On the role of the nonlocal Hartree-Fock exchange in \textit{ab initio} quantum transport: H$_2$ in Pt nanocontacts revisited

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Abstract

We propose a practical way to overcome the ubiquitous problem of the overestimation of the zero-bias and zero-temperature conductance, which is associated to the use of local approximations to the exchange-correlation functional in Density-Functional Theory when applied to quantum transport. This is done through partial substitution of the local exchange term in the functional by the nonlocal exchange term.
Hartree-Fock exchange. As a non-trivial example of this effect we revisit the smallest molecular bridge studied so far: a H$_2$ molecule placed in between Pt nanocontacts. When applied to this system the value of the conductance diminishes as compared to the local-exchange-only value, which is in close agreement with results predicted from Time-Dependent Current-Density-Functional Theory. Our results issue a warning message on recent claims of perfect transparency of a H$_2$ molecule in Pt nanocontacts.

It is widely admitted that a first-principles methodology based on Density-Functional Theory (DFT) is the only compromise between accuracy and computational resources that can help pave the way towards molecular-engineered nanoscale devices [1]. The DFT manageability is based, for the most part, in the use of the Kohn-Sham scheme (DFT-KS) [2,3]. In addition, the central track doing a practical DFT-KS scheme lies on the definition of an approach to the true exchange-correlation (xc) functional [4]. Initially, the manageability of DFT-KS comes upon the introduction of the Local-Density Approximation (LDA) to the xc functional [3]. (Henceforth, extensions beyond LDA within local exchange models, like generalized gradient approximations (GGA) [5], and Meta-GGA [6], are referred as semi-local methods and labeled as LDA methods for the sake of simplicity).

This ab-initio based method combined with Landauer’s formalism is nowadays routinely applied to compute the conductance, $G$, of nanoscaled systems, i.e metallic nanocontacts and single-molecule junctions [7–9]. However, the use of DFT-KS electronic structure within LDA approximations, would
present two problems in this regard: (i) an obvious one related to the use of LDA and related approximations to approach the true xc-potential, $v_{xc}$ [4,9]; and (ii) a much more subtle one which could be associated with the absence of dynamical corrections in the DFT-KS schemes [10,11].

Regarding the first point, the reliability of LDA results relies naturally on the existence of fairly homogeneous, well-behaved electronic densities. While this is the case for metallic nanocontacts, molecular bridges, definitely, do not satisfy this premise [10]. For weakly-coupled molecules conducting in the Coulomb blockade regime, where charge localization is strong, failures of LDA are traced back to the self-interaction and derivative discontinuity problems, which are inherent to local or semi-local approximations [9,12–14]. Interestingly, this problem is not present in more sophisticated exact exchange (EXX) nonlocal approaches, as recently emphasized by others [15].

Concerning the second point, the use of Time-Dependent Density-Functional Theory (TDDFT) [16] has been shown to give the exact total current if the exact $v_{xc}$ is known [10], and it reduces in the zero-frequency limit to the standard static treatment only when the adiabatic approximation is invoked [10]. Furthermore, as initially suggested by Vignale and Kohn [11], the apparent impossibility to approach the exact $v_{xc}$ through successive local approximations could be circumvented by a new form of functional where the local current density plays a central role or, equivalently, a nonlocal density-based theory. Recent work [10] based on Time-Dependent Current-Density-Functional Theory (TDCDFT) has shown that dynamical effects manifest themselves in the appearance of a dynamical potential, $v_{xc}^{\text{dyn}}$, that always opposes the electrostatic potential and lowers the conductance obtained within
LDA methods, even in linear response. The origin of this potential can be traced back to the nonlocal response to an electric field which is captured by TDCDFT [10, 11]. It is difficult to assess to what extent the resulting dynamical potential accounts for the lack of nonlocality of the starting LDA approximation or if it represents a true intrinsic dynamical effect which is present even for the exact DFT-KS potential [9] (probably both).

The role played by the dynamical term in increasing the resistance is compatible with another seemingly unrelated fact: The polarizability of molecular systems (e.g., hydrogen [17] or polymeric [18] chains) is severely overestimated by LDA, while Hartree-Fock (HF), TDCDFT, and exact many-body calculations—all of them nonlocal schemes—yield similar values. We note here that a recent work has shown that the conductance can be expressed in terms of the polarizability [19].

