

Supporting Information for

Integer *versus* Fractional Charge Transfer

at Metal(/Insulator)/Organic Interfaces: Cu(/NaCl)/TCNE

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1 Introduction.

As Perdew and coworkers have shown,¹ the total energy obtained from the exact density functional is piecewise linear between integer electron numbers, as indicated by the solid line in Figure S1. Unfortunately, many common functionals deviate from this straight-line behavior. This deviation is commonly known as the many-electron self-interaction error.² Functionals belonging to the generalized gradient approximation (GGA) class, including the PBE³ functional used in this work, systematically underestimate the energy at fractional electron numbers (indicated by the red line in Figure S1). In contrast, the Hartree-Fock (HF) approximation (which by construction is single-electron self-interaction free, but still suffers from many-electron self-interaction errors), consistently overestimates the total energy at fractional electron numbers (indicated by the blue line in Figure S1). In the PBEh⁴ hybrid functional family a fraction of HF exchange – denoted α – is mixed with a complementary fraction of PBE exchange. As indicated by the arrow in Figure S1, α has a strong effect on the many-electron self-interaction error.

In principle, it is possible to choose α such that the straight line condition is obeyed for any one segment.⁵ Indeed, this is sometimes done, giving rise to so-called optimally tuned functionals, which improve the description of e.g., charge-transfer energies over common semi-local functionals.⁶ In practice, to obtain the α that is required to satisfy the straight-line condition, it is necessary to compute the ionization potential and/or the electron affinity. For isolated atoms or molecules, this is a straightforward task that can be done by subtracting the total energy of the neutral moiety from the energy of the singly (positively or negatively) charged moiety. For periodic surfaces and interfaces, however, this is not a viable approach. Instead, one would have to compute the ionization energies *via* many-body perturbation theory, such as *GW*. However, at present *GW* is not tractable for systems of the size considered in this work.

Therefore, we refrain from any attempt to “optimally tune” our functional. Instead, we compare PBE, which consistently underestimates the total energy (the red region in Figure S1), with one distinct representative of the PBEh family that consistently overestimates the total energy (the blue region in Figure S1).

Before we proceed to justify our choice for α in section 3, we shall briefly discuss the qualitative differences between the red and the blue region in Figure S1. In section 4, we will discuss the impact of the choice of α as well as the impact of the molecular geometry, for a hypothetical, free-standing monolayer of TCNE. Furthermore, in this section we will also briefly discuss another functional family, namely the range-separated hybrid functional HSE.^{7,8} Finally, in section 5, we briefly discuss what we would expect to happen for the standard parameterization of the PBEh functional, i.e. $\alpha=0.25$.

