

Electronic level alignment at a metal-molecule interface from a short-range hybrid functional

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Hybrid functionals often exhibit a marked improvement over semi-local functionals in the description of the electronic structure of organic materials. Because short-range hybrid functionals, notably the Heyd-Scuseria-Ernzerhof (HSE) functional, can also describe the electronic structure of metals reasonably well, it is interesting to examine to which extent they can correctly describe the electronic structure at metal-organic interfaces. Here, we address this question by comparing HSE calculations with many-body perturbation theory calculations in the GW approximation, or with experimental photoemission data, for two prototypical systems: benzene on graphite and benzene diamine on gold. For both cases, we find that while HSE yields results that are somewhat closer to experiment than those of semi-local functionals, the HSE prediction is still lacking quantitatively by ~ 1 eV. We show that this quantitative failure arises because HSE does not correctly capture the fundamental gap of the organic or its renormalization by the metal. These discrepancies are traced back to missing long-range exchange and correlation components, an explanation which applies to any conventional or short-range hybrid functional. © 2011 American Institute of Physics. [doi:10.1063/1.3655357]

I. INTRODUCTION

A basic hurdle to understanding and rationally designing organic electronic devices at the molecular scale is to predict the electronic structure in general, and electronic energy level alignment in particular, of organic molecules adsorbed on metallic substrates.¹⁻⁷

Ideally, one would like to predict the level alignment from first principles using density functional theory (DFT).⁸ DFT is the standard method of choice for fully quantum-mechanical calculations of relatively large-scale systems (see, e.g., Ref. 9). Unfortunately, level alignment predicted from the eigenvalues of a Kohn-Sham calculation within the local density approximation (LDA) or the generalized gradient approximation (GGA) is typically in gross error with respect to experiment. Usually, both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies are too close to the Fermi level of the metal, often by well over an eV, resulting in an overestimate of the conductance of metal-molecule junctions by as much as two orders of magnitude.¹⁰⁻¹⁴

This failure is not surprising.¹⁵ Within Kohn-Sham theory, if one were to use the exact (and generally unknown) exchange-correlation functional, the HOMO eigenvalue would be equal and opposite to the ionization potential,^{16,17} but the molecular Kohn-Sham gap, $\epsilon_{\text{KS}}^{\text{LUMO}} - \epsilon_{\text{KS}}^{\text{HOMO}}$, where ϵ_{KS} is a Kohn-Sham eigenvalue, would still underestimate the fundamental gap of the molecule (defined as the difference between the molecular ionization potential, IP, and the electron affinity, EA).¹⁸⁻²⁰ This is because

the Kohn-Sham gap must be smaller than the fundamental gap by the derivative discontinuity,¹⁶ a finite “jump” that the exchange-correlation potential must exhibit as the number of particles in the system crosses an integer number.²¹ Practically, LDA and GGA possess no derivative discontinuity and their averaging over it invariably results in a small HOMO-LUMO gap, such that the IP and EA inferred from the HOMO and LUMO eigenvalues are too small and too large, respectively.^{18,22}

Because electronic level alignment at a metal-molecule interface must depend on the molecular IP and EA, it is necessary to go beyond the Kohn-Sham theory for quantitative accuracy. One way of achieving this task is by using many-body perturbation theory, typically in the GW approximation.²³⁻³¹ However, this can be, and often is, associated with prohibitive computational cost. It is, therefore, interesting to explore beyond Kohn-Sham methods within DFT.

Hybrid functionals, i.e., functionals that “mix” a fraction of GGA exchange and a fraction of Fock exact-exchange,²⁰ have proven to be quite effective in improving the predictive power of DFT for molecular properties such as geometries, vibrational spectra, and formation enthalpies.³²⁻³⁶ Here, we focus on a special class of hybrid functionals, known as short-range hybrid functionals.^{20,37} In such hybrid functionals, the exchange term is partitioned into a short-range (SR) and a long-range (LR) contribution, by means of splitting the Coulomb repulsion term, e.g., as $1/r = \text{erf}(\mu r)/r + \text{erfc}(\mu r)/r$. μ is a range-separation parameter that determines the relative length scale of the SR and LR contributions. Short-range hybrids differ from conventional hybrid functionals in that only the SR Fock-exchange is “mixed” with GGA exchange, whereas the LR exchange is all GGA. These functionals are of particular interest for the metal-molecule level

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alignment problem, because evaluation of the slowly decaying LR component of the Fock exchange in periodic solids is associated with a very large computational cost, especially for metallic systems that require dense Brillouin zone sampling.^{38,39} The best-known functional of this kind is the Heyd-Scuseria-Ernzerhof one,^{38,40} which is the short-range version of PBE0,⁴¹ a conventional hybrid functional based on the Perdew-Burke-Ernzerhof (PBE) GGA functional,⁴² with μ determined semi-empirically.

