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First-principles scheme for spectral adjustment in nanoscale transport

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Abstract. We implement a general method for correcting the low-bias transport properties of nanoscale systems within an *ab initio* methodology based on linear combinations of atomic orbitals. This method consists of adjusting the molecular spectrum, i.e. shifting the position of the occupied and unoccupied molecular orbitals to match the experimental highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO (HL)) gap. Thus we show how the typical problem of an underestimated HL gap can be corrected, leading to quantitative and qualitative agreement with experiments. We show that an alternative method based on calculating the position of the relevant transport resonances and fitting them to Lorentzians can significantly underestimate the conductance and does not accurately reproduce the electron transmission coefficient between resonances. We compare this simple method in an ideal system of a benzene molecule coupled to featureless leads to more sophisticated approaches, such as GW, and find rather good agreement between both. We also present the results of a benzenedithiolate molecule between gold leads, where we study different coupling configurations for straight and tilted molecules, and show that this method yields the observed evolution of two-dimensional conductance histograms. We also explain the presence of low-conductance zones in such histograms by taking into account different coupling configurations.

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Contents

1. Introduction

Theories of coherent electron transport through nanostructures are commonly based on a mean-field Hamiltonian H, describing a scattering region connected to crystalline current-carrying leads. Starting from H, a scattering matrix S (or equivalent Green's function) is calculated and transport properties such as the electrical conductance G obtained by evaluating Landauer-type formulae. For example, at zero temperature and bias, $G = (2e^2/h)T(E_F)$, where $T(E)$ is the transmission coefficient for electrons of energy E passing from one side of the scattering region to the other and E_F is the Fermi energy. The mathematical machinery for computing S and $T(E)$ from H is well established and is often referred to as 'the scattering approach' or 'non-equilibrium Green's function approach' to transport. When implemented with the same level of rigor, these are mathematically equivalent. Such theories have been used to predict transport properties of a large number of molecules between metallic leads [1]–[3], [5]–[9].

The problem of identifying the most accurate mean-field Hamiltonian for predicting nanoscale transport is a more open question. Density functional theory (DFT) [10, 11] is a versatile tool for generating self-consistent, mean-field Hamiltonians at both zero- and finite-applied voltages. For metallic systems, such as atomic chains between electrodes of the same material, there is quantitative agreement between experiment and predictions derived from DFT-based mean-field Hamiltonians. In contrast, for low-conductance systems such as single molecules attached to metallic electrodes, predictions can differ from experiments by orders of magnitude [5], due to limitations inherent to DFT [12]–[16]. These discrepancies mainly arise from an underestimation of the HOMO–LUMO (HL) gap, with theoretical predictions of the order of 40% of the experimental values [17, 18]. Approximated exchange-correlation functionals also contain self-interaction errors [14, 19], which are particularly important for localized states. Such errors, which worsen the agreement between the removal energy and the last occupied Kohn–Sham eigenvalue, produce an incorrect alignment between the HOMO and the Fermi energy [20] and can also affect the width of the resonances when the coupling is small [21]. Even in strongly coupled molecules, such as molecules with thiol anchor groups, where the HOMO has a large weight on the sulfur atoms, localized states can still have large self-interaction errors and produce peaks very close to the Fermi energy. When the self-interaction correction (SIC) is applied, such states move downward and the zero-bias conductance decreases [22]. Other approaches that avoid the self-interaction error, at least partially, are hybrid functionals, such as the B3LYP [23, 24], that include part of exact exchange obtained from Hartee–Fock. The main effect of such functionals on the transport properties is the opening of the HL gap, especially when the molecule is strongly coupled to the leads and

charge transfer is small [21]. Exact exchange approaches (EXX), such as Hartree–Fock (HF) or DFT with exact exchange [25], also produce wider HL gaps [21]. A complementary method to the SICs is LDA + U [26, 27], where a parameter U, that represents the orbital-dependent Coulomb repulsion between electrons on the same level, is included to account for the intratomic repulsion felt by the d electrons. This approximation then uses the LDA on the s and p states and the LDA plus a U-correction on the d states. The main effect of the U is again the opening of the HL gap, which reduces the zero-bias conductance [28]. Another alternative method applies Hedin's GW approximation [29] on the extended molecule to correct its electronic properties [30]–[33]. This method is a many-body approximation that calculates quasiparticle band structures by including a self-energy that is approximated as the product in real space of the Green's function (G) and the dynamically screened Coulomb interaction (W). GW is known to reproduce energy gaps more accurately and also takes into account screening effects of the leads. However, this method has technical difficulties related to the connection between the GW-corrected extended molecule and the leads and is also very expensive. Consequently, to date, this method has only been applied to small molecules.

