Energy lowering of current-carrying single-particle states in open-shell atoms due to an exchange-correlation vector potential

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Abstract

Current-density-functional theory is used to perturbatively calculate single-particle energies of open-shell atoms prepared in a current-carrying state. We focus on the highest occupied such energy, because its negative is, in principle, the exact ionization energy. A variety of different density functionals and calculational schemes are compared with each other and experiment. When the atom is prepared in a current-carrying state, a current-dependent exchange-correlation functional is found to slightly lower the single-particle energy of the current-carrying orbital, as compared to a calculation using standard (current independent) density functionals for the same system. The current-dependent terms in the exchange-correlation functional thus provide additional stabilization of the current-carrying state.

Keywords: density-functional theory, atomic energy levels, current density, magnetism, ionization energies
I. INTRODUCTION

Density-functional theory (DFT) [1, 2, 3, 4] is widely recognized as a powerful reformulation of the many-electron problem in terms of the charge-density distribution $n(r)$. In practice the most common version of DFT is spin-DFT (SDFT), which employs spin-resolved charge densities $n_\uparrow(r)$ and $n_\downarrow(r)$. While SDFT satisfactorily accounts for magnetic effects associated with the electron spin, it does not explicitly deal with magnetic effects associated with the current density. In the presence of symmetry-broken states with orbital currents (or in strong external fields), a useful alternative to SDFT is provided by current-DFT (CDFT) [5, 6, 7], which allows explicit calculation of the orbital currents and their effect on, e.g., total and single-particle energies. In CDFT the exchange-correlation ($xc$) energy $E_{xc}$ depends on $n(r)$ and the current density

$$j_p(r) = \frac{1}{2i} \sum_k [\psi_k^*(r) \nabla \psi_k(r) - (\nabla \psi_k^*(r)) \psi_k(r)]$$

(atomic units are used in all equations). The derivative of the functional $E_{xc}[n, j_p]$,

$$A_{xc}(r) = \frac{1}{c} \frac{\delta E_{xc}[n, j_p]}{\delta j_p(r)},$$

(2)

gives rise to an $xc$ vector potential $A_{xc}$ in the Kohn-Sham equations, in addition to the usual scalar $xc$ potential $v_{xc}(r) = \delta E_{xc}/\delta n(r)$ [5, 6, 7]. Within (S)DFT $A_{xc} \equiv 0$. Consequences of a nonzero $A_{xc}$ are little explored in quantum chemistry.

Both SDFT and CDFT share the fundamental property that the negative of the highest occupied single-particle eigenvalue equals the exact first ionization energy $I$ [8]. It is well known that in actual (approximate) SDFT calculations the highest occupied eigenvalue provides only an unsatisfactory approximation to $I$ if the local-density approximation (LDA) or any of the common generalized-gradient approximations (GGA’s) are used. The main reason for this failure is incomplete self-interaction correction (SIC). We have recently explored numerically the question if the application of CDFT corrections on top of a converged SDFT LDA calculation can mitigate this problem, or reduce the remaining difference to experiment after a SIC has been applied [9].

This investigation was partially motivated by the observation that in order to prepare a current-carrying single-particle state in an atom one must selectively occupy certain $m$-substates, and leave others unoccupied. In the absence of orbital currents and external fields
all single-particle states differing only in the occupation of $m$-substates are degenerate, but in
the presence of currents this degeneracy is broken, and it becomes a legitimate question to ask
if one of the resulting single-particle energies is a better approximation to the experimental
$-I$ than the one obtained by spherical averaging (i.e., restoring the original degeneracy).
This becomes an interesting question in particular for open-shell systems, where orbital
currents can flow. The numerical results obtained in Ref. [9] did not allow to give a conclusive
answer since, although the proposed calculation turned out to be numerically feasible, no
systematic improvement of ionization energies with respect to SDFT was achieved. While
this was discussed in some detail in Ref. [9], another interesting aspect of those data was
mentioned there only in passing, namely that the current-dependent correction tends to
lower the single-particle energy, as compared to an (S)DFT calculation for the same state.