Because hybrid functionals employ a non-local operator, they can be considered as a special case of *generalized* Kohn-Sham theory, where some of the missing derivative discontinuity can be “absorbed” in the non-local operator.^{20,43–46} Accordingly, even though HSE was originally developed with computational cost considerations in mind,³⁸ it has also been found empirically to produce reasonable prediction of gaps in semiconducting solids, yet retain a Fermi surface for metallic solids.^{37,39,47} Furthermore, for gas phase molecules it has also been shown to improve agreement with photoemission experiments substantially, as compared to PBE, owing to a reduction of self-interaction errors.^{37,48–50} From this perspective, the HSE functional would appear to be a natural candidate for the level alignment problem. On the other hand, it has been previously shown that PBE0 does not offer any meaningful improvement over PBE for this problem:²⁵ both underestimate the molecular fundamental gap and fail to describe its renormalization upon metal adsorption. One could thus argue that HSE, whose SR and LR components are PBE0- and PBE-like, respectively, would also fail in this respect. It is therefore interesting to examine whether, and to which degree, HSE can assist in improving the accuracy of level alignment predictions, a question made particularly timely by the recent availability of HSE in popular DFT packages such as GAUSSIAN,^{38,40,51} VASP,^{39,52} and QUANTUM ESPRESSO.⁵³

In this work, we assess the accuracy of the HSE short-range hybrid functional by considering two benchmark systems – benzene on graphite and benzene diamine (BDA) on Au. First, we evaluate the accuracy of HSE eigenvalues for describing the electronic structure of the solid metal and the IP and EA of the isolated molecule. Then, by judicious comparison against benchmark results from many-body perturbation theory or photoemission spectroscopy, we determine its accuracy for the metal-molecule interface. We find that HSE provides only a modest improvement over PBE, which we rationalize in terms of a systematic, but only partial, cancellation of errors between the absence of long-range exchange and long-range correlation – a picture which holds for any GGA-based hybrid, whether conventional or short range.

II. COMPUTATIONAL DETAILS

All periodic system calculations are performed using the VASP software package⁵² while treating the core electrons with the projector augmented wave (PAW) method,⁵⁴ using PAW operators based on the PBE functional. Because of the heavy computational cost associated with use of the HSE functional in conjunction with large supercells in VASP, PAW operators used for first-row elements are the softer ones provided with the code. In order to further decrease the computa-

tional costs, we use the built-in VASP options for employing a coarse FFT grid for the overlap integrals and a reduced q -grid for the potential matrix elements in all the procedures involving exact exchange. Convergence of eigenvalues with respect to the accuracy settings is carefully tested and we estimate residual errors of each eigenvalue to be no larger than 0.05 eV. For single molecule calculations, we employ both VASP (using a large cubic supercell) and GAUSSIAN 09.⁵¹ For the latter, the aug-cc-pVTZ basis set is used. Quantitative agreement between the two approaches is found.

Because PBE- and HSE-based geometries are known to be similar (see, e.g., Refs. 39 and 48) and because we are interested in an electronic structure comparison that is not affected by small geometrical differences, the geometry of all bulk and gas phase systems discussed below is optimized using the PBE functional. We investigated the following systems: Au and Al as bulk metals; benzene and BDA as single molecules; benzene adsorbed on graphite and BDA adsorbed on Au. We find the PBE-based lattice parameters for Au and Al to be 4.16 Å and 4.04 Å, respectively, in good agreement with literature values.⁵⁵ Following previous work,²⁴ the benzene molecule is placed 3.24 Å above and parallel to the (0001) surface of graphite. The latter is represented by four graphene sheets of 18 carbon atoms each. The lateral separation between the benzene molecule and its nearest periodic image is 7.34 Å and the vertical distance between the benzene molecule and the nearest graphite periodic image is 19.9 Å. Using a geometry informed by experiment⁵⁶ and vdW-DF calculations⁵⁷ the BDA molecule is placed 3.49 Å above and parallel to the Au(111) surface, built from four layers of 16 gold atoms each. Here, the lateral and vertical distances to the molecule and substrate periodic images, respectively, are 10.25 and 21.69 Å.