Errors in the predicted spectrum of the DFT Hamiltonians lead to erroneous predictions for the positions of resonances in $T(E)$. In order to overcome this deficiency, spectral adjustment in nanoscale transport (SAINT) can be used to adjust the peak positions of $T(E)$ [34, 35]. For a molecule attached to a metallic surface, the correct positions of the HOMO and LUMO levels could be determined experimentally from photoemission measurements. Alternatively, they can be estimated theoretically by noting that the HOMO (ε_{H}) and the LUMO (ε_{L}) energies should coincide with the negative of the ionization potential (IP) and electron affinity (EA), defined as $\mathrm{IP} = E_{N-1} - E_N$ and $\mathrm{EA} = E_N - E_{N+1}$, where N is the number of electrons in the neutral molecule [36, 37]. These quantities can be approximated by taking into account the Coulomb energy required to charge the molecule, E_{C}, as $\mathrm{IP} = -\varepsilon_{\mathrm{H}} + E_{\mathrm{C}}$ and $\mathrm{EA} = -\varepsilon_{\mathrm{L}} - E_{\mathrm{C}}$,[4] so that the charging energy is equal to $\mathrm{IP} - \mathrm{EA} = \Delta_{\mathrm{HL}} + 2E_{\mathrm{C}}$ [38], which is larger than the HL gap. However, when the molecule is placed in a polarizable environment, such as metallic surfaces, the charging energy is reduced from the gas phase value by the polarization energies P_+ and P_-, which reduce both the HL gap and the Coulomb energy. The change $\Delta\Sigma$ of each frontier orbital can be decomposed into Coulomb-hole ($\Delta\Sigma_{\mathrm{CH}}$), screened exchange ($\Delta\Sigma_{\mathrm{SX}}$) and bare exchange or Fock ($\Delta\Sigma_{\mathrm{X}}$) contributions [16]. The bare exchange is, in general, small and the screened exchange satisfies $\Delta\Sigma_{\mathrm{SX}} \sim -2\Delta\Sigma_{\mathrm{CH}}$ for the HOMO and $\Delta\Sigma_{\mathrm{SX}} \sim 0$ for the LUMO, so that typically $P_+ \sim -P_-$ [16]. From a physical point of view, the reduction of the IP can be understood by noting that the work required to take one molecular electron to infinity is decreased, since the attraction of the positively charged molecule that the electron leaves behind is screened. The EA is increased because the positive image charges help to stabilize the extra electron placed on the molecule. Finally, to account for all effects, in the presence of coupling to the leads, a further shift occurs due to the coupling self-energy.

Once the positions of the HOMO and LUMO resonances are known, the question arises of how to obtain the most accurate $T(E_{\mathrm{F}})$. In the literature, there are two approaches to this question and one of the aims of this paper is to compare the two. The first method selects either the HOMO or LUMO resonance ε closest to the Fermi level and fits this to a Lorentzian $T'(E) = \Gamma^2/[(E-\varepsilon)^2 + \Gamma^2]$, whose width Γ is obtained from the original DFT-based H. The zero-bias conductance is then given by $G = (2\mathrm{e}^2/\mathrm{h})T'(E_{\mathrm{F}})$ [39]–[41]. This method has been

[4] In general the Coulomb energies that enter in the definition of IP and EA are not the same.

shown to give results in close agreement with experiments, but it is only reliable when the relevant orbital is close to the Fermi level and the transmission in the gap is described by the tail of a single Lorentzian.

In our paper, we compare this approach with an alternative method for achieving SAINT, which adjusts the diagonal elements of the mean-field Hamiltonian [34, 42] to reproduce known values of the IP and EA. In particular, we show how to adjust the energy spectrum of a molecule or nanoscale object between electrodes to make it closer to more accurately predicted gaps or gaps measured from experiments and thus obtain transport results that agree much better with experiments, both qualitatively and quantitatively. This method has the advantage that it is numerically very cheap, i.e. the computational time does not increase significantly after including it, and it is easy to implement and gives in many cases results that are very similar to those obtained with more expensive methods, such as GW. We show how to derive this method in section 2 and how it compares to GW in the case of a benzene ring between featureless leads in section 3. In section 4, we study a more realistic case of a Benzenedithiolate (BDT) between gold leads and explain the evolution of the conductance as a function of the tip–surface separation in some recent experiments. Finally, we summarize the main results in section 5.

2. The theoretical approach

The starting point of the SAINT method is a projection $\hat{H}^0$ of the self-consistent mean-field Hamiltonian onto the atomic orbitals associated with the molecule, whose eigenvalues and eigenvectors are $\{\epsilon_n\}_{n=1,\ldots,M}$ and $\{\Psi_n\}_{n=1,\ldots,M}$, respectively, where M is the number of basis functions (atomic orbitals) on the molecule. From this, it is possible to build a new Hamiltonian,

$$\hat{H} = \hat{H}^0 + \Delta_o \sum_{n_o} |\Psi_{n_o}\rangle\langle\Psi_{n_o}| + \Delta_u \sum_{n_u} |\Psi_{n_u}\rangle\langle\Psi_{n_u}|, \tag{1}$$

whose eigenvalues corresponding to the occupied and unoccupied levels are shifted by Δ_o and Δ_u, respectively; n_o and n_u sum to the occupied and unoccupied levels, respectively. Taking into account the definition of the density matrix, $\hat{\rho} = \sum_{n=1}^{M} |\Psi_n\rangle\langle\Psi_n| f(\epsilon_n - \mu_e)$, where μ_e is the chemical potential, and the completeness relation, $\hat{1} = \sum_{n=1}^{M} |\Psi_n\rangle\langle\Psi_n|$, one notes that in the limit of zero temperature $f(E - \mu_e) = \Theta(\mu_e - E)$, and $\hat{\rho} = \sum_{n_o} |\Psi_{n_o}\rangle\langle\Psi_{n_o}|$, so that $\sum_{n_u} |\Psi_{n_u}\rangle\langle\Psi_{n_u}| = \hat{1} - \hat{\rho}$. Finally,

$$\hat{H} = \hat{H}^0 + (\Delta_o - \Delta_u)\hat{\rho} + \Delta_u \hat{1}. \tag{2}$$

In the general framework of non-orthogonal basis sets, the matrix elements $H_{\mu\nu}$ of this Hamiltonian are obtained by adding to the matrix elements of $\hat{H}^0$, the molecular matrix elements of the density matrix operator and the identity operator multiplied by the respective constants. In the case of the density matrix, one has

$$\langle\mu|\hat{\rho}|\nu\rangle = \sum_{n=1}^{M} \langle\mu|\Psi_n\rangle\langle\Psi_n|\nu\rangle f(\epsilon_n - \mu_e) = \sum_{\alpha,\beta=1}^{M} S_{\mu\alpha}\tilde{\rho}_{\alpha\beta}S_{\beta\nu}, \tag{3}$$

where $\hat{S}$ is the overlap matrix. In this expression, the matrix elements $\tilde{\rho}_{\alpha\beta}$ are defined to be $\tilde{\rho}_{\alpha\beta} = \sum_{n=1}^{M} c_{n\alpha}c^*_{n\beta} f(\epsilon_n - \mu_e)$, where $\{c_{n\alpha}\}$ are coefficients in the expansion $|\Psi_n\rangle = \sum_{\alpha=1}^{M} c_{n\alpha}|\alpha\rangle$.