This lowering suggests that inclusion of the current-dependent part of the full exchange-
correlation functional — and hence of $A_{xc}$ — provides extra stabilization of the current-
carrying state, relative to a current-independent calculation for the same state. In the present
paper we continue this investigation of current-carrying single-particle states, and show that
the lowering of the single-particle energy of the current-carrying orbital due to $xc$ effects is
robust against a variety of technical and conceptual changes in the calculational procedure.

II. METHODS

In general, the ionization energy of a many-body system is defined as $I = E(N - 1) -
E(N)$, where $E(M)$ is the many-body ground-state energy of the $M$-electron system. Simi-
larly, the current flowing in a many-body system in the absence of externally applied mag-
netic fields is the expectation value of

$$\hat{J}_p(r) = \frac{1}{2i} \sum_i \nabla_i \delta(r - r_i) + \delta(r - r_i) \nabla_i,$$  \hspace{1cm} (3)

taken with the many-body wave function. Within DFT, SDFT and CDFT the ioniza-
tion energy can also be calculated from the negative of the highest occupied single-particle
eigenvalue [8], and within CDFT (but not DFT or SDFT) the current can also be calculated
from Eq. (1), which is obtained by taking the expectation value of $\hat{J}_p(r)$ with the Kohn-Sham
Slater determinant [5, 6, 7]. Note that these are exact properties, which hold regardless of
the fact that the quantum numbers $(l, m)$ used to label the noninteracting atomic states are
not the same used for the interacting states, $^{2S+1}L_J$.

Consequently, it is not necessary to construct current-carrying many-body states to calculate the ionization energy of the current-carrying system. The (at least $m$-fold degenerate) highest eigenvalue of the unperturbed noninteracting Kohn-Sham system already yields the ionization energy in the absence of currents. A current-carrying state is then described by selectively occupying single-body substates with definite value of $m$, obtained by multiplying a numerical radial function with the appropriate spherical harmonic $Y_{m}^{l}(\theta, \Phi)$. Within SDFT these current-carrying states are still degenerate, but CDFT is capable of picking up the energetic contribution of the current to the highest occupied single-particle state, and will thus in general make a different prediction for the ionization energy. The original motivation for this work was to see if the resulting ionization energies of current-carrying single-particle states were better approximations to the experimental ones, in particular for atoms whose many-body configuration has $L \neq 0$ or $J \neq 0$. This expectation was not borne out by the numbers in Ref. [9]. The present paper is concerned with the question whether this is due to computational approximations made in that work, or a real physical phenomenon.

The computational approach of Ref. [9] was to apply CDFT not self-consistently, but perturbatively, following a converged (S)DFT calculation. This strategy, denoted perturbative CDFT (pCDFT) was proposed by one of us in Ref. [10], and leads to a major simplification of the CDFT equations. While similar in spirit to post-LDA applications of GGA [11], or post-GGA applications of Meta-GGA [12, 13], pCDFT is not simply obtained by substituting SDFT orbitals in CDFT expressions (as in ‘post’ methods), but amounts to low-order perturbation theory with respect to $A_{xc}$, taking as unperturbed system the Kohn-Sham equations of (S)DFT. In this sense there is some conceptual similarity between pCDFT and Möller-Plesset perturbation theory, and also between pCDFT and the SDFT derivation of the Stoner approximation to the theory of itinerant ferromagnetism [14]. Since the basic equations of CDFT and pCDFT have been described in detail in Refs. [5, 6, 7] and [9, 10], respectively, we refer the interested reader to these papers, and here focus directly on numerical results and their interpretation. For later reference we record, however, the explicit expression for the perturbative shift of the $k$’th single-particle eigenvalue due to the presence of the current in the orbital $\psi_k(r)$ [10],

$$\delta \epsilon_k = \frac{1}{e} \int d^3r \mathbf{j}_{p,k}(r) \cdot \mathbf{A}_{xc}[n,\mathbf{j}_p](r),$$  \hspace{1cm} (4)
where
\[ j_{p,k}(r) = \frac{1}{2k} [\psi_k^*(r) \nabla \psi_k(r) - (\nabla \psi_k^*(r)) \psi_k(r)] . \] (5)