III. RESULTS

A. Bulk electronic structure

To quantify the performance of HSE for the metallic electronic structure, we consider gold because it is frequently used as an inert electrode in experiments. The PBE- and HSE-computed occupied density of states for bulk gold is shown in Fig. 1, where it is additionally compared to experimental photoemission data. We find that the HSE bandwidth (10.3 eV) is larger than PBE (9.4 eV) and experiment (9.6 eV). This is despite the fact that in both cases, we find the difference in work function (for the (111) surface) between PBE and HSE to be smaller than 0.1 eV. This finding is in agreement with previous observations on other metals,^{39,58,59} as well as with additional calculations we performed for Al – a “simple” metal, with no potential complications due to the presence of d electrons. For Al, we found the HSE bandwidth (13.0 eV) to be larger than both PBE (11.4 eV) and experiment (10.6 eV).⁶⁰

The onset of the d -band is lower in HSE (~ 2.0 eV below the Fermi level) than in PBE (~ 1.3 eV below the Fermi level), bringing it into better agreement with experiment (~ 1.7 eV below the Fermi level). This agrees well with a similar observation made previously for platinum.⁵⁸ We also note that the

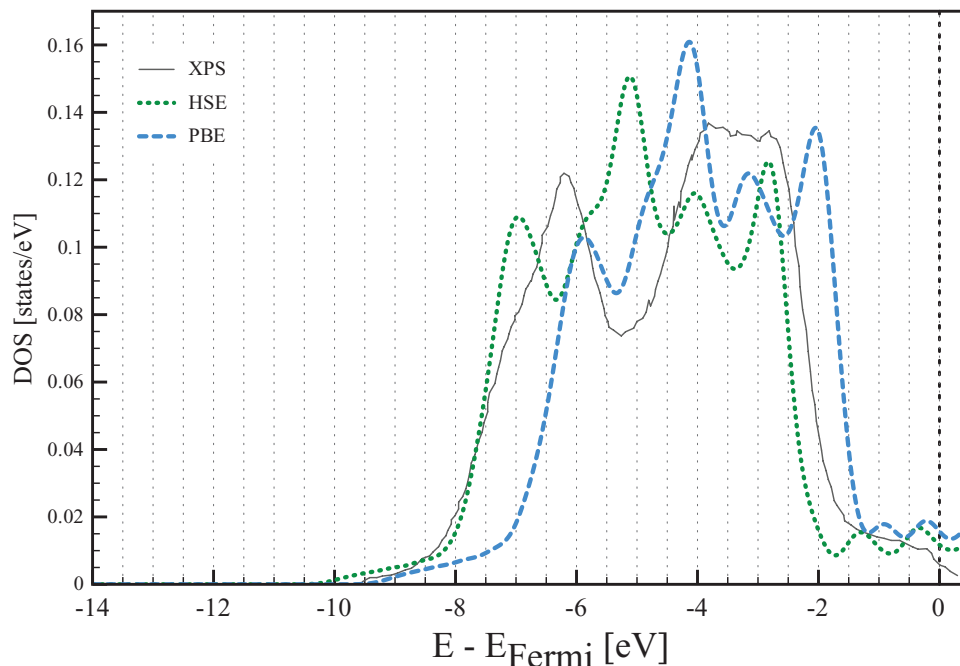


FIG. 1. The electronic density of states of gold computed using HSE and PBE. Computational data have been broadened by convolution with a 0.2 eV wide Gaussian to facilitate comparison with x-ray photoemission spectroscopy (XPS) data (see Ref. 62) that are also shown in the figure. The experimentally observed splitting in the d -band is absent from the calculations as it is associated with spin-orbit coupling (see Ref. 61), which was not included in the calculations.

experimentally observed splitting in the d -band is absent from our calculations as it is associated with spin-orbit coupling,⁶¹ which we neglect.

