PHYSICAL REVIEW B **89**, 195134 (2014)

Bridging density-functional and many-body perturbation theory: Orbital-density dependence in electronic-structure functionals

Andrea Ferretti,[1,*] Ismaila Dabo,[2] Matteo Cococcioni,[3,†] and Nicola Marzari[4]
[1]*Centro S3, CNR–Istituto Nanoscienze, 41125 Modena, Italy*
[2]*Department of Materials Science and Engineering, Materials Research Institute, and Penn State Institutes of Energy and the Environment, The Pennsylvania State University, University Park, Pennsylvania 16802, USA*
[3]*Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, USA*
[4]*Theory and Simulations of Materials, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland*

(Received 17 February 2012; revised manuscript received 18 April 2014; published 27 May 2014)

Energy functionals which depend explicitly on orbital densities, rather than on the total charge density, appear when applying self-interaction corrections to density-functional theory; this is, e.g., the case for Perdew-Zunger and Koopmans-compliant functionals. In these formulations the total energy is not invariant under unitary rotations of the orbitals, and local, orbital-dependent potentials emerge. We argue that this is not a shortcoming, and that instead these potentials can provide, in a functional form, a simplified quasiparticle approximation to the spectral potential, i.e., the local, frequency-dependent contraction of the many-body self-energy that is sufficient to describe exactly the spectral function. As such, orbital-density-dependent functionals have the flexibility to accurately describe both total energies and quasiparticle excitations in the electronic-structure problem. In addition, and at variance with the Kohn-Sham case, orbital-dependent potentials do not require nonanalytic derivative discontinuities. We present numerical solutions based on the frequency-dependent Sham-Schlüter equation to support this view, and examine some of the existing functionals in this perspective, highlighting the very close agreement between exact and approximate orbital-dependent potentials.

DOI: 10.1103/PhysRevB.89.195134 PACS number(s): 71.15.−m, 71.10.−w, 78.20.Bh

I. INTRODUCTION

Density-functional theory (DFT) is one of the most used and most successful approaches to solve accurately and inexpensively the electronic-structure problem for interacting electrons [1]. Being exact in principle but approximate in practice, it has seen much theoretical work spent in searching for accurate approximations of the unknown total-energy functional [2]. Some shortcomings identified early on stem from the remnants of electronic self-interactions [3] in the functionals used, leading to qualitative failures in describing fractional occupations [4–7], and by extension dissociation processes, charge-transfer excitations [8–10], and single-particle energy levels [11,12]. Self-interaction-corrected (SIC) functionals able to deal with these failures have been proposed [3,13–15]; these depend explicitly on individual orbital densities $\rho_i(\mathbf{r})$, and their direct minimization leads to local but orbital-dependent Hamiltonians that are not invariant for unitary rotations of the electronic wave functions. Such schemes have been labeled orbital-density-dependent (ODD) functionals [16], and Perdew-Zunger (PZ) [3] and Koopmans-compliant (KC) [14,15,17] functionals belong to this class.

This loss of unitary invariance and the emergence of orbital-dependent operators may hint at an intrinsic strength of ODD functionals, rather than a shortcoming, which readily emerges from a direct comparison with many-body formulations [18]. In fact, when solving orbital equations with frequency-dependent (i.e., dynamical) potentials, such as the self-energy, a simplified representation of the frequency space by means of discrete poles is often adopted, leading to the quasiparticle (QP) approximation [18] and orbital-dependent potentials. We suggest here that ODD nonunitary invariant schemes can be seen as QP approximations to many-body potentials, and argue that local and orbital-dependent Hamiltonians have the flexibility to describe accurately not only total energies but also orbital energies for the problem at hand. We also show how orbital-dependent potentials naturally capture the physics of electrons' additions and removals, without requiring derivative discontinuities in the potentials, as is otherwise the case in density-functional theory. Accurate numerical solutions of a one-dimensional (1D) model are presented, based on Sham-Schlüter equations, to support these arguments and to further illustrate the theory, followed by ODD calculations of the electronic structure in realistic case studies, and their comparison with experimental photoemission data. The central message of this paper is that broken unitary invariance is indeed not an accident, but rather a natural bridge to more general frameworks that allow one to describe with functional theories many-body spectral properties.

