

# Strong polarization-induced reduction of addition energies in single-molecule nanojunctions

## Supporting Information

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## 1 Theoretical Framework

Here we show how to include the polarizable environment of a molecular single-electron transistor (SET) in a total energy calculation of the molecule. The main idea is the following: when treating the metallic leads and gate dielectric in a continuum description they enter only in the molecular Hamiltonian as an effective potential.

In order to address the position of the ionization potential and electron affinity in the molecular junction, the full junction Hamiltonian (i.e. molecule, metallic leads, gate dielectric and their mutual interaction) must be considered

$$H = H_S + H_E + H_{SE}. \quad (1)$$

The first term is the Hamiltonian of a nanoscale system  $S$  (here a molecule). In general,  $H_S$  is a quantum mechanical many-body Hamiltonian that can be treated with quantum chemical methods of required accuracy. For now  $H_S$  will not be specified further. The second term is the Hamiltonian of the polarizable environment ( $E$ ), which accounts for the energy cost due to build-up of the polarization charge in the metallic electrodes and the gate dielectric. Since the dynamical polarization response of the environment is orders of magnitude faster than the electronic tunneling rates between the molecule and leads, an electrostatic treatment of the interaction will be sufficient. Therefore we replace the environments by their classical electrostatic energies, which are functionals of the charge distributions and polarizations in the leads and in the dielectric. This approximation neglects the kinetic energy and the exchange-correlation energy associated with the charge build up.

For the metallic environment where the electrons are free to move around

the electrostatic energy is

$$H_m = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho_m(\mathbf{r}) V_C(\mathbf{r} - \mathbf{r}') \rho_m(\mathbf{r}'), \quad (2)$$

where  $\rho_m$  is the charge density of the metal and  $V_C(\mathbf{r}) = 1/|\mathbf{r} - \mathbf{r}'|$  is the Coulomb interaction (atomic units are used throughout this note if not otherwise stated). In the dielectric environment the polarization charge is bound in small dipoles  $\mathbf{p}_i$ , giving rise to a macroscopic polarization  $\mathbf{P} = \sum_i \mathbf{p}_i$  of the dielectric. The energy of a polarized dielectric can be expressed as

$$H_d = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho_b(\mathbf{r}) V_C(\mathbf{r} - \mathbf{r}') \rho_b(\mathbf{r}') + \frac{1}{2} \int d\mathbf{r} \frac{4\pi}{\chi(\mathbf{r}, \mathbf{r})} |\mathbf{P}(\mathbf{r})|^2, \quad (3)$$

where  $\rho_b = -\nabla \cdot \mathbf{P}$  is the bound charge of the dielectric and  $\chi$  the electric susceptibility. The first term in equation (3) describes the electrostatic dipole-dipole interaction. The second local term, which is equivalent to the energy of a spring  $\frac{1}{2} kx^2$ , accounts for the energy stored in the dipoles  $\mathbf{p}_i$ . Utilizing that  $\nabla \cdot \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^2} = \delta(\mathbf{r} - \mathbf{r}')$  this term can recast in the form  $\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho_b(\mathbf{r}) \tilde{V}(\mathbf{r}; \mathbf{r}') \rho_b(\mathbf{r}')$ , where  $\tilde{V}$  is a complicated interaction between the bound charges. The total Hamiltonian of the environment can now be written

$$H_E = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho_E(\mathbf{r}) V(\mathbf{r}; \mathbf{r}') \rho_E(\mathbf{r}'), \quad (4)$$

where  $\rho_E = \rho_m + \rho_d$  and  $V$  is either  $V_C$  or  $V_C + \tilde{V}$ . As we shall see in the following, a further specification of  $V$  is not required. The last term in equation (1) accounts for the interaction between the molecule and the environment. Since we are focusing on the Coulomb blockade regime where the molecule has small tunnel couplings to the leads, the hybridization term of  $H_{SE}$  can be neglected. What remains is the Coulomb interaction between the spatially separated charges of the molecule and of the environment

$$H_{SE} = \int d\mathbf{r} \int d\mathbf{r}' \rho_S(\mathbf{r}) V_C(\mathbf{r} - \mathbf{r}') \rho_E(\mathbf{r}'). \quad (5)$$

