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Molecular properties of molecules between electrodes

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Abstract. We consider methods for determining properties of molecules between electrodes. We utilize a heterogeneous and structured solvation model for describing the physical situation of a molecule located between electrodes. This method includes directly the polarization terms of the surrounding environment in the quantum mechanical equations.

Keywords: heterogeneous solvation – molecular properties – conductance – ab-initio – wave functions

1 Introduction

In order to determine relevant and measureable molecular properties of molecules located between electrodes it is beneficial to invoke response theory in order to calculate time-dependent electromagnetic properties. The utilization of response methods has mainly been for computing static and dynamic molecular properties of molecules in the gas phase [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. The response methods have been extended to include solvated molecular systems [13, 14, 15, 16, 17]. For the solvent response methods, one encounters a model where the solute is enclosed in a spherical cavity which is embedded in a dielectric medium. The electronic structure of the solute is represented by either uncorrelated or correlated electronic wave functions. The electromagnetic molecular properties such as excitation energies and transition matrix elements, one-photon and two-photon transition moments, can be obtained from an analysis of the poles and residues of the response functions, respectively and mixed electric–magnetic properties along with first-order and second-order hyperpolarizability tensors are also obtained from the response functions. The models have been developed for nonequilibrium [13, 14, 15, 16] and equilibrium [17] solvent response models. The electronic structure methods include Hartree–Fock (HF), multiconfigurational self-consistent reaction field (MCSCRF) and coupled-cluster SCRF (CCSCRF) and response functions up to the level of cubic response have been developed.

The research area involving the development of electronic structure methods for molecules embedded in a dielectric medium has been a very active one [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52]. The occurrence of nonequilibrium solvation states which appear when considering optical processes has been handled by the introduction of optical and inertial polarization vectors [47, 53]. Most of these models utilize uncorrelated electronic structure methods for the solute [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 31, 32, 33, 34, 35]. The use of correlated electronic methods for solvated molecules has been presented at the second-order Møller–Plesset (MP2) level [44, 46], the MCSCRF level [29, 36] and the CCSCRF level [52].

In order to describe a solvated molecule in a dielectric film which is adsorbed on a metallic surface or a heterogeneously solvated molecule or a molecule located between electrodes/metal plates, one has to develope new methods. Our present aim is to investigate how energies and linear along with nonlinear optical electromagnetic properties of molecular systems are influenced by the presence of two or more dielectric media. These concerns are of importance for many areas of chemistry, such as electrochemistry, photocatalysis, molecular wires, surface photochemistry and surface-enhanced two-photon transitions or hyperpolarizabilities. Therefore, our focus is on how to develop methods for determining linear and nonlinear response molecular properties of molecules enclosed within two electrodes where the metal is given as a perfect conductor and the electronic structure of the solvated molecular systems is given by an uncorrelated or a correlated electronic structure wave function. Our response methods for this physical situation enable the determination of molecular properties up to fourth order and they include

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- Frequency-dependent second-order hyperpolarizabilities (γ).
- One-, two- and three-photon absorptions.
- Two-photon absorption between excited states.
- Frequency-dependent polarizabilities.
- Frequency-dependent polarizabilities of excited states.
- Frequency-dependent first-order hyperpolarizability tensors.
- One-, two- and three- photon matrix elements.

The manufacture and development of photonic and optoelectronic devices have been performed with the intention of making new materials within telecommunication, data storage and information processing [54, 55, 56, 57, 58, 59, 60, 61, 62, 63]. Theoretical investigations and numerical computations are helpful for understanding and predicting the molecular properties of molecular structures that are coupled to the surrounding media. Here, it is important to investigate the relationship between the molecular structure and its molecular properties along with the effects of the surrounding media [1, 2, 3, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76].

Within molecular electronics, electronic transport in molecular systems or the notion of molecular wires is a rapidly expanding research field both theoretically and experimentally [77, 78, 79, 80]. Useful devices have been designed and manufactured utilizing molecular units [81, 82, 83, 84, 85, 86, 87]. For future design and improved understanding of the fundamental physics behind the multitude of molecular devices it is pertinent to have theoretical and computational tools suited for these tasks. The theoretical investigations have to be based on the actual layout of the molecular device and include the various externally applied fields or potentials. Our present contribution enables theoretical investigations and computational studies of molecules located between electrodes and subjected to external fields, either static or frequency-dependent electromagnetic fields.

We start out by developing a model that describes how a molecular system is coupled to electrodes and exposed to an externally applied field or bias. This section contains a derivation of how to couple a quantum mechanical representation of the molecular system with the bulk electrodes and classical external electromagnetic fields. We present the equations for describing the physical situation that the molecules are influenced by. The quantum mechanical equations are presented in connection with the classical electrostatic equations. Thereby, we are able to obtain and calculate wave functions and energies for the molecule coupled to the electrodes. The following section (Sect. 3) contains a derivation of a response method concerning the calculations of molecular properties of a molecule between electrodes. The calculated molecular properties in Sect. 4 form the basis for a model determining the conductance of a molecule between two electrodes and exposed to an external electric field or bias. The methods in the Sects. 2 and 3 enable us to calculate the necessary energies and molecular properties of the molecular system located between the two electrodes that are used in the model presented in Sect. 4. The last section concludes this presentation and outlines some of our future work within this area.

2 The coupling of a molecular system with dielectric media

Theoretical and computational methods involving the coupling of a molecular system with the surrounding media have been utilized [18–49, 88, 89, 90, 91]. The molecular system, the subsystem of principal interest, is described using quantum mechanics and the surrounding media are treated by a simpler method. The interactions between the molecular system and the surrounding media are given by the interactions between charges and/or induced charges and a van der Waals term [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34]. Effectively, these interactions are represented by an interaction operator which is included in the quantum mechanical equations and the quantum state for the prinicipal system is determined in the presence of the other subsystems [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 31, 32, 33, 35, 40, 42, 44, 45, 46, 47, 48, 49].

A simple example is to think of a molecule embedded in a dielectric medium as a model of a homogeneously solvated molecule. In fact such models can be generalized to incorporate any number of external media. Each such medium then represents a solvent, a solid surface, an electrode or perhaps a polymer phase. The dielectric media are modeled as continuous media, each being linear, homogeneous and isotropic and they are characterized by a scalar, optical, inertial or static dielectric constant. In this context a metallic phase is thought of as a dielectric medium with infinite dielectric constant, $\epsilon = \infty$.

