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Impact of Exchange-Correlation Effects on the *IV* Characteristics of a Molecular Junction

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The role of exchange-correlation effects in nonequilibrium quantum transport through molecular junctions is assessed by analyzing the *IV* curve of a generic two-level model using self-consistent many-body perturbation theory (second Born and *GW* approximations) on the Keldysh contour. It is demonstrated how the variation of the molecule's energy levels with the bias voltage can produce anomalous peaks in the dI/dV curve. This effect is suppressed by electronic self-interactions and is therefore underestimated in standard transport calculations based on density functional theory. Inclusion of dynamic correlations introduces quasiparticle (QP) scattering which in turn broadens the molecular resonances. The broadening increases strongly with bias and can have a large impact on the calculated *IV* characteristic.

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Over the last decade, it has become possible to contact single molecules by metallic electrodes and measure the *IV* characteristic of the resulting nano junction [1–3]. Experiments of this kind can be seen as the first step towards the realization of a molecule based electronics. On a more fundamental level, the *IV* characteristics provide a spectroscopic fingerprint of the molecular junction containing information about the positions and lifetimes of the electronic energy levels. In view of this, the interpretation of *IV* curves in terms of the electronic structure of the junction represents a fundamental challenge for molecular electronics.

So far, almost all *ab initio* calculations of conductance in molecular junctions have been based on the single-particle Kohn-Sham (KS) scheme of Density Functional Theory (DFT) [4–6]. This approach has been successfully applied to junctions characterized by strong coupling between molecule and leads [7,8], but has generally been found to overestimate the low-bias conductance of larger and more weakly coupled molecules [9–11]. Recently, this shortcoming of the DFT approach has been attributed to the presence of self-interaction (SI) errors in the standard exchange-correlation (xc) functionals [12]. Inclusion of electronic correlations beyond the single-particle approximation could also be important; however, attempts in this direction have so far been limited [13].

While the theory of nanoscale conductance in the low-bias limit and its relation to the ground state electronic structure has been studied in depth, the finite-bias regime has received much less attention [13–15]. The main reason for this unbalance is presumably the larger complexity of the latter problem: linear-response properties can be obtained from the ground state, e.g., via the Kubo formula [16], whereas finite-bias properties require the construction of a nonequilibrium steady state which, unlike the ground state, is not a variational quantity.

In this Letter, we analyze the mechanisms governing the shape of molecular *IV* characteristics with particular focus on the role of exchange and correlation. The molecular junction is modeled by two electronic states, representing the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), coupled symmetrically to leads as sketched in Fig. 1(a). It is easy to anticipate that the slope of the *IV* curve is largest when a molecular level is aligned with one of the bias window edges. This will show as peaks in the dI/dV curve. In the simplest picture, the distances between peaks in the dI/dV curve are thus a direct measure of the distances between the energy levels of the molecule, and the width of the peaks gives the lifetime of the levels. This simple picture breaks down because the electronic structure of the molecule will

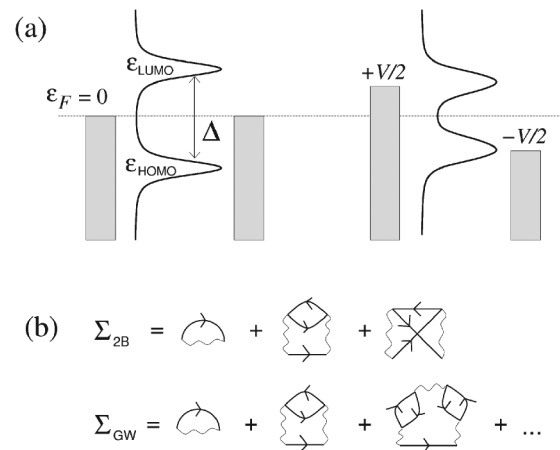


FIG. 1. (a) Density of states for a molecular junction under zero and nonzero bias voltage. As indicated, the bias changes the molecule's DOS which in turn affects the dI/dV . (b) Diagrams for the second Born (2B) and *GW* self-energies. Full lines represent the Green's function of the molecule *with* coupling to leads. Wiggly lines represent the interaction.

change in response to the applied bias, and as we will see, this effect can be surprisingly large even for very simple systems.