B. Fundamental gap of gas phase molecules

A comparison of the HOMO and LUMO eigenvalues to IP and EA values, obtained from total energy differences (i.e., with the Δ SCF method) within PBE and HSE for single-molecule BDA in the *cis* conformation, is given in Table I. Results for the *trans* conformation were the same to within 0.01 eV and are omitted for brevity. The IP values obtained using Δ SCF with the two functionals are remarkably similar to each other and within 0.5 eV of the experimental value.^{63,64} The HOMO of both functionals significantly underestimates the Δ SCF IP. The underestimate is ~ 2.1 eV with HSE, as compared to ~ 2.6 eV with PBE, i.e., with HSE the error is smaller by ~ 0.5 eV. Likewise, the LUMO with HSE is higher than the PBE one by ~ 0.5 eV. This means that the overall, ~ 1 eV HOMO-LUMO gap increase, observed on going from PBE to HSE, is contributed to equally by both frontier

TABLE I. A comparison of the HOMO and LUMO eigenvalues to IP and EA values obtained with the Δ SCF method, within PBE and HSE, for single-molecule BDA in the *cis* conformation. All values are in eV.

	PBE		HSE	
	ϵ_{KS}	Δ SCF	ϵ_{KS}	Δ SCF
EA/LUMO	-1.02	Unbound	-0.56	Unbound
IP/HOMO	-4.21	6.80	-4.81	6.93

orbitals. However, the LUMO is bound with both functionals despite the fact that the EA as obtained from Δ SCF is negative.

A similar trend is observed in Figure 2 for single molecule benzene: While the HSE HOMO-LUMO gap (6.27 eV) is over an eV larger than the PBE one (5.16 eV), it is still a very substantial underestimate, by 4.23 eV, of the quasiparticle gap obtained from GW (Ref. 24) (10.5 eV).

C. Metal-adsorbed molecules

Figure 2 further shows the PBE, HSE, and GW gaps of graphite-adsorbed benzene. Here, the highest occupied and lowest unoccupied states of benzene are deduced from analyzing the projected density of states on the molecule. The

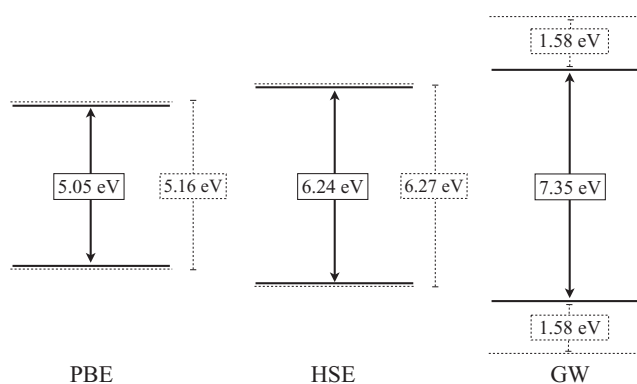


FIG. 2. The fundamental gap of a benzene molecule, as computed from eigenvalue differences within PBE, HSE, and GW, for the gas-phase (dashed lines) and graphite-physisorbed (solid lines) molecule.

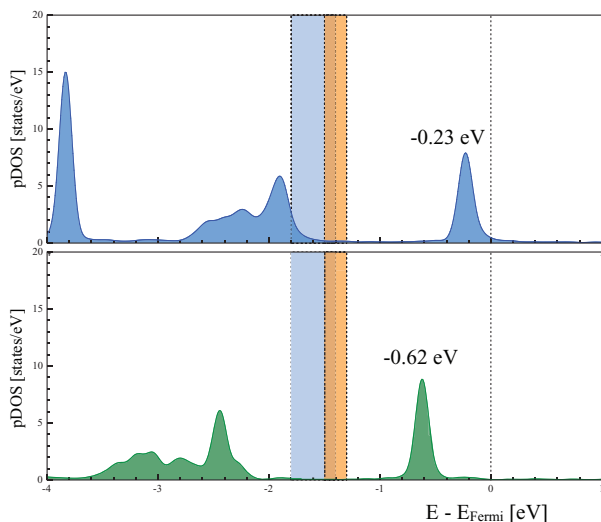


FIG. 3. BDA-projected density of states for the BDA on Au(111) system, computed using PBE (upper panel) and HSE (lower panel). The position of the HOMO relative to E_{Fermi} is indicated for each. The vertical shaded areas show the experimental windows for the HOMO binding energy based on UPS (1.4 ± 0.1 eV, right rectangle) and resonant XPS (1.6 ± 0.2 eV, left rectangle) data (see Ref. 56).

figure clearly shows that with either PBE or HSE, the HOMO-LUMO eigenvalue difference fails to capture the significant, GW-predicted 3.2 eV polarization-induced reduction of the gap in the presence of the metal.