We are interested in the situation where a molecule is placed between two metal electrodes. The electrostatic interaction with the metals will be included in the molecular Hamiltonian and in the case where an external bias is applied to the metal electrodes we have a simple electrostatic model of a molecular wire experiment.

Since there is no charge-transfer mechanism in such a model no current will run through the molecular wire. However, much insight can be obtained from an electrostatic model since in such systems the molecule couples only weakly to the electrodes and the molecule–metal interactions are dominated by electrostatics. Thus, an electrostatic model should give a good description of how much the molecular levels are shifted by the electrodes. This is a vital piece of information if one wants to model the conductance of a molecular wire.

To model contemporary molecular wire experiments, a third electrode should be taken into account. This electrode is situated below the substrate on which the desired nanostructure is synthesized. To this electrode a so-called gate voltage is applied which effectively shifts the molecular levels compared to the Fermi levels of the source and drain electrodes.

We represent the quantum state of the molecular system, M, by the electronic wave function, Ψ, and we denote the charge distribution by ρ_{M}. The presence of the charge distribution between the two electrodes gives rise to polarization charges in the two surrounding dielectric media and the creation of a reaction field and a polarization potential, $\Phi^{\text{ind}}(\boldsymbol{r})$, in the dielectric. The induced reaction field interacts with the molecular charge distribution, ρ_{M}, at a point $\boldsymbol{r}$ inside the cavity and the polarization energy is determined by

$$E_{\text{pol}} = \frac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\rho_{\text{M}}(\boldsymbol{r})\Phi^{\text{ind}}(\boldsymbol{r}) \tag{1}$$

and the interaction energy is given by

$$E_{\text{int}} = \int \mathrm{d}\boldsymbol{r}\,\rho_{\text{M}}(\boldsymbol{r})\Phi^{\text{ind}}(\boldsymbol{r}) \ . \tag{2}$$

The models for calculating molecular properties of a molecule between surrounding media require that we must solve simultaneously a quantum mechanical problem (the Schrödinger equation) and a classical electrostatic problem (the Poisson equation). Additionally, the equations for the quantum mechanical and electrostatic problems have to be solved subject to the boundary conditions defined by the geometry of the electrodes.

2.1 The Quantum mechanical problem

We solve the Schrödinger equation using the following Hamiltonian

$$H_{\text{M}}(\mathbf{q};\mathbf{Q})\Psi(\mathbf{q};\mathbf{Q}) = E(\mathbf{Q})\Psi(\mathbf{q};\mathbf{Q}) \ , \tag{3}$$

where we have included the couplings to the dielectric media and this is solved for a fixed nuclear configuration. The effective molecular Hamiltonian, H_{M}, is given as

$$H_{\text{M}}(\mathbf{q};\mathbf{Q}) = H^0_{\text{M}}(\mathbf{q};\mathbf{Q}) + W_{\text{pol}} \ , \tag{4}$$

where the coordinates of N_{el} electrons and M nuclei are termed $\mathbf{q} \equiv \mathbf{q}_1, \ldots, \mathbf{q}_{N_{\text{el}}}$ and $\mathbf{Q} \equiv \mathbf{Q}_1, \ldots, \mathbf{Q}_{\text{M}}$, respectively. The effective molecular Hamiltonian contains two terms:

- The Hamiltonian of the molecular system in a vacuum with fixed nuclear configuration, H^0_{M}.
- The interaction, W_{pol}, between the molecular system and the dielectric media.

The interaction operator, W_{pol}, describing the interactions between the molecule and the dielectric media, depends on the induced potential, $\Phi^{\text{ind}}(\boldsymbol{r})$, in the surrounding dielectric media along with the molecular charge distribution $\rho_{\mathbf{m}}(\boldsymbol{r})$. The latter is given by

$$\rho_{\text{m}}(\boldsymbol{r}) = \sum_{i=1}^{M} Q_i\delta(\boldsymbol{r} - \boldsymbol{R}_i) \ , \tag{5}$$

where Q_i is the partial charge on the ith nucleus at position $\boldsymbol{R}_i$.

We assign the molecular charge distribution using the approach proposed by Cioslowski [92, 93]. Previously, it was demonstrated by Åstrand et al. [94] that this type of charge assignment follows the normal convergency rules with respect to one- and many-electron basis sets.

2.2 The classical electrostatic problem

For a given molecular charge distribution – in our case a Cioslowski-type point-charge distribution – we want to determine the induced potential from the electrodes. Thus, we need to solve the Poisson equation subject to the appropriate boundary conditions.

In the case of metallic electrodes these are particularly simple. We want to specify the potential applied to each electrode, thus we impose Dirichlet boundary conditions on the potential. With a simple electrode geometry it may be possible to obtain the corresponding Green's function $G_D(\boldsymbol{r}, \boldsymbol{r}')$ subject to the constraint that $G_D(\boldsymbol{r}, \boldsymbol{r}') = 0$ when $\boldsymbol{r}'$ is on a surface.

Now the potential due to a charge distribution $\rho(\boldsymbol{r}')$ in the presence of grounded surfaces is given by

$$\Phi(\boldsymbol{r}) = \frac{1}{4\pi\varepsilon_0}\int \mathrm{d}\boldsymbol{r}'\rho(\boldsymbol{r}')G_{\text{D}}(\boldsymbol{r}, \boldsymbol{r}') \ . \tag{6}$$

Since we only want the induced potential we subtract a free- space Coulomb potential:

$$\Phi^{\text{ind}}(\boldsymbol{r}) = \frac{1}{4\pi\varepsilon_0}\int \mathrm{d}\boldsymbol{r}'\rho(\boldsymbol{r}')\left\{G_{\text{D}}(\boldsymbol{r}, \boldsymbol{r}') - \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}\right\} \ . \tag{7}$$

When the sufaces are held at finite voltages the molecule is exposed to an external potential. In general we have [95]:

$$\Phi^{\text{bias}}(\boldsymbol{r}) = -\frac{1}{4\pi}\int_S \mathrm{d}a'\Phi^{\text{bias}}(\boldsymbol{r}')\frac{\partial G_{\text{D}}}{\partial n'} \ , \tag{8}$$

where the normal derivative of the Green's function is defined as

$$\frac{\partial G_{\text{D}}}{\partial n'} = \mathbf{\nabla}_{\boldsymbol{r}'}G_{\text{D}}(\boldsymbol{r}, \boldsymbol{r}')\cdot\boldsymbol{n}(\boldsymbol{r}') \ . \tag{9}$$