In the light of the above discussion, one might ask: to what extent can nonlocal approaches to the $v_{xc}$ (out of the realm of standard static DFT-KS theory) mimic the missing dynamical corrections? In this work we explore the influence of a nonlocal potential—such as HF exchange—on the conductance of a molecular bridge (see Figure 1). To this end we choose to study electron transport in a H$_2$ molecule bridging Pt nanocontacts [20–22] (see inset in Figure 2), using nonlocal functionals customized for this problem. We show that the HF-like exchange has a strong influence on the conductance of this bridge, rapidly decreasing as the percentage of HF-like increases in the hybrid functional. By adjusting this percentage, with the aid of accurate quantum chemistry calculations in clusters, we conclude that previously reported calculations based on LDA might have systematically overestimated
the value of the conductance in this system. Finally, for this benchmark system, we compare the numerical results derived from our method, the nonlocal functionals for an effective DFT-KS formalism, with those obtained within TDCDFT [10]. The conductance values are quite similar, which further supports the conclusions reached here. The average value of the conductance for such system turns out to be \( \approx 0.2 \times 2e^2/h = 0.2 \times G_0 \), in stark contrast to LDA calculations yielding \( \approx 1.0 \times G_0 \) and in support of a previous work by some of us [21].

Our theoretical approach have been thus developed in accordance with the scheme that follows. The central track doing an effective DFT-KS scheme lies on the definition of the \( v_{xc} \) [1, 4, 23]. Rooted on the adiabatic connection theorem, which formally justified the design of nonlocal functionals (usually referred as hybrid functionals [24]), and based on the experience gained after original Becke’s proposal [25], we adopt the following expression for an approach to the \( v_{xc} \):

\[
v_{xc} = \alpha v_{HF}^x + (1 - \alpha) v_{local}^x + v_{local}^c,
\]

where \( v_{HF}^x \) is the HF-like potential contribution, which accounts for nonlocal effects, the \( v_{local}^{x,c} \) contributions are given by any of the available exchange (x) or correlation (c) local functionals and, finally, \( \alpha \) is a fitting parameter. With this parameterized potential, we will solve the mean-field equations derived from DFT-KS formalism for a finite system, the cluster. This finite cluster is selected in such a way that the boundary conditions determined by the problem are fulfilled, as discussed in the next paragraphs. Finally, the electronic states derived from the DFT-KS are deployed in conjunction with
Landauer formalism for zero temperature quantum transport characterization [26]. Concerning the software employed for the numerical calculations, we use the code ALACANT (ALicante Ab initio Computation Applied to NanoTransport) [27] which is interfaced to GAUSSIAN03 [28].

We first compute the LDA conductance ($\alpha = 0$) of the system shown in the inset of Figure 2 where the H$_2$ molecule lies along the Pt nanocontacts axis [29]. In agreement with previous works [20,22,30], we obtain a single fully conducting channel at the Fermi level which yields $G \approx 1.0 \times G_0 = 2e^2/h$. This result supports the implementation for the computation of the current [31].

To probe in a systematic way the influence of the nonlocal exchange on the electronic structure and concomitant change in the conductance, the coefficient $\alpha$ is now varied. Strictly speaking $\alpha$ should not be a constant, but a function of spatial coordinates, $\alpha = \alpha(\vec{r})$. It is expected that HF-like exchange is more needed to describe electronic density regions governed by just one electron where the self-interaction error is more notorious [32]. This is particularly the case for the H$_2$ molecule. The value of $\alpha$, on the other hand, should decrease as we move into the bulk electrodes where LDA or GGA is expected to perform better. As a compromise between both situations we take $\alpha$ to be constant in the nanocontacts region close to the H$_2$ molecule where the coordination is low, i.e., the bridge Pt-H$_2$-Pt (see inset in Figure 3). The rest of the system is described by the self-energy corresponding to a parameterized Bethe lattice. Figure 1 shows the effect of the HF-like exchange on the conductance. For values close to 50% the conductance has almost dropped to zero.
The drop in conductance as the amount of HF-like exchange increases at the bridge can also be understood from a purely microscopic point of view. This construction is based on the approach to the exact non-correlated density-based scheme for determine the electronic structure [23], and its combination with the accepted Landauer formalism for determine the electronic conductance [7]. Therefore, under these two conditions, the electronic structure limited to the HOMO-LUMO gap, $\Delta_{HOMO-LUMO}$, will play a key role in the final outcome of the electronic conductance [33]. Figure 3 shows the effect of the HF-like contribution on the HOMO-LUMO gap ($\Delta_{HOMO-LUMO}$) for the isolated Pt-H$_2$-Pt bridge. This effect is well known in molecules and bulk semiconductors where LDA approximations usually underestimate the real value of the charge gap [34–36]. The one electron Green’s function ($g(\epsilon)$) of the isolated Pt-H$_2$-Pt bridge has poles at the position of the molecular orbitals energies. Once the isolated system is coupled to the rest of the electrodes these poles shift and broaden in a way dictated by the self-energies $\Sigma_L$ and $\Sigma_R$ representing the electrodes:

$$g^{(\pm)}(\epsilon) = [(\epsilon \pm i\delta)I - H - \Sigma_L - \Sigma_R]^{-1}. \tag{2}$$

