\gamma} \tag{29}$$

where it is obvious that $F^{i}_{\beta}(\mathbf{r}_s)$ contributes with the dependence of the electron density to the induced dipole and hence to the polarization energy in the MM region. The electrostatic energy $E^{\mathrm{el}}_{\mathrm{MM}}$ and the van der Waals energy $E^{\mathrm{vdw}}_{\mathrm{MM}}$ were found to be independent of the electron density and can therefore be ignored in the optimization of the electron density.

The energy contribution from $E_{\mathrm{DFT/MM}}$ is likewise split up as in the general QM/MM method where we found the electrostatic energy and the polarization energy to depend on the electron density

$$E_{\mathrm{DFT/MM}}[\rho] = E^{\mathrm{el}}_{\mathrm{DFT/MM}}[\rho] + E^{\mathrm{pol}}_{\mathrm{DFT/MM}}[\rho] + E^{\mathrm{vdw}}_{\mathrm{DFT/MM}} \tag{30}$$

and hence only the van der Waals energy in the DFT/MM can be ignored according to the optimization of the electron density. Note that the van der Waals contribution does not come from the DFT expressions but due to the DFT/MM calculation. However, as mentioned previously, the polarization and the electrostatic energy can be separated into a nucleus-dependent part and an electron-dependent part, and hence $E^{\mathrm{el},m}_{\mathrm{DFT/MM}}$ and $E^{\mathrm{pol},m}_{\mathrm{DFT/MM}}$ can be ignored in the optimization. Further, the electric fields arising from the nuclei in the QM region $F^{m}_{\beta}(\mathbf{r}_s)$ and the charges in the classical region $F^{s}_{\beta}(\mathbf{r}_s)$ can be ignored. The only contributions left to the electron density optimization are $E^{\mathrm{pol}}_{\mathrm{MM}}, E^{\mathrm{pol},i}_{\mathrm{DFT/MM}}$ and $E^{\mathrm{el},i}_{\mathrm{DFT/MM}}$, and collecting these terms gives rise to the DFT/MM interaction functional $v_{\mathrm{DFT/MM}}$ given by

$$\begin{aligned} v_{\mathrm{DFT/MM}} = {} & \frac{1}{2}\sum_{s}\sum_{s'>s}\sum_{\alpha\beta\gamma}\Big(\mu^{\mathrm{ind},s}_{\alpha}T^{\alpha}_{ss'}q^{s'} \\ & -\mu^{\mathrm{ind},s}_{\alpha}T^{\alpha\beta}_{ss'}\left(\mu^{s'}_{\beta} + \mu^{\mathrm{ind},s'}_{\beta}\right) + \frac{1}{3}\mu^{\mathrm{ind},s}_{\alpha}T^{\alpha\beta\gamma}_{ss'}\Theta^{s'}_{\beta\gamma}\Big) \\ & - \int\rho(\mathbf{r})\sum_{s}\left(T_{is}q^{s} + \sum_{\alpha}\left(T^{\alpha}_{is}\mu^{s}_{\alpha} + \frac{1}{3}\sum_{\alpha\beta}T^{\alpha\beta}_{is}\Theta^{s}_{\alpha\beta}\right)\right)\mathrm{d}\mathbf{r} \\ & - \frac{1}{2}\sum_{s}\sum_{\alpha}\mu^{\mathrm{ind},s}_{\alpha}\int T^{\alpha}_{is}\rho(\mathbf{r})\mathrm{d}\mathbf{r} \end{aligned} \tag{31}$$

where $\mu^{\mathrm{ind}_r,s}_{\alpha}$ is the reduced induced dipole moment $\mu^{\mathrm{ind}_r,s}_{\alpha} = \alpha^{s}_{\alpha\beta}(F^{\mathrm{pol},i}_{\beta}(\mathbf{r}_s) + F^{i}_{\beta}(\mathbf{r}_s))$. We combine this with the Kohn Sham vacuum energy from vacuum DFT, and we obtain the total energy functional as

$$E_{\mathrm{total}}[\rho] = E_{\mathrm{vacum}}[\rho] + v_{\mathrm{DFT/MM}}[\rho]. \tag{32}$$

3 Response theory

A majority of all experiments carried out on molecules can be understood as the interaction of a molecule with an electromagnetic field [68–70]. The term electromagnetic field can be illustrated in several ways: the static external electric field in a capacitor, an oscillating electric field and a magnetic field of electromagnetic radiation, an electric field due to another molecule nearby and so on.

The desired molecular properties in this presentation can be obtained using linear response theory, where the response functions are derived from time-dependent perturbation theory. This is done for an exact state, where it is required to know the exact eigenstates of the unperturbed Hamiltonian, but since it is not possible we also introduce methods of approximate states and it should be noted that second quantization is used [68–71].

3.1 Perturbation theory

In the presence of a time-dependent field $\boldsymbol{F}$, one has to find solutions to the time-dependent Schrödinger equation.

$$i\hbar\frac{\partial}{\partial t}|t\rangle = \hat{H}(t)|t\rangle \tag{33}$$

where the Dirac notation has been used for the simplicity indicating the time-dependent wave function $|t\rangle$. The total Hamiltonian of the system is composed of an unperturbed time-independent part $\hat{H}^{(0)}$ and a perturbed part $\hat{V}(t)$:

$$\hat{H}(t) = \hat{H}^{(0)} + \hat{V}(t) \tag{34}$$

where $\hat{V}(t)$ describes the interactions between the system and the field $\boldsymbol{F}$ causing the perturbation. It should be noted that the total Hamiltonian is only time-dependent in the presence of a time-dependent perturbation. In the state without perturbation, referred to as $|0\rangle$, it is assumed that $|0\rangle$ is an eigenfunction to the unperturbed Hamiltonian.

$$\hat{H}^{(0)}|0\rangle = E|0\rangle \tag{35}$$

and generally we have

$$\hat{H}^{(0)}|n\rangle = E_n|n\rangle \tag{36}$$

The perturbation will be adiabatically switched on in order to avoid any transient effects, and to ensure the adiabatically switching on of the field, a positive infinitesimal ϵ is incorporated. Taking the Fourier transformation of $\hat{V}(t)$, we obtain

$$\hat{V}(t) = \sum_{\omega} \hat{V}_{\alpha}^{\omega}\boldsymbol{F}_{\alpha}^{\omega}\mathrm{e}^{-i\omega t}\mathrm{e}^{\epsilon t} \tag{37}$$

where the integrals have been replaced with discrete sums due to a monochromatic perturbation i.e., a constant frequency ω. Further, the summation over the Cartesian axes is implied. $\boldsymbol{F}_{\alpha}^{\omega}$ are the Fourier amplitudes of the field along the molecular axis α, where the exponential function is the time-oscillating component; hence, the field is considered to be composed of a static component multiplied with a time-oscillating part, and $\hat{V}_{\alpha}^{\omega}$ could be the electric dipole.

