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Renormalization of Molecular Quasiparticle Levels at Metal-Molecule Interfaces: Trends across Binding Regimes

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When an electron or a hole is added into an orbital of an adsorbed molecule the substrate electrons will rearrange in order to screen the added charge. This polarization effect reduces the electron addition and removal energies of the adsorbed molecule relative to those of the free molecule. Using a microscopic model of the metal-molecule interface, we illustrate the basic features of this renormalization mechanism through systematic GW, Hartree-Fock, and Kohn-Sham calculations for the molecular energy levels as function of the model parameters. We identify two different polarization mechanisms: (i) polarization of the metal (image charge formation) and (ii) polarization of the molecule via charge transfer across the interface. The importance of (i) and (ii) is found to increase with the metal density of states at the Fermi level and metal-molecule coupling strength, respectively.

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The position of an adsorbed molecule’s frontier orbitals with respect to the substrate Fermi level determines the threshold energies at which electron transfer can take place across the metal-molecule interface. Such electron transfer processes represent the basis of surface photochemistry and nonadiabatic chemistry, organic and molecular electronics, as well as scanning tunneling and photoemission spectroscopy [1–7]. Accurate descriptions of adsorbate energy spectra are thus fundamental for quantitative modeling within these important areas.

Recently, a number of experiments probing transport and optical properties of molecules at metal surfaces have found strong reductions of electron addition or removal energies due to polarization effects in the metal substrate [4–8]; see Fig. 1(a). Theoretical studies of metal-molecule interfaces are usually based on density functional theory (DFT) and rely on an interpretation of Kohn-Sham (KS) eigenvalues as quasiparticle energies. This interpretation is unjustified in principle and questionable in practice—even with the exact exchange-correlation functional—because single-particle schemes like KS and Hartree-Fock (HF) take no account of dynamical effects such as screening of added electrons or holes. Inclusion of dynamical polarization effects through classical image charge models have been applied to correct DFT calculations of quantum transport in molecular contacts [9–11]. Only recently, GW calculations by Neaton et al. have demonstrated that the energy gap of benzene is reduced by more than 3 eV when physisorbed on graphite due to image charge effects [12]. As a complementary study, this work focuses on qualitative trends and explores different binding situations including strong-weak coupling and narrow-wide band substrates.

To illustrate the problem, suppose we add an electron into the lowest unoccupied molecular orbital (LUMO) of an adsorbed molecule. The associated energy cost is given by the quasiparticle (QP) spectral function

FIG. 1 (color online). (a) Schematic of a molecule’s HOMO and LUMO energy levels as it approaches a metal surface. For weak coupling (physisorbed molecule) the gap is reduced due to image charge formation in the metal. For strong coupling (chemisorbed molecule) dynamic charge transfer between molecule and metal reduces the gap further. (b) The model used in this study. (c) The semielliptical band at the terminal site of the TB chain and the resonances of the molecule.
A_L(\varepsilon) = \sum_n |\Psi_n^{N+1}\rangle [c_i^{\dagger} \Psi_n^{N}]^2 \delta(\varepsilon - E_n^{N+1} + E_0^N), \quad (1)

where \(|\Psi_n^{N}\rangle\) and \(|\Psi_n^{N+1}\rangle\) denote the many-body \(N\)-particle ground state and \((N + 1)\)-particle excited states, respectively. The qualitative shape of \(A_L\) is mainly dictated by the hybridization with the metal states. On the other hand, quantitative features such as the precise position of its peak(s) depend on the system’s response to the extra electron in the LUMO. This follows by noting that peaks in \(A_L\) appear at dominant Fourier components of the time-dependent state \(c_i^{\dagger} |\Psi_n^{N}\rangle(t)\). Dynamical effects of this type can be incorporated within an effective single-particle framework where the electron-electron interaction is represented by an energy-dependent potential known as a self-energy. In practice the self-energy must be approximated using, e.g., many-body perturbation theory. For weak metal-molecule coupling, total energy calculations with constrained occupations of the molecule represent a simple alternative to the many-body approach [13]. However, such calculations only provide a lower (upper) bound for the LUMO (HOMO) energies and, as we show here, these bounds can differ from the true QP energies.