Here $\boldsymbol{n}(\boldsymbol{r}')$ is unit vector normal to the surface at $\boldsymbol{r}'$ and pointing into the electrode. If electrode number i is held at potential Φ^{bias}_i the total potential is given by

$$\Phi^{\text{bias}}(\boldsymbol{r}) = -\frac{1}{4\pi}\sum_i \Phi^{\text{bias}}_i \int_{S_i} \mathrm{d}a'\frac{\partial G_{\text{D}}}{\partial n'} \ . \tag{10}$$

So the total external potential to which a molecule is exposed is given by

$$\Phi(\boldsymbol{r}) = \Phi^{\text{ind}}(\boldsymbol{r}) + \Phi^{\text{bias}}(\boldsymbol{r}) \tag{11}$$

2.2.1 Model potentials

For a simple electrode configuration the Green's function can be obtained by the method of image charges. As is well known, a point charge in the vicinity of a metal surface induces an image charge within the metal. For a charge at the point $\boldsymbol{r}' = (x', y', z')$ near a surface in the $x = 0$ plane the image charge is at $\boldsymbol{r}'' = (-x', y', z')$. The Green's function to describe the situation is given by:

$$G_D(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} - \frac{1}{|\boldsymbol{r}-\boldsymbol{r}''|} \quad . \tag{12}$$

If a second electrode is set in the $x = l$ plane an infinite number of point charges are induced in each electrode. Let $\hat{\boldsymbol{x}}$ be a unit vector in the x-direction. Now $\boldsymbol{r}'' = \boldsymbol{r}' - 2x'\hat{\boldsymbol{x}}$. The Green's function is given by

$$G_D(\boldsymbol{r},\boldsymbol{r}') = \sum_{n=-\infty}^{\infty} \left[\frac{1}{|\boldsymbol{r}-(\boldsymbol{r}'+2nl\hat{\boldsymbol{x}})|} - \frac{1}{|\boldsymbol{r}-(\boldsymbol{r}'-2x'\hat{\boldsymbol{x}}+2nl\hat{\boldsymbol{x}})|} \right] \quad . \tag{13}$$

The induced potential can now be calculated using Eq. (7).

If we want to include a third electrode – a gate electrode – the electrostatic problem becomes much harder to solve. An approximative procedure would be to disregard the gate electrode when calculating the induced potential $\Phi^{\mathrm{ind}}(\boldsymbol{r})$. The problem remaining is then to solve the Laplace equation with the full electrode configuration. If needed, this problem can also be divided into two. The constant electric field from the simpler two-electrode problem is then superimposed on the solution to the case where a potential, V, is applied to the gate electrode and the other two electrodes are grounded.

A simple extention to the previous problem is to put a surface, held at V, in the $y = 0$ plane. The solution to this problem is given by [95]

$$\Phi^{\mathrm{bias}}(x,y) = \frac{4V}{\pi} \sum_{n\ \mathrm{odd}} \frac{1}{n} \exp\left(-\frac{n\pi y}{l}\right) \sin\left(\frac{n\pi x}{l}\right) \quad . \tag{14}$$

2.2.2 The reaction field

We find by introducing the wave function that we are able to write the interaction operator between the dielectric media and the molecule as

$$W_{\mathrm{pol}} = \sum_j \sum_k \Phi^{(k)}(\boldsymbol{r}_j) \sum_{rs} \langle \phi_r |\ q_j | \phi_s \rangle E_{rs} \quad , \tag{15}$$

where

- ϕ_r and ϕ_s represent molecular the orbitals r and s, respectively.
- The excitation operator, E_{rs}, is defined as:

  $$E_{rs} = \sum_\sigma a^\dagger_{r\sigma} a_{s\sigma} \quad . \tag{16}$$

- The operators $a^\dagger_{r\sigma}$ and $a_{r\sigma}$ are the creation and annihilation operators for an electron in the spin orbital $\phi_{r\sigma}$, respectively.

3 MCSCRF response theory for a molecule surrounded by dielectric media

This section considers how to obtain the response of a molecular system coupled to surrounding dielectric media of the reference state when the total system is exposed to a time-dependent perturbation. The application of a time-dependent perturbation to the system gives a nonstationary state and this implies that the time-dependent Schrödinger equation must be considered. We do this by applying Frenkel's variation principle in the form of the Ehrenfest equation and for the operator A we have

$$\frac{\mathrm{d}\langle A \rangle}{\mathrm{d}t} = \left\langle \frac{\partial A}{\partial t} \right\rangle - i\langle [A,H] \rangle \quad , \tag{17}$$

where the total Hamiltonian for the molecular system interacting with an external field is

$$H = H_0 + W_{\mathrm{pol}} + V(t) \quad . \tag{18}$$

The underlying assumptions are

- The terms $(H_0 + W_{\mathrm{pol}})$ form the time-independent Hamiltonian of the unperturbed system.
- The term $V(t)$ is the time-dependent perturbation corresponding to the external field.
- The expectation values are determined from the time-dependent wave function, $|0^t\rangle$, at time t

  $$\langle \cdots \rangle = \langle {}^t0 | \cdots | 0^t \rangle \tag{19}$$

- The time-dependent wave function $|0^t\rangle$ at time t is given as

  $$|0^t\rangle = \exp[i\kappa(t)] \exp[iS(t)] |0\rangle \quad . \tag{20}$$

- The electronic wave function $|0\rangle$ is given by an optimized multiconfigurational self-consistent reference wave function

  $$(H_0 + W_{\mathrm{pol}})|0\rangle = E_0|0\rangle \quad , \tag{21}$$

- The electronic wave function satisfies the generalized Brillouin condition

  $$\langle 0 | [\lambda, H_0 + W_{\mathrm{pol}}] | \rangle \tag{22}$$

  for both the orbital and configurational variation parameters, λ.

Overall, we have a wave function that has been optimized in the presence of the surrounding dielectric media. The two transformation operators, $\exp[iS(t)]$ and $\exp[i\kappa(t)]$, perform unitary transformations in the configuration and orbital space, respectively. Their definitions are

$$S(t) = \sum_n [S_n(t)R^\dagger_n + S^*_n(t)R_n] \tag{23}$$

and

$$\kappa(t) = \sum_k [\kappa_k(t)c^\dagger_k + \kappa^*_k(t)c_k] \quad . \tag{24}$$

The transformation operators within the configuration and orbital spaces are defined by

- The excitation operator, c_k, which is written as

  $$c_k = E_{pq} \quad p > q \quad . \tag{25}$$

- The state-transfer operator, R_n, which is given as

  $$R^\dagger_m = |n\rangle\langle 0| \tag{26}$$

with $|n\rangle$ belonging to the orthogonal complement space to $|0\rangle$.