II. THEORETICAL FRAMEWORK

We briefly formulate the problem by considering an expression for the total energy where the exchange-correlation functional becomes explicitly dependent on orbital densities, i.e., $E^{\mathrm{OD}}_{\mathrm{xc}}[\{\rho_i\}]$. As alluded to above, this is, for instance, the case for the PZ and KC functionals. Following this notation, the total charge density $\rho(\mathbf{r})$ is written in terms of the orbital densities $\rho_i(\mathbf{r})$ of the occupied orbitals $\phi_i(\mathbf{r})$:

$$\rho(\mathbf{r}) = \sum_i^{\mathrm{occ}} \rho_i(\mathbf{r}) = \sum_i^{\mathrm{occ}} |\phi_i(\mathbf{r})|^2. \tag{1}$$

---

[*] Corresponding author: andrea.ferretti@nano.cnr.it

[†] Present address: Theory and Simulations of Materials, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland.

These energy functionals are minimized with respect to the above set of orbitals, together with the orthogonality constraint

$$\frac{\delta}{\delta\langle\phi_i|}\left[E-\sum_{jk}\Lambda_{jk}\langle\phi_k|\phi_j\rangle\right]=0 \tag{2}$$

yielding the Euler-Lagrange equations

$$h_i^{\rm OD}|\phi_i\rangle \equiv h_0|\phi_i\rangle + v_{{\rm xc},i}^{\rm OD}|\phi_i\rangle = \sum_j \Lambda_{ji}|\phi_j\rangle, \tag{3}$$

where $h_0 = T + v_{\rm ext} + v_{\rm H}$ and $v^{\rm OD}_{{\rm xc},i}(\mathbf{r}) = \frac{\delta E^{\rm OD}_{\rm xc}}{\delta\rho_i(\mathbf{r})}$. At the minimum, the Pederson condition [19]

$$\langle\phi_i|h_i|\phi_j\rangle = \langle\phi_i|h_j|\phi_j\rangle \tag{4}$$

is satisfied and the Λ matrix becomes Hermitian [20,21]. As was recognized long ago [19], as a consequence of Eq. (4) the orbitals $\{\phi_i\}$ minimizing the ODD functional (henceforth labeled variational orbitals) are usually localized. Nevertheless, Λ can be diagonalized via a unitary transformation ($\Lambda = U^\dagger\lambda U$), allowing [19,22] to define canonical (delocalized) orbitals $|\psi_m\rangle = \sum_i |\phi_i\rangle\, U^\dagger_{im}$ and to cast Eq. (3) as:

$$\left[h_0+\bar{v}^{\rm OD}_{{\rm xc},m}\right]|\psi_m\rangle=\lambda_m\,|\psi_m\rangle. \tag{5}$$

The canonical potentials $\bar{v}^{\rm OD}_{{\rm xc},m}(\mathbf{r})$ are related to the variational ones $v^{\rm OD}_{{\rm xc},i}(\mathbf{r})$ through the transformation

$$\bar{v}^{\rm OD}_{{\rm xc},m}(\mathbf{r})\,\psi_m(\mathbf{r})=\sum_i v^{\rm OD}_{{\rm xc},i}(\mathbf{r})\,U^\dagger_{im}\,\phi_i(\mathbf{r}). \tag{6}$$

A similar construction can be worked out also for empty states [17,23]. While the interpretation of the eigenvalues of Λ as (canonical) orbital energies according to Eq. (5) has been recently questioned [24], it is common practice [19,22] and has been clearly argued for in Ref. [21]. Our findings support such interpretation, as shown by the numerical examples presented below.

We point out first that similar equations, where each orbital is related to a different Hamiltonian are routinely found when dealing with frequency-dependent potentials. In order to address this point, we refer to Green's function theory [18,25,26], one of the most well-known approaches involving dynamical potentials [the nonlocal self-energy $\Sigma(\mathbf{r},\mathbf{r}',\omega)$]. In fact, when computing the interacting Green's function (GF) G, the full complexity of the many-body problem can be embodied in the self-energy Σ, leading to a non-Hermitian frequency-dependent operator. Once an approximate Σ is defined (as it is done, e.g., in the GW approach), the interacting GF can be obtained by inverting the Dyson equation

$$G(\omega) = [\omega I - h_0 - \Sigma(\omega)]^{-1} \tag{7}$$

(here spatial indices are left implicit). The exact solution of Eq. (7) can be written as [18,26]

$$[h_0+\Sigma(\omega)]|\psi_{s\omega}\rangle = E_s(\omega)|\psi_{s\omega}\rangle \tag{8}$$

$$G(\omega)=\sum_s \frac{|\psi_{s\omega}\rangle\langle\psi^{s\omega}|}{\omega-E_s(\omega)}, \tag{9}$$