Our previous results for the pCDFT corrections to the highest occupied DFT-LDA eigenvalue for open-shell atoms prepared in a current-carrying state indicate that, without applying a SIC, CDFT eigenvalues are about as far from the experimental first ionization energies as SDFT ones, whereas after applying a SIC the remaining difference between experiment and LDA-SIC is comparable to (but still larger than) the pCDFT corrections \[ 9 \]. We found the pCDFT corrections to be mostly negative, i.e., to stabilize the current-carrying state as compared to a (current-insensitive) SDFT calculation for the same current-carrying configuration. Since LDA+SIC sometimes underestimates and sometimes overestimates the true ionization energy, a negative correction cannot consistently improve agreement with experiment. However, the fact that the single-particle energy is lowered upon including \( A_{xc} \) is interesting in its own right, even if the deviation of LDA-SIC from experimental ionization energies is not dominated by current-related effects, and it is important to check whether it is robust against changes in the approximations and computational procedures.

To further investigate these issues we consider, in the present paper, three methodological changes with respect to the calculations of Ref. \[ 9 \]. First, we obtain the orbitals and energies of the unperturbed system (i.e., the DFT Kohn-Sham equations) not with LDA but from two common GGAs: B88-LYP \[ 11, 16 \] and PW91 \[ 17 \]. Either choice should yield an improved description of the input orbitals needed for perturbatively calculating the effect of \( A_{xc} \). In a first step we made only this change, to single out the consequences of passing from LDA to GGA without changing anything else.

In a second step, we analyse the role played by the orbital susceptibility \( \chi \) in the CDFT LDA, \( E_{xc}^{LDA}[n,j_p] \) (cf. Eqs. (8,9) of Ref. \[ 9 \] or Eq. (17) of Ref. \[ 5 \] for the explicit form of this functional). In the spirit of the ordinary LDA, this functional is derived from the interacting uniform electron gas \[ 5, 6, 7 \]. Current-related many-body effects enter via the orbital (Landau) susceptibility \( \chi \), which has been calculated numerically for the electron gas by Vignale, Rasolt and Geldart \[ 18 \] and parametrized by Lee, Colwell and Handy (LCH) \[ 19, 20, 21 \] and in Ref. \[ 9 \]. We observe that of these two parametrizations the five-term interpolation \[ 9 \]

\[ s_5(r_s) = 1.1038 - 0.4990 r_s^{1/3} + 0.4423 \sqrt{r_s} - 0.06696 r_s + 0.0008432 r_s^2, \] (6)
provides a better fit of the 10 data points of Ref. [18], while the LCH expression

$$s_{LCH}(r_s) = (1.0 + 0.028 r_s) \exp(-0.042 r_s)$$

(7)

has the correct limiting behaviour as \( r_s \to 0 \) and \( r_s \to \infty \), and a smoother derivative. In addition to calculations employing consistently the LCH or the five-term interpolations, we thus tentatively also implemented a hybrid calculation that employs (6) for \( s(r) \), but (7) for its gradient

$$\nabla s(r) = \frac{ds(r_s)}{dr_s} \frac{dr_s(n)}{dn} \nabla n(r).$$

(8)

In these expressions \( r_s \) is related to the density via \( n = 3/4\pi r_s^3 \), and \( s = \chi/\chi_0 \), where \( \chi_0 \) is the (known) orbital susceptibility of the noninteracting electron gas.

Third, we observed that either expression for the orbital susceptibility is derived from the Vignale-Rasolt-Geldart data for the electron gas [18], which clearly has a susceptibility that is very different from that of an open-shell atom. We thus also considered a semi-empirical expression of the LCH form,

$$s_{se}(r_s) = (1.0 + b r_s^c) \exp(-0.042 r_s),$$

(9)

whose parameters \( b \) and \( c \) were fitted to reproduce the experimental value of \(-I\) for the Carbon atom and then employed unchanged for the other atoms. This semi-empirical calculation can provide a valuable additional piece of information: If it turned out that with a semi-empirical susceptibility, fitted to one atom only, good ionization energies were obtained also for the other atoms this would suggest that the form of the employed functional for \( A_{xc} \) is in principle correct, but handicapped by the input data from the electron gas. If, on the other hand, replacing the electron-gas susceptibility by a semi-empirical one did not improve the ionization energies for the other atoms considered, this would suggest that the functional itself may not be adequate for this type of calculation, independently of the origin of the susceptibility used in it.