In order to describe the evolution of the molecular system we introduce a set of operators, $\mathbf{T}$:

$$\mathbf{T} = (\mathbf{c}^\dagger, \mathbf{R}^\dagger, \mathbf{c}, \mathbf{R}) \ , \tag{27}$$

where the individual components are given as

$$c_k^{\dagger,t} = \exp{[i\kappa(t)]} c_k^\dagger \exp{[-i\kappa(t)]} \ , \tag{28}$$

$$c_k^t = \exp{[i\kappa(t)]} c_k \exp{[-i\kappa(t)]} \ , \tag{29}$$

$$R_n^{\dagger,t} = \exp{[i\kappa(t)]}\exp{[iS(t)]}R_n^\dagger \exp{[-iS(t)]}\exp{[-i\kappa(t)]} \ , \tag{30}$$

and

$$R_n^t = \exp{[i\kappa(t)]}\exp{[iS(t)]}R_n \exp{[-iS(t)]}\exp{[-i\kappa(t)]} \ . \tag{31}$$

Therefore, we are able to formulate the Ehrenfest equation for the time- transformed operator $\mathbf{T}^{t,\dagger}$ as:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle \mathbf{T}^{\dagger,t}\rangle = \left\langle \frac{\partial \mathbf{T}^{\dagger,t}}{\partial t}\right\rangle - i\langle[\mathbf{T}^{\dagger,t}, H_0]\rangle - i\langle[\mathbf{T}^{\dagger,t}, V(t)]\rangle \\ - i\langle[\mathbf{T}^{\dagger,t}, W_{\mathrm{pol}}]\rangle \ ,\end{aligned} \tag{32}$$

where the expectation values are obtained from the time-dependent wave function, $|O^t\rangle$.

We switch on the perturbation of the field adiabatically at $t = -\infty$ and we represent the the perturbation as

$$V(t) = \int_{-\infty}^{\infty} \mathrm{d}\omega V^\omega \exp[(-i\omega + \epsilon)t] \ , \tag{33}$$

where ϵ is positive infinitesimal number ensuring that the perturbation is zero at $t = -\infty$. V^ω is the Fourier transform of $V(t)$. It is required that the perturbation is Hermitian and therefore $(V^\omega)^\dagger = V^{-\omega}$.

Additionally, we assume that $|0^t\rangle$ is an eigenfunction (also denoted as a reference state) $|0\rangle$ of H_0 at $t = -\infty$ and fulfills the Brillouin conditions.

We obtain the following expression of the time-dependent expectation value of a time-independent operator A:

$$\begin{aligned}&\langle 0^t|A|0^t\rangle \\ &= \langle 0|A|0\rangle + \int_{-\infty}^{\infty} d\omega_1 exp[(-i\omega_1 + \epsilon)t]\langle\langle A; V^{\omega_1}\rangle\rangle_{\omega_1} \\ &+ \frac{1}{2}\int_{-\infty}^{\infty}\mathrm{d}\omega_1 \int_{-\infty}^{\infty}\mathrm{d}\omega_2 exp[(-i(\omega_1+\omega_2) + 2\epsilon)t] \\ &\times \langle\langle A; V^{\omega_1}, V^{\omega_2}\rangle\rangle_{\omega_1,\omega_2} + \cdots \ ,\end{aligned} \tag{34}$$

where the functions $\langle\langle A; V^{\omega_1}\rangle\rangle_{\omega_1}$ and $\langle\langle A; V^{\omega_1}, V^{\omega_2}\rangle\rangle_{\omega_1,\omega_2}$ are the linear and quadratic response functions, respectively [9].

In the case of a concrete external field as a homogeneous periodic electromagnetic field we find that the interaction operator is given by

$$V^t = -(\mu\mathbf{F}^0)\cos\omega t \ , \tag{35}$$

where

– the vector $\mu = (\mu^x, \mu^y, \mu^z)$ represents the electric dipole moment operator of the molecular.

– The electric field has frequency ω and the strength of the electric field, $\mathbf{F}^0$, is given by

$$\mathbf{F}(t) = \frac{1}{2}\mathbf{F}^0[exp(-i\omega t) + exp(i\omega t)] = \mathbf{F}^0\cos\omega t \ . \tag{36}$$

Finally, we have the following expression for the interaction operator between the external field and the molecular system

$$V^\omega = -\frac{1}{2}(\mu\mathbf{F}^0)[\delta(\omega - \omega_0) + \delta(\omega + \omega_0)] \ . \tag{37}$$

We are able to express the total dipole moment, μ_i^{ind}, induced in the molecule by the electric field, $\mathbf{F}(t)$, as a Taylor expansion with respect to the electric field:

$$\begin{aligned}\mu_i^{\mathrm{ind}} = \mu_i^{\mathrm{T}} &+ \sum_j \alpha_{ij}^{\mathrm{T}}(-\omega;\omega)F_j^\omega \\ &+ \frac{1}{2}\sum_{j,k}\beta_{ijk}^{\mathrm{T}}(-2\omega;\omega,\omega)F_j^\omega F_k^\omega \\ &+ \frac{1}{6}\sum_{j,k,l}\gamma_{ijkl}^{\mathrm{T}}(-3\omega;\omega,\omega,\omega)F_j^\omega F_k^\omega F_l^\omega + \cdots\end{aligned} \tag{38}$$

The subscripts i, j, k and l denote the molecular axes x, y and z. The terms entering this expansion give the molecular response properties of the molecular system surrounded by the dielectric media. We have denoted these as μ_i^{T}, α_{ij}^{T}, β_{ijk}^{T}, and $\gamma_{ijkl}^{\mathrm{T}}$ and they are

- The dipole moment, μ_i^{T} (an expectation value).
- Frequency - dependent polarizability, $\alpha_{ij}^{\mathrm{T}}(-\omega;\omega)$ (a linear response property).
- Frequency - dependent first order hyperpolarizability, $\beta_{ijk}^{\mathrm{T}}(-2\omega;\omega,\omega)$ (a quadratic response property).
- Frequency dependent second - order hyperpolarizability, $\gamma_{ijkl}^{\mathrm{T}}(-3\omega;\omega,\omega,\omega)$ (a cubic response property).