showing that for each frequency ω a non-Hermitian eigenvalue problem for $h_0+\Sigma(\omega)$ has to be solved, with complex orbital energies $E_s(\omega)$ and biorthogonal left-right eigenvectors $\langle\psi^{s\omega}|\psi_{s'\omega}\rangle=\delta_{ss'}$ (a covariant-contravariant notation has been adopted). A common approach to obtaining the solution of Eq. (9) is the quasiparticle (QP) approximation, whereby the continuous index ω is dropped for E's and ψ's, and only some relevant poles are retained. This can be done, e.g., according to the condition

$$E_s\left(z_m^{\rm QP}\right) = z_m^{\rm QP}, \tag{10}$$

using, if needed, an analytical continuation of $E_s(\omega)$ out of the real axis (see, e.g., Ref. [26] for the full mathematical treatment). The quasiparticle approximation is equivalent to representing the most relevant structures of G in Eq. (9) by a finite number of poles. Setting $\Sigma_m^{\rm QP}=\Sigma(z_m^{\rm QP})$, Eq. (8) then becomes:

$$\left[h_0+\Sigma_m^{\rm QP}\right]\left|\psi_m^{\rm QP}\right\rangle = z_m^{\rm QP}\left|\psi_m^{\rm QP}\right\rangle. \tag{11}$$

While Σ here is non-Hermitian, and nonlocal, the similarity between Eqs. (5) and (11) is apparent, and will be one of the central points of this work.

Indeed, this similarity is not restricted to the special case of the self-energy in GF theories, but it is general to any frequency-dependent potential. An interesting case of such potentials has been recently pointed out by Gatti *et al.* in Ref. [27] (see also—closely related—Ref. [28]), where it is shown that a local, Hermitian, dynamical potential $v^{\rm SP}(\mathbf{r},\omega)$ [hereby referred to as the spectral potential (SP)] is flexible enough to reproduce exactly the spectral density $\rho(\mathbf{r},\omega)$ (i.e., the local spectral function) of an interacting system described by the many-body interacting Green's function G:

$$\rho(\mathbf{r},\omega)=\frac{1}{\pi}|{\rm Im}G(\mathbf{r},\mathbf{r},\omega)|. \tag{12}$$

In other words, if instead of the true nonlocal, non-Hermitian $\Sigma(\mathbf{r},\mathbf{r}',\omega)$ a suitable local, real $v^{\rm SP}(\mathbf{r},\omega)$ is used to construct an auxiliary Green's function[1] $G^{\rm SP}$, the resulting $G^{\rm SP}$ can still reproduce the correct spectral density. Note this is not otherwise possible with a local and static potential, such as $v^{\rm KS}(\mathbf{r})$ in KS theory, which can only provide the exact density $\rho(\mathbf{r})$. A frequency-dependent Sham-Schlüter-like equation can be solved to explicitly determine the spectral potential $v^{\rm SP}(\mathbf{r},\omega)$ by imposing that the local spectral functions of $G^{\rm SP}$ and G are the same [27]. Then, for each frequency we have

$$\begin{aligned}\int d\mathbf{r}_1\, v^{\rm SP}(\mathbf{r}_1,\omega)\,{\rm Im}[G^{\rm SP}(\mathbf{r},\mathbf{r}_1,\omega)\,G(\mathbf{r}_1,\mathbf{r},\omega)]\\ = {\rm Im}[G^{\rm SP}\Sigma G]_{\mathbf{r},\mathbf{r}}.\end{aligned} \tag{13}$$

We refer to this equation as the spectral-potential Sham-Schlüter equation (SP-SSE), and we provide in Appendix A a variational derivation of its linearized version, allowing us to define the energy functional associated with the SP-SSE. Applying a discretization of the frequency to $v^{\rm SP}(\mathbf{r},\omega)$ (as is done in QP approximations) we obtain a local and orbital-dependent potential, exactly as in Eq. (5). Thus, orbital-dependent ODD

---

[1] Here $v^{\rm SP}$ and $v^{\rm KS}$ are defined as the xc contribution to the total potential.

Hamiltonians can be used to define quasiparticle approximations to $v^{\text{SP}}(\mathbf{r},\omega)$, and are in principle able to reproduce orbital energies (in this context, we identify orbital energies with the quasiparticle excitations, i.e., the peaks in the spectral function corresponding to the charged excitations of the system at $N\pm1$ particles; such peaks are usually divided [18,29] into main peaks and satellites according to their intensities, and when making a QP approximation only the main peaks are retained).