What is left to determine is how the wave function evolves in time and this event depends on the chosen parametrization. In order to construct the time-dependent wave function, the following parametrization has been chosen.

$$|\psi(t)\rangle = \sum_n d_n(t)\mathrm{e}^{-iE_nt/\hbar}|n\rangle \tag{38}$$

In the reference state $|0\rangle$, the coefficient d_n is simply Kronecker delta and only contributes when $n = 0$. When inserting Eq. 38 into the Schrödinger Eq. 33 and multiplying both sides of the equation with the ket $|m\rangle$

$$\begin{aligned}&\langle m|i\hbar\frac{\partial}{\partial t}\sum_n d_n(t)\mathrm{e}^{-iE_nt/\hbar}|n\rangle\\ &\quad= \langle m|(\hat{H}^{(0)} + \hat{V}(t))\sum_n d_n(t)\mathrm{e}^{-iE_nt/\hbar}|n\rangle\end{aligned} \tag{39}$$

First, the right-hand side, (RS), of the equation is expanded and thereafter the left-hand side, (LS).

$$\mathrm{RS} = \langle m|(\hat{H}^{(0)} + \hat{V}(t))\sum_n d_n(t)\mathrm{e}^{-iE_nt/\hbar}|n\rangle \tag{40}$$

$$\begin{aligned}&= \langle m|\hat{H}^{(0)}\sum_n d_n(t)\mathrm{e}^{-iE_nt/\hbar}|n\rangle\\ &\quad+ \langle m|\hat{V}(t)\sum_n d_n(t)\mathrm{e}^{-iE_nt/\hbar}|n\rangle\end{aligned} \tag{41}$$

The left-hand side of Eq. 39 expanded:

$$\mathrm{LS} = \langle m|i\hbar\frac{\partial}{\partial t}\sum_n d_n(t)\mathrm{e}^{-iE_nt/\hbar}|n\rangle \tag{42}$$

$$= \langle m|i\hbar\sum_n\left(\frac{\partial d_n(t)}{\partial t}\mathrm{e}^{-iE_nt/\hbar} + d_n(t)\left(-\frac{iE_n}{\hbar}\right)\mathrm{e}^{-iE_nt/\hbar}\right)|n\rangle \tag{43}$$

$$= i\hbar\sum_n\langle m|\frac{\partial d_n(t)}{\partial t}\mathrm{e}^{-iE_nt/\hbar}|n\rangle + \sum_n\langle m|d_n(t)E_n\mathrm{e}^{-iE_nt/\hbar}|n\rangle \tag{44}$$

$$= i\hbar\frac{\partial d_m(t)}{\partial t}\mathrm{e}^{-iE_mt/\hbar} + \sum_n\langle m|d_n(t)\hat{H}^{(0)}\mathrm{e}^{-iE_nt/\hbar}|n\rangle \tag{45}$$

Setting RS = LS, some contributions vanish and we obtain:

$$i\hbar\frac{\partial d_m(t)}{\partial t}\mathrm{e}^{-iE_mt/\hbar} = \langle m|\hat{V}(t)\sum_n d_n(t)\mathrm{e}^{-iE_nt/\hbar}|n\rangle \tag{46}$$

$$= \sum_n\langle m|\hat{V}(t)|n\rangle d_n(t)\mathrm{e}^{-iE_nt/\hbar}|n\rangle \tag{47}$$

$$= \sum_n V_{mn}(t)d_n(t)\mathrm{e}^{-iE_nt/\hbar}|n\rangle \tag{48}$$

which is rewritten as

$$i\hbar\frac{\partial d_m(t)}{\partial t}=\sum_n V_{mn}(t)d_n(t)\mathrm{e}^{i(E_m-E_n)t/\hbar} \tag{49}$$

The equation is solved by considering expansions of the coefficients in power of series of the perturbation:

$$d_n(t)=d_n^{(0)}+d_n^{(1)}(t)+d_n^{(2)}(t)+\cdots \tag{50}$$

where the solution to the Nth order is

$$d_m^N(t)=\frac{1}{i\hbar}\int_{-\infty}^{t}\sum_n V_{mn}(t')d_n^{(N-1)}(t')\mathrm{e}^{i(E_m-E_n)t'/\hbar}dt' \tag{51}$$

with the corresponding wave function

$$|\psi(t)\rangle=|\psi^{(0)}(t)\rangle+|\psi^{(1)}(t)\rangle+|\psi^{(2)}(t)\rangle+\cdots \tag{52}$$

where the Nth order wave function is given by

$$|\psi^{(N)}(t)\rangle=\sum_n d_n^{(N)}(t)\mathrm{e}^{-iE_nt/\hbar}|n\rangle \tag{53}$$

Since we are only interested in the linear response in this presentation, only the first-order solution is given; however, higher-order solution can be obtained if the procedure is repeated. The first-order solution is given via Eq. 51 where it should be noted as previously that $d_n^0=\delta_{0n}$

$$d_m^{(1)}(t)=\frac{1}{i\hbar}\int_{-\infty}^{t}\sum_n\langle m|\sum_{\omega_1}\hat{V}_\alpha^{\omega_1}\boldsymbol{F}_\alpha^{\omega_1}\mathrm{e}^{-i\omega_1t}\mathrm{e}^{\epsilon t}|n\rangle\mathrm{e}^{i\omega_{mn}t'}\delta_{0n}dt' \tag{54}$$

$$=-\frac{1}{\hbar}\sum_{\omega_1}\frac{\langle m|\hat{V}_\alpha^{\omega_1}|0\rangle\mathbf{F}_\alpha^{\omega_1}}{\omega_{m0}-\omega_1-i\epsilon}\mathrm{e}^{i(\omega_{m0}-\omega_1)t}\mathrm{e}^{t\epsilon} \tag{55}$$

where $\omega_{mn}=(E_m-E_n)/\hbar$, and Eq. 37 has been used for V_{mn}. Finally, the first-order corrected wave function can be written if Eqs. 53 and 55 are combined.

$$|\psi(t)\rangle=|\psi^{(0)}(t)\rangle+|\psi^{(1)}(t)\rangle \tag{56}$$

$$=|0\rangle\mathrm{e}^{-iE_0t/\hbar}-\frac{1}{\hbar}\sum_n\sum_\omega\frac{\langle n|V_\alpha^\omega|0\rangle F_\alpha^\omega}{\omega_{n0}-\omega-i\epsilon}\mathrm{e}^{-i\omega t}\mathrm{e}^{t\epsilon}|n\rangle\mathrm{e}^{-iE_0t/\hbar} \tag{57}$$

where $\omega=\omega_1$ since only the linear perturbation is considered and hence only one field with one frequency.

