Deleterious Effects of Exact Exchange Functionals on Predictions of Molecular Conductance

Qingguo Feng,† Atsushi Yamada,† Roi Baer,*‡ and Barry D. Dunietz*†

†Department of Chemistry and Biochemistry, Kent State University, Kent, Ohio 44242, United States
‡Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Supporting Information

ABSTRACT: Kohn–Sham (KS) density functional theory (DFT) describes well the atomistic structure of molecular junctions and their coupling to the semi-infinite metallic electrodes but severely overestimates conductance due to the spuriously large density of charge-carrier states of the KS system. Previous works show that inclusion of appropriate amounts of nonlocal exchange in the functional can fix the problem and provide realistic conductance estimates. Here however we discover that nonlocal exchange can also lead to deleterious effects which artificially overestimate transmittance even beyond the KS-DFT prediction. The effect is a result of exchange coupling between nonoverlapping states of diradical character. We prescribe a practical recipe for eliminating such artifacts.

Computational studies of molecular junctions often employ Kohn–Sham density functional theory (KS-DFT) for determining their nuclear and geometric structure in thermal equilibrium.1−8 For conductance, the Kohn–Sham theory is however not a reasonable choice, because the energy gap \( \varepsilon_{\text{L}} - \varepsilon_{\text{H}} \) between the lowest unoccupied and highest occupied KS eigenvalues is much smaller than the electron–hole quasiparticle (QP) gap,9−13 often leading to gross overestimation of the low voltage conductance.14−22

One way to overcome this failure is to include a portion of exact Hartree–Fock (HF) exchange in the exchange-correlation functional, within a generalized KS (GKS)6,23−35 approach to DFT. When a proper tuning procedure is applied, the GKS eigenvalue gap comes close to the QP gap,36−38 and a quantitative improvement in the predictions of conductance in comparison to experimental results is seen.21,39,40

Here we discover that exact-exchange can also have an opposite role, similar to the potential spurious effect first revealed in ref 41, where artificially high electronic transmission can be found depending on the employed electrode model. In ref 41 it was shown that artificially high transmission in gapped but ghosted systems (that is where bridge atoms are only included as ghost atoms) is likely a result of imposing a diradical nature across the two electrode regions rather than reflecting a basis set related artifact as suggested in an earlier report.42 In this manuscript we focus on a different and novel issue, namely the detrimental effects of nonlocal exchange interactions causing unphysical couplings of diradical states in the lead. Furthermore, we prescribe a way to generically avoid the spurious predictions in practical calculations.

In order to demonstrate the problem in using exact exchange for conductance calculations we use HF theory to calculate the transmission function \( T(E) \) (shown in Figure 1) of two nearly identical molecular junctions composed of a single phenyl ring connected to gold leads through sulfur atoms. (The details of the computational approach are provided in the Appendix.) The two systems, tagged Au31 and Au41, differ by one atom on each lead. Both systems have the same chemical potential \( \mu_{\text{HF}} = \frac{1}{2}(\varepsilon_{\text{L}} + \varepsilon_{\text{H}}) \approx -3.9 \) eV (see Figure 2(a)), but Au31 features substantially higher transmission than Au41. This drastically elevated transmission upon a seemingly benign change in the electrode region is clearly an artifact.

To understand this remarkable result we study the HF frontier eigenvalues for Au41 and Au31 shown in Figure 2(a).

Published: July 25, 2016
\(\phi_R(-x,y,z)\), situated on the left and right leads. The effect of each such pair on the conductance can be analyzed using a symmetric double-well Hamiltonian

\[ \hat{H} = -t (\phi_L \langle \phi_R \rangle - \phi_R \langle \phi_L \rangle) \]

where the parameter \(t\) is the tunneling matrix element (\(t/2\pi\) is the average rate of transition between the left and right states). Diagonalization of the Hamiltonian produces

\[ \hat{H} = t (\psi_+ \langle \psi_+ \rangle - \psi_- \langle \psi_- \rangle) \]

where \(\psi_\pm = (\phi_L \pm \phi_R)/\sqrt{2}\) are the ground and excited states of \(\hat{H}\) and evidently \(t\) is also half the energy splitting between the eigenvalues. Hence it is clear that degenerate states, where \(t = 0\), do not contribute to transmission.

This explains why in Au41, where all frontier levels come in (nearly) degenerate pairs, transmission is low (see Figure 2 (a)). As Au31 is “obtained” from Au41 by removal of two atoms (one from each lead) it has one less frontier orbital in each lead. The only rather mysterious issue is why the HOMO and LUMO delocalize and split in energy. This is a mystery since it would seem reasonable that localized versions can be formed such that the energy would be degenerate. Often, when a structural symmetry involves a HOMO-LUMO degeneracy the system spontaneously breaks the symmetry through a nuclear configuration distortion thereby lowering the energy of the HOMO (structural Jahn-Teller effect\(^4\)). This however is not the case here: we do not allow for nuclear relaxation, and yet the system breaks the degeneracy as a purely nonlocal electronic effect.