On the basis of the two-level model, we identify a simple mechanism which can lead to the formation of anomalously strong peaks in the dI/dV curve. The mechanism is driven by the applied bias voltage and can be viewed as a collapse of the HOMO-LUMO gap by which both levels move simultaneously into the bias window, giving rise to a large increase in the current. The mechanism is suppressed by SI and is therefore only partly present in DFT transport calculations which suffer from SI errors [12]. The second result of the Letter is that the inclusion of dynamic correlations, at the levels of the second Born (2B) and GW approximations, can have a strong influence on the IV curve, due to the strong enhancement of QP scattering at finite bias which broadens the molecular resonances.

We denote the noninteracting HOMO and LUMO energies by ξ_0 and $\xi_0 + \Delta_0$, respectively. We take the charging energy of the HOMO and LUMO levels to be the same (U_{11}) whereas the charging energy between an electron in the HOMO and an electron in the LUMO is set to $U_{12} = 0.75U_{11}$. As discussed later, our conclusions are not sensitive to this choice as long as $U_{12} > 0.5U_{11}$. We neglect the exchange energy between the HOMO and LUMO states as it is generally much smaller than the charging energies [17]. The Hamiltonian of the molecule is written $\hat{H}_{\text{mol}} = \hat{H}_0 + \hat{U}$, where

$$\hat{H}_0 = \sum_{\sigma} \xi_0 \hat{n}_{H\sigma} + (\xi_0 + \Delta_0) \hat{n}_{L\sigma} \quad (1)$$

$$\hat{U} = \sum_{i=H,L} U_{11} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \sum_{\sigma,\sigma'} U_{12} \hat{n}_{H\sigma} \hat{n}_{L\sigma'}, \quad (2)$$

with $\hat{n}_{H\sigma}$ and $\hat{n}_{L\sigma}$ being the number operator for an electron with spin σ in the HOMO and LUMO states, respectively. The interactions can also be written $\hat{U} = \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{i,j \in \{L,H\}} \tilde{U}_{i\sigma,j\sigma'} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma'}^\dagger \hat{c}_{j\sigma'} \hat{c}_{i\sigma}$, where $\tilde{U}_{i\sigma,j\sigma'} = U_{11} \delta_{ij} (1 - \delta_{\sigma\sigma'}) + U_{12} (1 - \delta_{ij})$. By working with this spin-dependent interaction, i.e., using $\tilde{U}$ to represent the wiggly lines in the diagrams of Fig. 1(b), SI errors are automatically avoided to all orders in the interaction since $\tilde{U}_{i\sigma,i\sigma} = 0$. [18] This can be illustrated by noting that both the first- and second-order exchange diagrams (first and last diagram of Σ_{2B}) vanish when evaluated using $\tilde{U}$. [19] In the present model, these diagrams should exactly cancel the SI in the Hartree and second-order bubble diagrams, respectively. By using $\tilde{U}$ for the calculation of the GW self-energy, we get similar diagrams included “for free” to all orders in the interaction. In particular, the resulting SI-free GW is exact to second order, i.e., includes the 2B (at least for our model). This is in contrast to standard GW calculations, including previous GW model calculations [20], which suffer from higher order SI errors.

The retarded Green’s function describing the molecule in contact with leads is written

$$G^r(\omega) = [(\omega + i\Gamma)I^{2 \times 2} - H_0 - \Sigma_H^r - \Sigma^r(\omega)]^{-1}. \quad (3)$$

Spin dependence has been suppressed as we specialize to the spin unpolarized case, i.e., $G_{\uparrow\uparrow} = G_{\downarrow\downarrow} = G$. The coupling to leads is included via the wide-band tunneling rate Γ . Σ_H and Σ denote the Hartree and xc self-energies, respectively. In this work, Σ can be either zero (corresponding to the Hartree approximation), exchange, 2B or (SI-free) GW . The self-energies, $\Sigma_H[G]$ and $\Sigma[G]$, are calculated self-consistently in conjunction with the Dyson Eq. (3) using the nonequilibrium Keldysh formalism to account for the difference in chemical potentials. The calculational procedure is described in detail in Ref. [18].

