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Towards a theoretical description of molecular junctions in the Coulomb blockade regime based on density functional theory

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Nonequilibrium Green's function techniques (NEGF) combined with density functional theory (DFT) calculations have become a standard tool for the description of electron transport through single molecule nanojunctions in the coherent tunneling regime. However, the applicability of these methods for transport in the Coulomb blockade (CB) regime is still under debate. Here we present NEGF-DFT calculations performed on simple model systems in the presence of an effective gate potential. The results show that (i) the CB addition energies can be predicted with such an approach with reasonable accuracy and (ii) neither the magnitude of the Kohn-Sham gap nor the lack of a derivative discontinuity in the exchange-correlation functional represent a problem for this purpose.

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Interest in electron transport between nanoscale contacts has recently intensified due to its possible applicability in molecular electronics and recent progress in its experimental characterization.[1] Electron transport is generally described within two limiting regimes, namely, coherent transport (CT) for strong coupling between the molecule and the electrodes and Coulomb blockade (CB) for weak coupling. Transport in the CB regime is characterized by the so-called CB diamonds depicting frontiers between low- and high-conductivity domains in the source/drain bias gate voltage coordinates.[2–4] Key quantities in this stability diagram are the energy differences between the ionization and affinity levels of a quantum dot or single molecule, which are referred to as addition energies E_{add}.

First-principles nonequilibrium Green's function (NEGF) methods are typically implemented[5–8] in combination with density functional theory (DFT) to theoretically describe electron transport through single molecule junctions. This approach proves to be very useful for the description of the CT regime. For electron transfer in the CB regime, however, an integer charge is transferred and it results in a relaxation of the electronic structure of the central molecule. Only a many-body approach such as a multideterminant configuration-interaction scheme provides a general solution to the latter problem,[9,10] which is difficult to apply to an open system with the leads usually described by mean-field band-structure calculations. Quasiparticle calculations based on the GW approximation, on the other hand, were found to not accurately represent the impact of local spin and charge fluctuations on CB.[11]

It has also been suggested that a standard DFT framework has inherent problems for describing electron transport in both the CB and CT regimes[12,13] due to the self-interaction (SI) of electrons[14] in a Kohn-Sham (KS) framework and the lack of a derivative discontinuity[15] in the evolution of the eigenenergy of the highest occupied molecular orbital (HOMO) as a function of its occupancy, which can be fractional. In Ref. 12, these two issues have been portrayed as intimately linked and a SI correction scheme has been devised as a remedy. Independently, optimized effective potentials and hybrid methods have been employed for reducing or removing SI from DFT-based electron-transport calculations.[16,17]

In this Brief Report, we present NEGF-DFT calculations performed in the presence of an effective gate potential V_{gate}, which allows for an explicit charge transfer between one-dimensional lithium chains as electrodes, and H_2 and benzene molecules as the central unit (see Fig. 1). The results obtained for these model systems show that (i) quantitatively realistic values can be derived for the addition energies E_{add} associated with CB diamonds despite the fact that our calculations are carried out in the local-density approximation (LDA) and introduce a distortion in the charging process characteristic for DFT and (ii) the size of the KS gap estimated from the electronic eigenenergies of the frontier orbitals is not directly related to E_{add}. Our approach follows a similar philosophy as a constrained DFT,[18] where sometimes a potential confined to only a part of the system is also applied but with the condition of a fixed occupation for a given orbital rather than a fixed potential as in our case.

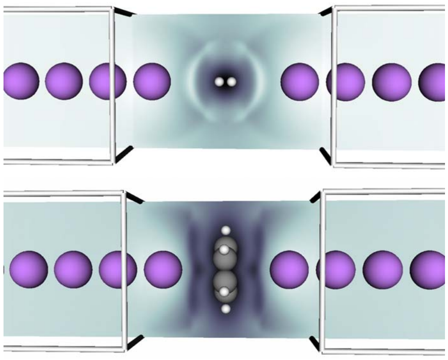

FIG. 1. (Color online) Geometry and applied gate potential in the two molecular junctions of our study; a H_2 molecule (top) and a benzene molecule (bottom) are attached to lithium chains with a fixed separation of 4.37 and 4.00 Å, respectively. The profile of V_{gate} (taken from the differences in spatial resolution for calculations at 1 and 0 V) is shown with gray shading in both junctions, where its maximum is located in the black regions.