The frequency dependency (or orbital dependency within the QP approximation) of Σ and v^{SP} makes these methods more general than KS-DFT. In principle, the standard Sham-Schlüter equation (here referred to as KS-SSE) [30,31]

$$\int d\mathbf{r}_1\, v^{\text{KS}}(\mathbf{r}_1) \int \frac{d\omega}{2\pi i}\, e^{i\omega 0^+}\, G^{\text{KS}}(\mathbf{r},\mathbf{r}_1,\omega)G(\mathbf{r}_1,\mathbf{r},\omega) = \int \frac{d\omega}{2\pi i}\, e^{i\omega 0^+}\, [G^{\text{KS}}\Sigma G]_{\mathbf{r},\mathbf{r}} \tag{14}$$

or the optimized-effective potential (OEP) technique [32] could be used to bring a SP framework back to KS-DFT (G^{KS} here is the GF of the KS system), at the price of losing spectral information, as will be argued in the next Sections; similar OEP techniques [22] have also been proposed to bring ODD formulations back into a proper KS framework.

While these approaches are appealing, in this work we argue that orbital-dependent Hamiltonians [as in Eqs. (3) and (5)] can be seen as functional formulations that go beyond DFT and that can address both the total energy and the single-particle spectrum of a given system. The actual accuracy in doing so would depend on the details of the ODD functional, but it is relevant to note that for Koopmans-compliant functionals one can correct orbital energies (and obtain excellent agreement with experiments [11]) while preserving the underlying DFT potential energy surface either very accurately [14] or exactly [33].

III. NUMERICAL MODELS

In order to investigate numerically these ideas we study a 1D model system for a diatomic molecule with eight interacting, spin-unpolarized electrons, using soft Coulomb potentials of the form $v(r) = v_0/\cosh^2(\beta r)$, as in Ref. [10] [the M1 parametrization is reported in Appendix B, and the external potential for this model dimer is depicted in Fig. 1(a), thick black line]. We first compute for this system the self-consistent HF solution, and once the nonlocal HF exchange potential is determined, we obtain from the KS-SSE the local Kohn-Sham potential for which the DFT solution provides exactly the HF ground-state density. Here the HF exchange potential has been taken as the simplest approximation to the electron-electron self-energy. The corresponding $v^{\text{KS}}(\mathbf{r})$ is then the KS exact-exchange potential (EXX) (while EXX usually refers to the solution of the linearized KS-SSE, we solve here the exact KS-SSE). This local $v^{\text{KS}}(\mathbf{r})$ is plotted in Fig. 1(a) and, as is well known, it reproduces exactly the HF ground-state charge density, but not the eigenspectrum [which differs considerably from the HF one, as shown in Fig. 1(c)]. Of course, the HOMO eigenvalue is reproduced, since it determines the decay of the charge density in the vacuum region [34].

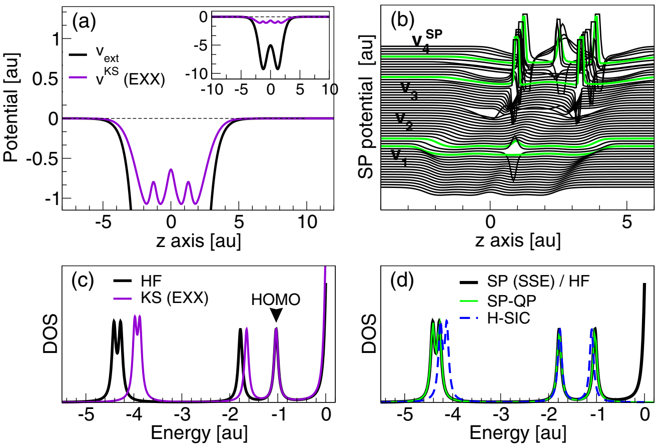

FIG. 1. (Color online) Comparison of the KS-SSE and SP-SSE for an eight-electron, spin-unpolarized one-dimensional model of a diatomic molecule (M1, discussed in Appendix B); the interacting electronic structure is calculated at the HF level. (a) External potential $v_{\text{ext}}(\mathbf{r})$ and local KS-EXX potential $v^{\text{KS}}(\mathbf{r})$. (b) Dynamical potential $v^{\text{SP}}(\mathbf{r},\omega)$ from the SP-SSE. Potentials at the occupied HF energies are highlighted (green). (c), (d) DOS corresponding to HF, KS-EXX, full SP-SSE (numerically identical to HF, not shown), SP-SSE within the QP approximation (SP-QP), and Hartree-SIC (discussed later in the text).