In order to establish the unphysical nature of the energy splitting we emphasize the absence of overlap between the left and right leads by removing the phenyl bridge, obtaining two gapped systems. Sulfur atoms are also removed, where only the gold atoms are left intact. The electron transmission function of the gapped system is shown in Figure 2 (b) (compare to the bridge case in [a]), and one immediately notices a switch: Au31, which is conductive in the bridged system, is an insulator in the gap system, and Au41, which is insulating in the bridged system, is conductive in the gapped case!

The energy eigenvalues of the gapped systems are shown in Figure 2 (b). This time the orbitals of Au31 form degenerate pairs explaining the low transmission. In going from the nonconducting gapped Au31 to Au41 we add an atom to each of the two leads and therefore obtain two additional orbitals. Due to the symmetry and spatial separation we expect the two additional orbitals to be localized and degenerate. As in the bridged system, but once again, surprisingly, these orbitals interact and become delocalized and nondegenerate. This exaggerates the calculated transmission for Au41, a qualitatively wrong prediction due to the presence of the wide gap.

In the gapped system there is no overlap between the left and right orbitals. This emphasizes the fact that the coupling between the orbitals is not due to kinetic energy, external potential, or Hartree potential operators as all these interactions are local, i.e. require overlap between orbitals on the two leads.

---

**Figure 1.** Transmission as a function of electron energy through two molecular junctions, Au41 and Au31, calculated using HF theory. The lead is represented in Au41 by 29 Au gold atoms, arranged in parallel planes each containing 4 gold atoms and an utmost (first) layer of a single atom which participates in the Au–S bond. The lead of Au31 has 28 in total of gold atoms, where the second layer has only 3 gold atoms. Thus, the leads in Au41 are identical to Au31 except for the one additional gold atom (encircled in the figure) in the second layer. The bridge is also shown and is composed of a phenyl ring with two sulfur atoms in opposite positions for connecting to the outermost gold atom of each lead.

**Figure 2.** Frontier orbitals and eigenvalues of the Au41 and Au31 systems for (a) the bridged system at the Hartree–Fock level, (b) the gapped system at the Hartree–Fock level, and (c) the LDA level. The energy scale in the case of LDA is much smaller than in the case of HF, as indicated by the arrows between the panels. A larger presentation of the panel figures is provided in SI Figures S1–S3.
The only explanation for the energy splitting is the nonlocal orbital coupling caused by exact exchange interaction. In SI section 1 we demonstrate in detail how exact exchange causes splitting of degeneracy in a pair of levels occupied by 2 electrons (but not in a pair occupied by 4 or 0 electrons). For this reason the pair HOMO−1 and HOMO−2 and the pair LUMO+1 and LUMO+2 in the Au31 gap/HF panel of Figure 2 stay degenerate in spite of the presence of the exchange operator. In Au41 nonlocal exchange splits the HOMO−LUMO levels because they are occupied by only 2 electrons (the number of valence electrons in Au41 is not divisible by 4, as it has $2 \times 29$ highest valence band electrons from $2 \times 29$ gold atoms). In contrast, the Au31 system has $2 \times 28$ highest valence band electrons, and all its degenerate pairs of orbitals are either occupied by 4 electrons or zero electrons.

To verify this theory, we study the behavior of these systems using the local density approximation (LDA) where exchange interaction is purely local (i.e., depending on the electron density and not the reduced density matrix [see further discussion in SI section 1]). The frontier eigenvalues of the LDA calculations for the Au31 and Au41 systems are shown in Figure 2(c) where all levels indeed remain degenerate for both Au31 and Au41. This proves that the splitting is necessarily a result of nonlocal exchange. Furthermore, Figure 3(c) shows that both Au31 and Au41 with LDA have similar low transmission due to this full level degeneracy.

The final issue we discuss now is how to avoid the nonlocal exchange coupling which leads to spuriously high transmission. One obvious solution is to choose the leads such that there is no diradical character. However, we emphasize, that it is not always obvious how to accomplish this. In our system, for example, we could move continuously from the bridged to the gapped configuration by gradually stretching the Au−S bonds. At some stage during this process the system would “switch” the parity of the leads representation, but it is not easy to determine in general when.

A systematic approach can be obtained by taking into account the spin state of the model system. Studying the transmission as a function of spin state in Figure 3(a) and (b) and comparing the energies in Table 1, it turns out that whenever the conductance is spuriously high the singlet energy is higher than the triplet energy by as much as 1 eV. This correlates nicely with the fact that one should base the low bias conductance calculations on the lowest possible energy state.