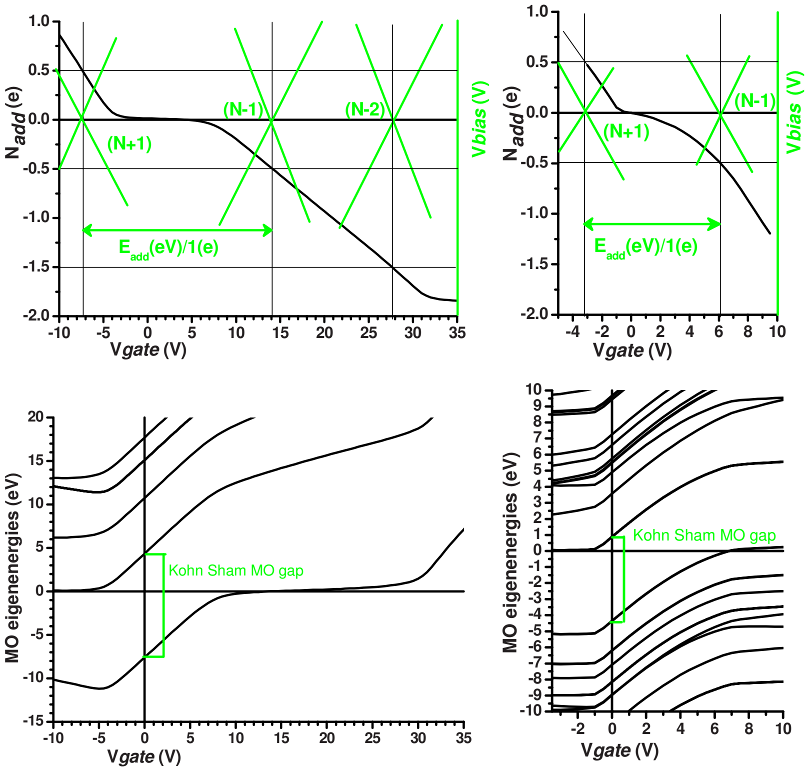

FIG. 2. (Color online) (Top) Evolution of the surplus electrons on the molecules (N_{add}) as a function of V_{gate} and schematic description of the CB diamonds at the predicted threshold voltages for the junction with H_2 (left) and benzene (right), respectively. (Bottom) Corresponding evolution of MO eigenenergies as a function of V_{gate}. N_{add} is determined by integrating charge-density differences with $V_{\text{gate}}=0$ V as a reference and where the spatial border between the molecule and the electrode is the region invariant in charge to V_{gate}. The MO eigenenergies have been extracted from NEGF-DFT calculations by using a projection scheme (Ref. 20) where the zero energy is the Fermi level of the Li electrodes.

Figure 1 illustrates the two systems of our study for which we performed NEGF-DFT calculations with the commercially available ATK software.[19] A single-Li atom is included in the scattering region on each side of the central unit and each electrode part contains six atoms. A self-consistent solution for the electron density of the open system as a whole is carried out within the Keldysh formalism[5–8] for every value of V_{gate} on a grid of 0.5 V; a small source-drain bias of 20 mV has been applied in order to generate a current through the junction. The voltage V_{gate} is introduced in the Keldysh Hamiltonian as $H_{\mu\nu}=H_{\mu\nu}+V_{\text{gate}}S_{\mu\nu}$, where $S_{\mu\nu}$ is the overlap matrix and the indices μ and ν run only over the atomic basis functions of the molecules (i.e., V_{gate} is not applied to the electrodes); the term containing V_{gate} is added to the Hamiltonian at every step in the self-consistent cycle. The shape of the resulting potential is shown as gray shades in Fig. 1. In all the calculations presented in this Brief Report, LDA has been used for the exchange-correlation (XC) functional and a double-zeta polarized basis set for both the molecules and the electrodes.

Figure 2 shows the evolution of the charge on the molecules (N_{add}) and the KS-molecular orbital (MO) eigenenergies as a function of V_{gate} for both systems. The range of gate voltages is larger in the positive region than in the negative one due to the well-known convergence problems for anions when using localized basis sets.[21] The correct physical behavior would show electrons moving between the electrodes and the molecule one by one at given threshold voltages. A spin-polarized treatment would be required to properly describe this situation. Given that the total electron density in the scattering region remains practically constant irrespective of V_{gate} in our calculations, a spin-polarized solution would imply spatially different spin-up and spin-down densities in the scattering region together with the same integrated number of spin-up and spin-down electrons as in the absence of charge transfer. In practice, only nonpolarized solutions are obtained throughout this Brief Report with N_{add} evolving linearly from 0 to almost 2 electrons with V_{gate} due to the use of a closed-shell ansatz and the lack of a derivative discontinuity in DFT.[10] This general deficiency of DFT allows for any fractional value between 0 and 2 for the occupation of frontier orbitals of the molecules, even if they are only weakly coupled to metal electrodes (as it is the case in the present calculations).