The final result is a phenomenological Hamiltonian with matrix elements

$$H_{\mu\nu} = H^0_{\mu\nu} + (\Delta_o - \Delta_u)\langle\mu|\hat{\rho}|\nu\rangle + \Delta_u S_{\mu\nu}. \quad (4)$$

From this Hamiltonian one obtains a $T(E)$ that possesses accurately positioned resonances.

In order to implement the above SAINT, we utilize the quantum transport code SMEAGOL [43], which uses the Hamiltonian provided by the *ab initio* code SIESTA [44] to compute self-consistently the density matrix and the transmission coefficients. We first compare the zero-bias conductance $T(E_F)$ obtained from this method, with the value obtained by making a Lorentzian fit to the resonance closest to E_F. We also compare this method with most sophisticated approaches, such as the GW approximation, in case of a benzene molecule between featureless leads, and study how the qualitative and quantitative trends in the conductance are modified when this method is used to correct the transmission of a BDT molecule between gold leads.

3. Benzene ring between featureless leads

In order to illustrate how SAINT works and compare it with other methods such as the GW method, we first study the simple case of a benzene molecule coupled to featureless leads. We compare our results for the bias-dependent conductance to the results obtained by Thygesen and Rubio [32]. We used SMEAGOL with a double-ζ polarized basis set (DZP) for both carbon and hydrogen atoms and a real space grid defined with an energy cutoff of 200 Ry. The DFT exchange and correlation energy was evaluated with the generalized gradient approximation (GGA) as parametrized by Perdew *et al* [45]. With these approximations, we obtain an HL gap of 5.99 eV and a quasiparticle gap, calculated by energy differences, of 10.00 eV, which is in very good agreement with previous results [32].

We first analyze how to implement the SAINT method. In the case of a completely isolated molecule, the method is unambiguous. However, when a molecule is coupled to electrodes, one has to separate the Hamiltonian and density matrix of the molecule from those of the electrodes[5]. The Hamiltonian of the whole extended molecule cannot be shifted, because that would introduce a discontinuity at the interface between the surfaces of the extended molecule and the bulk leads. Therefore, as explained in the previous section, we project onto orbitals belonging to atoms of the molecule and define $\hat{H}_0$ to be the sub-matrix of the Hamiltonian involving these orbitals only. The molecular density matrix is obtained by diagonalizing $\hat{H}_0$.

In case of featureless leads, which act only as electron reservoirs, the only effect of the coupling to the electrodes is a broadening of the molecular levels by the imaginary part of the self-energies, Γ. The retarded Green's function can therefore be written as $\hat{G}^R(E) = [(E + 2i\Gamma)\hat{S} - \hat{H}]^{-1}$. From the retarded Green's function, we compute the lesser Green's function, both in and out of equilibrium, and obtain the density matrix to make the process self-consistent [43]. At the end of the self-consistent cycle, for a given voltage, we apply the SAINT correction and calculate the density of states (DOS), the transmission, which in this case can be simplified to $T(E) = (i\Gamma/2)\mathrm{Tr}\{[\hat{G}^R(E) - \hat{G}^{R\dagger}(E)]\hat{S}\}$, and the current. We define the SAINT shifts via the parameter $\bar{\Delta} = (\Delta_o, \Delta_u)$.

[5] In the case of a molecule coupled to featureless leads, we only have the orbitals of the molecule. In that sense, defining the Hamiltonian of the molecular part has no ambiguity.

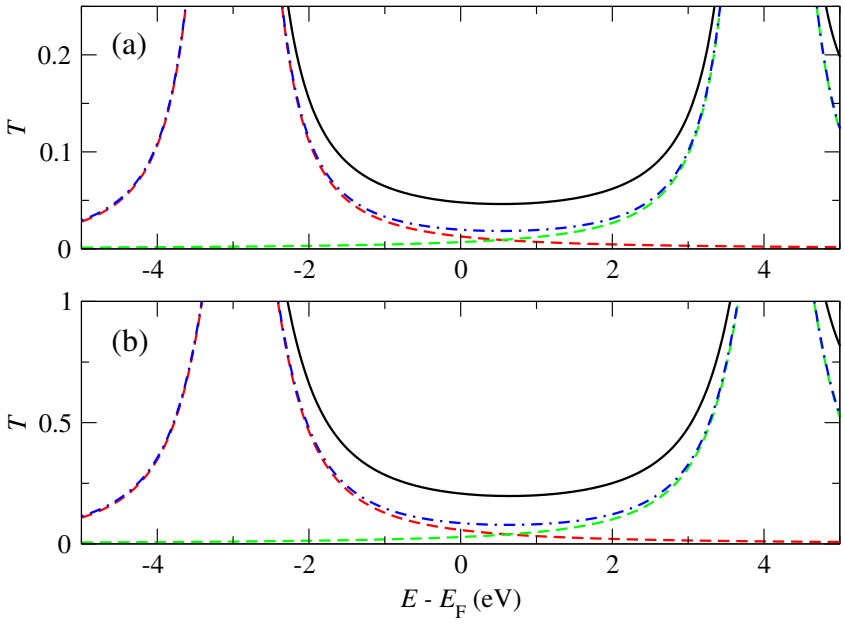

Figure 1. Comparison between the full transmission curve corrected with a SAINT $\bar{\Delta} = (-1, 1)$ eV and the transmission obtained by fitting the HOMO or the LUMO to Lorentzians (dashed lines) and summing both (dashed-dotted line). $\Gamma = 0.12$ eV in (a) and 0.25 eV in (b). Note that we had to use different vertical scales on each panel because the transmission in panel (a) is much smaller due to the lower value of Γ. The Lorentzians reach a transmission of 2 in both the HOMO and the LUMO due to the double degeneracy of such states produced by rotational symmetry.