The Fermi level is likely to lie in the gap between the HOMO and LUMO states of the Pt-H$_2$-Pt cluster since no significant charge transfer is expected between Pt atoms. As can be seen in Figure 3, the LDA gap is almost zero for this bridge. From the opening of the gap as $\alpha$ increases one could easily have anticipated a strong decrease in conductance since this depends on the Green’s functions through the well-known expression [26]:

$$G = \frac{2e^2}{h} Tr[\Gamma_L(\epsilon)\ g^+(\epsilon)\ \Gamma_R(\epsilon)\ g^-(\epsilon)]. \tag{3}$$
Finally, to estimate $\alpha$ we follow a well-established methodology in semiconductors and insulators. The value is chosen so that $\Delta_{\text{HOMO-LUMO}}$ matches the charge gap, $GAP$. Accordingly, it is defined as $GAP = 2E_0(N) - E_0(N + 1) - E_0(N - 1)$, where $N$ represents the number of electrons, and $E_0$ is the total energy for the selected ground states in a Kohn-Sham system of independent electrons. Matching between $\Delta_{\text{HOMO-LUMO}}$ and $GAP$ will be enough to guarantee accuracy for mean-field Green’s functions [37,38], and therefore for the conductance value, expressions 2 and 3. The choice of the finite region where to perform the search of $\alpha$ is constrained by three conditions: (i) it must contain the zone which is restricting the current flow, in our case the H$_2$ molecule; (ii) the HOMO and LUMO must not be localized on the electrodes; and (iii) screening effects from the contacts should be -at least- partially included. These three conditions reduce the range of possibilities to the cluster shown in Figure 3, and limit the selection of system (previously referred as the extended molecule [9,39]). One way to estimate to what extent screening is included in such small cluster is to look for a quantity such as the internal mode frequency of the H$_2$ molecule, $w_{H_2}$, and check how much it changes with increasing the size of the cluster. We find that larger clusters do not appreciably change that quantity, which is given by $w_{H_2} \approx w_{H_2}^0/2$ where $w_{H_2}^0$ is the internal mode of an isolated H$_2$. This change in the frequency with respect to the free molecule suggests an intermediate regime of coupling.

To find out ground state energies and therefore the right $GAP$, we begin by considering the mean-field HF method. To approach the exact many-body solution to the $GAP$, we invoke hierarchical correlated $ab\ initio$ methods such as Möller-Plesset perturbation (MP) or Coupled-Cluster (CC) theories.
The corresponding results are presented in Figure 4. The GAP for this system, $\sim 5$ eV, critically differs from the $\Delta_{HOMO-LUMO}$, described from the electronic structure in pure DFT-LDA calculations $\sim 0$ eV, see Figure 3. Therefore, and considering the scheme we propose to correct this pitfall, the $\Delta_{HOMO-LUMO}$ for the system is extracted from Figure 4. Comparing those results with the whole information contained in curve of Figure 3, we estimate that the percentage of HF exchange in Eq. 1 should be $\sim 60$ percent, which gives a very low value for the conductance (see Figure 1). It is the main result we should draw from this paper.

Note that there is an increasing concern about the influence of exact exchange for conduction phenomena at the molecular level [40,41]. Although a rule of thumb for the needed admixture of exact exchange is provided here, we indeed believe that it will be difficult to unambiguously give the optimum weight of exact exchange for an uniformly good description of all systems. Instead of this, we would like to remark how the results clearly show that inclusion of exact exchange is necessary for accurate descriptions. We should point that the same amount of HF exchange is obtained (with error band of 10 percent), if the contour condition to find out its value is limited to the matching between the HOMO eigenvalue and the negative of the ionization potential, $\epsilon_{HOMO} = -IP$ [42]. Concerning future work and despite being technically challenging, it would be definitionally interesting to investigate the performance on these benchmark systems of a new generation of functionals describing $v_{xc}$. For instance, we should mention orbital-based functionals [43], self-interaction corrected functionals [44,45], the hybrid functionals based on a screened Coulomb potential [46,47], and the last generation of $v_{xc}$ density-
functionals belonging to the M06 suite of methods [48, 49]. Furthermore, more studies for closely related molecules and nanocontacts will be highly welcomed too.