Nevertheless, the addition energies E_{add} associated with the CB diamonds can be calculated as

$$\begin{aligned} E_{\text{add}} &= [E(N+1)-E(N)]-[E(N)-E(N-1)] \\ &= \int_0^1 dN_{\text{add}}V_{\text{gate}}(N_{\text{add}}) - \int_{-1}^0 dN_{\text{add}}V_{\text{gate}}(N_{\text{add}}) \\ &= V_{\text{gate}}(N_{\text{add}}=+0.5e)-V_{\text{gate}}(N_{\text{add}}=-0.5e). \end{aligned} \tag{1}$$

In Eq. (1), the first line is a general expression for calculating the difference between the redox levels from the total energies of the neutral and charged isolated molecules (as we did hereafter using Gaussian[22]), which does not suffer from the lack of a derivative discontinuity in the exchange-correlation functional in contrast to the differences of KS eigenenergies for a fixed particle number N.[23] The second line is general in electrostatics and makes use of the relationship between a total energy E, a voltage V, and a charge N. In the last step, threshold voltages obtained from NEGF-DFT calculations are introduced, where a midpoint rule for the integration over the charge has been used;[24] E_{add} is thus evaluated from the gate voltages required to add or subtract half an electron to

TABLE I. Addition energies E_{add} calculated as V_{gate} ($N_{\mathrm{add}}=+0.5e$)$-V_{\mathrm{gate}}$ ($N_{\mathrm{add}}=-0.5e$) from NEGF DFT for the junctions shown in Fig. 1 and as $E(N+1)+E(N-1)-2E(N)$ from the total energies of the neutral and charged isolated molecules. The KS HOMO-LUMO gap extracted from the NEGF-DFT calculations and reliable values for E_{add} of the isolated molecules provided by the experiment for H_2 (Ref. 27) and GW calculations for benzene (Ref. 28) are also given for comparison. All values are given in eV.

Molecule	NEGF-DFT	DFT-E_{total}	KS-MOs	Lit (IP-EA)
H_2	21.30	21.35	11.95	18.56
Benzene	9.80	11.54	5.23	10.51

the molecule.[25] With this general procedure, the more linear the dependence of V_{gate} with respect to N_{add}, the more precise is the application of the midpoint rule. Recently, it has been demonstrated that total energies calculated from DFT for noninteger occupation numbers yield an increased error due to one-electron self-interaction effects in comparison to integer occupations.[26] We point out, however, that these deviations from the correct functional behavior of the total energy vs N are always quite symmetric with respect to the integer values of N and therefore cancel out to a large extent in the energy differences used for defining E_{add} in Eq. (1).

Table I collects the values of E_{add} calculated for both junctions using the two expressions in Eq. (1) with the same basis set and XC functional. For comparison, we also provide the Kohn-Sham gap between the highest occupied (HOMO) and lowest unoccupied MO (LUMO) taken from NEGF-DFT calculations at $V_{\mathrm{gate}}=0$ V by projecting the eigenstates of the semi-infinite junction on the sub-Hamiltonian defined by the part of the basis set that is localized exclusively on the molecule[20]—reliable values for E_{add} are also listed for the isolated H_2 (Ref. 27) and benzene[28] molecules. Although the KS-MO gap is, as expected, about a factor of 2 smaller than all the other values, Table I shows that the results obtained from the NEGF-DFT approach match the two reliable sets of E_{add} values obtained for the isolated molecules rather well. N_{add} has been estimated by integrating the voltage-dependent differences in the self-consistent charge density over the molecular part. The counter charges are located on the Li chains with the main part on the atoms directly in contact with the molecule and the remainder decaying into the wires in Friedel oscillations (not shown here). Since the addition and removal of electrons on the Li leads occur at the Fermi level, the energetically significant effect is the actual charging of the molecule in contrast to neutral excitations on molecules as measured, e.g., in photoabsorbtion experiments.[29] The electrons and holes on metal and molecule interact, however, through long-range electrostatics, which might explain some of the differences between columns one and two in Table I. We also stress that the scaling factor α, used in experiments[2,3] to distinguish between the applied gate voltage and the effective potential felt by the molecule, is equal to 1 in our calculations.