In order to illustrate the power of the response functions, we consider a situation where for an exact reference state $|0\rangle$ we are able to write the linear response function in a basis of eigenfunctions $|n\rangle$ of $(H_0 + W_{\mathrm{pol}})$

$$\begin{aligned}\langle\langle A; V^\omega\rangle\rangle_\omega = \lim_{\epsilon\to 0}\sum\nolimits_{n\neq 0}\frac{\langle 0|A|n\rangle\langle n|V^\omega|0\rangle}{\omega - \omega_n + i\epsilon} \\ - \lim_{\epsilon\to 0}\sum\nolimits_{n\neq 0}\frac{\langle 0|V^\omega|n\rangle\langle n|A|0\rangle}{\omega + \omega_n + i\epsilon} \ ,\end{aligned} \tag{39}$$

where $\omega_n = E_n - E_0$. From this expression we note that the linear response function is characterized by having

- poles at frequency $\omega = \pm\omega_n$ that are the excitation and deexcitation energies of the unperturbed system.

- Residues which give the corresponding transition moments.

The representation of the linear response function as in Eq. (39) is only true for exact wave functions. It is an inaccurate and inefficient approach for calculating molecular properties but it illustrates rather nicely the properties that one is able to obtain[9, 10, 11, 12, 13, 14, 15, 16, 17].

Within the sum - of states - approach we are able to express the quadratic response functions as

$$
\begin{aligned}
&\langle\langle B; V^{\omega_m}, V^{\omega_n}\rangle\rangle_{\omega_m,\omega_n} \\
&\quad = \sum_{p,q>0}\Bigg[\frac{\langle 0|B|p\rangle\left[\langle p|V^{\omega_m}|q\rangle - \delta_{pq}\langle 0|V^{\omega_m}|0\rangle\right]\langle q|V^{\omega_n}|0\rangle}{(\omega_m+\omega_n-\omega_{p0})(\omega_n-\omega_{q0})} \\
&\qquad + \frac{\langle 0|V^{\omega_n}|q\rangle\left[\langle q|V^{\omega_m}p\rangle - \delta_{pq}\langle 0|V^{\omega_m}|0\rangle\right]\langle p|B|0\rangle}{(\omega_m+\omega_n+\omega_{p0})(\omega_n+\omega_{q0})} \\
&\qquad - \frac{\langle 0|V^{\omega_m}|p\rangle\left[\langle p|B|q\rangle - \delta_{pq}\langle 0|B|0\rangle\right]\langle q|V^{\omega_n}|0\rangle}{(\omega_m+\omega_{p0})(\omega_n-\omega_{q0})} \\
&\qquad + \frac{\langle 0|B|p\rangle\left[\langle p|V^{\omega_n}|q\rangle - \delta_{pq}\langle 0|V^{\omega_n}|0\rangle\right]\langle q|V^{\omega_p}|0\rangle}{(\omega_m+\omega_n-\omega_{p0})(\omega_m-\omega_{q0})} \\
&\qquad + \frac{\langle 0|V^{\omega_m}|q\rangle\left[\langle q|V^{\omega_n}|p\rangle - \delta_{pq}\langle 0|V^{\omega_n}|0\rangle\right]\langle p|B|0\rangle}{(\omega_m+\omega_n+\omega_{p0})(\omega_m+\omega_{q0})} \\
&\qquad - \frac{\langle 0|V^{\omega_n}|p\rangle\left[\langle p|B|q\rangle - \delta_{pq}\langle 0|B|0\rangle\right]\langle q|V^{\omega_m}|0\rangle}{(\omega_n+\omega_{p0})(\omega_m-\omega_{q0})}\Bigg] ,
\end{aligned}
\tag{40}
$$

where we have that the energy difference between the excited state $|q\rangle$ and the ground state $|0\rangle$ is given by $\omega_{q0} = E_q - E_0$. The frequencies of the external electric field are ω_m and ω_n. From Eq. (40) we note that the spectral representation of the quadratic response function provides information about

- Poles when either ω_n or ω_m equals an excitation or deexcitation energy and when the sum of the two frequencies, $\omega_n + \omega_m$, is equal to an excitation or deexcitation energy.
- Residues concerning two-photon transistion matrix elements and transition moments between nonreference states.

Furthermore, within the sum-over-states approach the cubic response functions can be written as

$$
\begin{aligned}
&\langle\langle\langle B; V^{\omega_m}, V^{\omega_n}, V^{\omega_l}\rangle\rangle\rangle_{\omega_m,\omega_n,\omega_l} = \sum P(m,n,l) \\
&\sum_{p,q,r>0}\frac{\langle 0|B|p\rangle\left[\langle p|V^{\omega_m}|q\rangle - \delta_{pq}\langle 0|V^{\omega_m}|0\rangle\right]\left[\langle q|V^{\omega_n}|r\rangle - \delta_{qr}\langle 0|V^{\omega_n}|0\rangle\right]\langle r|V^{\omega_l}|0\rangle}{(\omega_m+\omega_n+\omega_l-\omega_{p0})(\omega_n+\omega_l-\omega_{q0})(\omega_r-\omega_{l0})} ,
\end{aligned}
\tag{41}
$$

where we see from Eq. (41) that the information obtainable from a cubic response function gives

- The energy difference between the excited state for example $|p\rangle$ and the ground state or reference state. The energy difference is given by $\omega_{p0} = E_p - E_0$.
- The operator P is the permutation operator.
- The frequencies of the external electric field are ω_m,ω_n and ω_l.
- ω_n, ω_m or ω_l equals an excitation or deexcitation energy for a one-photon transition.
- $\omega_n + \omega_m$, ω_n, ω_l, or $\omega_m + \omega_l$ equal an excitation or deexcitation energy for a two-photon transition.
- $\omega_n + \omega_m + \omega_l$ equals an excitation or deexcitation energy for a three-photon transition.
- The residues from the cubic response function provide information about three-photon transition matrix elements and transition moments between nonreference states (excited states).