3.2 Exact state

In order to determine the properties of interest, the time-dependent expectation value of the given observable has to be evaluated and this gives rise to the response functions. Let $\hat{\Omega}$ be the operator of the observable of interest, such as the electric dipole moment. The following expansion is considered

$$\langle\psi(t)|\hat{\Omega}|\psi(t)\rangle=\langle\psi^{(0)}|\hat{\Omega}|\psi^{(0)}\rangle \tag{58}$$

$$+\langle\psi^{(1)}|\hat{\Omega}|\psi^{(0)}\rangle+\langle\psi^{(0)}|\hat{\Omega}|\psi^{(1)}\rangle \tag{59}$$

$$+\cdots \tag{60}$$

and this expansion can be continued, but will not be considered in this presentation. Taking the Fourier transformation, we obtain

$$\langle\psi(t)|\hat{\Omega}|\psi(t)\rangle=\langle 0|\hat{\Omega}|0\rangle \tag{61}$$

$$+\sum_{\omega_1}\langle\langle\Omega;V_\beta^{\omega_1}\rangle\rangle\boldsymbol{F}_\beta^{\omega_1}\mathrm{e}^{-i\omega_1t}\mathrm{e}^{\epsilon t} \tag{62}$$

$$+\cdots \tag{63}$$

From the above equations, it is seen that the first-order properties are simply given by the expectation value of the operator of interest with respect to the reference state. The second-order properties are given with respect to the first-order correction to the expectation value evaluated by insertion of the zero-order wave function as well as the first-order correction given by the combination of Eqs. 55 and 53.

$$\begin{aligned}
\langle\Omega\rangle^{(1)}&=\langle\psi^{(1)}|\hat{\Omega}|\psi^{(0)}\rangle+\langle\psi^{(0)}|\hat{\Omega}|\psi^{(1)}\rangle\\
&=-\langle 0|\mathrm{e}^{iE_0t/\hbar}\Omega\sum_n\frac{1}{\hbar}\sum_{\omega_1}\frac{\langle n|\hat{V}_\beta^{\omega_1}|0\rangle\boldsymbol{F}_\beta^{\omega_1}}{\omega_{no}-\omega_1-i\epsilon}\mathrm{e}^{i(\omega_{n0}-\omega_1)t}\mathrm{e}^{\epsilon t}\mathrm{e}^{-iE_nt/\hbar}|n\rangle\\
&\quad-\sum_n\frac{1}{\hbar}\sum_{\omega_1}\frac{\langle 0|\hat{V}_\beta^{\omega_1}|n\rangle[\boldsymbol{F}_\beta^{\omega_1}]^*}{\omega_{n0}-\omega_1+i\epsilon}\mathrm{e}^{-i(\omega_{n0}-\omega_1)t}\mathrm{e}^{\epsilon t}\mathrm{e}^{iE_nt/\hbar}\langle n|\Omega\mathrm{e}^{iE_0t/\hbar}|0\rangle\\
&=-\sum_{\omega_1}\frac{1}{\hbar}\sum_n\frac{\langle 0|\hat{\Omega}|n\rangle\langle n|\hat{V}_\beta^{\omega_1}|0\rangle}{\omega_{no}-\omega_1-i\epsilon}\boldsymbol{F}_\beta^{\omega_1}\mathrm{e}^{-i\omega_1t}\mathrm{e}^{\epsilon t}\\
&\quad-\sum_{\omega_1}\frac{1}{\hbar}\sum_n\frac{\langle 0|\hat{V}_\beta^{\omega_1}|n\rangle\langle n|\hat{\Omega}|0\rangle}{\omega_{no}-\omega_1+i\epsilon}[\boldsymbol{F}_\beta^{\omega_1}]^*\mathrm{e}^{i\omega_1t}\mathrm{e}^{\epsilon t}\\
&=-\sum_{\omega_1}\frac{1}{\hbar}\sum_n\left[\frac{\langle 0|\hat{\Omega}|n\rangle\langle n|\hat{V}_\beta^{\omega_1}|0\rangle}{\omega_{no}-\omega_1-i\epsilon}+\frac{\langle 0|\hat{V}_\beta^{\omega_1}|n\rangle\langle n|\hat{\Omega}|0\rangle}{\omega_{no}+\omega_1+i\epsilon}\right]\boldsymbol{F}_\beta^{\omega_1}\mathrm{e}^{-i\omega_1t}\mathrm{e}^{\epsilon t}
\end{aligned} \tag{64}$$

where it has been used that ω runs over both negative and positive frequencies and the fact that the field is real and thereby $F^\omega=[F^{-\omega}]^*$.

The second-order properties, or linear response function, can now be expressed by Eq. 63 as

$$\langle\langle\hat{\Omega};\hat{V}_\beta^\omega\rangle\rangle=-\frac{1}{\hbar}\sum_n\left[\frac{\langle 0|\hat{\Omega}|n\rangle\langle n|\hat{V}_\beta^\omega|0\rangle}{\omega_{no}-\omega-i\epsilon}+\frac{\langle 0|\hat{V}_\beta^\omega|n\rangle\langle n|\hat{\Omega}|0\rangle}{\omega_{n0}+\omega+i\epsilon}\right] \tag{65}$$

The properties of interest can now be obtained if the excitation energies as well as the transition moments are known.

If we wish to obtain the polarizability tensor α, the substitution of $\hat{\Omega}=\hat{\mu}_\alpha$ and $\hat{V}_\beta^\omega=-\hat{\mu}_\beta$ is made.

$$\alpha_{\alpha\beta}(-\omega;\omega) = \frac{1}{\hbar}\sum_{n}{}' \left[\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle}{\omega_{no} - \omega - i\epsilon} + \frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle}{\omega_{n0} + \omega + i\epsilon}\right] \tag{66}$$

where the subscript in the summation indicates that we exclude the sum over the ground state, hence only sums over excited states.

3.3 Time-dependent DFT

In case of exact state, the eigenstates of the Hamiltonian of the unperturbed system were known; however, this is not the case in approximate state response theory, and thereby, the reference state is made by an approximation depending on the chosen quantum method. In this presentation, DFT is considered, and therefore, the linear response function is expressed within time-dependent density functional theory, TD-DFT. Further, the second quantization will be used [58]. It should be kept in mind that the expectation value of an operator is still at interest, like in the previous section, but for the simplicity ϵ is neglected in the following.