The evolution of the MO eigenenergies as a function of the gate voltage in Fig. 2 reflects the corresponding curves obtained for N_{add}, since the occupation of a given MO can only vary between 0 and 2 while it stays pinned to the Fermi level. N_{add} thus changes with V_{gate} while the eigenenergies stay constant and vice versa. The pinning of the MOs to Fermi-level E_F is also reflected in the transmission functions shown in Fig. 3 for the LUMO peak of the Li-H_2-Li junction. As long as the energy of the transmission peak does not reach E_F, it shifts as a function of V_{gate} with a slope of 1; this evolution is stopped when progressive charging is initiated in our mean-field calculations, instead of the correct stepwise charging, as already discussed above. As a consequence, the peak in the current/V_{gate} curve shown in the inset of Fig. 3 is unphysically broadened by up to 10 V; in reality, this peak is expected to be much narrower due to the weak coupling between the molecule and the electrodes. The inset does show the high- and low-conductivity domains characteristic of the CB behavior when the gate voltage is modulated; the point is, however, that the position of the boundaries along the V_{gate} axis is distorted by the mean-field character of the calculations and should be extracted properly in the way as illustrated in Fig. 2.

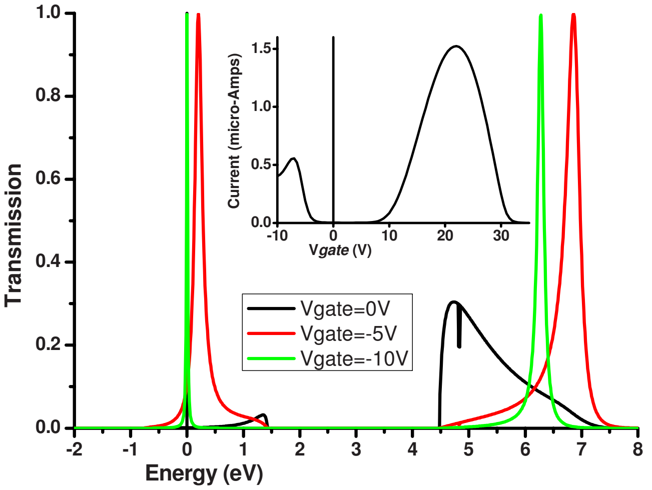

FIG. 3. (Color online) Transmission functions for the Li-H_2-Li junction for different values of V_{gate}, where the Fermi level E_F of the Li chain defines zero on the energy axis. The peak corresponding to the LUMO moves from $\sim+5$ eV at $V_{\mathrm{gate}}=0$ V to $\sim+0.2$ eV at $V_{\mathrm{gate}}=-5$ V; for $V_{\mathrm{gate}}=-10$ V, it becomes pinned to E_F. In the transmission functions obtained for the two finite values of V_{gate}, an additional peak associated with a higher-lying unoccupied MO can also be seen above 6 eV. The inset shows the current in the same junction with an applied source-drain bias of 20 mV as a function of V_{gate}.

At this stage, we refrain from addressing the issue of screening or image charge effects, which are highly relevant for the interpretation of recent experimental data. These are expected to be only significant when considering large surface areas; so in our study, the surface consists of just a single atom on each side. A recent comparison between DFT-LDA versus GW results for the adsorption of benzene on graphite[28] suggests that DFT is likely to fail in describing such polarization effects. We note, however, that the adsorbed molecule was not explicitly charged in this study and the focus was on the KS-MO gap, which is fundamentally different from our approach.

It would be highly desirable to conduct similar calculations for more realistic electrodes and junctions, e.g., where the molecule is chemisorbed on the leads via anchoring groups and the weakness of the coupling required for the CB regime promoted by spacers.[3] From a practical viewpoint, such a study would require considerable computational effort since going to rather high gate voltages is required even for molecules with a moderate gap size, and convergence can only be achieved if the voltage is varied in small steps as the electronic structure of the systems is significantly perturbed. Furthermore, the rather crude way we used to introduce V_{gate} does not allow for the introduction of chemical bridges without ambiguity. Since the primary goal of the current Brief Report is to establish a proof of principle for our approach, we leave the evaluation of the latter issues to future work.

In conclusion, we have addressed the issue whether NEGF-DFT techniques can be employed for deriving relevant parameters in the Coulomb blockade regime. In our approach, we explicitly introduced a gate voltage in order to induce a charge transfer from the electrodes (Li chains) to the inserted molecules (H_2 and benzene). We obtained realistic results for addition energies (a key quantity in CB experiments) and also illustrated why our results are not affected by the widely known shortcomings of DFT such as the lack of a derivative discontinuity in the exchange-correlation functional.