Notice that the molecular charge has contributions from both the ionic cores and the valence electrons of the molecule:  $\rho_S(\mathbf{r}) = \rho_{ion}(\mathbf{r}) + \rho_e(\mathbf{r}) = \sum_i Z_i \delta(\mathbf{r} - \mathbf{r}_i) - \psi^\dagger(\mathbf{r}) \psi(\mathbf{r})$ .

With the Hamiltonian in place we now proceed to eliminate the environment degrees of freedom. Since the part of the Hamiltonian involving  $\rho_E$  is classical and has no dynamics, the solution for  $\rho_E$  can be found by minimizing with respect  $\rho_E$ , i.e. by setting  $\delta H / \delta \rho_E = 0$ . The resulting equation can be solved for  $\rho_E$  giving (in matrix notation)

$$\rho_E = -[V_{EE}]^{-1} V_{ES} \rho_S \equiv \rho_{ind}, \quad (6)$$

which represents the charge density induced by the system charge  $\rho_s$ . Inserting this expression for the induced charge of the environment back into the full Hamiltonian in equation (1), the terms involving  $\rho_e$  can be recast in the form

$$H_E + H_{SE} = -\frac{1}{2}\rho_s V_{SE} (V_{EE})^{-1} V_{ES} \rho_s, \quad (7)$$

in which the degrees of freedoms of the environment has been substituted by an effective interaction between molecular charges. By inserting the expression in equation (6) for the induced charge density into equation (7), we find that  $H_E + H_{SE} = \frac{1}{2}\rho_s V_{SE} \rho_{ind}$ , which is one half of  $H_{SE}$  in equation (5). This result, which is a generalization of the classical image charge problem (a point charge placed at a distance  $z$  from a perfect conducting surface where  $H_E + H_{SE} = -1/4z$ ), states that the energy cost associated with the build up of the polarization charge is always one half of the energy gained by the system  $S$  through its interaction with the polarization charges.

Due to the presence of the electronic field operators in  $\rho_s$  the effective interaction in equation (7) must be approximated. In our scheme we use a Hartree approximation. This is justified because i) correlation effects due to the effective interaction are small given the absence of a short range interaction and ii) exchange is not relevant since self-interactions are possible via the image charges. Introducing the induced potential  $\Phi_{ind}(\mathbf{r}) = \int d\mathbf{r}' \rho_{ind}(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$ , the Hartree version of equation (7) can be written as

$$H_E + H_{SE} = \int d\mathbf{r} \rho_s(\mathbf{r}) \Phi_{ind}(\mathbf{r}) - \frac{1}{2} \int d\mathbf{r} \langle \rho_s(\mathbf{r}) \rangle \Phi_{ind}(\mathbf{r}), \quad (8)$$

where the last term subtracts the double counted contributions to the total energy in the first term.

The induced potential can be obtained by solving Poisson's equation

$$-\nabla \cdot [\epsilon_r(\mathbf{r}) \nabla \Phi_{tot}(\mathbf{r})] = 4\pi \rho_s(\mathbf{r}) \quad (9)$$

with Dirichlet boundary-conditions on the electrode surfaces  $S_i$ , i.e.  $\Phi_{tot} = 0$  if  $\mathbf{r} \in S_i$ . Here, the total potential is the sum of the potential from the system charges plus the potential from the induced charges:  $\Phi_{tot} = \Phi_s + \Phi_{ind}$ .

The present approach thus allows us to combine a continuum description of the junction environment with a quantum chemical description of the molecule.