III. RESULTS AND DISCUSSION

Our results are summarized in Table I, which for each atom and current-carrying (cc) single-particle (sp) state considered lists the difference \( \Delta I \) between the LDA+SIC data of Ref. [15] and the experimental data [22]. The other columns contain data for the negative
of the pCDFT shift of the highest occupied eigenvalue, \(-\delta \epsilon\), obtained from Eq. (4) with the various calculational schemes described above. In every case the unperturbed DFT orbitals and energies were obtained using the fully numerical (basis-set free) Kohn-Sham code \textit{opmks} [23].

In Table I the current-carrying single-particle states are characterized succinctly by the values of \(m\) of the single-particle orbitals occupied in the open shell. As an example of our notation, for the Carbon atom the numbers \(\{1, 0\}\) in the second column mean that of the two electrons in the open p-shell one is in a state with \(m = 1\), the other in a state with \(m = 0\). Note that states with \(m = 0\) do not make a contribution to either \(j_P\) or \(A_{xc}\). States with \(m = 1\) and with \(m = -1\) make a contribution of same magnitude but opposite sign to each \(j_P\) and \(A_{xc}\). Hence both lead to the same value for the resulting energy shift, which is determined by the product \(j_P \cdot A_{xc}\). Here we consider only one single-particle configuration for each open shell. Ref. [9] contains data for other choices of occupation.

We now systematically discuss each of the calculational schemes described above, and the resulting conclusions. Although we do not find that ionization energies are systematically improved by pCDFT, we still present, in Sec. III A, a rather detailed discussion of the corresponding numbers, since they justify our conclusion that the difference between experiment and LDA+SIC is most likely \textit{not} due to current-related effects. In Sec. III B we then turn to the possible self-induced stabilization of current-carrying states via formation of a nonzero \(xc\) vector potential \(A_{xc}\).

### A. Ionization energies

In column three of Table I we reproduce the results obtained with LDA for \(v_{xc}\) and the LCH expression (7) for \(s = \chi/\chi_0\). These are the same data listed in Table I of Ref. [9] and are repeated here for comparison purposes [24]. As pointed out in Ref. [9], there is no overall systematic trend as to when the pCDFT correction improves the LDA+SIC value and by what margin, although we note that for the first-row elements there is a systematic correlation between the atomic number \(Z\) and the size of \(\Delta I\), while for first and second-row elements there is a correlation between \(\delta \epsilon\) and the size of the current. The deviation between the LDA+SIC+pCDFT values and experiment is, however, in most cases larger than the pCDFT correction itself, which leads us to believe that other effects, not related to orbital
currents, must play a more important role in explaining the remaining differences. Some possible sources for these are explored in the following.

The next two columns list data obtained using the B88-LYP and PW91 GGAs for \( v_{xc} \). As anticipated in Ref. [9], the resulting changes are very small. This shows that for the remaining calculations we can use either functional, without significant changes in the final numbers. It also implies that an improved treatment of the unperturbed system does not improve agreement with experiment, suggesting, as expected, that the critical ingredient in the calculation is the current-dependent part of the full \( xc \) functional, not the charge-density dependent one.

The following column contains results obtained with the five-term expression \((6)\) for the susceptibility ratio \( s = \chi/\chi_0 \) in the current-dependent part of the functional. These values replace the ones listed in Table I of Ref. [9], which suffered from a numerical error. This correction does lead to somewhat different numbers, but does not affect any of the conclusions drawn in Ref. [9]. In particular, it remains still true that the numbers are more strongly dependent on the choice made for the orbital susceptibility than on the one for the charge-dependent part of the functional (LDA/GGA). The next column contains data from the hybrid implementation using the LCH expression \((7)\) for determining \( \nabla s(r) \) and the five-term expression \((6)\) for \( s(r) \). The results are on average closer to those obtained with only the LHC expression than to those obtained with only the five-term interpolation.