The Kohn–Sham reference determinant is built from an unperturbed Kohn–Sham determinant and an exponential parametrization of the time-evolution antihermitian operator $\hat{\kappa}(t)$ in the following manner:

$$|\Phi^{\mathrm{KS}}(t)\rangle = \mathrm{e}^{-\hat{\kappa}(t)}|\Psi^{\mathrm{KS}}_{(0)}\rangle \tag{67}$$

with the unperturbed determinant defined as

$$|\Psi^{\mathrm{KS}}_{(0)}\rangle = \prod_{p,\sigma}\hat{a}^{+}_{p\sigma}|vac\rangle \tag{68}$$

where $a^{+}_{p\sigma}$ is the creation operator, which adds electrons to the vacuum state.

The time-evolution operator is defined as

$$\hat{\kappa}(t) = \sum_{pq}\kappa_{pq}(t)\hat{E}_{pq} = \sum_{pq}\kappa_{pq}(t)\sum_{\sigma}\hat{a}^{+}_{p\sigma}\hat{a}_{q\sigma} \tag{69}$$

with $\hat{a}_{q\sigma}$ being the annihilation operator, which removes electrons from an orbital p or q. The excitation operator is therefore composed of operators removing and adding electrons from different orbitals, and furthermore, it should be noted that the reference determinant satisfies the equation:

$$(\hat{H} + \hat{V}(t))|\Psi^{\mathrm{KS}}(t)\rangle = i\hbar\frac{\partial}{\partial t}|\Psi^{\mathrm{KS}}(t)\rangle \tag{70}$$

where the Hamiltonian in the Kohn–Sham model is represented by

$$\hat{H} = \sum_{i} f(\mathbf{r}_i, t) \tag{71}$$

and depends implicitly on time due to the time-dependent electron density and $f(\mathbf{r}_i, t)$ is the Kohn–Sham operator. To obtain the time-dependent electron density, we have to introduce the density operator:

$$\hat{\rho}(\mathbf{r}) = \sum_{pq}\phi^{*}_{p}(\mathbf{r})\phi_{q}(\mathbf{r})\hat{E}_{pq} \tag{72}$$

and evaluating the expectation value of the operator

$$\rho(\mathbf{r},t) = \langle\Psi^{\mathrm{KS}}_{(0)}|\mathrm{e}^{\hat{\kappa}(t)}\hat{\rho}(\mathbf{r})\mathrm{e}^{-\hat{\kappa}(t)}|\Psi^{\mathrm{KS}}_{(0)}\rangle \tag{73}$$

where the exponential of an operator is equivalent to the Taylor expansion of exp:

$$\mathrm{e}^{\hat{\kappa}(t)} = \sum_{m}\frac{\hat{\kappa}^{m}(t)}{m!} \tag{74}$$

With this expansion up to second term, Eq. 73 can be expanded in a Baker–Campbell–Hausdorff expansion:

$$\rho(\mathbf{r},t) = \langle\Psi^{\mathrm{KS}}_{(0)}|(1+\hat{\kappa}(t))\hat{\rho}(\mathbf{r})(1-\hat{\kappa}(t))|\Psi^{\mathrm{KS}}_{(0)}\rangle \tag{75}$$

$$= \langle\Psi^{\mathrm{KS}}_{(0)}|\hat{\rho}(\mathbf{r})|\Psi^{\mathrm{KS}}_{(0)}\rangle + \langle\Psi^{\mathrm{KS}}_{(0)}|\hat{\kappa}(t)\hat{\rho}(\mathbf{r})|\Psi^{\mathrm{KS}}_{(0)}\rangle - \langle\Psi^{\mathrm{KS}}_{(0)}|\hat{\rho}(r)\hat{\kappa}(t)|\Psi^{\mathrm{KS}}_{(0)}\rangle \tag{76}$$

$$= \rho(\mathbf{r},0) + \langle\Psi^{\mathrm{KS}}_{(0)}|[\hat{\kappa}(t),\hat{\rho}(\mathbf{r})]|\Psi^{\mathrm{KS}}_{(0)}\rangle \tag{77}$$

where the non-linear terms have been neglected.

The time evolution operator is expanded in powers of perturbation in order to obtain the parameters $\kappa_{pq}(t)$

$$\hat{\kappa}(t) = \hat{\kappa}^{(1)}(t) + \hat{\kappa}^{(2)}(t) + \cdots \tag{78}$$

where the respective term can be expressed as its Fourier transformation, but only the linear perturbation is considered:

$$\hat{\kappa}^{(1)}(t) = \int\hat{\kappa}^{\omega}\mathrm{e}^{-i\omega t}\mathrm{d}\omega \tag{79}$$

For a monochromatic perturbation, the integrals would be replaced with sums.

The perturbed density matrices up to first order can now be introduced by combining Eqs. 78 and 77 yielding:

$$D^{(0)}_{pq} = \langle\Psi^{\mathrm{KS}}_{(0)}|\hat{E}_{pq}|\Psi^{\mathrm{KS}}_{(0)}\rangle \tag{80}$$

$$D^{(1)}_{pq} = \langle\Psi^{\mathrm{KS}}_{(0)}|\left[\hat{\kappa}^{(1)}(t),\hat{E}_{pq}\right]|\Psi^{\mathrm{KS}}_{(0)}\rangle \tag{81}$$

with the n'th order correction

$$\rho^{(n)}(\mathbf{r},t) = \sum_{pq}\phi^{*}_{p}(r)\phi_{q}(r)D^{(n)}_{pq}(t). \tag{82}$$

3.3.1 *The Kohn–Sham operators*

In order to proceed, the Kohn–Sham operators have to be evaluated in the perturbation; hence, expanding the operators in order of perturbation and the Kohn–Sham Hamiltonian is dependent on the electron density and thereby, it needs to be expanded in order of the perturbation.

$$\hat{H} = \sum_n \hat{H}^{(n)} = \sum_n \sum_{pq} \hat{f}^{(n)}_{pq} \hat{E}_{pq} \tag{83}$$

with

$$\hat{f}^{(n)}_{pq} = \delta_{n0} h_{pq} + j^{(n)}_{pq} + v^{(n)}_{xc,pq} \tag{84}$$

The first contribution is the one-electron integral over the kinetic energy and the nuclear attraction

$$h_{pq} = \left\langle \phi_p \middle| -\frac{1}{2}\nabla^2 + \sum_a \frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|} \middle| \phi_q \right\rangle \tag{85}$$

The second term is the n'th order Coulomb interaction

$$j^{(n)}_{pq} = \sum_{rs} g_{pqrs} D^{(n)}_{rs} \tag{86}$$

with g_{pqrs} being the two-electron integral

$$g_{pqrs} = \left\langle \phi_p(1)\phi_r(2) \middle| \frac{1}{r_{12}} \middle| \phi_q(1)\phi_s(2) \right\rangle \tag{87}$$

The n'th order exchange-correlation potentials are

$$v^{(n)}_{xc,pq} = \langle \phi_p | \hat{v}^{(n)}_{xc}(\mathbf{r}, t) | \phi_q \rangle \tag{88}$$

which depends on the chosen DFT functional.