In this Letter, we introduce a simple model of a metal-molecule interface and use it to investigate the effect of dynamical polarization on the molecular levels as a function of microscopic key quantities such as the metal-molecule coupling strength \(\Gamma\) and the metal density of states (DOS). We find that polarization effects consistently reduce the molecular gap as compared to the gas phase value. This effect is completely absent in HF theory which systematically overestimates the gap. On the other hand, the KS spectrum is indirectly affected through the “exact density” requirement; however, the KS gap is always found to be too small. On the basis of \(GW\) calculations, we find that the gap reduction due to polarization of the metal, i.e., image charge formation, is insensitive to \(\Gamma\) but increases with the metal DOS at \(E_F\). On the other hand, polarization of the molecule via charge transfer to or from the metal increases strongly with \(\Gamma\) leading to a direct correlation between adsorbate bond strength and the gap renormalization.

Our model Hamiltonian consists of three parts, \(\hat{H} = \hat{H}_{\text{met}} + \hat{H}_{\text{mol}} + \hat{V}\), describing the metal, the molecule, and their mutual interaction; see Fig. 1(b). The metal is modeled by a noninteracting, semi-infinite tight-binding (TB) chain,

\[ \hat{H}_{\text{met}} = \sum_{i \rightarrow -\infty}^{0} \sum_{\sigma = \uparrow, \downarrow} t(c_{i\sigma}^{\dagger} c_{i-1\sigma} + c_{i-1\sigma}^{\dagger} c_{i\sigma}). \quad (2) \]

The molecule is modeled as two interacting levels representing the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals

\[ \hat{H}_{\text{mol}} = \xi_H \hat{n}_H + (\xi_H + \Delta_0) \hat{n}_L + \hat{U}_{\text{mol}} \quad (3) \]

where, e.g., \(\hat{n}_H = c_H^{\dagger} c_H + c_H^{\dagger} c_H + c_{L}^{\dagger} c_{L}\) is the number operator of the HOMO level. Notice that, despite the interactions, the eigenstates of \(\hat{H}_{\text{mol}}\) are simply Slater determinants build from the orbitals \(|H\sigma\rangle\) and \(|L\sigma\rangle\). Finally, hybridization and interaction between the molecule and the terminal site of the chain is described by

\[ \hat{V} = \sum_{\nu = H, L} \sum_{\sigma = \uparrow, \downarrow} t_{\text{hyb}} (c_{0\sigma}^{\dagger} c_{\nu\sigma}^{\dagger} + c_{\nu\sigma}^{\dagger} c_{0\sigma}^{\dagger}) + U_{\text{ext}} \delta \hat{n}_0 \delta \hat{N}_{\text{mol}}. \quad (5) \]

Here \(\delta \hat{n}_0 = (\hat{n}_0 - 1)\) and \(\delta \hat{N}_{\text{mol}} = (\hat{N}_{\text{mol}} - 2)\) represent the excess charge on the chain’s terminal site and the molecule, respectively. We set \(E_F = 0\) corresponding to a half filled band, and adjust \(\xi_H\) so that the molecule holds exactly two electrons in the ground state. Specifically this means \(\xi_H = -\Delta_0/2 - U_0/2 - U_{HL}\). The model neglects interactions within the TB chain and between the molecule and interior TB sites \((i < 0)\). These approximations are, however, not expected to influence the qualitative trends described by the model.