In figure 1, we compare the results obtained by shifting the molecular Hamiltonian levels with those obtained by fitting to Lorentzians. The results are shown for the case $\bar{\Delta} = (-1, 1)$ eV and two different couplings to the leads, to illustrate again the effect of the broadening of the molecular levels. We fit Lorentzians to the nearest resonances and compare these to the $T(E)$ obtained from the spectrally adjusted Hamiltonian. As can be seen, simply by fitting to the nearest resonances (either the HOMO or the LUMO), the resulting zero-bias transmission is much smaller than the SAINT result. Furthermore, adding both Lorentzians does not significantly improve the results. This disagreement arises because for a system with many resonances, the Breit–Wigner formula does not accurately describe the electron transmission coefficient between resonances, even though it may be accurate in the vicinity of a resonance [46].

We plot in figure 2(a) the bias-dependent conductance obtained by differentiating the current. The uncorrected DFT result is very similar to the result of Thygesen and Rubio [32]. It has, however, a slightly larger value, due to our use of more basis states that produce additional resonances above the Fermi level, in contrast with the minimal and truncated Wannier function basis used in [32], which gives rise to only one resonance above the LUMO. We apply the SAINT correction with $\bar{\Delta} = (-2, 2)$ eV and $\bar{\Delta} = (-3, 3)$ eV, which roughly correspond to the correction to the HOMO and LUMO with and without taking into account the correction due to the image charges, respectively. The former would also approximately correspond to the GW

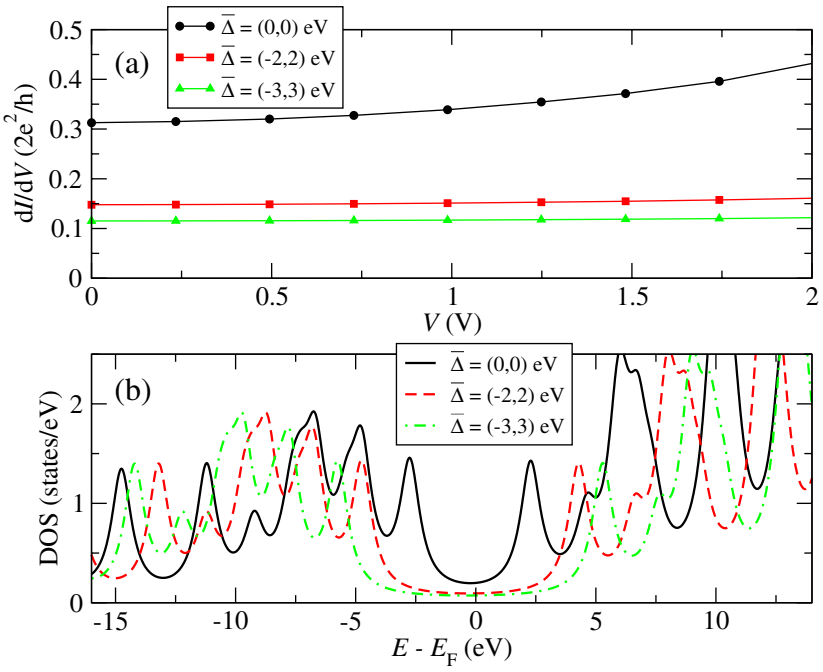

Figure 2. Conductance obtained by numerical differentiation of the current (a) and the corresponding DOS at equilibrium (b) for various values of the SAINT correction. $\Gamma = 0.25\,\mathrm{eV}$.

case and the latter to the HF case. As can be seen, the SAINT-corrected curves are significantly lower and flatter than the DFT result, which agrees with the GW and HF results. This change in the conductance can be explained by the opening of the gap and the subsequent reduction of the DOS in the middle of the gap, as can be seen in figure 2(b), which reduces the transmission. Compared with [32], the absolute values are again slightly higher, which may be due to the use of different basis sets[6]. Since the main effect of the GW and HF methods is the opening of the gap, which is exactly the same effect produced by SAINT, the origin of the good agreement between these calculations is clear. The GW and HF give rise, however, to additional structure in the occupied and unoccupied levels due to the energy-dependent GW self-energy and the different electronic structure method, respectively. Such structure can slightly modify the value of the transmission in the gap due to modifications in the tails of the resonances, but does not produce differences as large as those found between the exact result and the Lorentzian approximation.