Finally, we list data obtained with the semi-empirical expression \((9)\). In this case the value for the \( m_1 = 1 \) and \( m_2 = 0 \) single-particle (Kohn-Sham) configuration of the Carbon atom was used to determine the parameters \( b \) and \( c \), while the other values were obtained holding these parameters fixed. The optimal values \( b = 0.161 \) and \( c = 0.689 \) exactly reproduce the first ionization energy of Carbon. This procedure allows us to disentangle the form of the functional from the electron-gas origin of the original expression for the susceptibility. Clearly, some improvement for the other atoms is obtained in this way, in particular as regards the sign of the corrections, but the improvement is still not fully satisfactory or consistently obtained for all considered systems. This observation suggests that future work should go into deducing CDFT functionals adequate for finite systems, instead of improving on the electron-gas data.

Our conclusion from all these calculations is that currents in open shells do not make a decisive contribution to atomic ionization energies.
B. Possible self-stabilization of current-carrying states

We now focus on the CDFT shifts $\delta \epsilon$ themselves, independently of the question how
they change ionization energies. For this purpose we have to disregard the second-to-last
(semi-empirical) column of Table I because the values of $\delta \epsilon$ listed there were forced to have
the sign and size required to obtain perfect agreement with experimental ionization energies
for the Carbon atom, and can thus not be used to discuss sign and size of the calculated
correction.

A notable feature of the non-empirical data collected in Table I is that, with exception of
a few cases using the five-term interpolation for the derivative of $\chi$, the pCDFT correction
$\delta \epsilon$ is negative throughout. (Data obtained with the five-term interpolation for the derivative
of the orbital susceptibility may be less reliable because of the wrong $r_s \to 0$ and $r_s \to \infty$
limits and the polynomial fit involved.) To appreciate that this lowering of the single-
particle eigenvalue of the current-carrying state is not entirely trivial, consider the following
two observations: (i) Both $j_p(r)$ and $A_{xc}(r)$ individually have positive and negative values
for some $r$, it is only the integral over their product, Eq. (4), which is negative. (ii) $A_{xc}$ itself
is nonzero only due to the presence of the current, so that the energy lowering is not simply
due to the accomodation of a current in the system in response to some external field.

On the single-particle level, inclusion of the $xc$ vector potential thus provides additional
stabilization of the current-carrying state, as compared to ordinary DFT or SDFT calcu-
lations, which are insensitive to the current. While this stabilization is apparently not a
decisive factor in determining ionization energies, it may have significant consequences in
other situations, since it implies that a proper assessment of the energetics of processes
involving electron flow should consider the $xc$ effects associated with charge currents, and
not only those associated with the charge density. In the present case the pCDFT shifts
are relatively small, but within the accuracy of modern density functionals. A systematic
exploration of current-related many-body effects could hold some surprises, in particular for
nearly degenerate or symmetry-broken states, or in the presence of strong external fields.

We stress that this energy lowering is obtained for a fixed current-carrying state, com-
paring a calculation that is insensitive to the current (the LDA of SDFT) with a calculation
that explicitly accounts for current-dependent correlations (the LDA of CDFT, implemented
within pCDFT). A related result was recently reported in Ref. [12] — employing another
current-dependent density functional, not constructed within the framework of CDFT — where the total energies of some current-dependent states were found to be lower in a current-dependent calculation than in a current-independent one.

In this context it is also interesting to recall the suggestion by Rasolt and Perrot[25] that the ground state of a strongly inhomogeneous many-body system can develop spontaneous self-induced currents. This result was obtained using the same formal framework as here (CDFT), but with a quite different choice of the density functional (optimized for two-dimensional systems), and by performing a direct minimization of the total energy (thus avoiding any self-consistent calculations). Clearly a spontaneously current-carrying ground state is an extreme example of self-stabilization, in which the energy lowering due to current-dependent correlations does not only reduce the energy below the one of a current-independent calculation for the same current-carrying state, but even below the one of the not current-carrying state. It remains to be explored whether our above result, obtained for single-particle energies, can be related to this type of novel many-body ground state.