It is instructive first to consider the model in the limit \(t_{\text{hyb}} = 0\) (weak physisorption) where the metal and molecule interact only via the Coulomb term \(\hat{U}_{\text{ext}}\). It is straightforward to verify that in this limit the many-body eigenstates coincide with the HF solutions. More precisely they are single Slater determinants constructed from the molecular orbitals, \(|H\sigma\rangle\) and \(|L\sigma\rangle\), and the eigenstates of the Hamiltonian, \(\hat{H}^\text{HF}_{\text{mol}}(\delta \hat{N}_{\text{mol}}) = \hat{H}_{\text{mol}} + U_{\text{ext}}(\delta \hat{N}_{\text{mol}})\hat{n}_0\), where \(\langle \delta \hat{N}_{\text{mol}} \rangle = -2, \ldots, 2\) is the excess number of electrons on the molecule as given by the number of molecular orbitals in the Slater determinant. Although the eigenstates are single Slater determinants, the situation is different from the noninteracting case because the single-particle orbitals of the metal depend on the occupation of the molecule (each electron on the molecule will shift the potential of the terminal site by \(U_{\text{ext}}\)). As we will see below, this has important consequences for the position of the molecule’s QP levels.

In order to test the accuracy of the \(GW\) approximation for the problem at hand, we have compared it to exact diagonalization results in the case where the TB chain is truncated after the first two sites; see the supplementary material [14]. The \(GW\) spectral function is essentially identical to the exact result, also for strong interactions, demonstrating that \(GW\) captures the essential physics of the model accurately.

To study how the molecular levels depend on the model parameters, we vary one parameter at a time keeping the remaining fixed at the following reference values: \(t = 10\), \(t_{\text{hyb}} = 0.4\), \(U_0 = 4\), \(U_{HL} = 3\), \(U_{\text{ext}} = 2.8\), \(\Delta_0 = 2\). The reference values correspond to weak coupling \((\Gamma = 0.02)\) and a wideband metal \((W = 4t = 40)\). The positions of the HOMO and LUMO levels are defined as the maximum of the corresponding spectral functions (1) which we calcul-
late from the Green function, \( A_n(e) = -(1/\pi) \text{Im} G_{nn}^r(e) \); see supplementary material for plots of a representative set of spectral functions [14]. The Green function is obtained by solving the Dyson equation fully self-consistently in conjunction with the self-energy (\( \Sigma_{GW}[G] \) or \( \Sigma_{hyb}[G] \)) as described in Ref. [15]. Following the lattice version of DFT [16], we define the KS Hamiltonian as the noninteracting GW \(^\wedge\) by solving the Dyson equation fully self-consistently in of spectral functions [14]. The Green function is obtained see supplementary material for plots of a representative set of\(^\wedge\) describes the dynamical effects responsible for the gap reduction. The explanation is that the KS levels are affected indirectly: the KS levels are forced to follow the GW levels in order to reproduce the GW occupations. In the upper right-hand panel of Fig. 2 we show the dependence of the QP levels on the molecule’s intrinsic gap \( \Delta_0 \). The fact that the renormalization of the QP gap due to image charge formation is independent of \( \Delta_0 \) follows from the discussion above since \( \tilde{H}_{\text{met}} \) is independent of \( \Delta_0 \).

It seems intuitively clear that the size of the gap reduction (for fixed \( U_{\text{ext}} \)) should depend on the polarizability of the metal, i.e., how much the electron density changes in response to the perturbing field created by the added electron or hole. In the lower left-hand panel of Fig. 2 we show the QP levels as function of the chain hopping \( t \) [18]. The gap reduction is larger for small \( t \) corresponding to a narrow band. This is easily understood by noting that a narrow band implies a large DOS at \( E_F \), which in turn implies a larger density response function. In the lower right-hand panel of Fig. 2 we show the diagonal elements of the static component of the response function, \( \chi_{nn}(\omega = 0) \), for the HOMO, LUMO, and terminal site of the chain, respectively. In this weakly coupled regime, the response function of the HOMO and LUMO is clearly negligible for all values of \( t \), while the response of the terminal site is significant and increases as \( t \) is reduced. This clearly demonstrates that the QP levels are renormalized by screening inside the metal. In general, only the response at frequencies \( |\omega| \leq \Gamma \) is relevant as \( \Gamma^{-1} \) sets the decay time of the states \( c_i^\dagger |\Psi_0\rangle \) and \( c_i |\Psi_0\rangle \).