Two notes of caution should be added when the SAINT method is applied to more realistic systems. In some special cases, when the Fermi level is pinned at the HOMO or the LUMO and the charge on the molecule is significantly altered from its neutral value, the self-consistent charge transfer, corresponding to that given by the uncorrected DFT result, would introduce additional shifts in the levels and possibly additional structure. Such charge transfer would have

[6] We performed tests with single-ζ polarized (SZP), double-ζ (DZ) and single-ζ (SZ) basis sets and indeed found that the conductace decreased to lower values and the relative differences converged with the results of Thygesen and Rubio [32]. The zero-bias conductances (in units of G_0) obtained for each basis set for $\bar{\Delta} = (0, 0), (-2, 2)$ and $(-3, 3)$ eV, respectively, were the following. DZP: 0.31, 0.15, 0.11; SZP: 0.29, 0.13, 0.10; DZ: 0.26, 0.12, 0.09; SZ: 0.23, 0.10, 0.05.

been different if the gap had been bigger. Since the SAINT is non-self-consistent and the gap is opened at the end, the amount of charge transfer in such cases would be wrong. However, the charge transfer in most of the systems is small [47] and large distortions due to it are not expected to be common. Another aspect that should be considered is related to molecular states located on the coupling atoms and that penetrate into the leads due to the strong coupling, such as the typical thiol–gold connections [34]. In these systems, such molecular states have some weight inside the leads and therefore when the SAINT is applied only to the molecular orbitals, these states can be distorted. The main effect in the transport properties would be a change in the width of the associated resonances. These changes are not expected, however, to have an effect on the qualitative trends and would affect only slightly the quantitative predictions[7]. A special case, which would produce states that would penetrate deep into the leads, can occur when the coupling between the molecule and the leads is very strong and the on-site energies of both parts are very similar, but this is not very common in molecular electronic systems unless the molecule is very small [48].

4. Benzenedithiolate (BDT) between Au leads

An archetypic example that has been extensively studied, both experimentally [49]–[55] and theoretically [56]–[70], is the BDT molecule coupled to gold leads. Recent experiments analyzed by means of two-dimensional (2D) conductance histograms [40], [71]–[73], on similar molecules (oligo(phenylene ethynylene) (OPE) molecules capped with thiols) contacted on one side to a surface and on the other side to a scanning tunneling microscope (STM), show a decrease of the conductance as the separation between the tip and the surface increases and a 2D zone with an upper and a lower edge of high and low conductances, respectively[8]. Some histograms also show at large tip–surface separations a circular zone of low conductances [40, 73]. Such histograms suggest that these molecules can be contacted with a tilted configuration for small tip–surface separations; as the tip retracts from the surface, the angle increases and the conductance is reduced. This can happen, as we shall see, if at least one of the sulfurs is in contact with an adatom, which corresponds to the most probable coupling configuration to the tip.

Many theoretical calculations have been carried out with the benzene molecule oriented normal to the surfaces and coupled in a hollow configuration, which is predicted to be the most stable contact configuration and gives strong coupling. When the molecule is contacted on top of a gold atom and normal to the surface, however, the coupling between the HOMO orbital, which is mainly made of perpendicular x and y p orbitals, to the s orbital of the gold adatom, is rather small due to symmetry. When the molecule is tilted, the x and y orbitals of the sulfur

[7] Tests performed on a BDT molecule coupled to gold leads with only s orbitals, which produce a smooth DOS and allow us to clearly observe the effect of the SAINT corrections, indeed showed reductions in the resonance width. However, such reductions were small and the resonances were not distorted.

[8] 2D conductance histograms are constructed by measuring thousands of traces of conductance when an STM tip retracts from a surface partially covered with molecules and plotting in a graph the number of values (z-axis) for a given conductance (y-axis) and separation between tip and surface (x-axis). By using such graphs, it is possible to have an idea of the most probable values of molecular conductance for a given separation between tip and surface, which are those that have the largest number of traces (highest z-coordinates), and understand how the junction evolves. In general, the zone with the largest number of traces has a certain width along the conductance axis, which means that there are various molecule–electrode configurations that give different conductances for a particular distance and move to lower values of conductance as the distance increases.

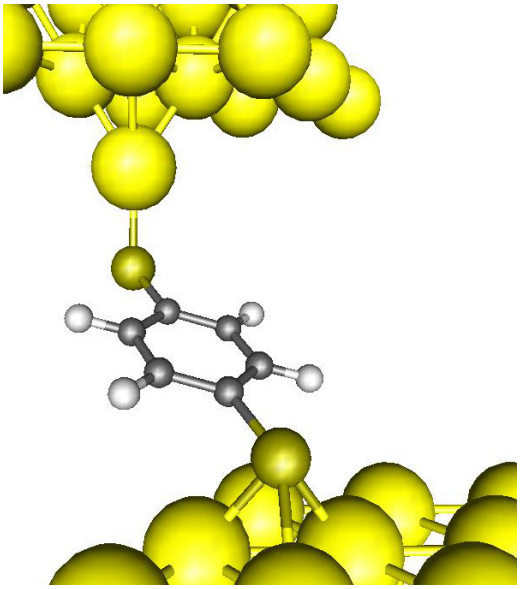

Figure 3. A BDT molecule between (111) Au leads, tilted 70° from the normal and contacted on the bottom surface in a hollow configuration and in the top surface to an adatom.

increase the overlap with the adatom orbitals and the coupling increases. The same does not happen, however, when the sulfur is contacted in a hollow configuration because the coupling of such orbitals to the gold surrounding atoms is already large and it is not severely reduced by symmetry. One would therefore expect a rather strong angular dependence when one of the sulfurs is in contact with an adatom and a weaker angular dependence when both sulfurs are contacted in a hollow configuration. The additional low-conductance zone in the histogram could be produced by another gold adatom on the surface, which would increase the distance between the tip and the surface and further decrease the conductance due to the small coupling on both sides.

In order to test these assumptions, we carried out *ab initio* calculations again using the SMEAGOL code. The parameters were the same as for the benzene molecule, but in this case we had to explicitly include the leads. We chose (111) gold leads with nine atoms per slice, two slices on each side of the extended molecule, and three additional slices to include the bulk leads. We also included periodic boundary conditions along the perpendicular directions to make sure that the transmission coefficients were smooth. We chose a SZ basis set for the gold atoms, which included the s and d orbitals[9]. An example of one of the configurations, where the molecule is tilted and in contact with an adatom in one of the surfaces, can be seen in figure 3. We studied three coupling configurations, hollow–hollow (HH), adatom–hollow (AH) and adatom–adatom (AA), and in each case we compared the normally aligned molecule ($\theta = 0^\circ$ from the normal to the surface) with a tilted molecue ($\theta = 70^\circ$).