## 2 Semi-empirical Method

The molecular part of the total junction Hamiltonian in equation (1) is split up into two parts: i) one that accounts for the isolated molecule and ii) one

that accounts for polarization/redistribution of charge due to interactions with the junction environment and/or charging of the molecule,

$$H_s = H_0 + H_{pol}. \quad (10)$$

In the following our semi-empirical treatment is described in detail. It is similar to the one presented in Ref. [1], however, here applied to total energy calculations and generalized to include dielectrics in the determination of the induced potential  $\Phi_{ind}$ .

The part describing the isolated molecule is an effective tight-binding Hamiltonian

$$H_0 = \sum_i \varepsilon_i c_i^\dagger c_i + \sum_{i \neq j} t_{ij} c_i^\dagger c_j, \quad (11)$$

where the sums run over atomic valence orbitals  $\{\phi_i\}$  and  $i$  is a collective index referring to atom, orbital and spin index:  $i \rightarrow \mu i \sigma$ . We use Extended Hückel parameters by Hoffmann [2] for the onsite and hopping energies

$$\varepsilon_i = -V_i \quad (12)$$

$$t_{ij} = \frac{1}{2} k S_{ij} (\varepsilon_i + \varepsilon_j). \quad (13)$$

Here  $V_i$  is associated with the ionization energy of the valence orbital  $\phi_i$ ,  $k$  is a fitting parameter usually set to 1.75 and  $S_{ij} = \langle \phi_i | \phi_j \rangle$  is the overlap between the non-orthogonal atomic orbitals. Notice that electron-electron interactions are implicitly included in  $H_0$  due to its parametrized form.

In the part of the Hamiltonian that accounts for polarization and charging of the molecule, electron-electron interaction are treated at the Hartree level. Since the Hartree potential of the isolated molecule is indirectly accounted for in  $H_0$ , only changes in the Hartree potential due to variations in the electron density from its value,  $n_0$ , in the isolated molecule are considered

$$\delta V_H(\mathbf{r}) = \int d\mathbf{r}' \frac{\delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (14)$$

where  $\delta n = n - n_0$ . Since the Hartree potential depends on the electron density, this poses a self-consistent problem that must be iterated to convergence.

To simplify the numerics the integral in equation (14) is approximated by a sum over atomic point charges given by the Mulliken populations  $n_\mu = \text{Tr}[\rho S]_\mu$ , where  $\rho$  is the density matrix

$$\delta V_H(\mathbf{r}) = \sum_\mu \frac{\delta n_\mu}{|\mathbf{r} - \mathbf{r}_\mu|}. \quad (15)$$

To avoid problems with the diverging point charge potential when evaluated at the atomic positions,  $\mathbf{r}_\mu$ , the onsite contribution to the sum is replaced by a species dependent Hubbard  $U$  taking into account the energy cost of adding an electron to the atom. These parameters are taken from the quantum chemical CNDO method [3, 4]. In order to keep consistency between the onsite and the offsite interactions, the Magata-Nishimoto [5] interpolation formula is used for the latter

$$U_{\mu\nu} = \frac{1}{R_{\mu\nu} + \frac{2}{U_\mu + U_\nu}}. \quad (16)$$

With these approximation the final form of the Hartree potential in equation (14) becomes

$$\delta V_H(\mathbf{r}_\mu) = \delta n_\mu U_\mu + \sum_{\nu \neq \mu} \delta n_\nu U_{\mu\nu}. \quad (17)$$

In our atomic basis the polarization/charging part of the Hamiltonian is written

$$H_{pol} = \sum_{i,j} V_{ij} c_i^\dagger c_j - \frac{1}{2} \sum_{\mu} n_\mu V_H(\mathbf{r}_\mu), \quad (18)$$

where the last term subtracts double counting in the first term and  $H_0$ . The matrix representation of the Hartree potential has been approximated as follows

$$\begin{aligned} V_i &= \langle \phi_i | \delta V_H | \phi_i \rangle \approx \delta V_H(\mathbf{r}_\mu) \\ V_{ij} &= \langle \phi_i | \delta V_H | \phi_j \rangle \approx \frac{1}{2} S_{ij} (V_i + V_j). \end{aligned} \quad (19)$$

The part of the Hamiltonian involving the induced potential is written similarly

$$H_E + H_{ES} = \sum_{i,j} V_{ij} c_i^\dagger c_j - \frac{1}{2} \sum_{\mu} (Z_\mu - n_\mu) \Phi_{ind}(\mathbf{r}_\mu) \quad (20)$$

with  $V_{ij} = \langle \phi_i | V_{ind} | \phi_j \rangle$  evaluated as above in equation (19).