Interestingly, the deviation between the GW levels and \( \Delta E_{\text{tot}} \) becomes significant for small \( t \). We stress that this does not imply that the GW results are wrong. In fact, \( \Delta E_{\text{tot}} \) only represents an upper or lower bound for the true QP energies, and the deviation thus indicates that the overlap of \( c_i^\dagger |\Psi_0\rangle \) and \( c_i |\Psi_0\rangle \) with higher lying excited states of the \((N+1)\)-particle system [see Eq. (1)] is more important for small \( t \).

We now leave the regime of weak molecule-metal coupling and consider the dependence of the molecular spectrum on \( t_{\text{hyb}} \); see Fig. 3. At finite \( t_{\text{hyb}} \) the molecular levels broaden into resonances; however, it is still possible to define the level position as the resonance maximum [19]. In addition to the GW, HF, and KS levels, we also show the result of a calculation where only \( \tilde{U}_{\text{mol}} \) is treated at the GW level while \( \tilde{U}_{\text{ext}} \) is treated at the HF level. This means that the only dynamical effects included in the GW(mol) calculation are those due to \( \tilde{U}_{\text{mol}} \). In particular, image charge formation in the metal is ignored.
Focusing on the $GW$ and $GW$(mol) results, we conclude that the reduction of the QP gap as function of $t_{hyb}$ is mainly due to the interactions internally on the molecule. On the other hand, the reduction due to the molecule-metal interaction is largely insensitive to $t_{hyb}$ [this reduction is given by the difference between the $GW$ and $GW$(mol) levels]. From the right-hand panel of Fig. 3, we see that $\mid \chi_{mol}\mid$ for the HOMO and LUMO states increases with $t_{hyb}$ indicating that the gap reduction due to $\hat{U}_{mol}$ is of a similar nature as the image charge effect, but with the molecule itself being polarized instead of the metal. Polarization of the molecule can occur via dynamic charge transfer to or from the metal as illustrated in the drawing of Fig. 3. Note that this picture is consistent with the fact that no polarization of the molecule occurs without coupling to the metal [see $GW$(mol) result in the limit $t_{hyb} \rightarrow 0$ in Fig. 3].

The fact that dynamical polarization becomes more important as the molecular DOS at the Fermi level increases has important consequences for charge transport in molecular junctions. Indeed, as the chemical potential, $\mu_\alpha$, of one electrode approaches a molecular level, polarization effects become stronger and the level is shifted towards $\mu_\alpha$. This effect was recently shown to have a large impact on the junction $IV$ characteristics [20]. Finally, we mention that the correlation between chemisorption bond strength and gap renormalization suggested by Fig. 3 has in fact been observed in inverse photoemission spectroscopy experiments [7].

In summary, we have used a simple model of a metal-molecule interface to identify universal trends in the way dynamical polarization effects renormalize molecular interface states. The effect of polarization is to reduce the gap between occupied and unoccupied molecular orbitals. The size of the gap reduction correlates directly with the static response function, and is promoted by larger metal and/or molecular DOS at the Fermi level. The latter suggests that transition metals with partially filled $d$ band should be more effective in reducing the gap of molecular adsorbates than, e.g., alkali and $sp$ metals. The results strongly indicate that dynamical polarization is of fundamental importance for charge transfer at metal-molecule interfaces.

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[17] In the relevant limit $t_{hyb} \rightarrow 0$, $\Delta E_{ext}$ can be obtained from the change in total energy upon shifting the on-site energy of the terminal site of a semi-infinite TB chain by $\pm U_{ext}$, which in turn can be accurately calculated.
[18] We stress that even though $\Gamma$ depends on $t$, all results of Fig. 2 are essentially unchanged as $t_{hyb}$ is reduced below the reference value and thus represent the limit $t_{hyb} \rightarrow 0$.
[19] Because of the interactions, the resonance width is slightly enlarged relative to the noninteracting value of $\Gamma^{-1} \approx |t|/|t_{hyb}|^2$.