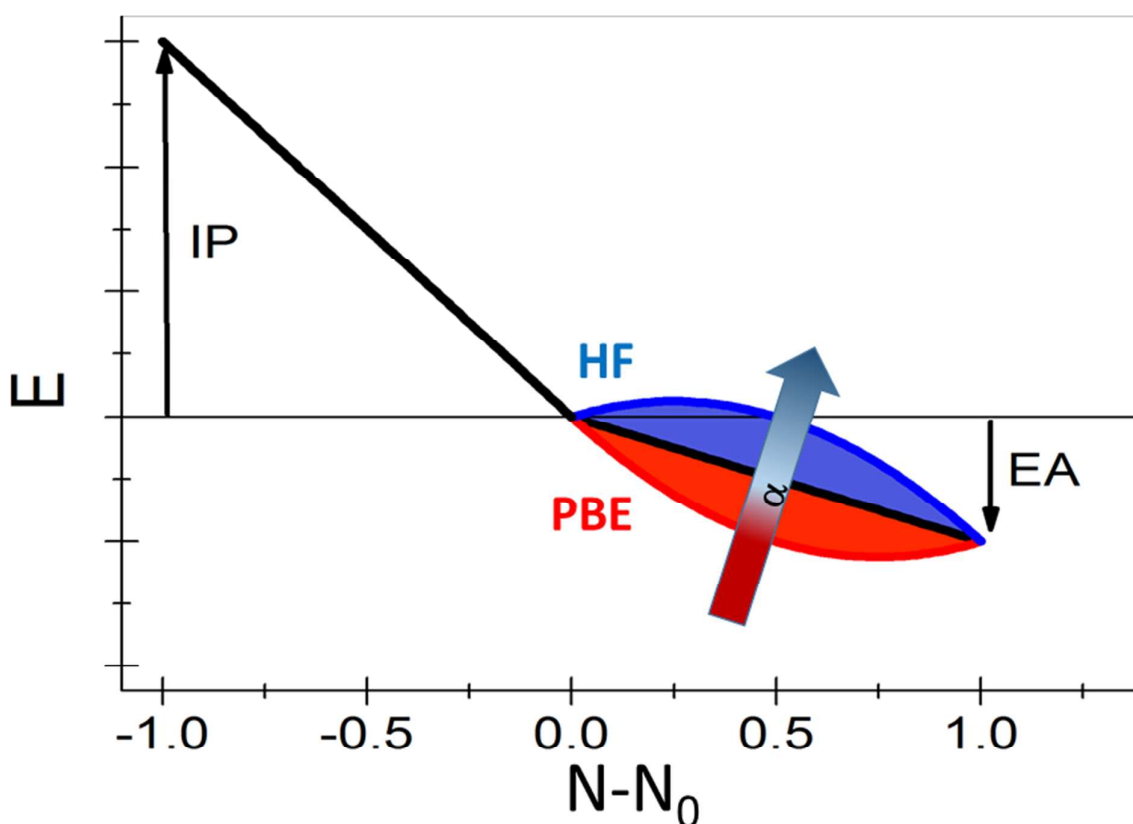


Figure S1: Total energy E vs. the number of electrons in the system N , relative to the number of electrons in the neutral system, N_0 . IP and EA denote ionization potential and electron affinity, respectively. The black line corresponds to exact functional. Deviations from linearity are shown for electron addition.

2 The role of many-electron self-interaction for the charge-transfer mechanism.

In the Cu/NaCl/TCNE system, PBE leads to FCT, while PBEh* leads to ICT. The reason for this difference is rooted in the many-electron self-interaction error. To understand this qualitative difference, it is instructive to recall Janak’s theorem,⁹ which states that the orbital energy of the

highest occupied orbital (ϵ) is equivalent to the derivative of the total energy with respect to the total energy

$$\epsilon = \frac{dE}{dN} \quad (1)$$

From Figure S1, it becomes evident that ϵ may be a function of the orbital occupation f . In PBE, which over-delocalizes charge, ϵ *increases* as it becomes filled. Conversely, in functionals that over-localize charge (blue region), ϵ *decreases* with increasing occupation. Only for a functional that is many-electron self-interaction free, ϵ is *independent* of f .² Let us now consider a simplified system consisting of two (initially empty) levels belonging to two non-interacting moieties. Let us further assume that the molecules are of the same chemical species, but that the symmetry is slightly broken, e.g., due to the presence of a non-regular substrate in their vicinity, due to fluctuations in their geometry, or similar. Such a situation is depicted in the left panel of Figure S2.

If we now gradually add a single electron to the system, the lower-lying orbital of the two will become occupied first. In the case of the PBE functional, this leads to an increase of the orbital's energy until it is in resonance with the higher lying orbital. From this point on, any further charge add to the system will be equally distributed between both orbitals. Thus, when the system is completely charged, the electron density will be delocalized and evenly distributed between both molecules, and the levels of both molecules will be found at (almost) the same energy.

The situation is entirely different when we follow the same procedure with a functional that over-localizes charge. As the lower-lying orbital starts to get occupied, it moves to lower energy and thus further away from the other level. The orbital will eventually take up the entire electron, resulting in one charged and one uncharged molecule. The two corresponding levels will have significantly different energies.