IV. SUMMARY

Concerning the calculation of ionization energies, we find that neither the description of the charge-dependent part of the functional (LDA or GGA) nor the quality of the interpolation used for the electron-gas susceptibility (LCH or five-term interpolations) decisively influence the quality of the final results, whereas a semi-empirical expression for the susceptibility yields better results than expressions based on the electron gas. Although it is thus possible that current-dependent functionals designed specifically for finite systems will further improve results, as compared to electron-gas based functionals, the remaining differences to experiment are sufficiently large to suggest that they are not due to orbital currents.

While ionization energies thus do not seem to be systematically affected by current-dependent corrections, the single-particle energy of the current-carrying states is. The self-stabilization of these states by means of the exchange-correlation vector potential, $A_{xc}[n,\mathbf{j}_p]$, is found to be robust against a variety of numerical and conceptual changes in the computational procedure. This self-stabilization is completely missed in current-independent calculations, but may be relevant for studies of the energetics of processes
involving electron flow and states with orbital currents in general.

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TABLE I: Current-induced changes in the ionization energies of atoms with open $p$ ($B$ to $Cl$) and $d$ ($Sc, Y$) shells. Column one: atom. Column two: selected current-carrying (cc) single-particle (sp) state, characterized by the occupied $m$-substates in the open shell. As in Ref. [9] we have normally considered several current-carrying configurations for each atom, but here we list only one for each, since the numbers for the others do not affect any of the conclusions. Column three: Negative of the pCDFT correction obtained with LDA, using the LCH expression for the susceptibility $\chi$. Column four: Negative of the pCDFT correction obtained with B88-LYP GGA, using the LCH $\chi$. Column five: Negative of the pCDFT correction obtained with PW91 GGA, using the LCH $\chi$. Column six: Negative of the pCDFT correction obtained with LDA using the five-term (5t) Eq. (6) for $\chi$. Column seven: Negative of the pCDFT correction obtained with LDA using Eq. (6) for $\chi$ itself, but the LCH expression for its gradient. Column eight: Negative of the pCDFT correction obtained with LDA, using the semi-empirical (se) expression for $\chi$. Column nine: deviation of zero-current ionization energy calculated within LDA-SIC [15] from experimental ionization energies [22]. All values are in eV.

| cc sp state | $-\delta\epsilon$ | $-\delta\epsilon$ | $-\delta\epsilon$ | $-\delta\epsilon$ | $-\delta\epsilon$ | $-\delta\epsilon$ |
|-------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|             | LDA               | B88LYP            | PW91              | LDA               | LDA               | LDA               |
| B           | 1                 | 0.072             | 0.070             | 0.071             | 0.016             | 0.034             | -0.32             | -0.018             |
| C           | 1,0               | 0.045             | 0.044             | 0.044             | -0.012            | 0.023             | -0.34             | -0.34             |
| N           | 1,1,0             | 0.14              | 0.14              | 0.14              | -0.085            | 0.086             | -1.3              | -0.42             |
| O           | 1,1,0,0           | 0.11              | 0.11              | 0.11              | -0.10             | 0.39              | -1.2              | -0.71             |
| F           | 1,1,0,0,-1        | 0.023             | 0.023             | 0.023             | -0.032            | 0.17              | -0.27             | -1.2              |
| Al          | 1                 | 0.043             | 0.043             | 0.044             | 0.025             | 0.027             | -0.092            | -0.42             |
| Si          | 1,0               | 0.022             | 0.021             | 0.021             | 0.0061            | 0.016             | -0.093            | 0.35              |
| P           | 1,1,0             | 0.059             | 0.059             | 0.059             | 0.0082            | 0.046             | -0.34             | 0.42              |
| S           | 1,1,0,0           | 0.044             | 0.044             | 0.044             | -0.0054           | 0.082             | -0.32             | -0.050            |
| Cl          | 1,1,0,0,-1        | 0.0091            | 0.0091            | 0.0091            | -0.0017           | 0.020             | -0.073            | -0.11             |
| Sc          | 1                 | 0.036             | 0.036             | 0.036             | 0.012             | 0.043             | -0.26             | -                  |
| Y           | 1                 | 0.035             | 0.034             | 0.034             | 0.015             | 0.035             | -0.19             | -                  |