3.3.2 *Linear response*

In order to determine the evolution parameters κ_{pq}, the Ehrenfest method is used, where we set up equations to determine the first-order term of Eq. 78 and hence the linear response functions. This is done by considering the time development of the expectation value of a given operator. On the basis of "Appendix", we obtain

$$\langle \Psi^{\mathrm{KS}}_{(0)} | \left[\hat{\mathbf{q}}, \mathrm{e}^{\hat{\kappa}} \left(\hat{H} + \hat{V}(t) - i\frac{\partial}{\partial t} \right) \mathrm{e}^{-\hat{\kappa}} \right] | \Psi^{\mathrm{KS}}_{(0)} \rangle = 0 \tag{89}$$

with $\hat{\mathbf{q}}$ representing the vector collecting the excitation operators $\hat{E}_{pq}$

$$\hat{\mathbf{q}} = \begin{pmatrix} \vdots \\ \hat{E}_{pq} \\ \vdots \end{pmatrix} \tag{90}$$

To obtain the linear response functions, Eq. 89 is expanded to first order (see "Appendix") giving

$$\begin{aligned} &\langle \Psi^{\mathrm{KS}}_{(0)} | \left[\hat{\mathbf{q}}, \left[\hat{\kappa}^{(1)}, \hat{H}^{(0)} \right] + \hat{H}^{(1)} \right] | \Psi^{\mathrm{KS}}_{(0)} \rangle \\ &\quad + i \langle \Psi^{\mathrm{KS}}_{(0)} | \left[\hat{\mathbf{q}}, \hat{\kappa}^{(1)} \right] | \Psi^{\mathrm{KS}}_{(0)} \rangle = \end{aligned} \tag{91}$$

$$-\langle \Psi^{\mathrm{KS}}_{(0)} | [\hat{\mathbf{q}}, \hat{V}(t)] | \Psi^{\mathrm{KS}}_{(0)} \rangle \tag{92}$$

By Fourier transformation of Eq. 92 into the frequency domain, we obtain

$$\begin{aligned} &\langle \Psi^{\mathrm{KS}}_{(0)} | \left[\hat{\mathbf{q}}, \left[\hat{\kappa}^{(\omega)}, \hat{H}^{(0)} \right] + \hat{H}^{(\omega)} \right] | \Psi^{\mathrm{KS}}_{(0)} \rangle \\ &\quad + \omega \langle \Psi^{\mathrm{KS}}_{(0)} | \left[\hat{\mathbf{q}}, \hat{\kappa}^{(\omega)} \right] | \Psi^{\mathrm{KS}}_{(0)} \rangle = \end{aligned} \tag{93}$$

$$-\langle \Psi^{\mathrm{KS}}_{(0)} | [\hat{\mathbf{q}}, \hat{V}^{\omega}(t)] | \Psi^{\mathrm{KS}}_{(0)} \rangle \tag{94}$$

To carry out the above equation in matrix structure, we start by expressing the first-order parameters in matrix form:

$$\hat{\kappa}^{\omega} = \left(\cdots \hat{E}_{pq} \cdots \right) \begin{pmatrix} \vdots \\ \hat{\kappa}^{\omega}_{pq} \\ \vdots \end{pmatrix} = \hat{\mathbf{q}}^{\dagger} \kappa^{\omega} \tag{95}$$

Right-hand side of Eq. 94 is expressed as the following perturbation vector

$$\mathbf{V}^{\omega} = \langle \Psi^{\mathrm{KS}}_{(0)} | [\hat{\mathbf{q}}, \hat{V}^{\omega}(t)] | \Psi^{\mathrm{KS}}_{(0)} \rangle \tag{96}$$

The left side can be expressed as the following

$$\mathbf{E}\kappa^{\omega} = \langle \Psi^{\mathrm{KS}}_{(0)} | \left[\hat{\mathbf{q}}, \left[\hat{H}^{(0)}, \hat{\kappa}^{(\omega)} \right] - \hat{H}^{(\omega)} \right] | \Psi^{\mathrm{KS}}_{(0)} \rangle \tag{97}$$

and the overlap matrix $\mathbf{S}$

$$\mathbf{S} = \langle \Psi^{\mathrm{KS}}_{(0)} | [\hat{\mathbf{q}}, \hat{\mathbf{q}}^{\dagger}] | \Psi^{\mathrm{KS}}_{(0)} \rangle \tag{98}$$

which can be recognized as the second term in Eq. 94 with Eq. 95 substituted in.

Finally, we have Eq. 94 expressed as a matrix structure

$$(\mathbf{E} - \omega\mathbf{S})\kappa^{\omega} = \mathbf{V}^{\omega} \tag{99}$$

The linear response functions can now be obtained considering Eqs. 63 and 77

$$\langle\langle \hat{\Omega}, \hat{V}^{\omega} \rangle\rangle = \langle \Psi^{\mathrm{KS}}_{(0)} | \left[\hat{\kappa}^{\omega}, \hat{\Omega} \right] | \Psi^{\mathrm{KS}}_{(0)} \rangle \tag{100}$$

$$= \langle \Psi^{\mathrm{KS}}_{(0)} | \left[\hat{\mathbf{q}}^{\dagger} \kappa^{\omega}, \hat{\Omega} \right] | \Psi^{\mathrm{KS}}_{(0)} \rangle \tag{101}$$

$$= \langle \Psi^{\mathrm{KS}}_{(0)} | \left[\hat{\mathbf{q}}^{\dagger}, \hat{\Omega} \right] | \Psi^{\mathrm{KS}}_{(0)} \rangle \kappa^{\omega} \tag{102}$$

$$= \langle \Psi^{\mathrm{KS}}_{(0)} | \left[\hat{\mathbf{q}}^{\dagger}, \hat{\Omega} \right] | \Psi^{\mathrm{KS}}_{(0)} \rangle (\mathbf{E} - \omega\mathbf{S})^{-1} \mathbf{V}^{\omega} \tag{103}$$

$$= -\mathbf{\Omega}^{\dagger} (\mathbf{E} - \omega\mathbf{S})^{-1} \mathbf{V}^{\omega} \tag{104}$$

with

$$\mathbf{\Omega} = \langle \Psi^{\mathrm{KS}}_{(0)} | \left[\hat{\mathbf{q}}, \hat{\Omega} \right] | \Psi^{\mathrm{KS}}_{(0)} \rangle \tag{105}$$

where the two vectors $\mathbf{\Omega}$ and $\mathbf{V}^{\omega}$ are denoted as property gradient vectors and give the desired properties just as Eq. 65 in the exact state theory. We have now obtained a method within DFT to calculate the desired properties.