For BDA on Au, there are no experimental results for the change in the BDA gap upon metal adsorption. Nevertheless, recent photoemission data do provide an accurate measurement of the HOMO binding energy compared to the Fermi level of gold.⁵⁶ Specifically, the BDA HOMO was reported to be 1.4 ± 0.1 eV below the Fermi level when measured with ultraviolet photoemission spectroscopy (UPS), and 1.6 ± 0.2 eV within resonant XPS. In that work, it was further shown that PBE is unable to correctly predict the molecule-metal level alignment. Agreement with experiment was obtained only when a model self-energy correction including explicit electrode polarization was applied.

Figure 3 shows the BDA-projected density of states for the BDA on Au(111) system, computed within both PBE and HSE. We do not find significant differences in the BDA-related surface dipole, as the difference in PBE- and HSE-predicted work function for the metal-adsorbate system is smaller than 0.15 eV. We do find that the use of HSE brings the HOMO position 0.3 eV closer to the mean experimental value, relative to PBE. However, it still falls well short, at least 0.7 eV from the error bar and almost 1 eV from the mean experimental value.

IV. DISCUSSION

The results shown in Fig. 3 clearly establish that the predictions of HSE for the level alignment problem at the molecule-metal interface are still in significant error with respect to experiment. Therefore, they cannot serve as a basis for the quantitative calculations required for interpreting spectroscopy or transport measurements. This is consistent with a

similar observation for the band-offsets obtained from HSE for the Si/SiO₂ interface.⁶⁵

It is often observed that despite their shortcomings with respect to orbital energies, semi-local functionals do predict bare-substrate work functions and adsorbate-induced dipole effects accurately.^{56,66,67} Because the HSE predictions for these values are essentially the same as those of PBE, the HSE failure must then be due to significant errors in the HSE-based eigenvalues. Indeed, the above-presented results reveal three different such errors: an overestimate of the metallic bandwidth; an underestimate of the molecular fundamental gap, associated with a HOMO that is too high and a LUMO that is too low; and a failure to capture adsorption-related changes in the molecular energy levels.

To understand the first failure – an overestimate of the metallic bandwidth – recall that the difference between HSE and PBE is in mixing in a fraction of SR Fock exchange. It is well known that addition of non-local exchange generally tends to “stretch” the density of states over a wider energy range. For molecules, this usually improves agreement with experiment,^{68–71} because introduction of non-local exchange mimics the first-order correction for the difference between Kohn-Sham and quasiparticle eigenvalues.⁷² However, for metals it is equally well known⁷³ that dynamical correlation effects generally decrease the bandwidth. Such correlations are absent from both PBE and HSE. Thus, increasing long-range exchange without a corresponding increase in long-range correlation is detrimental for metals.

Importantly, the above failure is *not* of primary relevance for the level alignment problem, for several reasons. First, the molecules presented here are only weakly adsorbed on the metal and therefore should not be sensitive to details of substrate band structure. Second, as shown in Fig. 1, the differences in band structure due to the increased bandwidth are most pronounced further away from the Fermi level, in an energy region that is not of direct relevance for the problem at hand. And most importantly, for *d*-electron metals like gold, the density of states from HSE closer to the Fermi level is overall superior to that obtained from PBE. This is because the *d*-band in PBE is too high in energy owing to self-interaction errors associated with these localized states.⁷⁴ We have mentioned above that with HSE such localized-state self-interaction errors are reduced on the molecular side, but they are also known to be similarly reduced for both metallic^{58,59} and non-metallic^{75–79} solids.

