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Integer particle preference during charge transfer in Kohn-Sham theory

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We investigate the static and dynamic charge transfer that is triggered by external electric fields in model molecular wires. A self-interaction correction in Kohn-Sham density functional theory leads to the desired integer electron transfers that do not occur with standard functionals which miss Coulomb blockade effects. Analysis of the multiplicative exchange-correlation potential in stationary cases and during real-time propagation shows how the local exchange-correlation potential builds up step and reverse-step structures that enforce the integer particle preference. The role of spin-symmetry breaking is discussed.

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The large error that "standard density functionals" such as (semi)local functionals and regular hybrids show for long-range charge-transfer (CT) problems has been one of the most serious deficiencies of (time-dependent) density functional theory [(TD)DFT]. That standard functionals seriously overestimate CT has long been known,[1–5] and the CT problem shows up in many guises. Yet, the various manifestations of TDDFT's CT problem typically fall into one of two important areas. The first one is the calculation of CT excitations that are part of linear response absorption spectra. Great progress has been made in this field in recent years.[6] The second is the area of quantum transport and molecular electronics. In the latter field the performance of (TD)DFT in practice is still debated. DFT has frequently been combined with nonequilibrium Green's function theory for calculating transport characteristics. However, there are fundamental limitations when these two approaches are combined.[7] Very early, Ref. 8 pointed out the importance of dynamical exchange-correlation (xc) corrections to the conductance, and the influence of self-interaction errors[3–5,9] and the derivative discontinuity[10–12] has been discussed.

Therefore, alternative schemes have been proposed that aim at exploiting the power of real-time propagation methods.[13–15] These works have shown the conceptual strengths of approaching the conductance CT problem in real time. With the open system quantum problem set up in such a way that real-time propagation in the central molecular region has a solid theoretical basis, the molecular conductance problem of TDDFT has been reduced to finding xc functional approximations that incorporate the physics that is decisive for this type of CT.

This is still a very considerable challenge, as there is a huge and even qualitative gap between the transport characteristics that standard functionals deliver, and the characteristics that are found in reality. With the present work we take a step towards closing this gap. We demonstrate that a Kohn-Sham (KS) self-interaction correction (SIC) not only remedies the large overestimation of the response that is obtained with (semi)local functionals, but can also enforce the principle of integer preference in CT. Integer preference can be seen in relation to Coulomb blockade[16] and has long been considered a correlation phenomenon that would be beyond the abilities of readily applicable functionals. Our approach is fully consistent and goes beyond previous implementations of the SIC that just corrected the eigenvalues. By analyzing the local KS potential, we can pinpoint step and reverse-step structures in the xc potential that are crucial for enforcing the integer preference. The results not only encourage the use of KS SIC. They stress the important role of spin-symmetry breaking and provide guiding insights for the further development of functionals that should yield reliable transport characteristics.

Due to the decisive role that self-interaction and the derivative discontinuity play in the conductance problem, it is a close lying idea to employ the SIC of Ref. 1 for studying the CT question. By its definition $E_{\mathrm{xc}}^{\mathrm{SIC}}[n_\uparrow,n_\downarrow] = E_{\mathrm{xc}}^{\mathrm{app}}[n_\uparrow,n_\downarrow] - \sum_{\sigma=\uparrow,\downarrow}\sum_{j=1}^{N_\sigma}[E_{\mathrm{H}}[n_{j\sigma}] + E_{\mathrm{xc}}^{\mathrm{app}}[n_{j\sigma},0]]$, i.e., by subtracting Hartree energy E_{H} and xc energy $E_{\mathrm{xc}}^{\mathrm{app}}$ contributions for all occupied orbital densities $n_{j\sigma}(\mathbf{r}) = |\varphi_{j\sigma}(\mathbf{r})|^2$ from a given xc approximation, the SIC energy is one-electron self-interaction free and incorporates a derivative discontinuity. Using recently developed ground-state[17] and TD KS SIC schemes[18] we can employ the SIC as a KS functional with one multiplicative potential. Thus, we can study the potential structure that develops during electron transfers in real space and real time, allowing to gain insight into the functioning of KS theory.