If we were able to follow unambiguously the same procedure for larger systems the value for $\alpha$ would probably be reduced, although we do not expect it to go to zero. Unable to get rid of this uncertainty we compare our results to those obtained with TDCDFT following the work by Sai et al. [10].

A dynamical counteracting potential appears whenever there is a change in the macroscopic density which modifies the local-density conductance:

$$G = \frac{G_{\text{local}}}{1 + G_{\text{local}} R^{\text{dyn}}}$$

From the average density profile along the $z$-direction (see Figure 5) we compute the corrections to the local conductance. The electronic density is fixed in the electrodes to the bulk value, considering for the number of free-electrons as the mean experimental atomic-point-contact transmission. In case of Pt-nanocontacts, this number implies a range between one- and two-free-electrons per Pt atom [20]. The rest of the parameters involved in the calculation of $R^{\text{dyn}}$ were estimated in agreement with the method proposed by Sai et al. [10]. Our calculations brings the conductance down to $\approx 0.2 \times G_0$. (Details are included in Ref. [50]). Nevertheless, this procedure is not free from ambiguities either, but it points towards similar conclusions as the ones drawn above.

In summary, we have presented a route to approach the DFT-KS electronic transport calculations based on the controlled addition of EXX contribution to $v_{xc}$. The selection of the fraction of HF-like needed is based on
first-principles procedures. Our results agree with the ones obtained with the method developed by Sai et al [10] within TDCDFT, and supports the functionality of DFT methods based on nonlocal models for $v_{xc}$. Its agreement opens up possibilities to formally justify a connection between nonlocal DFT and TDCDFT in the zero-frequency limit. Furthermore, more work is needed on this respect since the exact amount of nonlocality might be difficult to estimate given: (i) the difficulties for the definition of the region where it should operate; and (ii) the correct implementation of this behavior. However, we can at least define an upper limit for this nonlocal HF correction, and give arguments in favour of its non-zero value, as DFT-LDA methods considered. Within this context, the numerical calculation of the conductance for a H$_2$ molecule in Pt nanocontacts have been corrected, lowering in one order of magnitude the standard DFT-LDA calculation. Note, however, that the statements and the conclusions that will be made are not limited to calculations of conductance in this benchmark system. It is widely accepted that nonlocal contributions to $v_{xc}$ do play a significant role to get beyond DFT-LDA results either in molecular systems or bulk materials. For instance, we could mention the polarizability of polymeric chains [18], the magnetic coupling and the band structure in systems such as antiferromagnetic insulators [51, 52] and magnetic oxides [53]. Finally, our theory is that the overestimation of the conductance is not intrinsic to the DFT-KS approach. This wrong behavior could be greatly improved by a controlled design of an exchange-correlation potential which incorporates nonlocal contributions.

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• **Figure 1.** Reduction of the conductance due to the progressive substitution of the local xc-potential by the nonlocal HF-like contribution. The inset shows the conductance as function of energy calculated in a nonlocal DFT approximation for $\alpha = 0.6$.

• **Figure 2.** Transmission as a function of energy calculated in a local DFT approximation for the Pt-H$_2$-Pt bridge shown in the inset.

• **Figure 3.** Enhancement of the HOMO-LUMO gap ($\Delta_{HOMO-LUMO}$) due to the substitution of local xc potential by the nonlocal HF contribution. The inset shows the Pt-H$_2$-Pt system bridging the Platinum electrodes.

• **Figure 4.** Ground state energy calculations of the charge gap, $GAP$, for the system shown in the inset. $GAP = 2E_0(N) - E_0(N+1) - E_0(N-1)$, where N represents the number of electrons, and $E_0$ is the total energy for the selected ground states. Total energy calculations were done using wave-function based methods: Hartree-Fock (HF), Möller-Plesset perturbation theory at the second, third and fourth order (MP2, MP3, MP4, respectively) and Coupled-Cluster theory with single, doubles and single, doubles, and perturbatively estimated triples [CCSD, CCSD(T), respectively] methods.

• **Figure 5.** Electron density profile after planar average (dashed line) and three-dimensional average of the microscopic density.
Figure 1
Figure 2
Figure 4