For a many electron self-interaction-free functional, for which the orbital energies are independent of occupation, the final situation depends on the relative magnitude of the initial symmetry breaking and the width of the energy levels. If the separation of the orbitals is larger than the combined width, a pure ICT situation will occur. If the two orbitals overlap, the charge density will be distributed across both molecules. However, the molecule with the lower lying level will still receive significantly more charge, resulting in a situation that is still closer to ICT than to FCT.

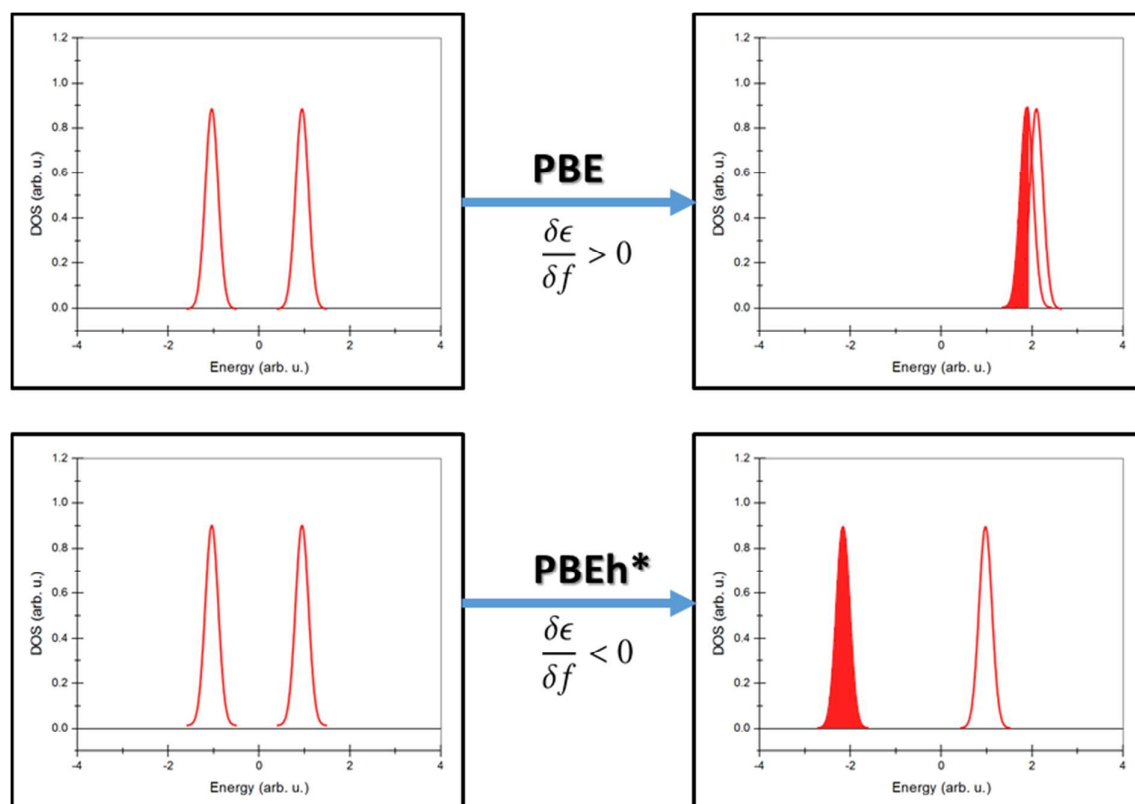


Figure S2: Schematic evolution of the level alignment for a two-state system with initially broken symmetry for PBE and PBEh*. Details see text.

3 – Choosing α for PBEh*

While the exact functional is, naturally, not known, it is in principle possible to generate a functional (by tuning α) that is self-interaction free for the LUMO of the adsorbate. The condition to fulfill this requirement is to choose α such that the LUMO corresponds to the electron affinity of the molecule *after adsorption on the substrate*, i.e., including the screening of the charged molecules by the substrate and by the surrounding layer. Unfortunately, as discussed before, obtaining this number is currently not tractable. Thus, to be on the safe side, for PBEh* we chose to use the α that fulfills the condition in the gas phase, i.e., in the absence of screening. This is possible because screening always lowers the energy of the charged moiety, while hardly affecting the energy of the neutral molecule. At the same time, in hybrid functionals the orbital energy of the neutral molecule is unaffected by the adsorption process. Therefore, the α that fulfills the straight-line condition in the gas phase must be above the value that fulfills the straight-line condition on the surface (i.e., is definitely in the blue region in Figure S1), and can be regarded as upper bound. For TCNE, the corresponding gas-phase value is $\alpha \sim 0.8$, slightly larger than the ~ 0.7 that were previously obtained for larger molecules⁶. From