We use real-valued ground-state KS orbitals, but for the reasons explained in Refs. 18 and 19, the energy minimizing orbitals, TD KS orbitals, and orbital transformations are complex and we use SIC only in combination with the local spin density approximation (LSDA). All calculations were done with the Bayreuth version[20] of the PARSEC real-space program package,[21] with parameters chosen in analogy to Ref. 18. Our SIC studies use the generalized optimized effective potential (GOEP) and the generalized Krieger-Li-Iafrate (GKLI) approximation (GKLI-SIC)[17,18] to the GOEP.

Hydrogen chains have frequently served as model systems that provide tough challenges in terms of a correct description of the CT physics while being technically transparent. Here we use the setup[4] that is depicted in the upper part of Fig. 1. Two hydrogen chains, both containing eight H atoms separated by 1 Å, are aligned along the x axis with a separation of 8 Å. We apply an electric field along the x axis and monitor how charge is transferred from the right H chain (donor, D) to the left H chain (acceptor, A) depending on the field strength. As the distance between the H chains is large, the interchain coupling is small and physical electron transfer occurs by integer electron jumps.[4] Thus, up to a certain field strength, no charge flow should take place. As soon as the field exceeds

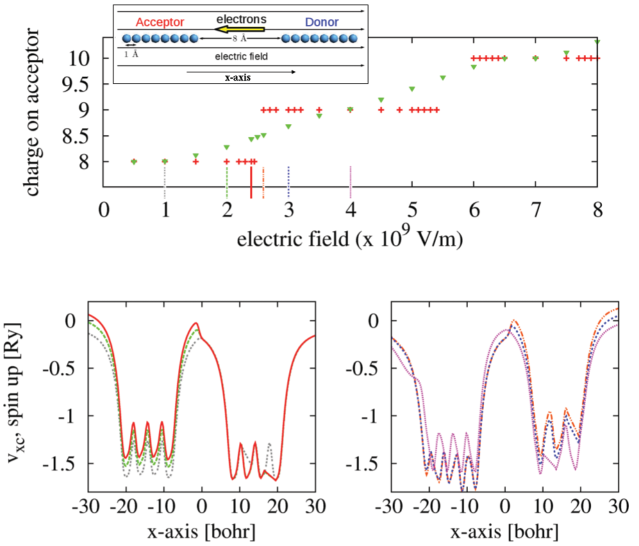

FIG. 1. (Color online) Upper panel: Charge on the left (acceptor, A) hydrogen chain as a function of an external electric field that is applied to the system of H atoms depicted in the inset. Triangles represent LSDA, and crosses GKLI-SIC results. The charge on A is obtained by integration of the density in the left half space of our real-space grid. The two lower panels show the up-spin v_{xc} of GKLI-SIC along the x axis for three field strengths before (left) and after (right) the first electron jump. The six field strengths are indicated by vertical lines in the upper panel. v_{xc} first builds a pronounced step that works against the electron transfer to A, and then a reverse step that ensures that the electron stays on A.

a specific strength, one electron, i.e., one (integer) unit of e, should jump from D to A and remain there unless the field strength is reduced. Increasing the field strength further, further integer electron jumps should occur.

However, the CT that one obtains from standard functionals as exemplified by LSDA (triangles in the upper panel of Fig. 1) is completely different and qualitatively wrong.[4] In LSDA, fractional CT occurs from a field strength of 1.5×10^9 V/m on. With increasing field strength there is a gradual transfer of charge to A until one unit of e has been transferred at a field strength of 4.0×10^9 V/m. Further increasing the field strength leads to further gradual CT until the electron number on A reaches a short plateau at a field strength of about 6.5×10^9 V/m, which indicates the second transferred unit of e. Using a hybrid functional, the plateaus are broader, but overall one obtains a similarly wrong CT picture.[4]

The picture changes completely as one goes from LSDA to SIC. Straightforward SIC of the LSDA functional within the KS framework is sufficient to recover the decisive physical principle of integer preference in CT. In the GKLI-SIC data (crosses in the upper panel of Fig. 1) one observes only integer numbers of electrons on the H chains with electron jumps occurring at field strengths of about 2.5×10^9 and 5.7×10^9 V/m. We also performed full GOEP calculations up to 3.5×10^9 V/m. They yield the same results as GKLI, i.e., the GKLI approximation is well justified. The electron jumps in GKLI-SIC occur at about the same field strengths at which half of an electron is transferred from D to A in LSDA.