The evolution of the molecular system represented by a MCSCRF or a SCRF wave function is given by a set of operators, $\mathbf{T}$,

$$
\mathbf{T} = (\mathbf{c}^\dagger, \mathbf{R}^\dagger, \mathbf{c}, \mathbf{R}) \ , \tag{42}
$$

where

$$
c_k^{\dagger,t} = \exp[i\kappa(t)]c_k^\dagger \exp[-i\kappa(t)] \ , \tag{43}
$$

$$
c_k^t = \exp[i\kappa(t)]c_k \exp[-i\kappa(t)] \ , \tag{44}
$$

$$
\begin{aligned}
R_n^{\dagger,t} = {} & \exp[i\kappa(t)]\exp[iS(t)]R_n^\dagger \\
& \times \exp[-iS(t)]\exp[-i\kappa(t)]
\end{aligned}
\tag{45}
$$

and

$$
\begin{aligned}
R_n^t = {} & \exp[i\kappa(t)]\exp[iS(t)]R_n \\
& \times \exp[-iS(t)]\exp[-i\kappa(t)] \ .
\end{aligned}
\tag{46}
$$

In the case of a MCSCRF wave function all four operator types are required, whereas for a SCRF wave function we only consider two operator types, $c_k^{\dagger,t}$ and c_k^t. This leads to an Ehrenfest equation for the time-transformed operator, $\mathbf{T}^{t,\dagger}$:

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\langle\mathbf{T}^{\dagger,t}\rangle = {} & \langle\frac{\partial\mathbf{T}^{\dagger,t}}{\partial t}\rangle \\
& - i\langle[\mathbf{T}^{\dagger,t}, H_0]\rangle - i\langle[\mathbf{T}^{\dagger,t}, V(t)]\rangle \ , \\
& - i\langle[\mathbf{T}^{\dagger,t}, W_{\mathrm{pol}}]\rangle
\end{aligned}
\tag{47}
$$

where the expectation values are obtained from the time-dependant wave function, $|O^t>$. In order to obtain the response functions from linear to cubic we solve the Ehrenfest equation for each order of the perturbation. The only term that has not been considered previously is the last term in Eq. (47) [9, 10, 11, 12]. Physically, this last term describes the changes of the response function due to the presence of the induced charges in the dielectric media. We are able by using Eq. (15) to express the last term of Eq. (47) as

$$
\begin{aligned}
&- i\langle[\mathbf{T}^{\dagger,t}, W_{\mathrm{pol}}]\rangle \\
&\quad = -i\sum_j\sum_k \Phi^{(k)}(r_j) \\
&\qquad \times \sum_{pq}\langle\phi_p|\, q_j|\phi_q\rangle\langle 0^t|[\mathbf{T}^{\dagger,t}, E_{pq}]|0^t\rangle \ .
\end{aligned} \tag{48}
$$

Performing an expansion of $|0^t\rangle$ and $\mathbf{T}^{\dagger,t}$ we obtain the terms to the linear, quadratic and cubic contributions due to the presence of the dielectric media:

$$
\begin{aligned}
&- i\langle[\mathbf{T}^{\dagger,t}, W_{\mathrm{pol}}]\rangle \\
&\quad = G^{(0)}(\mathbf{T}^{\dagger,t}) + G^{(1)}(\mathbf{T}^{\dagger,t}) + G^{(2)}(\mathbf{T}^{\dagger,t}) + G^{(3)}(\mathbf{T}^{\dagger,t}) + \cdots \ .
\end{aligned} \tag{49}
$$

The modifications of the MCSCF(SCF) equations for obtaining the linear response functions for a molecule coupled to dielectric media are obtained by considering only linear terms in $\kappa(t)$ and $S(t)$. For the orbital operator, c_k^t, we find the modifications to be

$$
\begin{aligned}
G^{(1)}(c_k^t) = &-\sum_j\sum_k \Phi^{(k)}(r_j) \\
&\times \sum_{pq}\langle\phi_p|q_j|\phi_q\rangle\big(\langle 0|[S(t),[c_k,E_{pq}]]|0\rangle \\
&+\langle 0|[c_k,[\kappa(t),E_{pq}]]|0\rangle\big)
\end{aligned} \tag{50}
$$

and we find for the operator $c_k^{\dagger,t}$ the same expression except we replace c_k by $c_k^\dagger$ everywhere. If the focus is on a SCF approach it is only the last term in Eq. (50) that contributes. For the configurational operator R_n^t we find the linear response contribution to be

$$
\begin{aligned}
G^{(1)}(R_n^t) = &-\sum_j\sum_k \Phi^{(k)}(r_j) \\
&\sum_{pq}\langle\phi_p|\, q_j|\phi_q\rangle\big(\langle 0|[R_n,[S(t),E_{pq}]]|0\rangle \\
&+\langle 0|[R_n,[\kappa(t),E_{pq}]]|0\rangle\big)
\end{aligned} \tag{51}
$$

and again the equation for the configurational operator $R_n^{\dagger,t}$ is similar to this except all R_n are replaced by $R_n^\dagger$. In the case of the quadratic response function we find that the extra terms due to the coupling to the dielectric media are given by

$$
\begin{aligned}
G^{(2)}(c_k^t) = &\frac{i}{2!}\sum_j\sum_k \Phi^{(k)}(r_j)\sum_{pq}\langle\phi_p|q_j|\phi_q\rangle \\
&\times (\langle 0|[S(t),[S(t),[c_k,E_{pq}]]]|0\rangle \\
&+ \langle 0|[c_k,[\kappa(t),[\kappa(t),E_{pq}]]]|0\rangle \\
&+ 2\langle 0|[S(t),[c_k,[\kappa(t),E_{pq}]]]|0\rangle) \ .
\end{aligned} \tag{52}
$$

At the HF level we are only concerned with contributions from the second term to the second-order response function. As before, we obtain the contributions to the second-order response function for $c_k^{\dagger,t}$ by replacing c_k with $c_k^\dagger$.

The extra terms due to the coupling to the dielectric media related to the configurational operator R_n^t give the following extra terms for the quadratic response function

$$
\begin{aligned}
G^{(2)}(R_n^t) = &\frac{i}{2!}\sum_j\sum_k \Phi^{(k)}(r_j)\sum_{pq}\langle\phi_p|\, q_j|\phi_q\rangle \\
&\times \big(\langle 0|[R_n,[S(t),[S(t),E_{pq}]]]|0\rangle \\
&+\langle 0|[R_n,[\kappa(t),[\kappa(t),E_{pq}]]]|0\rangle \\
&+2\langle 0|[R_n,[S(t),[\kappa(t),E_{pq}]]]|0\rangle\big) \ .
\end{aligned} \tag{53}
$$

The equation for the configurational operator $R_n^{\dagger,t}$ is given by a similar expression where we replace all R_n by $R_n^\dagger$.