In the special case of symmetric coupling, the particle current can be written [22]

$$I(V) = \Gamma \int_{\varepsilon_F - V/2}^{\varepsilon_F + V/2} \varrho(V; \omega) d\omega, \quad (4)$$

where $\varrho(\omega) = (i/2\pi) \text{Tr}[G^r(\omega) - G^r(\omega)^\dagger]$ is the (non-equilibrium) density of states (DOS). It has peaks at the position of the QP energy levels, ε_i , which represent the electron addition/removal energies of the junction. The width of a peak equals the inverse lifetime of the QP, $\tau_i^{-1} \approx \Gamma + \text{Im}\Sigma_{ii}^r(\varepsilon_i)$. Because single-particle approximations are characterized by a real, frequency independent xc self-energy, the width of the spectral peaks obtained in Hartree and HF will be given by Γ . From Eq. (4), it is clear that the current will increase more rapidly when a peak in the DOS enters the bias window. We stress, however, that $\varrho(\omega)$ depends on V through Σ_H and Σ , and thus the overall shape of the DOS, in particular, the HOMO and LUMO positions, will change with the bias voltage. Clearly, this change in the DOS determines the shape of the dI/dV curve.

The following parameters have been used throughout: $\Delta_0 = 2$, $U_{11} = 2$, $U_{12} = 1.5$. By varying the one-particle energy ξ_0 , we can control the equilibrium occupation of the molecule, N_{el} . We consider the case of weak charge transfer to the molecule, i.e., N_{el} ranges from 2.0 to 2.1, corresponding to ε_F lying in the middle of the gap and slightly below the LUMO, respectively. The Fermi level is set to zero, and the bias is applied symmetrically, i.e., $\mu_L = V/2$ and $\mu_R = -V/2$.

In Fig. 2, we show the calculated dI/dV curves (obtained by numerical differentiation) for different values of Γ and N_{el} . We first notice that the 2B and GW approximations yield similar results in all the cases indicating that the higher order terms in the GW self-energy are fairly small. For $\Gamma = 1.0$, all methods yield qualitatively the same result. For even larger values of Γ (not shown), and independently of N_{el} , the results become even more similar. In this strong coupling limit, single-particle hybridization effects will dominate over the interactions.

For $\Gamma = 0.25$, the Hartree approximation severely overestimates the low-bias conductance. This is a consequence of the SI contained in the Hartree potential which leads to

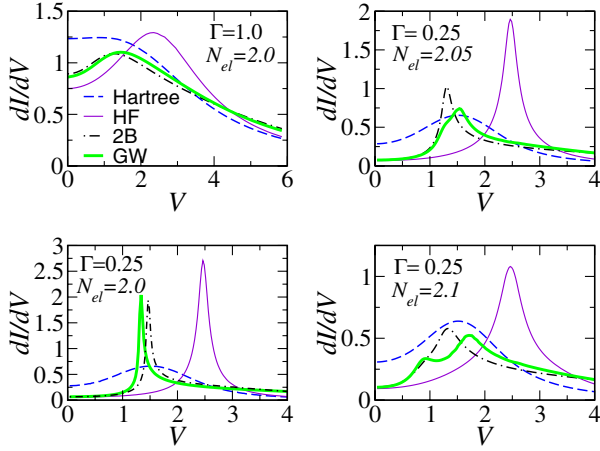


FIG. 2 (color online). dI/dV curves for different values of the tunneling strength Γ and occupation of the molecule, N_{el} . The curves are calculated using different approximations for the xc self-energy.

an underestimation of the (equilibrium) HOMO-LUMO gap. On the other hand, the HF, 2B, and GW methods lead to very similar conductances in the low-bias regime. This indicates that the inclusion of dynamic correlations does not change the (equilibrium) HOMO-LUMO gap significantly. It is well known that HF tends to overestimate band gaps and that the inclusion of correlations, e.g., at the GW level, has the effect of reducing the HF gap towards the true value. However, in finite systems where the electrons are confined in discrete, well separated energy levels, correlation effects are weak and HF already yields good spectra. In such cases, the inclusion of correlations is expected to have minor effects on the equilibrium gap, as observed in the present case.