### 3 Poisson's Equation and $\Phi_{ind}$

In the following section it is described how the induced potential is determined by solving Poisson's equation (9) for the total potential  $\Phi_{tot}$ .

### 3.1 Finite element approach

One of the major advantages of the finite element method (FEM) is its partitioning of the solution domain into a finite number of elements (typically triangles in 2D and tetrahedra in 3D). The possibility to refine the element size around sharp corners and in the vicinity of spatially rapidly varying source terms, allows FEM to handle a large variety of problems and solution domains of practically any geometry, hence making it very suitable for modelling of nanoscale devices.

In the present case we seek to solve Poisson's equation in the geometry of a single-molecule SET. To this end we use the finite element software from the FEniCS project [6].

The molecular charge density, which has both electronic and ionic contributions, is represented by a sum of atomic centered gaussian charge distributions:

$$\rho_s(\mathbf{r}) = (2\pi)^{-3/2} \sum_{\mu} \frac{q_{\mu}}{\sigma^3} e^{-|\mathbf{r}-\mathbf{r}_{\mu}|^2/2\sigma^2} \quad (21)$$

Here  $\sigma = a_0$  is the width of the gaussians and  $q_{\mu} = Z_{\mu} - n_{\mu}$  ( $Z_{\mu}$  being the atomic valence) is the net atomic charge.

Having obtained the total potential,  $\Phi_{tot}$ , the induced potential can be extracted by subtracting the potential,  $\Phi_s$ , from the molecular source charges, which for a gaussian charge distribution centered at the origin is:

$$\Phi_s(\mathbf{r}) = \frac{q}{r} \text{erf}\left(\frac{r}{\sqrt{2}\sigma}\right) \quad (22)$$

where erf is the error function.

The calculated induced potential has been converged (to 0.05 eV) with respect to the element size and the spatial dimensions of the device. In order to get an accurate description of the potential at the atomic positions, the molecule is enclosed in a box with a fine mesh of element size  $\sim a_0$ . The element size at the boundaries of the device are 20 times larger, which is illustrated by the boundary mesh in figure 1(a). The following device size was used to converge the potential: an electrode height of 50 a.u., a device width of 100 a.u. and a device length of 150 a.u..

### 3.2 Analytical solution

In the simplified device geometry shown in Fig. 1(b), Poisson's equation can be solved analytically. It can be shown that the Greens function satisfying:

$$-\nabla \cdot [\varepsilon_r(\mathbf{r}) \nabla G(\mathbf{r}, \mathbf{r}')] = \delta(\mathbf{r} - \mathbf{r}') \quad (23)$$