In the case of the cubic response function we have derived the following extra terms arising from the coupling to the dielectric media:

$$
\begin{aligned}
G^{(3)}(c_l^t) = &\frac{1}{3!}\sum_j\sum_k \Phi^{(k)}(r_j)\sum_{pq}\langle\phi_p|\, q_j|\phi_q\rangle \\
&\times \big\{\langle 0|[S(t),[S(t),[S(t),[c_l,E_{pq}]]]]|0\rangle \\
&+\langle 0|[c_l,[\kappa(t),[\kappa(t),[\kappa(t),E_{pq}]]]]|0\rangle \\
&+2\langle 0|[S(t),[S(t),[c_l,[\kappa(t),E_{pq}]]]]|0\rangle \\
&+2\langle 0|[S(t),[c_l,[\kappa(t),[\kappa(t),E_{pq}]]]]|0\rangle\big\} \ .
\end{aligned} \tag{54}
$$

Here, it is only the second term that is relevant for contributions to the cubic response function at the HF level. The extra terms involving the operator $c_l^{\dagger,t}$ are obtained by replacing c_l with $c_l^\dagger$.

Concerning the cubic response function, we find in the case of the configurational operator R_n^t the following equation for the terms related to the coupling to the dielectric media

$$
\begin{aligned}
G^{(3)}(R_n^t) = &\frac{1}{3!}\sum_j\sum_k \Phi^{(k)}(r_j)\sum_{pq}\langle\phi_p|\, q_j|\phi_q\rangle \\
&\times \big\{\langle 0|[R_n,[S(t),[S(t),[S(t),E_{pq}]]]]|0\rangle \\
&+\langle 0|[R_n,[\kappa(t),[\kappa(t),[\kappa(t),E_{pq}]]]]|0\rangle \\
&+2\langle 0|[R_n,[S(t),[S(t),[\kappa(t),E_{pq}]]]]|0\rangle \\
&+2\langle 0|[R_n,[\kappa(t),[\kappa(t),[S(t),E_{pq}]]]]|0\rangle\big\} \ .
\end{aligned} \tag{55}
$$

For the configurational operator $R_n^{\dagger,t}$ we derive a similar expression with all R_n replaced by $R_n^\dagger$.

The model and associated response method presented enable us to perform correlated and uncorrelated calculations of molecular properties such as the energies of excited states for molecules located between electrodes and exposed to a static or a time-dependent electric field.

4. Conductance of a molecule between two electrodes

In the field of mesoscopic physics, quantum transport theory based on the non-equilibrium many-particle Green's function formalism has been used to derive expressions for the current through mesoscopic semiconductor structures [96, 97, 98]. To describe the current through molecular wires such an approach should be merged with a quantum chemical treatment of the molecular problem. In this section we present a derivation of an expression for the current through a molecule coupled to two leads. The model utilizes a division of the system into three subsystems, where the molecule is one subsystem and the two leads are the other two subsystems. The section defines the Hamiltonian of the system and the expressions for the current.

4.1 Hamiltonian

The total Hamiltonian of the system is divided into three terms, where the two terms describe the molecule, H^{mol} and the leads H^{leads}, and the last term V describes the coupling between the three subsystems and it is written as

$$H = H^{\text{leads}} + H^{\text{mol}} + V \ . \tag{56}$$

The leads are described by a noninteracting Hamiltonian which is given as a sum over the states at the right and left lead

$$H^{\text{leads}} = \sum_{l \in \text{L,R}} \varepsilon_l c_l^\dagger c_l \ . \tag{57}$$

The molecular Hamiltonian could include full electron-electron interaction. We will also derive a simpler transport equation valid at the HF level only.

$$H^{\text{mol}} = \sum_n \varepsilon_n d_n^\dagger d_n \ . \tag{58}$$

Finally, we describe the coupling as

$$V = \sum_{l,n} (V_{ln} c_l^\dagger d_n + V_{ln}^* d_n^\dagger c_l) \ , \tag{59}$$

where the summation includes the interations between the lead on the left or right, $c_l^\dagger$, c_l and the molecular states $d_n^\dagger$, and d_n.

4.2 Continuity equation

The current from the left electrode to the molecule is given by

$$J_\text{L} = -e\langle \dot{N}_\text{L} \rangle = -\frac{ie}{\hbar}\langle [H, N_\text{L}] \rangle \ . \tag{60}$$

Only the coupling term of the Hamiltonian does not commute with the operator $N_L = \sum_{l \in L} c_l^\dagger c_l$. We find by using standard operator algebra that the current is given as

$$J_L = \frac{ie}{\hbar} \sum_{l,n} (V_{ln} \langle c_l^\dagger d_n \rangle - V_{ln}^* \langle d_n^\dagger c_l \rangle) \ . \tag{61}$$

This is basically the current to be evaluated. In the following we invoke the full machinery of nonequilibrium Green's functions. This turns out to be fruitful since we will be able to confine the problem to the molecular subspace.

4.3 Green's Functions

First we define the following:

$$G_{kl}^{>}(t,t') = -i\langle c_k(t) c_l^\dagger(t') \rangle, \tag{62}$$

$$G_{kl}^{<}(t,t') = i\langle c_l^\dagger(t') c_k(t) \rangle. \tag{63}$$

These are the building blocks of several other Green's functions, for example the retarded and advanced Green's functions, respectively,

$$G_{kl}^{r}(t,t') = \vartheta(t-t')\{G_{kl}^{>}(t,t') - G_{kl}^{<}(t,t')\} \tag{64}$$

$$G_{kl}^{a}(t,t') = -\vartheta(t'-t)\{G_{kl}^{>}(t,t') - G_{kl}^{<}(t,t')\} \ , \tag{65}$$

For a full account of many-particle Green's functions we refer to Refs [99,98]. Our interest is to express Eq. (61) in terms of the Green's function $G_{kl}^{<}(t,t')$. Since the full Hamiltonian Eq. (56) is time- independent the Green's function Eq. (63) should only depend on the time difference $t-t'$. And since the operators in Eq. (61) describe instantaneous particle transfer we should write

$$i\langle c_l^\dagger d_n \rangle = \lim_{(t-t') \to 0} i\langle c_l^\dagger(t') c_k(t) \rangle = \lim_{(t-t') \to 0} G_{kl}^{<}(t-t') \ . \tag{66}$$

To be able to take this limit we first Fourier transform the Green function with respect to $t-t'$. In terms of energy – dependent Green's functions we obtain the following expression for the current

$$J_L = \frac{e}{\hbar} \sum_{l,n} \int \frac{d\varepsilon}{2\pi} [V_{ln} G_{nl}^{<}(\varepsilon) - V_{ln}^* G_{ln}^{<}(\varepsilon)] \ . \tag{67}$$