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[1] *Introducing Molecular Electronics*, Lecture Notes in Physics Vol. 680, edited by G. Cuniberi, G. Fagas, and K. Richter (Springer, New York, 2005).

[2] L. P. Kouwenhoven, D. G. Austing, and S. Tarucha, Rep. Prog. Phys. **64**, 701 (2001).

[3] S. Kubatkin, A. Danilov, M. Hjort, J. Cornil, J. L. Brdas, N. Stuhr-Hansen, P. Hedegård, and T. Bjørnholm, Nature (London) **425**, 698 (2003); A. Danilov, S. Kubatkin, S. Kafanov, P. Hedegård, N. Stuhr-Hansen, K. Moth-Poulsen, and T. Bjørnholm, Nano Lett. **8**, 1 (2008).

[4] A. Nitzan and A. Ratner, Science **300**, 1384 (2003).

[5] M. Brandbyge, J. L. Mozos, P. Ordejon, J. Taylor, and K. Stokbro, Phys. Rev. B **65**, 165401 (2002).

[6] Y. Xue, S. Datta, and M. A. Ratner, Chem. Phys. **281**, 151 (2002).

[7] A. R. Rocha, V. M. Garcia-Suarez, S. W. Baily, C. J. Lambert, J. Ferrer, and S. Sanvito, Nat. Mater. **4**, 335 (2005).

[8] K. S. Thygesen and K. W. Jacobsen, Chem. Phys. **319**, 111 (2005).

[9] S. M. Lindsay and M. A. Ratner, Adv. Mater. (Weinheim, Ger.) **19**, 23 (2007).

[10] S. Datta, arXiv:cond-mat/0603034 (unpublished); B. Muralidharan, A. W. Ghosh, and S. Datta, Phys. Rev. B **73**, 155410 (2006); Mol. Simul. **32**, 751 (2006).

[11] X. Wang, C. D. Spataru, M. S. Hybertsen, and A. J. Millis, Phys. Rev. B **77**, 045119 (2008).

[12] C. Toher, A. Filippetti, S. Sanvito, and K. Burke, Phys. Rev. Lett. **95**, 146402 (2005).

[13] M. Koentopp, C. Chang, K. Burke, and R. Car, J. Phys.: Condens. Matter **20**, 083203 (2008).

[14] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[15] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).

[16] J. J. Palacios, Phys. Rev. B **72**, 125424 (2005); I. Yanov, Y. Kholod, J. Leszczynski, and J. J. Palacios, Chem. Phys. Lett. **445**, 238 (2007).

[17] S. H. Ke, H. U. Baranger, and W. Yang, J. Chem. Phys. **126**, 201102 (2007).

[18] Q. Wu and T. Van Voorhis, Phys. Rev. A **72**, 024502 (2005).

[19] ATK, Version 2.2, atomistix a/s, 2004, www.atomistix.com.

[20] K. Stokbro, J. Taylor, and M. Brandbyge, J. Am. Chem. Soc. **125**, 3674 (2003).

[21] F. Jensen, J. Chem. Phys. **117**, 9234 (2002).

[22] GAUSSIAN 98, Revision A.11.3, Gaussian, Inc., Pittsburgh, PA, 2002; www.gaussian.com.

[23] W. Kohn, Phys. Rev. B **33**, 4331(R) (1986).

[24] A. R. Williams, R. A. deGroot, and C. B. Sommers, J. Chem. Phys. **63**, 628 (1975).

[25] It might seem counterintuitive to rely on a threshold voltage for the transfer of half an electron since the concept of fractional charges is somewhat artificial in quantum theory. This concept is, however, implicit in DFT where the central variable is the electron density. In correlated quantum-chemical approaches, the relation between E, V, and N in Eq. (1) still holds since the transfer of ± 0.5 e and ± 1.0 e occurs at the same voltages due to the step-like change in the charge N as a function of the voltage V.

[26] A. Ruzsinszky, J. P. Perdew, G. I. Csonka, O. A. Vydrov, and G. E. Scuseria, J. Chem. Phys. **126**, 104102 (2007); A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, Phys. Rev. B **77**, 115123 (2008); P. Mori-Sanchez, A. J. Cohen, and W. T. Yang, Phys. Rev. Lett. **100**, 146401 (2008).

[27] B. S. Jursic, J. Mol. Struct.: THEOCHEM **491**, 11 (1999).

[28] J. B. Neaton, M. S. Hybertsen, and S. G. Louie, Phys. Rev. Lett. **97**, 216405 (2006).

[29] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).