the adsorption of comparable molecules on graphene¹⁰ and on metal surfaces¹¹, we know that the reduction due to screening amounts to approximately 1 - 1.5 eV.

4 – Impact of α for charge-localization in a free-standing monolayer.

In order to see how sensitive the results of our calculations are to the choice of the functional, and in particular the parameter α , we have calculated the localization of charge for a hypothetical, free-standing monolayer of TCNE. The individual molecules were aligned in the same way they would align on the Cu(100) surface (cf. Fig 3 in the main manuscript). The monolayer was charged by a single extra electron, which was compensated by a homogenous positive background. We stress that these calculations were therefore done at a constant particle number N , while the calculations in the manuscript are performed for an adsorbate that is in contact with a charge reservoir, i.e. at a constant chemical potential μ . Here, to quantify how the extra electron is localized, we define the localization as

$$L = \frac{Q_{\max} - Q_{\min}}{Q_{\text{total}}} ,$$

where Q_{\max} is the (Mulliken) charge of the most charged and Q_{\min} the (Mulliken) charge of the least charged molecule in the supercell. Q_{total} is the total charge of the supercell, i.e. 1 in the present case. By definition, $L = 1$ if the charge is fully localized, and $L=0$ if the charge is completely delocalized. Figure S3 shows the results for the PBEh family as function of α . The black squares refer to calculations with fixed geometry (at the PBE level), while the red circles include full relaxation at the corresponding α^* . Without relaxation, we find that at low α (including $\alpha=0.25$), $L=0$, while for $\alpha > 0.6$, L becomes 1. For α between 0.4 and 0.5, we obtain an intermediate situations with partly localized charge. As the red circles show, this intermediate solution vanishes when we switch on relaxation. In other words, the partly broken symmetry of the electron density for intermediate cases leads to a distortion of the translation symmetry, which in turn leads to further –in fact, complete – electron localization.

These results indicate that there are only two qualitatively different situations – full localization or full delocalization – when we let the system relax. For the main paper, this allows us to choose any functional that is clearly “high- α ” and compare it with a “low- α ” solution. We are confident that qualitatively equivalent results would be obtained over a large range of α -values.

* The z-coordinate of all atoms was constrained at a fixed value (0) for all electron during the optimization.