An alternative approach is to perform the calculation in the spin unrestricted framework that represents an ensemble average of the conductance of the two spin states. In Figure 3 we show that the transmission of the spin-unrestricted state is qualitatively correct in the sense that it is similar to that of the lower energy restricted spin state avoiding the spurious elevated values of the high energy spin state.

In summary, we have discussed the spurious effects of exact nonlocal exchange on predictions of molecular junction conductance:

1. Nearly identical junctions are predicted by Hartree–Fock based transmittance calculations to yield widely different conductances: Au31 has much higher $T(E)$ than Au41. The trend reverses when we remove the molecular bridge (gapped systems): Au31 has much lower $T(E)$ than Au41.
2. Our junctions are symmetric and therefore produce pairs of molecular orbitals which are either exactly or approximately mirror images and energy-degenerate. A pair of states becomes degenerate as their coupling is reduced, and therefore they stay localized on the two sides of the junction, similar to the symmetric double-well with zero coupling. Hence, the transmittance of the junction can be understood almost solely in terms of the apparent degeneracies of the frontier energy levels.

3. We show that when each lead is a closed shell system the energy levels form degenerate pairs and support low conductance (in the absence of interactions that break these degeneracies). However, when a closed shell Hamiltonian is used to describe the conductance in a case where each lead has on the average an odd number of electrons, nonlocal exchange can split the energy degeneracy of the HOMO–LUMO pair, leading to prediction of unusually high transmittance. We proved the essential role of nonlocal exchange by showing that the degeneracy splitting does not occur in an LDA treatment.

4. Hence we concluded that use of Hartree–Fock exact exchange may lead to spuriously high conductance even in cases where it should be close to zero and that it occurs when the leads acquire a diradical nature in the electronic structure calculation.

5. We find that employing unrestricted or high spin framework of the electronic structure calculations remedies the problem as it correctly treats the two leads as separate uncoupled systems.

To conclude, the use of portions of exact exchange opens frontier orbital gaps to their proper energies and helps to correct the severe overestimation of (semi) local KS conductance calculations. However, we present a scenario where such an energy gap deleteriously elevates the conductance due to artificial coupling by nonlocal exchange.

While the discussion here focused on the Hartree–Fock method, the spurious effects we discovered are expected to plague all density functionals that deploy nonlocal exchange, such as hybrids and range-separated hybrids with varying degrees of extent. For example, B3LYP follows the same trend as observed with the HF level for the gapped case, where the transmission is spuriously enhanced for the Au41 based system (see Figure 3(d), with the corresponding orbitals shown in the SI Figure S4). The effect is also expected to prevail when the GW approximation is used to estimate the junction transmittance because nonlocal exchange is part of the GW self-energy.

The remedy for this problem is similar to the practical fix of the H2 molecular bond-breaking problem by the use of unrestricted spin calculations or restricted lowest energy spin state calculations. However, the bond-breaking conundrum differs from the presented problem in one important aspect: The former appears in both restricted HF and LDA treatments, while the latter shows up only in restricted HF (i.e., due only to long-range exchange). Our proposed remedy removes a qualitative deficiency, one that can cause artificially high transmission by orders of magnitude. The performance of the method, screening for possible remaining imperfections, can be assessed by comparing to conductance measurements.

APPENDIX

Computational Details

We used the Q-Chem quantum chemistry software package with the Los Alamos double zeta effective core potential (LANL2DZ) to do all quantum chemical and geometry calculations. (We confirm the trends presented in this study with a larger basis set (Stuttgart-Bonn ECP (SRSC) shown in SI Figure S5.) The latter were done using the B3LYP functional and include single gold atoms that are each attached to thiol groups to which an electrode representation is added for the transmission analysis. The coordinates of the bridge with the Au41 electrode model is given in SI Table S1. The transmission was calculated using T-Chem software package. Further information on the transmission calculation procedure is provided in the SI section 1 along with a sample of the T-Chem input file.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.6b00493.

Enlarged figures of Figure 2 (Figures S1–S3), orbitals calculated with the B3LYP functional for the gapped system (Figure S4), SRSC-based transmission (Figure S5), broadening factor study (Figure S6), bridged Au41 atomic coordinates (Table S1), and a T-Chem input section (SI appendix) (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: roi.baer@huji.ac.il.

E-mail: bdunietz@kent.edu,

Author Contributions

Q.F. and A.Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

B.D.D. would like to acknowledge the financial support by a DOE-BES award through the Chemical Sciences Geosciences and Biosciences Division (Grant No. 357 DE-SC0004924 and DE-FG02-10ER16174), as well as for computational support through access to the Ohio supercomputer and the Kent State University College of Arts and Sciences resources. R.B. gratefully acknowledges the support of the Israel Science Foundation (grant no. 189/14).

REFERENCES


(40) Yamada, A.; Feng, Q.; Fenk, K.; Dunietz, B. D. Submitted.