Returning to Fig. 2, we notice that the lower left graph shows an interesting feature. Namely, the HF, 2B, and GW curves all contain an anomalously strong conductance peak. Interestingly, the peak height is significantly larger than 1 which is the maximum conductance for a single level (Anderson impurity model). Moreover, the full width at half maximum (FWHM) of the peak is only $\sigma_{HF} = 0.27$ and $\sigma_{2B/GW} = 0.12$, respectively, which is much smaller than the tunneling broadening of $2\Gamma = 0.5$. We note in passing that the peak loses intensity as N_{el} is increased and that the Hartree approximation does not produce the anomalous peak at all.

To understand the origin of the anomalous peak(s), we plot in Fig. 3 the evolution of the HOMO and LUMO positions as a function of the bias voltage (the 2B result is left out as it is similar to GW). Focusing on the upper panel of the figure ($N_{el} = 2.0$), we notice a qualitative difference between the Hartree and the SI-free approximations: While the Hartree gap expands as the levels move into the bias window, the HF and GW gaps shrink leading to a dramatic increase in current around $V = 2.5$ and $V = 1.3$, respectively. This is clearly the origin of the anomalous dI/dV peaks. But why do the SI-free gaps collapse?

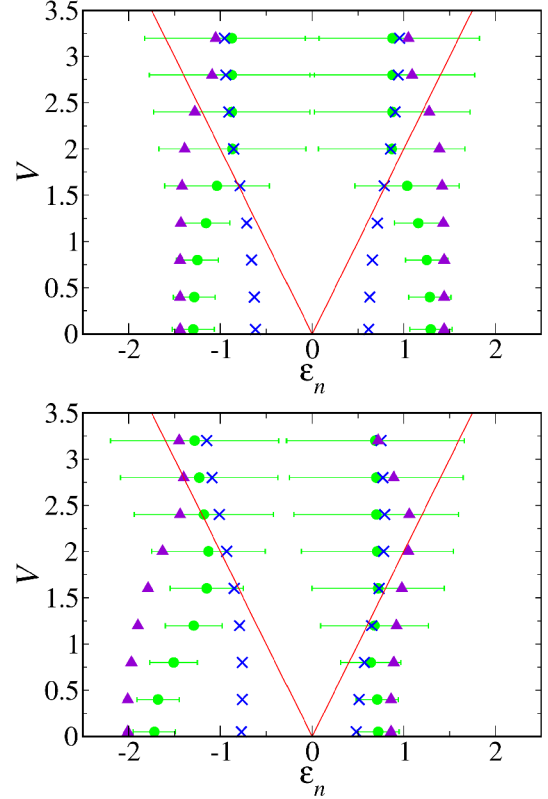


FIG. 3 (color online). Position of the HOMO and LUMO levels as a function of the bias voltage for the Hartree (crosses), HF (triangles), and GW (circles) approximations. The horizontal lines show the FWHM of the GW resonances. The FWHM of the Hartree and HF resonances is 2Γ independently of V . Notice the differences in the way the levels enter the bias window: The Hartree gap opens while the HF and GW gaps close. In the upper graph $\Gamma = 0.25$, $N_{el} = 2.0$ (symmetric case). In the lower graph $\Gamma = 0.25$, $N_{el} = 2.1$.