Further insight into how the different xc approximations realize the CT can be gained by analyzing the calculations in detail. Restricting the occupation numbers of the KS scheme to integers leads to nonconvergent calculations for LSDA. The self-consistent LSDA iterations converged only when fractional occupation numbers were allowed, and the converged calculations then showed fractional charges on each of the H_8 subunits. In the generalized SIC scheme, however, integer occupation numbers are natural as the unitary transformation that connects KS orbitals and energy minimizing orbitals is intrinsically defined only for integer occupations,[22] and the integer occupation calculations converge.

Looking at the situation in which the electrons are initially equally distributed over D and A and in which spin is treated explicitly, there are in principle four possibilities for realizing a single integer electron jump: (i) One D spin-up (↑) electron jumps to A ↑, (ii) one D spin-down (↓) electron jumps to A ↓, (iii) one D ↑ electron transfers to the ↓ channel of A, and (iv) one D ↓ electron transfers to the ↑ channel of A. Out of these four possible realizations, (i) and (ii) are analogous with respect to v_{xc} features and so are (iii) and (iv). Therefore, it suffices to discuss explicitly only one of each class. One may argue that cases (iii) and (iv) are unphysical as the transferring electric field can hardly induce a spin flip. Yet, we deliberately discuss this situation because it contributes to revealing how the SIC describes CT.

Our calculations show that all four realizations in GKLI-SIC give the same total energy, and the electron jumps occur at the same field strengths. Also, the two different CT scenarios both lead to a weak Aufbau principle violation:[23] Although the Aufbau principle is guaranteed within both spin channels separately, one electron should be transferred between the spin channels to fulfill the Aufbau principle in the entire system. In other words, there is an unoccupied KS eigenstate in one of the spin channels that is lower in energy than the highest occupied orbital of the other spin channel. In this way, one type of realization "points back" to the other one, and vice versa. This reflects that physically the transfer of one ↑ electron is as likely as the one of one ↓ electron. The situation is thus reminiscent of the "static correlation" situations that are notoriously difficult for DFT. Yet, GKLI-SIC successfully realizes a one-electron CT by breaking the spin symmetry. The important observation is that the spin-symmetry breaking here occurs in a system with a considerable number of electrons (not just two) and that it is systematic: When we average over (i) and (ii), or (iii) and (iv), or all four possible realizations—which are energetically degenerate—-then there remains no spin polarization. Thus, KS SIC yields the physically correct picture. We therefore argue that spin-symmetry breaking[24,25] can be seen as a positive feature of KS theory.

How exactly KS theory with its multiplicative, local potential realizes the integer CT is an important question. The two lower panels of Fig. 1 depict the GKLI-SIC xc potential of the spin-up channel in which the electron jump occurs [i.e., realization (i)] for three external fields of increasing strength before (left) and after (right) the electron jump. As the field increases, a step structure of increasing height builds up in between the two H chains, together with a relative shift of the potential between D and A sides (lower left panel). With these features the SIC xc potential works against a spurious fractional CT. After the field has become so strong that an electron transfers from D to A, another important feature