[9] A SZ basis set with s and d orbitals for the gold atoms allowed us to perform quick-enough calulations without compromising the accuracy of the results. Tests performed involving only s orbitals, however, showed a strong reduction in the conductance due to the orthogonality of the gold s orbital and the sulfur p_x and p_y orbitals when one or two adatoms were in contact with the molecule. The inclusion of d orbitals in gold is therefore necessary to produce reasonable results in such configurations.

Table 1. Distance between the image plane, located 1 Å above the surface, and the center of the molecule (a), image charge correction (W) and final corrections to the occupied (Δ_o) and unoccupied (Δ_u) levels.

	a (Å)	W (eV)	Δ_o (eV)	Δ_u (eV)
HH 0°	4.34	1.15	−1.36	1.45
HH 70°	2.68	1.86	−0.65	0.74
AH 0°	4.54	1.10	−1.41	1.50
AH 70°	2.88	1.73	−0.78	0.87
AA 0°	4.74	1.05	−1.46	1.55
AA 70°	3.07	1.62	−0.89	0.98

Before showing the results, it is necessary to comment on a technical detail. In the case of BDT and other molecules with degenerate levels, one has to take additional care to obtain the correct shifts. The HOMO resonance in the transmission coefficients given by this molecule is composed of two resonances, which correspond to two nearly degenerated molecular orbitals, one of which is empty in the isolated molecule without leads [48]. These states become occupied when the molecule is saturated with hydrogens, which are added to the sulfurs, or when the molecule is coupled to the leads. Consequently, if levels are shifted using the occupation obtained from the Hamiltonian of the isolated molecule, the empty level associated with the HOMO moves upward, which is not the desired outcome. In such cases, to avoid this problem, the LUMO has to be shifted downwards by Δ_o and only the LUMO+1 and higher-energy eigenstates shifted upward.

In order to define the precise SAINT shifts, it is necessary to know the DFT HOMO and LUMO, and the IP and EA (obtained by total energy differences) of the molecule in the gas phase and the image charge corrections. The DFT HOMO, DFT LUMO, IP and EA are, respectively, −4.68, −1.38, 7.19 and −1.22 eV, from where we obtain gas phase corrections of −2.51 and 2.60 eV, for the occupied and unoccupied levels, respectively. The precise gap varies, however, from configuration to configuration, because it depends on the distance between the molecule and the image charge planes, which changes with the coupling configuration and the tilting angle of the molecule. We assume that the image charge plane is 1 Å above the surface and the point charge is in the middle of the molecule, so that the charging contribution can be approximated by $W = (e^2 \ln 2)/(8\pi\epsilon_0 a)$ [40], where $a = d/2 - 1$, and d is the distance between surfaces. The values of a, W and the final corrections to the occupied (Δ_o) and unoccupied (Δ_u) states are shown in table 1.

The results for the HH configuration are shown in figure 4. As said before, the HOMO peak in this system is composed of two almost degenerated resonances coming from bonding and antibonding molecular orbitals generated by the states of the sulfur atoms near the Fermi level [48]. This peak is very high in energy due to self-interaction errors [20] and produces very high conductances, compared with experiments. When the molecule is tilted, the peak widens and moves down in energy due to the increase in coupling[10]. Therefore, as can be seen

[10] The LUMO is, however, not much affected because this orbital is located in the carbon ring and is not so strongly influenced by changes in the coupling. Note that in our calculation, the values of $T(E)$ associated with this orbital are not very well defined because it is located near the gold band edge. This is an artifact arising from the use of only a SZ basis set in the leads. However, since in equilibrium the Fermi level is very close to the HOMO (even after applying the SAINT corrections), the values of $T(E)$ around the LUMO are not important for our study.

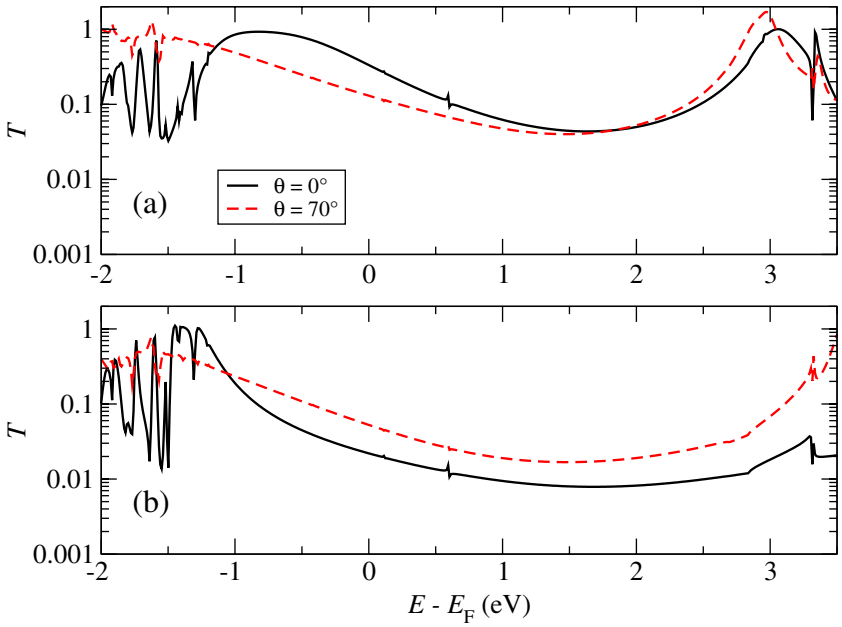

Figure 4. Transmission of a BDT molecule between (111) gold leads with both sulfur atoms contacted in the hollow configuration and the molecule normally aligned (continuous line) or tilted (dashed line). The results were obtained without (a) and with (b) the SAINT corrections given in table 1.