Let us consider the change in the HOMO and LUMO positions when V is increased by $2\delta V$. In general, this change must be determined self-consistently; however, a “first iteration” estimate yields a change in the HOMO and LUMO occupations of $\delta n_H \approx -\varrho_H(-V/2)\delta V$ and $\delta n_L \approx \varrho_L(V/2)\delta V$, respectively. At the HF level, this leads to

$$\delta \varepsilon_H \approx [-U_{11}\varrho(-V/2) + 2U_{12}\varrho(V/2)]\delta V \quad (5)$$

$$\delta \varepsilon_L \approx [U_{11}\varrho(V/2) - 2U_{12}\varrho(-V/2)]\delta V \quad (6)$$

where we have used that $\varrho_H(-V/2) \approx \varrho(-V/2)$ and $\varrho_L(V/2) \approx \varrho(V/2)$. The factor 2 in front of U_{12} includes interactions with both spin channels. In the symmetric case ($N_{el} = 2.0$), we have $\varrho(-V/2) = \varrho(V/2)$. Since $U_{11} < 2U_{12}$, this means that $\delta \varepsilon_H > 0$ and $\delta \varepsilon_L < 0$; i.e., the gap is reduced as V is raised. Moreover, it follows that the gap reduction is largest when $\varrho(\pm V/2)$ is largest, that is, just when the levels cross the bias window. In the general case ($N_{el} \neq 2.0$) the direction of the shift depends on the relative magnitude of the DOS at the two bias window edges: a

level will follow the edge of the bias window if the other level does not intersect the bias edge. It will move opposite to the bias, i.e., into the bias window, if the other level is close to the bias window edge. This effect is clearly seen in the lower graph of Fig. 3 (triangles). Thus the gap-closing mechanism has the largest impact on the dI/dV curve when the HOMO and LUMO levels hit the bias window simultaneously. Moreover, the effect is stronger the larger U_{12}/U_{11} , and the smaller Γ (the maximum in the DOS is $\sim 1/\Gamma$). At the Hartree level, Eqs. (5) and (6) are modified by replacing U_{11} by $2U_{11}$. This leads to an effective pinning of the levels to the bias window which tends to open the gap as V is increased, see Fig. 3 (crosses).

The effect of dynamic correlations can be identified by comparing the HF result with the $GW/2B$ results in Fig. 2. For $\Gamma = 0.25$, two qualitative differences are observed: (i) The $GW/2B$ conductance peaks occur at a lower bias voltage than the HF peak; (ii) the $GW/2B$ peaks have long, flat tails on the high-bias side while HF peaks are more symmetric. Returning to Fig. 3, we see that part of (i) can be explained from the fact that HF yields a larger equilibrium gap than GW . Indeed, for $V = 0$, the HF gap is ~ 0.3 larger than the GW gap. However, this effect alone cannot account for the shift in the conductance peak from $V \sim 2.5$ in HF to $V \sim 1.5$ in $GW/2B$.

In fact, both (i) and (ii) are consequences of a significant spectral broadening occurring at finite bias in the $GW/2B$ calculations. The broadening, indicated by horizontal lines in Fig. 3, is due to QP scattering. According to Fermi-liquid theory, QP scattering at the Fermi level is strongly suppressed in the ground state, i.e., $\text{Im}\Sigma_{ii}(\epsilon_F) = 0$ for $V = 0$. However, as the bias is raised, the phase space available for QP scattering is enlarged and $\text{Im}\Sigma$ increases accordingly. As a result of the additional level broadening, $\rho(\pm V/2)$ increases more rapidly as a function of V . Since this is exactly the driving force behind the gap-closing mechanism, the dI/dV peak occurs earlier in the GW than the HF calculation. Clearly, the long tails seen in the dI/dV of the $GW/2B$ calculations are also a result of the spectral broadening due to QP scattering.

In summary, we have investigated the mechanisms governing the shape of the IV characteristic of a generic molecular junction. We identified a simple gap-closing mechanism which can lead to anomalously strong peaks in the dI/dV . The mechanism is suppressed by SI errors and is therefore not likely to be correctly described in standard DFT calculations. This shows that the use of SI corrected xc-functionals, recently shown to be important for the linear-response conductance, could be equally important under finite-bias conditions. Finally, we found that the strong enhancement of QP scattering as function of bias voltage leads to significant smearing of spectral features, which in turn has a large impact on the dI/dV curve.

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