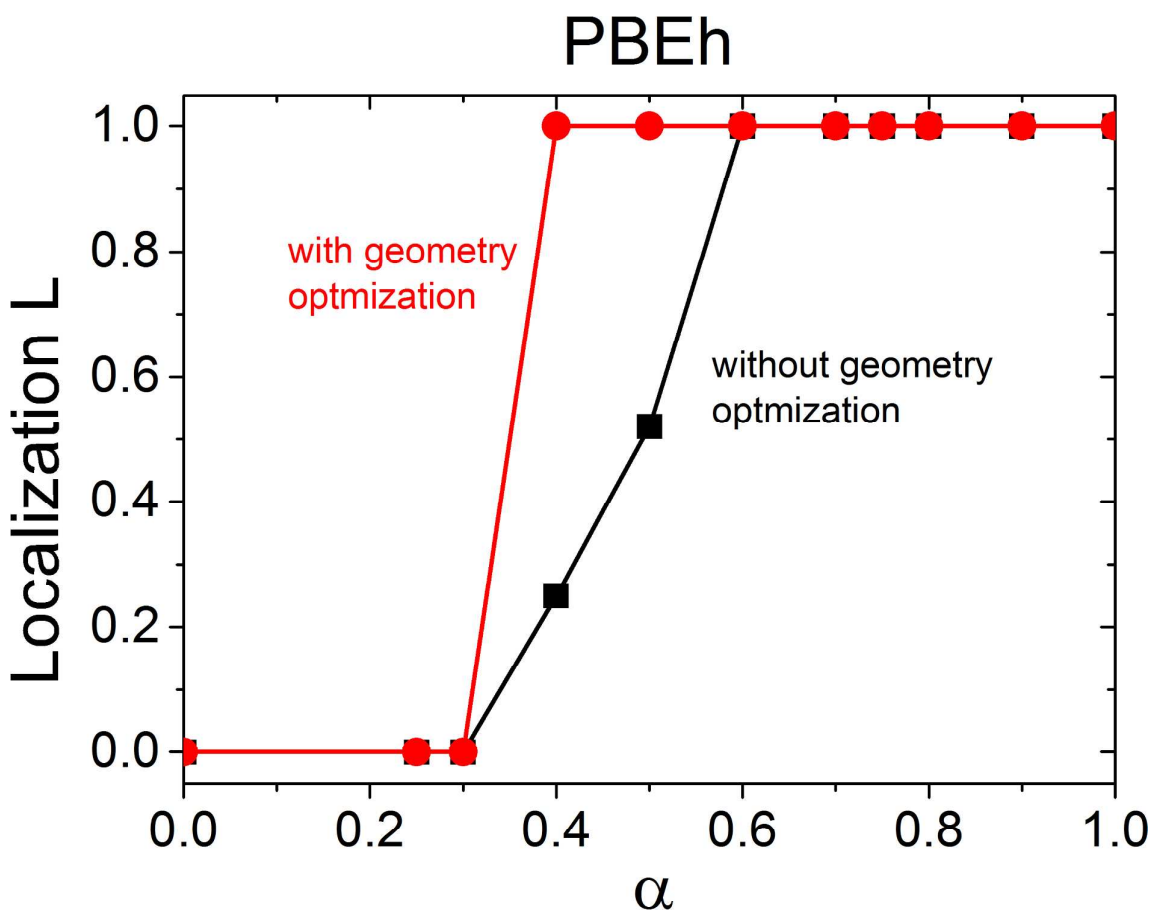


Figure S3: Localization of an extra electron in a TCNE layer as function of the fraction of Hartree-Fock exchange in PBEh

The HSE functional family is closely related to the PBEh family, but employs exact exchange only at short range, i.e., exact exchange is screened over a length of – by default – 5\AA . As a result, the orbitals of more distant molecules in the layer would interact only *via* PBE exchange. Figure S4 shows how α affects the localization in HSE. Qualitatively, the results are the same as for PBEh, i.e., at low α the electron is delocalized whereas at high α it is localized on a single molecule. We also obtain the intermediate situation when keeping the geometry fixed. For the main paper, we refrain from using HSE, since the screening length introduces a second, tunable parameter. More importantly, however, NaCl layers change the distance between the adsorbate and the metal, as described in Figure 2. As a consequence, for the adsorption on the NaCl double-layer the TCNE orbitals would not be able to interact with Cu electrons *via* HF exchange at all. For the adsorption on the NaCl single layer, each TCNE would only be able to interact (*via* HF exchange) with electrons in the Cu that are “right” below it. Without NaCl, however, the TCNE is much closer to the metallic substrate, and a much larger fraction of the metallic states can be found spatially within the screening length. Comparing these three systems, as done in the manuscript, would be difficult when using only a single screening parameter throughout.