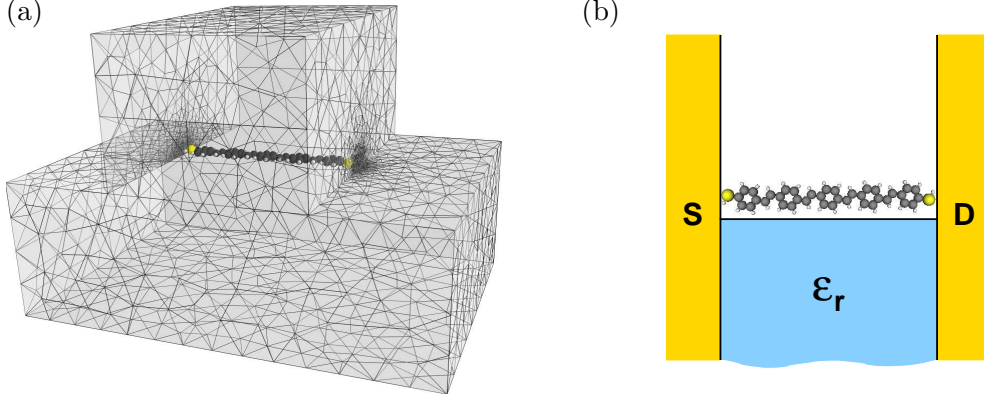


Figure 1: **Finite element mesh and simplified junction geometry.** (a) Surface mesh for the OPV5-SET. (b) Simplified junction for which Poisson's equation can be solved analytically. In this geometry the electrodes are modelled by infinite metallic surfaces and the gate oxide as a semi-infinite dielectric layer sandwiched between the electrode surfaces. The gate electrode is not included (see text).

has the following image charge solution:

$$G(\mathbf{r}, \mathbf{r}') = \sum_{\sigma=\pm 1} \sum_{\tau=\pm 1} \sigma \left( \frac{\varepsilon_r + \tau}{\varepsilon_r + 1} \right) \tau \left[ \frac{1}{\sqrt{(x - \sigma x')^2 + (y - \tau y')^2 + (z - z')^2}} + \sum_{n=1}^{\infty} \left( \frac{1}{\sqrt{(2nL - (x - \sigma x'))^2 + (y - \tau y')^2 + (z - z')^2}} + \frac{1}{\sqrt{(2nL + (x - \sigma x'))^2 + (y - \tau y')^2 + (z - z')^2}} \right) \right] \quad (24)$$

where  $L$  is the electrode spacing ( $z$  is the direction perpendicular to the paper plane in Fig. 1(b)) and the sums run over all repeated images of the source charge in the metallic surfaces and the dielectric. By leaving out the contribution from the source charge itself, only the induced potential remains:

$$\Phi_{ind}(\mathbf{r}) = \tilde{G}(\mathbf{r}, \mathbf{r}') \quad (25)$$

Here  $\tilde{G}$  denotes the Greens function which does not include the  $\sigma = 1$  and  $\tau = 1$  term outside the  $n$ -sum in equation (24).

In the calculations using the analytical solution, the molecular charge distribution has been approximated by point charges  $q_\mu$  located at the atomic positions. The induced potential follows directly from the Greens functions

of the individual point charges:

$$\Phi_{ind}(\mathbf{r}) = \sum_{\mu} q_{\mu} \tilde{G}(\mathbf{r}, \mathbf{r}_{\mu}) \quad (26)$$

### 3.3 FEM vs analytic

Table 1 summarizes the calculated polarization energies for the realistic junction modelled with FEM and the simplified junction shown in Fig. 1(b). The difference between the polarization energies in the two junctions is on the order of  $\sim 50$  meV for the different OPV-molecules. The slightly larger polarization energies in the simplified junction stem from the infinite metallic electrodes, which screen the Coulomb interactions on the molecule better than the semi-infinite metal blocks of the realistic junction. Notice that, due to its large distance to the molecule ( $\sim 5$  nm) and the metallic-like screening properties of the  $\text{Al}_2\text{O}_3$  gate oxide, the gate electrode does not contribute to the polarization energy in the realistic junction. This explains the relative small differences between the polarization energies in the two junction geometries.

Molecule	FEM	Analytic
OPV2	3.56	3.63
OPV3	3.11	3.17
OPV4	2.81	2.87
OPV5	2.59	2.63

Table 1: Calculated polarization energies  $P$  (in eV) for the two junction geometries illustrated in figure 1. The same electrode spacing has been used in the two geometries. Due to the infinite metallic surfaces, the polarization energy is slightly larger for the simplified junction geometry.

Hence, our analytical solution provides a realistic description of the potential in generic SET geometry (Fig. 2(a) in the main part of the paper) that can be used instead of computationally heavy Poisson solvers.

## References

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