To decompose these Green's functions we need the Langreth expression for "lesser than" components of matrix products.[98] In our case we need

$$G_{nl}^{<} = \sum_m V_{lm}^* [G_{nm}^{r} G_{ll}^{(0)<} + G_{nm}^{<} G_{ll}^{(0)a}] \tag{68}$$

$$G_{ln}^{<} = \sum_m V_{lm} [G_{ll}^{(0)r} G_{mn}^{<} + G_{ll}^{(0)<} G_{mn}^{a}] \ . \tag{69}$$

For this to be valid the leads must be non-interacting. The Green's functions with superscript (0) are uncoupled, i.e. they are Green's functions with respect to the uncoupled system Hamiltonian ($H^{\text{leads}} + H^{\text{mol}}$). Note, that Eqs. (68) and (69) contain uncoupled electrode Green's functions, $G_{ll}^{(0)<,r,a}$, and full Green's functions, $G_{mn}^{<,r,a}$, for the molecule. Inserting these expressions in Eq. (67) and interchanging the indices m and n in the last term, we find that the current from the left electrode to the molecule is given by

$$J_L = \frac{e}{\hbar} \sum_{lmn} \int \frac{d\varepsilon}{2\pi} V_{ln} V_{lm}^* [G_{ll}^{(0)<} \{G_{nm}^{r} - G_{nm}^{a}\} + G_{nm}^{<} \{G_{ll}^{(0)a} - G_{ll}^{(0)r}\}] \ . \tag{70}$$

The unperturbed Green's functions can be evaluated directly from Eqs. (63), (64) and (65) and can be expressed in terms of δ-functions:

$$G_{ll}^{(0)<} = 2\pi i f_L \delta(\varepsilon - \varepsilon_l) \tag{71}$$

$$G_{ll}^{(0)a} - G_{ll}^{(0)r} = 2\pi i \delta(\varepsilon - \varepsilon_l) \tag{72}$$

The spectral density of the molecular levels due to the coupling to the left electrode is defined as

$$\Gamma^{\mathrm{L}}_{mn} = 2\pi \sum_{l} \delta(\varepsilon - \varepsilon_l) V_{ln} V^{*}_{lm}. \tag{73}$$

The diagonal elements of this matrix represents the linewidth of the molecular levels. Finally, we find that the current expression reads

$$J_L = \frac{ie}{h} \sum_{mn} \int d\varepsilon \Gamma^{\mathrm{L}}_{mn} [f_L (G^r_{nm} - G^a_{nm}) + G^{<}_{nm}] \tag{74}$$

and in a matrix notation this becomes

$$J_L = \frac{ie}{h} \int d\varepsilon [\mathrm{Tr}\{f_L \mathbf{\Gamma}^{\mathrm{L}} (\boldsymbol{G}^r - \boldsymbol{G}^a)\} + \mathrm{Tr}\{\mathbf{\Gamma}^{\mathrm{L}} \boldsymbol{G}^{<}\}] \tag{75}$$

4.4 Total current

The current from the right electrode to the molecule is given by an expression exactly like Eq. (75). When a steady current is running we have $J_{\mathrm{L}} = -J_{\mathrm{R}}$. A symmetric expression for the total current is found by averaging:

$$J = \frac{1}{2}(J_{\mathrm{L}} + J_{\mathrm{L}}) = \frac{1}{2}(J_{\mathrm{L}} - J_{\mathrm{R}}) \tag{76}$$

In matrix notation this reads

$$\begin{aligned} J = \frac{ie}{2h} \int & \mathrm{d}\varepsilon [\mathrm{Tr}\{(f_{\mathrm{L}}(\varepsilon)\mathbf{\Gamma}_{\mathrm{L}} - f_{\mathrm{R}}(\varepsilon)\mathbf{\Gamma}_{\mathrm{R}})(\boldsymbol{G}^r - \boldsymbol{G}^a)\} \\ & + \mathrm{Tr}\{(\mathbf{\Gamma}_L - \mathbf{\Gamma}_R)\boldsymbol{G}^{<}\}] \ , \end{aligned} \tag{77}$$

4.5 HF Case

In the case of a non-interacting molecular Hamiltonian the molecular Green functions satisfy following identities:

$$\boldsymbol{G}^{<} = i f_{\mathrm{L}} \boldsymbol{G}^r \mathbf{\Gamma}^{\mathrm{L}} \boldsymbol{G}^a + i f_{\mathrm{R}} \boldsymbol{G}^r \mathbf{\Gamma}^{\mathrm{R}} \boldsymbol{G}^a \tag{78}$$

$$\boldsymbol{G}^r - \boldsymbol{G}^a = -i\boldsymbol{G}^r (\mathbf{\Gamma}^L + \mathbf{\Gamma}^R) \boldsymbol{G}^a \ . \tag{79}$$

With these expressions the integrand in Eq. (77) reduces to $-2i[f_{\mathrm{L}}(\varepsilon) - f_{\mathrm{R}}(\varepsilon)]\mathrm{Tr}\{\boldsymbol{G}^a \mathbf{\Gamma}^{\mathrm{R}} \boldsymbol{G}^r \mathbf{\Gamma}^{\mathrm{L}}\}$. Now the total current is given by

$$J = \frac{e}{h} \int \mathrm{d}\varepsilon [f_{\mathrm{L}}(\varepsilon) - f_{\mathrm{R}}(\varepsilon)] \mathrm{Tr}\{\boldsymbol{G}^a \mathbf{\Gamma}^{\mathrm{R}} \boldsymbol{G}^r \mathbf{\Gamma}^{\mathrm{L}}\} \tag{80}$$

This equation is in fact the starting point for most molecular wire calculations.

5. Conclusion

We have presented a model and associated response method for calculating molecular properties of relevance for the situation where a molecule is placed between electrodes and exposed to an external field. The procedure enables the calculations of linear, quadratic and cubic response functions that provide the possibility of calculating a substantial number of molecular properties that are of interest when designing molecular wires, photonic devices and electrooptical switches and a basic understanding of how the molecular system is influenced by the presence of the two electrodes and the externally applied bias.

This is the first model that enables a correlated electronic structure investigation of molecules located between electrodes and influenced by an external potential. Our method utilizes the classical idea of the image charge to represent the electrostatic interaction between the molecule and the surrounding dielectric media.

It is also the first contribution for this physical situation where it is possible to calculate frequency-dependent molecular properties up to fourth order at both the uncorrelated and the correlated electronic structure level.

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