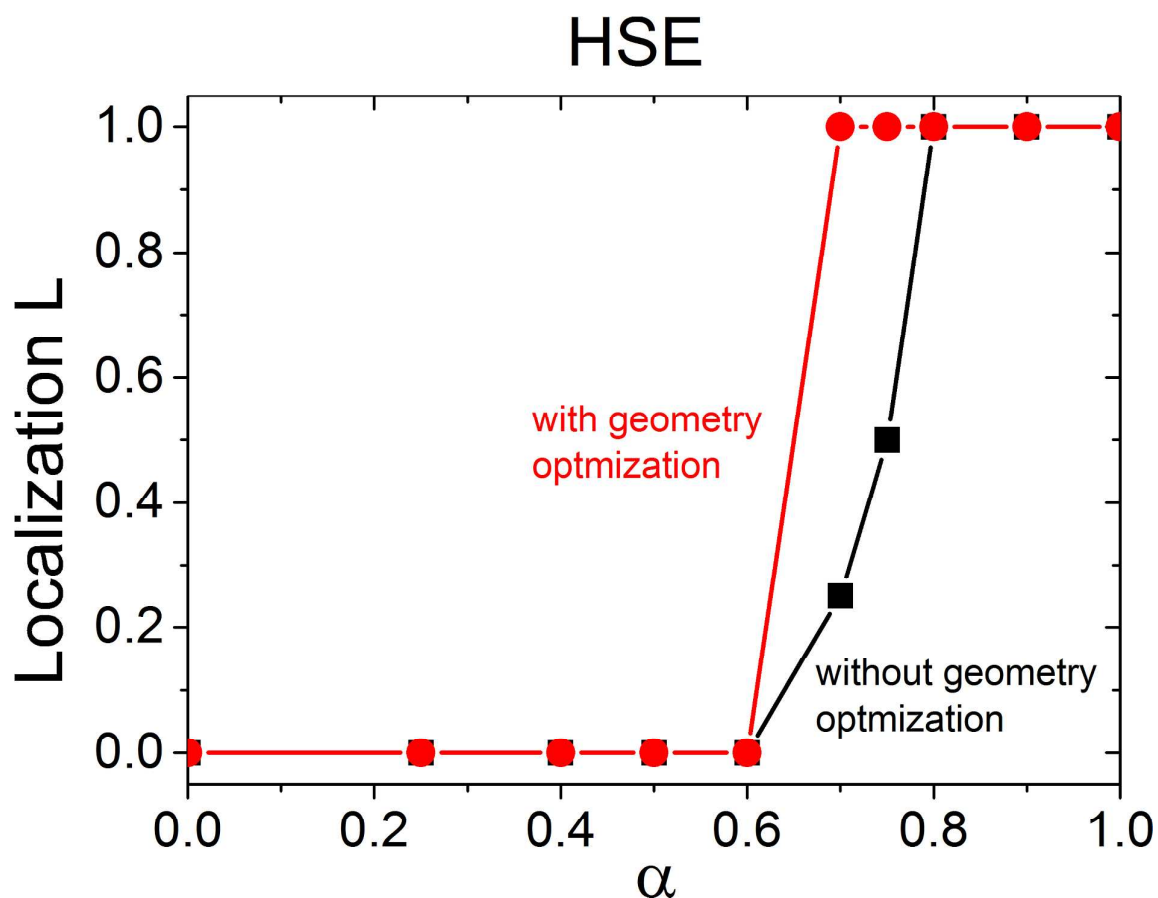


Figure S4: Localization of an extra electron in a TCNE layer as function of the fraction of Hartree-Fock exchange in HSE

5 – An expectation for the PBE0 functional for the TCNE/NaCl/Cu interface.

Naturally, it would be interesting to know what the charge-transfer mechanism would look like if we were to apply the default PBE0 functional (i.e., $a=0.25$), to the TCNE/NaCl/Cu system. Unfortunately, we were not able to converge these calculations. We ascribe this to the assumption that, due to screening, the TCNE LUMO would be almost many-electron self-interaction error free. Having a set of such orbitals means that shifting charge between them costs almost no energy, while still changing the electron distribution significantly in each step of the self-consistency cycle. The situation is reminiscent to that in a metallic slab, where convergence problems due to several, close lying states are solved through the introduction of occupation-smearing. This, however, would come at the cost of a (probably artificial) distribution of the electrons in the organic layer across all molecules, which would be more or less random. For the molecular layer on its own, the situation could be improved by reducing the smearing to zero. Unfortunately, the metal does not converge any more with such settings.

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