4 Summary and conclusion

Our strategy for investigating by theoretical and computational approaches how sandwiched organic molecules can transport electrons between metallic electrodes involves the determination of molecular structure of the molecules in vacuum and between two metal electrodes. Our previous investigations have utilized methods that are available within two standard quantum chemical program packages that are Gaussian [72] and Dalton [73]. We have previously performed calculations on two molecules 1,4 benzenedithiol (OPV1) and 4,4′ stielbendithiol (OPV2), and the calculations were performed under different circumstances. We perform several geometry optimizations with different basis sets and functionals, and based on these results, we select the molecular geometries further calculations. We perform for the selected molecular geometries calculations in vacuum and in the junction for five redox states $Q = 0,\ \pm 1,\ \pm 2$ to obtain the total energy, for which the junction calculations include the polarization energy. Furthermore, we utilize the described QM/MM response method for calculating molecular properties, such as the polarizability α and the excitation energies, of the organic molecules within the junction. On the basis of the calculated total energies, excitation energies, and polarizabilitites of organic molecule, we are able to calculate the conductance as a function of bias and gate voltage, hereby obtaining the harlequin pattern of Coulomb blockade diamonds. Furthermore, we are able to investigate the effect of including or excluding terminal hydrogens on the organic molecule and how changes in the molecular structure due to the different redox states affect the conductance as a function of bias and gate voltage. Our future work will focus on the utilization of this strategy on larger organic molecules, and thereby, we will be able to compare our calculated conductivity behavior directly with experimental observations. For the situations where it is crucial to address the chemical bonding between the molecule and the nanoparticles, it is important to include some of the nearby metal atoms in the quantum mechanical part of the system. The modeling of interfacial effects between nanoparticles and organic molecules is important to include dipole- and quadropole interaction terms.

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Appendix

The Ehrenfest method used in the response theory section can be derived in the following manner where the time development of the expectation value of the following operator is represented by

$$\hat{Q}(t) = \mathrm{e}^{-\hat{\kappa}(t)}\hat{Q}\mathrm{e}^{\hat{\kappa}(t)} \tag{106}$$

Considering the expectation value of the commutator between $\hat{Q}(t)$ and the operators in the Schrödinger equation yields

$$\langle t|[\hat{Q}(t), \hat{H}(t)]|t\rangle = \langle t|[\hat{Q}(t), i\frac{\partial}{\partial t}]|t\rangle \tag{107}$$

with $|t\rangle$ being the time-dependent wave function. As mentioned in the section on response theory, $|t\rangle = \mathrm{e}^{\hat{\kappa}(t)}|0\rangle$ and Eq. 107 can be expanded as

$$\left\langle 0\left|\mathrm{e}^{\hat{\kappa}(t)}\begin{pmatrix}\mathrm{e}^{-\hat{\kappa}(t)}\hat{Q}\mathrm{e}^{\hat{\kappa}(t)}(\hat{H}_{(0)} + \hat{V}(t)) - \\ (\hat{H}_{(0)} + \hat{V}(t))\mathrm{e}^{-\hat{\kappa}(t)}\hat{Q}\mathrm{e}^{\hat{\kappa}(t)}\end{pmatrix}\mathrm{e}^{-\hat{\kappa}(t)}\right|0\right\rangle = \tag{108}$$

$$\left\langle 0\left|\mathrm{e}^{\hat{\kappa}(t)}\begin{pmatrix}\mathrm{e}^{-\hat{\kappa}(t)}\hat{Q}\mathrm{e}^{\hat{\kappa}(t)}i\frac{\partial}{\partial t} - \\ i\frac{\partial}{\partial t}\mathrm{e}^{-\hat{\kappa}(t)}\hat{Q}\mathrm{e}^{\hat{\kappa}(t)}\end{pmatrix}\mathrm{e}^{-\hat{\kappa}(t)}\right|0\right\rangle \tag{109}$$

and by rearranging, we obtain

$$\begin{aligned}&\langle 0|\hat{Q}\mathrm{e}^{\hat{\kappa}(t)}(\hat{H}_{(0)}+\hat{V}(t))\mathrm{e}^{-\hat{\kappa}(t)} - \mathrm{e}^{\hat{\kappa}(t)}(\hat{H}_{(0)}+\hat{V}(t))\mathrm{e}^{-\hat{\kappa}(t)}\hat{Q}|0\rangle = \\ &\langle 0|\hat{Q}\mathrm{e}^{\hat{\kappa}(t)}i\frac{\partial}{\partial t}\mathrm{e}^{-\hat{\kappa}(t)} - \mathrm{e}^{\hat{\kappa}(t)}i\frac{\partial}{\partial t}\mathrm{e}^{-\hat{\kappa}(t)}\hat{Q}|0\rangle\end{aligned} \tag{111}$$

and we rewrite as

$$\begin{aligned}&\langle 0|\left[\hat{Q}, \mathrm{e}^{\hat{\kappa}(t)}(\hat{H}_{(0)} + \hat{V}(t))\mathrm{e}^{-\hat{\kappa}(t)}\right]|0\rangle \\ &\quad = \langle 0|\left[\hat{Q}, \mathrm{e}^{\hat{\kappa}(t)}i\frac{\partial}{\partial t}\mathrm{e}^{-\hat{\kappa}(t)}\right]|0\rangle\end{aligned} \tag{112}$$

Collecting the terms on the left-hand side

$$\left\langle 0\left|\left[\hat{Q}, \mathrm{e}^{\hat{\kappa}(t)}\left(\hat{H}_{(0)} + \hat{V}(t) - i\frac{\partial}{\partial t}\right)\mathrm{e}^{-\hat{\kappa}(t)}\right]\right|0\right\rangle = 0 \tag{113}$$

and remembering that the exponential function can be expanded as $\mathrm{e}^{\hat{\kappa}(t)} = 1 + \hat{\kappa}(t) + \cdots$ we obtain

$$\begin{aligned}&\left\langle 0\left|\left[\hat{Q}, \left(\hat{H}_{(0)} + \hat{V}(t) - i\frac{\partial}{\partial t}\right)\right]\right|0\right\rangle \\ &+ \left\langle 0\left|\left[\hat{Q}, \left[\hat{\kappa}(t), \left(\hat{H}_{(0)} + \hat{V}(t) - i\frac{\partial}{\partial t}\right)\right]\right]\right|0\right\rangle + \cdots \\ &= 0\end{aligned} \tag{114}$$