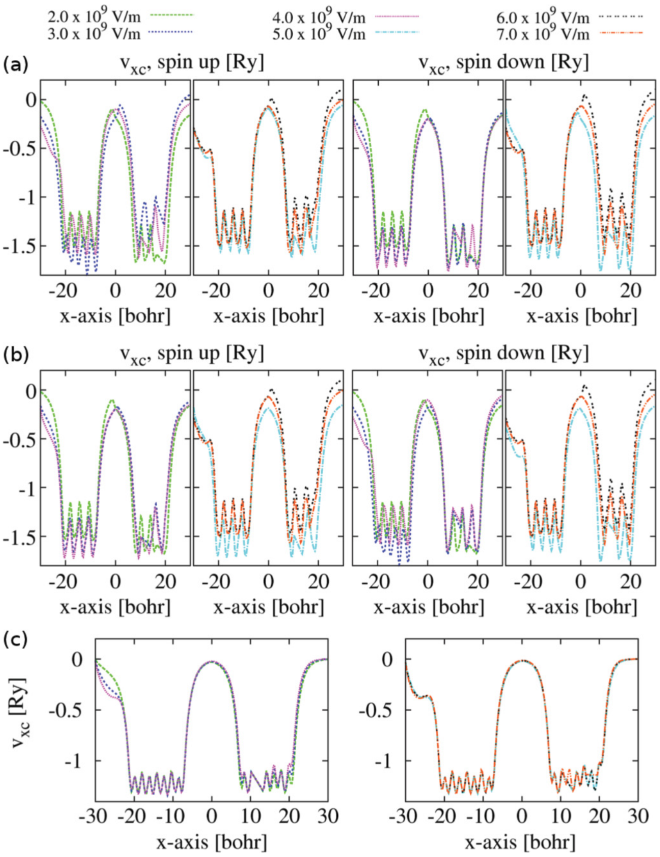

FIG. 2. (Color online) (a) depicts the GKLI-SIC xc potential along the x axis for external fields of strengths from 2.0×10^9 to 7.0×10^9 V/m. The up-spin v_{xc} is shown in the left two figures and the down-spin one in the right two figures. Both spin channels contain eight electrons. Step structures develop in v_{xc} of different spin channels and at different field strengths (see discussion in the main text). (b) depicts xc potentials similar to (a), but for the situation that after the first electron jump nine electrons are in the spin-down and seven in the spin-up channel. (c) shows v_{xc} of LSDA, which is identical for both spin channels and shows no step structures.

manifests: A *reverse* step and potential shift appear, keeping the newly arrived electron on A (lower right panel). With a further increase of the external field these features become less pronounced, "making room" for the next electron transfer.

Figure 2 extends the picture by comparing both spin channels for a larger range of external fields and for the different realizations that were discussed above. Figure 2(a) shows the realization in which both spin channels contain eight electrons throughout, i.e., this is the type of situation that we just looked at in the lower half of Fig. 1. As just discussed, with increasing external field the potential on the A side is shifted upwards with respect to the potential on the D side and a step appears in v_{xc}. As long as no electron transfer has occurred, both spin channels are the same. But as the external field goes beyond 2.5×10^9 V/m, spin symmetry breaks as one electron transfers in one of the spin channels. For the sake of this discussion and consistent with Fig. 1 we assume that the transferred electron has up spin. Then, the up-spin xc potential [left part of Fig. 2(a)] builds up the reverse step that we already discussed in the lower right panel of Fig. 1, and the right part of Fig. 2(a) shows that the step simply vanishes in the down-spin potential. As the external field is further increased, the step in the up-spin v_{xc} decreases, as discussed in Fig. 1, but a new step rises in the spin-down channel. This new step counteracts the second electron transfer, until finally a spin-down electron is transferred to A. After this second transfer, we observe a step in both spin channels that supports both electrons to stay on A.

Figure 2(b) depicts the GKLI-SIC xc potential for the situation that after the first electron jump nine electrons are in the spin-down and seven in the spin-up channel, i.e., number (iii) of the four realizations that were discussed above. In this case, the electron changes spin assignment when it hops from D to A and one more electron of each spin channel is on A than on D after the first electron jump. Therefore, the reverse step discussed in the previous situation builds up in both spin channels to counteract back transfer of the electron, but is less pronounced. These steps decrease as the field strength increases further, and new steps counteracting the second electron jump gradually emerge in v_{xc} of spin up and down. With the second electron jump, the symmetric distribution of eight electrons per spin channel is recovered and steps in both spin channels keep the electrons on A.