Table 2. Uncorrected and corrected zero-bias conductances G.

	$G_{\text{uncorrected}}$ (G_0)	$G_{\text{corrected}}$ (G_0)
HH 0°	3.3×10^{-1}	2.2×10^{-2}
HH 70°	1.3×10^{-1}	5.3×10^{-2}
AH 0°	5.0×10^{-1}	4.5×10^{-3}
AH 70°	9.8×10^{-2}	2.4×10^{-2}
AA 0°	8.1×10^{-1}	1.9×10^{-3}
AA 70°	1.2×10^{-1}	1.2×10^{-2}

in figure 4(a), for $\theta = 70°$, due to the movement of the HOMO to lower energies, the zero-bias conductance of the normally aligned molecule turns out to be higher than that of the tilted molecule. However, when the SAINT correction is applied, due to the facts that the transmission of the normally aligned molecule decays faster than that of the tilted molecule and the shift in the occupied levels in the first case is bigger than the shift in the second case due to a smaller image charge correction, when the SAINT corrections are applied, the situation reverses and the normally aligned molecule gives a lower conductance. The values of the transmission at the Fermi level can be seen in table 2.

In the normally aligned AH configuration, shown in figure 5, both the width and the height of the HOMO are smaller than those in the HH configuration. The decrease in the width of the resonance is due to the reduction of the coupling on the side of the molecule coupled to the adatom and the decrease in the height is due to the asymmetry of the contacts. When the

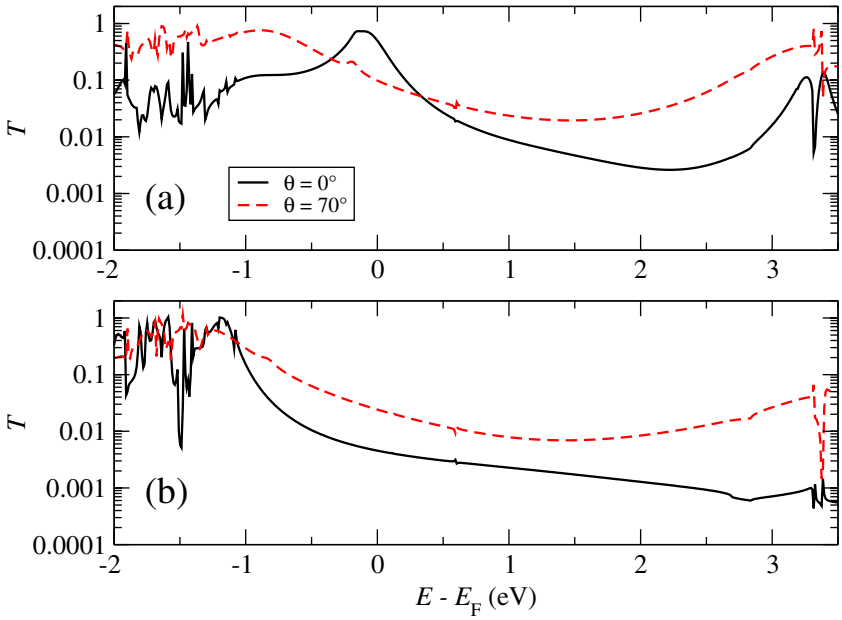

Figure 5. Transmission of a BDT molecule between (111) gold leads with one sulfur atom contacted in the hollow configuration and the other on top of an adatom and the molecule positioned normally aligned (continuous line) or tilted (dashed line). The results were obtained without (a) and with (b) the SAINT corrections given in table 1.

molecule is tilted, the width of the resonance increases dramatically and again moves down in energy. The LUMO is also affected this time by the increase in coupling, which allows better communication between the states in the carbon rings and the states in the leads than in the normally aligned configuration. At zero bias and without any correction, the conductance of the normally aligned molecule is again larger than that of the tilted molecule, which does not agree with recent theoretical and experimental predictions [73]. However, when the SAINT corrections are applied, the faster decay of the transmission and the larger shift of the occupied levels in the normally aligned configuration again reverse the trend and the tilted configuration gives the largest conductance, as can be seen in table 2.

Finally, in the AA configuration, shown in figure 6, the HOMO peak splits into a number of sharp resonances, one of which is pinned at the Fermi level. This movement of the HOMO toward the Fermi level in the AA or top–top (on top of surface gold atoms) configurations has been attributed to a reduction of the charge transfer, which moves the states upward and pins the HOMO at the Fermi energy [62]. This movement increases the zero bias conductance and, at the same time, decreases the transmission in the gap. When the molecule is tilted, the HOMO resonances merge into a single peak, whose width is much larger than that of the resonances of the normally aligned molecule. This peak moves downward again and gives a lower transmission at the Fermi level than that of the normally aligned case. However, when the SAINT corrections are applied, we see again that the situation reverses and now the tilted molecule gives a higher conductance. The results can be seen in table 2.