The second failure is more serious and obviously directly related to the level alignment: while the HSE HOMO-LUMO gap is substantially larger than the PBE one, it is still a severe underestimate of the fundamental gap in the gas phase molecule – of the order of several eV for both benzene and BDA – with the IP and EA severely underestimated and overestimated, respectively. It has been repeatedly observed (see, e.g., Refs. 37, 48, 80, and 81) that even though there is no rigorous justification for such comparison,^{20,48} HSE-derived gaps are often close to the optical gap, i.e., the lowest energy for a neutral excitation. The optical gap differs from the fundamental gap by the electron-hole interaction energy, which is usually sizable in small molecules. Similarity between the HSE and optical gap is also observed here. The experimental

optical gaps (i.e., first dipole allowed singlet transition) of benzene and BDA are, respectively, 6.1 eV (Refs. 82 and 83) and 4.26 eV,⁸⁴ which compare well to the respective HSE values found here, of 6.27 eV and 4.25 eV.

As mentioned in the introduction, a key feature of HSE is the absence of LR exchange, which makes it relatively easy to apply to solids in general and to metals in particular. Unfortunately, LR Fock exchange is important for the prediction of fundamental gaps in molecules from eigenvalue differences, as has been emphasized recently in several studies.^{46,85,86} Naturally, LR Fock exchange is not a sufficient condition (e.g., Hartree-Fock calculations do not yield reliable fundamental gaps). However, the absence of long-range exchange results in an incorrect asymptotic potential,⁸⁷ which vanishes exponentially instead of as $1/r$. With short-range correlation, as in conventional or short-range hybrids, this under-binds the electrons and results in a HOMO eigenvalue that is too small with respect to the IP. In addition, only some of the missing derivative discontinuity is “absorbed” in the asymptotically incorrect non-local operator, resulting in an EA that is too large. Consequently, the fundamental gap is seriously underestimated, unless additional exchange-correlation contributions are considered.^{46,85,86}

The third failure of HSE, which is also directly relevant to level alignment, is that the molecular HOMO and LUMO values are independent of environment, i.e., they remain essentially the same in the gas phase and the metal-adsorbed phase. This failure has been noted previously with semi-local functionals,²⁴ with conventional hybrid functionals,²⁵ and for insulating substrates with HSE.²⁹ In all cases the underlying physical origin of the problem is the same: The absence of non-local correlation makes it impossible for any of the above functionals to capture the polarization response of the substrate (or, indeed, any polarizable environment²⁴) and the appreciable renormalization of IP and EA values (and, for that matter, of the optical gap³¹) is entirely lost.

The above analysis shows that the two errors that affect level alignment the most are inherently of opposite sign. Using HSE, the gas-phase molecular fundamental gap is underestimated, with the IP being too small and the EA being too large. However, upon metal adsorption IP should decrease and EA should increase owing to the response of the metal to the quasi-hole or quasi-electron, respectively. In HSE this effect is missed. In some cases, these errors could fortuitously cancel each other, producing good agreement with experiment. However, the two above examples of benzene on graphite and BDA on Au clearly show that this cancellation is in general not sufficient for obtaining reliable level alignment. HSE does provide some improvement over PBE, but the IP and the gap for the metal-adsorbed molecule are still too small, suggesting that the underestimate of the gas-phase gap outweighs the absence of metal-induced level renormalization. Furthermore, if we accept at face value the assignment of the HSE gap to the optical one, then one can see that error cancellation will occur only if the gas-phase exciton binding energy is equal to the gap renormalization energy. But this result cannot be expected in general as the former depends, e.g., on the molecular size and the latter depends on the molecule-metal distance. Therefore, further progress requires that the missing physical

ingredients in the exchange-correlation functional be incorporated explicitly.

V. CONCLUSION

In conclusion, we have examined the extent to which the HSE short-range hybrid functional can describe the level alignment at a metal-organic interface. To that end, we performed HSE calculations for the metal, the gas phase molecule, and the metal-molecule interface for two important test cases – benzene on graphite and benzene diamine on gold. By comparing the HSE results with many-body perturbation theory calculations in the GW approximation and with experiment, we find that HSE underestimates the IP and overestimates the EA of the gas-phase molecule owing to the absence of long-range exchange. In addition, due to the absence of long-range correlation it does not capture the IP and EA metal-induced renormalization upon adsorption. Therefore, the HOMO and LUMO remain close to their gas-phase values and do not reflect the reduction of the IP and the increase of the EA. The two errors are inherently of opposite sign, but their magnitude is generally not the same and systematic error cancellation is neither expected nor obtained. We expect these conclusions to hold for any conventional or short-range hybrid functional and for a general metal-molecule interface, including, e.g., interfaces of metals with water or with inorganic molecules.

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