In the following, it will be useful to know the following commutator

$$\begin{aligned}&\left[\hat{\kappa}(t), -i\frac{\partial}{\partial t}\right]|t\rangle = \hat{\kappa}(t)\cdot\left(-i\frac{\partial}{\partial t}\right)|t\rangle + i\frac{\partial}{\partial t}\cdot\hat{\kappa}(t)|t\rangle \\ &= \hat{\kappa}(t)\cdot\left(-i\frac{\partial}{\partial t}\right)|t\rangle + i\kappa^{\bullet}(t)|t\rangle\ + i\hat{\kappa}(t)\cdot\left(\frac{\partial}{\partial t}\right)|t\rangle = i\kappa^{\bullet}(t)|t\rangle\end{aligned} \tag{115}$$

where $\kappa^{\bullet}(t)=\frac{\partial\kappa}{\partial t}$.

By expanding Eq. 114 in orders of first-order perturbation and neglecting higher-order terms, we obtain:

$$\left\langle 0\left|\left[\hat{Q},\left(\hat{H}^{(1)}_{(0)}+\hat{V}(t)\right)\right]\right|0\right\rangle + \left\langle 0\left|\left[\hat{Q},\left[\hat{\kappa}^{(1)}(t),\hat{H}^{(0)}_{(0)}-i\frac{\partial}{\partial t}\right]\right]\right|0\right\rangle = 0 \tag{116}$$

where it should be remembered that $\hat{V}(t)$ is of first order and we rewrite this as:

$$\left\langle 0\left|\left[\hat{Q},\left(\hat{H}^{(1)}_{(0)}+\hat{V}(t)\right)\right]\right|0\right\rangle + \left\langle 0\left|\left[\hat{Q},\left[\hat{\kappa}^{(1)}(t),\hat{H}^{(0)}_{(0)}\right]+\left[\hat{\kappa}^{(1)}(t),-i\frac{\partial}{\partial t}\right]\right]\right|0\right\rangle = 0 \tag{117}$$

Using Eq. 115, it can be written as

$$\left\langle 0\left|\left[\hat{Q},\left(\hat{H}^{(1)}_{(0)}+\hat{V}(t)\right)\right]\right|0\right\rangle + \left\langle 0\left|\left[\hat{Q},\left[\hat{\kappa}^{(1)}(t),\hat{H}^{(0)}_{(0)}\right]\right|0\right\rangle + i\langle 0|\left[\hat{Q},\kappa^{\bullet}(t)\right]\right]|0\right\rangle = 0 \tag{118}$$

Since the frequency domain is of interest, we perform a Fourier transform but first we start by rearranging the equation:

$$\begin{aligned}&\left\langle 0\left|\left[\hat{Q},-\left[\hat{H}^{(0)}_{(0)},\hat{\kappa}^{(1)}\right]+\hat{H}^{(1)}_{(0)}\right]\right|0\right\rangle + i\langle 0|\left[\hat{Q},\kappa^{\bullet}(t)\right]|0\rangle\\ &\quad = -\langle 0|\left[\hat{Q},\hat{V}(t)\right]|0\rangle\\ &\left\langle 0\left|\left[\hat{Q},\left[\hat{H}^{(0)}_{(0)},\hat{\kappa}^{(1)}\right]-\hat{H}^{(1)}_{(0)}\right]\right|0\right\rangle - i\langle 0|\left[\hat{Q},\kappa^{\bullet}(t)\right]|0\rangle\\ &\quad = \langle 0|\left[\hat{Q},\hat{V}(t)\right]|0\rangle\end{aligned} \tag{119}$$

The Fourier transform of the equation brings it into the frequency domain we start by multiplying by $\mathrm{e}^{i\omega t}$ and thereby taking the integral one the time-dependent terms.

$$\begin{aligned}&\left\langle 0\left|\left[\hat{Q},\left[\hat{H}^{(0)}_{(0)},\hat{\kappa}^{\omega}\right]-\hat{H}^{\omega}\right]\right|0\right\rangle - i\left\langle 0\left|\left[\hat{Q},\int \mathrm{d}t\,\mathrm{e}^{i\omega t}\kappa^{\bullet}(t)\right]\right|0\right\rangle\\ &\quad = \langle 0|\left[\hat{Q},\hat{V}^{\omega}\right]|0\rangle\end{aligned} \tag{120}$$

The second term can be solved considering the partial integration and remembering that the first term can be neglected

$$\begin{aligned}\int \mathrm{d}t\,\mathrm{e}^{i\omega t}\kappa^{\bullet}(t) &= -\int\left[\frac{\partial}{\partial t}\mathrm{e}^{i\omega t}\right]\kappa(t)dt\\ &= -i\omega\int \mathrm{e}^{i\omega t}\kappa(t)\mathrm{d}t\\ &= -i\omega\kappa^{\omega}\end{aligned} \tag{121}$$

Eq. 120 can now be written as:

$$\begin{aligned}&\left\langle 0\left|\left[\hat{Q},\left[\hat{H}^{(0)}_{(0)},\hat{\kappa}^{\omega}\right]-\hat{H}^{\omega}\right]\right|0\right\rangle - \omega\langle 0|\left[\hat{Q},\kappa^{\omega}\right]|0\rangle\\ &\quad = \langle 0|\left[\hat{Q},\hat{V}^{\omega}\right]|0\rangle.\end{aligned} \tag{122}$$