The conductances observed in previous experiments range from 10^{-4} G_0 [49] to 0.1 G_0 [53]. The values obtained by Reed *et al* [49] are rather small and could be produced

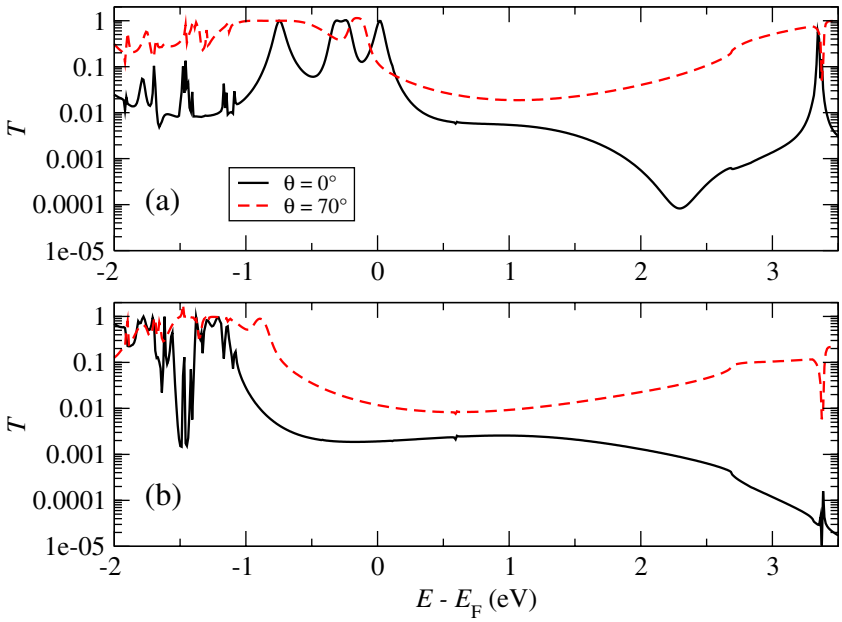

Figure 6. Transmission of a BDT molecule between (111) gold leads with both sulfur atoms contacted on top of an adatom and the molecule positioned normally aligned (continuous line) or tilted (dashed line). The results were obtained without (a) and with (b) the SAINT corrections given in table 1.

by specially stretched configurations. The rest of the values are roughly within the range of conductances we obtain after applying the SAINT correction. The differences between the high- and low-conductance zones in different molecules observed in recent experiments range between approximately 1 order of magnitude in pyridines [40] and 2 orders of magnitude in OPEs [73]. In our case, which is similar to that of the OPEs, we can see a difference of roughly 1 order of magnitude between the highest and lowest corrected values (excluding the HH configuration, which we predict would not be very probable in STM experiments). Probably the low-conductance zone could have lower conductances arising from stretched AA configurations.

5. Summary

In summary, we have shown how to shift the position of the occupied and unoccupied molecular resonances in *ab initio* transport calculations of molecules between electrodes to obtain HL gaps and transport properties that agree much better with experiments. This spectral adjustment easily solves one of the main problems of DFT-based mean-field Hamiltonians, which is an incorrect size of the HL gap and therefore an incorrect position of the resonances relative to the Fermi level of the electrodes. We found that this method, which is easy to implement and numerically very cheap, can improve both the qualitative and the quantitative agreements with experiments and is an improvement over an alternative approach based on Lorentzian fits.

We have shown how this method can be implemented by diagonalizing the projected Hamiltonian on the molecule and shifting its occupied and unoccpuied eingestates. We tested the accuracy of the method for the case of a benzene molecule coupled to featureless leads. We compared it with an alternative method based on using Lorentzian fits to correct the

transport properties of molecular junctions and found that such an approximation can severely underestimate the transmission in some cases. We also compared our method with previous GW results. We found a very good qualitative agreement, although the quantitative agreement was worsened by the presence of Lorentzian tails coming from unoccupied states. The agreement improved, however, when smaller numbers of basis functions were used.

We also used the SAINT method in a realistic junction of a BDT molecule between gold leads, in an attempt to explain the evolution of the conductance as a function of length in 2D histograms. We found that it was necessary to shift the molecular levels to obtain results that could explain the observed evolution, i.e. results where the zero-bias conductance of a normally aligned molecule coupled to one or two adatoms was smaller than the zero-bias conductance of a tilted molecule. We also predicted the existence of a low-conductance zone in the 2D histograms of these molecules located more than one order of magnitude below the main conductance zone.

As a final comment, we would like to say that the method works well due to the rather good description given by DFT of some physical quantities such as charge transfer and hybridization between the molecular states and the states of the electrodes (which is responsible for the width of the resonances). Since the main physical quantity that is not correctly described by DFT, even with a perfect exchange-correlation potential, is the HL gap, which is clearly underestimated, this method goes directly into the root of the problem and significantly improves the transport properties. So, once the main source of discrepancy is removed, the agreement between theory and experiments improves considerably, provided that the rest of quantities remain the same or very similar. Care, however, should be taken when many-body interaction terms are important. Such terms play a role in special situations, such as molecules very weakly coupled to the leads (physisorbed) or when molecular resonances are naturally very close to the Fermi level. Since in most molecular electronics systems the molecules are strongly coupled to the leads (chemisorbed) and the resonances are in reality relatively away from the Fermi level, these problems are absent. So, in all of these cases the agreement with experiments, at least at low voltages, depends basically on the width of the resonances and how far they are from the Fermi level, something that can be reasonably well described by a SAINT-corrected DFT.

Finally, we would also like to remark that the SAINT method can be used to correct mean-field Hamiltonians even when the IP, the EA and other corrections are not known from first principles, as is the case for long molecules, such as those reported in [3]. In order to obtain a corrected Hamiltonian in these cases, the SAINT shifts Δ_o and Δ_u can be treated as free parameters to adjust the transmission coefficient to yield agreement with some chosen property, such as the current–voltage characteristic, the temperature dependence of the conductance or the dependence of the conductance on a gate voltage in, for example, an electrochemical environment. Once Δ_o and Δ_u are chosen to fit one of these measurements, the SAINT-corrected Hamiltonian can then be used to predict the others.

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