Figure 2(c) demonstrates that the step structures are missing completely in v_{xc} of the LSDA functional. This explains why the LSDA leads to a gradual transfer of charge instead of realistic integer electron jumps.

Finally, we investigate the CT behavior of our model system time dependently. To this end, we apply an external field in dipole approximation along the x axis (grid spacing 0.4 bohr)

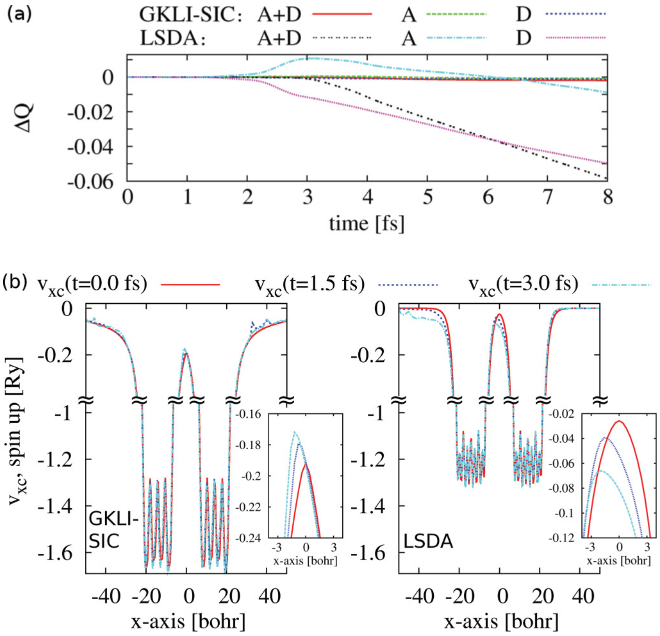

FIG. 3. (Color online) (a) Change of charge ΔQ of the acceptor (A), the donor (D), and the sum of A and D during time propagation using the GKLI-SIC and LSDA potentials and an external field of 8.0×10^9 V/m (see text). (b) Snapshots of the TD v_{xc} taken at different times. Left: GKLI-SIC. Right: LSDA. The insets in each case enlarge the xc potential in between the two chains. With time the potential barrier between A and D decreases for LSDA, but increases for GKLI-SIC.

and increase the field strength linearly within the first two fs of the propagation from zero to 8.0×10^9 V/m and then keep it constant. As part of the density may be accelerated to the boundary of our grid, we use an absorbing boundary to prevent this density from being spuriously reflected back to the system. Figure 3(a) reveals notable differences between LSDA and GKLI-SIC already at the early stages of the time evolution: In LSDA, almost from the start, a notable fraction of charge transfers from D to A. In addition, we observe ionization of the system at later times as fractions of the density arrive at the left boundary. GKLI-SIC shows a different behavior, as the integrated charges differ only slightly from their initial values.[26] This behavior may again be understood in terms of v_{xc} structures. Figure 3(b) shows snapshots of the TD xc potential. In analogy to the previously discussed static step structures, for GKLI-SIC a TD feature that counteracts spurious CT emerges between the chains. Due to the slowness of the tunneling process the buildup of the step occurs slowly and it is thus less pronounced here than in the static case. Steps also occur at the outer system boundaries and prevent the system from being ionized. The LSDA v_{xc} misses such structures. Instead, the potential barrier decreases when charge moves so that CT is too easy and spurious ionization occurs. Observing transfer of an integer charge is not possible with the present setup in either case, as the absorbing boundary changes the norm of the density and we thus observe not only effects of the transfer, but also effects of the boundary. Schemes such as the one of Ref. 14 can overcome this hurdle. Yet, our setup here already shows that also in a truly TD simulation the KS SIC approach cures deficiencies that standard functionals have with respect to the type of CT that is relevant for transport scenarios.

In conclusion, we showed that KS SIC enforces the important principle of integer preference in CT via an interplay of step structures and reverse-step structures appearing in turn in the different spin channels. KS SIC appears as a readily applicable, parameter-free functional that cures decisive transport deficiencies and may provide guiding lines for the further development of functionals that are useful for a real-time, first-principles description of transport.

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