References

1. Li X, Staykov A, Yoshizawa K Theo Chem Acc (accepted for the Imamura Festschriff). doi:10.1007/s00214-011-0968-y
2. Naleway CA, Curtiss LA, Miller JR (1991) J Phys Chem 95:8434
3. Larsson S (1981) J Am Chem Soc 103:4034
4. Marcus RA (1956) J Chem Phys 24:966
5. Marcus RA (1964) Ann Rev Phys Chem 15:155
6. Marcus RA (1965) J Chem Phys 43:679
7. Kuznetsov AM, Ulstrup J (1999) Electron transfer in chemistry and biology. Wiley, Chichester
8. Mikkelsen KV, Ratner MA (1987) Chem Rev 87:113
9. Beratan DN, Hopfield JJ (1984) J Am Chem Soc 106:1584
10. Rendell APL, Bacskay GB, Hush NS (1988) J Am Chem Soc 110:8343
11. Newton MD (1999) Adv Chem Phys 106:303
12. Reimers JR, Hush NS (1990) Chem Phys 146:89
13. Aviram A, Ratner MA (1974) Chem Phys Lett 29:277
14. Mujica V, Kemp M, Roitberg A, Ratner MA (1996) J Chem Phys 104:7296
15. Mujica V, Kemp M, Ratner MA (1994) J Chem Phys 101:6849
16. Nitzan A, Ratner MA (2003) Science 300:1384
17. Lindsay SM, Ratner MA (2007) Adv Mat 19:23
18. Park H, Park J, Lim AKL, Anderson EH, Alivisatos AP, McEuen PL (2000) Nature 407:57
19. Park J, Pasupathy AN, Goldsmith JI, Chang C, Yaish Y, Petta JR, Rinkoski M, Sethne JP, Abrua HD, McEuen PL, Ralph DC (2002) Nature 417:722
20. Liang W, Shores MP, Bockrath M, Long JR, Park H (2002) Nature 417:725
21. Kubatkin S, Danilov A, Hjort M, Cornil J, Brdas J-L, Stuhr-Hansen N, Hedegård P, Bjørnholm T (2003) Nature 425:698
22. Chen J, Reed MA, Rawlett AM, Tour JM (1999) Science 286:1550
23. Blum AS, Kushmerick JG, Long DP, Patterson CH, Yang JC, Henderson JC, Yao YX, Tour JM, Shashidhar R, Ratna BR (2005) Nat Mater 4:167
24. van der Molen SJ, Liljeroth P (2010) J Phys Condens Matter 22:133001
25. Mirkin CA, Ratner MA (1992) Ann Rev Phys Chem 43:719
26. Alivisatos AP, Barbara PF, Castleman AW, Chang J, Dixon DA, Klein ML, McLendon GL, Miller JS, Ratner MA, Rossky PJ, Stupp SI, Thompson ME (1998) Adv Mater 10:1297
27. Nitzan A, Ratner MA (2003) Science 300:1384
28. Health JR, Ratner MA (2003) Phys Today 56:43
29. Mikkelsen KV, Ratner MA (1989) J Chem Phys 90:4237
30. Taniguchi M, Tsutsui M, Mogi R, Sugawara T, Tsuji Y, Yoshizawa K, Kawai T (2011) J Am Chem Soc 133:11426
31. Saito T, Nishihara S, Yamanaka S, Kitagawa Y, Kawakami T, Yamada S, Isobe H, Okumura M, Yamaguchi K Theo Chem Acc. doi:10.1007/s00214-011-0941-9
32. Olsen ST, Hansen T, Mikkelsen KV (submitted) J Phys Chem C
33. Galperin M, Nitzan A (2005) Phys Rev Lett 95:206802
34. Galperin M, Nitzan A (2006) J Chem Phys 124:234709
35. Orrit M (2009) Nature 460:42
36. Hwang J, Pototschnig M, Lettow R, Zumofen G, Renn A, Goetzinger S, Sandoghdar V (2009) Nature 460:76
37. Ward DR, Halas JN, Ciszek JW, Tour JM, Wu Y, Nordlander P, Natelson D (2008) Nano Lett 8:919

38. Sukharev M, Galperin M (2010) Phys Rev B 81:165307
39. Song H, Kim Y, Jang YH, Jeong H, Reed MA, Lee T (2009) Nat Lett 462:1039
40. Hansen T, Solomon GC, Andrews DQ, Ratner MA (2009) J Chem Phys 131:194704-1
41. Kaasbjerg K, Flensberg K (2008) Nano Lett 8:3809
42. Stokbro K (2010) J Phys Chem C 114:20461
43. Hansen T, Mikkelsen KV (2004) Theo Chem Acc 111:122
44. Hansen T, Pedersen TB, Mikkelsen KV (2005) Chem Phys Lett 405:118
45. Kongsted J, Osted A, Mikkelsen KV, Christiansen O (2003) J Phys Chem A 107:2578
46. Kongsted J, Osted A, Mikkelsen KV, Christiansen O (2003) J Chem Phys 118:1620
47. Kongsted J, Osted A, Mikkelsen KV, Christiansen O (2003) J Chem Phys 119:10519
48. Kongsted J, Osted A, Mikkelsen KV, Christiansen O (2004) J Chem Phys 120:3787
49. Kongsted J, Osted A, Mikkelsen KV, Christiansen O (2002) Mol Phys 100:1813
50. Mikkelsen KV (2006) Ann Rev Phys Chem 57:365
51. Nielsen CB, Christiansen O, Mikkelsen KV, Kongsted J (2007) J Chem Phys 126:154112
52. Hansen T (2005) A molecule wired. Ph.D. thesis, University of Copenhagen
53. Hansen T, Mikkelsen KV Manuscript in preparation
54. Becke AD (1993) J Chem Phys 98:5648
55. Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ (1994) J Phys Chem 98:11623
56. Yanai T, Tew DP, Handy NC (2004) Chem Phys Lett 393:51
57. Peach MJG, Helgaker T, Sałek P, Keal TW, Lutnæs OB, Tozer DJ, Handy NC (2006) Phys Chem Chem Phys 8:558
58. Surjan PR (1989) Second quantized approach to quantum chemistry. Springer, Berlin, Germany
59. Tomasi J, Pomelli CS (1998) In: Encyclopedia of computational chemistry. Wiley, New York, p 2343
60. Hohenberg P, Kohn W (1964) Phys Rev 136:B864
61. Jensen F (2007) Introduction to computational chemistry, 2nd edn. Wiley, New York
62. Stone AJ (1996) The theory of intermolecular forces. Clarendon Press, Oxford
63. Jones JE (1924) Royal Soc Lond 106:441
64. Osted A, Kongsted J, Mikkelsen KV, Christiansen O (2004) J Phys Chem A 108:8646
65. Poulsen TD, Kongsted J, Osted A, Ogilby PR, Mikkelsen KV (2001) J Chem Phys 115:2393
66. Poulsen TD, Ogilby PR, Mikkelsen KV (2002) J Chem Phys 116:3730
67. Nymand TM, Astrand P-O, Mikkelsen KV (1997) J Phys Chem B 101:4105
68. Sauer SPA (2011) Molecular electromagnetism. A computational chemistry approach. Oxford University Press, Oxford, UK
69. Olsen J, Jørgensen P (1985) J Chem Phys 82:3235
70. Salek P, Vahtras O, Helgaker T, Ågren H (2002) J Chem Phys 117:9630
71. Norman P (2011) Notes on response theory
72. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, . Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2009) Gaussian09, Revision A.1, Gaussian, Inc, Wallingford, CT
73. Dalton Quantum Chemistry Program (2005) http://www.kjemi.uio.no/software/dalton/dalton.html