We then use the SP-SSE to calculate the local and dynamical $v^{\text{SP}}(\mathbf{r},\omega)$, which reproduces exactly the HF spectral function $\rho(\mathbf{r},\omega)$. We highlight in Fig. 1(b) (light green) the potentials corresponding to the bound HF spectrum (labeled $v_1^{\text{SP}},\ldots,v_4^{\text{SP}}$). We apply the QP approximation to these potentials [i.e., we used $v_1^{\text{SP}},\ldots,v_4^{\text{SP}}$ to build an effective GF in the spirit of Eq. (11); see Appendix B], and report the resulting spectral function in Fig. 1(d). This is found to be in perfect agreement with the exact solution of the SP-SSE (therefore, identical by construction to the HF spectral function). Thus, the spectral function of the nonlocal HF Hamiltonian has been reproduced by a set of local and orbital-dependent potentials, illustrating numerically the arguments presented above. In the more general case of a genuinely frequency-dependent self-energy, a similar picture would apply, the only difference being that a QP approximation as the one adopted here would fail to describe many-body features such as satellites and QP lifetimes, but would still considerably improve over KS-DFT.

As a final remark, we note that in principle v^{SP} is uniquely defined only where the spectral function is not identically zero, while infinitely many solutions can be obtained where the spectral function is zero [27,35]. This indeterminacy makes it numerically challenging to compute v^{SP} in the regions where it is irrelevant (e.g., where the spectral density is practically zero). Moreover, spikes in the computed $v^{\text{SP}}(\mathbf{r},\omega)$ potential [Fig. 1(b)] appear where the spectral density has a node or is very low, and are therefore harmless. In fact, when multiplying the spectral potential (at a given energy) by the spectral density (or by the relevant wave functions), spikes are matched by nodes, and their product is perfectly well behaved. This is shown in Fig. 2, where we plot (green triangles) the bare spectral potentials for the four frequencies of the HF bound spectrum (left panels) and compare these with $v^{\text{SP}}(\mathbf{r},\omega)\psi_m(\mathbf{r})$ (right panels), showing that the spikes in the

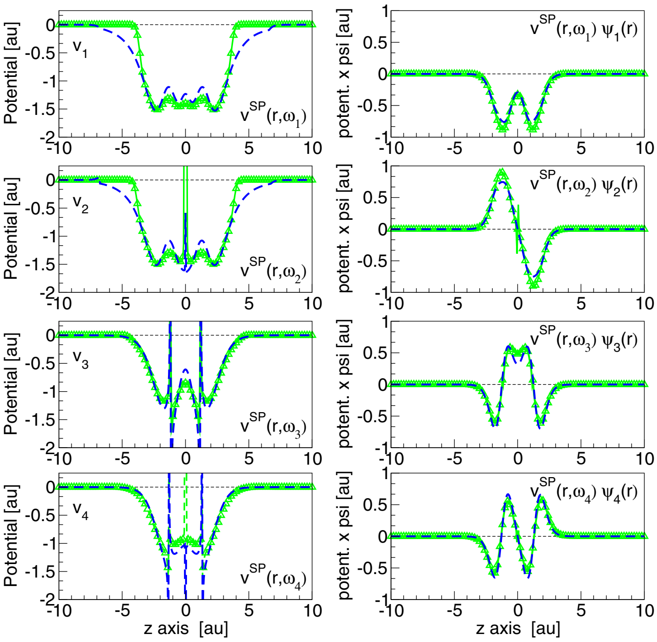

FIG. 2. (Color online) Left: spectral potentials $v^{\mathrm{SP}}(\omega_m)$ at the four HF energies ω_1–ω_4 (green triangles). Right: $v^{\mathrm{SP}}(\omega_m)$ times $\psi_m(\mathbf{r})$ (green triangles), where ψ_m are the eigenvectors corresponding to the orbital energies $\omega_1 = -4.42$, $\omega_2 = -4.28$, $\omega_3 = -1.78$, and $\omega_4 = -1.03$ a.u. We also compare to a simple, approximate ODD (H-SIC, blue dashed lines). Since the product of potential and wave function is the key physical quantity, the left panels highlight how this simple ODD approximation is remarkably close, qualitatively and quantitatively, to the exact solution.

potentials indeed cause no harm. The same picture holds when multiplying $v^{\mathrm{SP}}(\mathbf{r},\omega)$ by the spectral density $\rho(\mathbf{r},\omega)$. These considerations are particularly relevant when considering the task of identifying functional approximations to the spectral potential, since no ill-conditioned or nonanalytic features are required (including no derivative discontinuities; see Sec. V).

IV. ODD POTENTIALS AS A REPRESENTATION OF v^{SP}

So far we have highlighted a formal analogy between the framework of ODD functionals and that of the discretized spectral density, both leading to local and orbital-dependent potentials. This analogy suggests that ODD functionals could be used to derive useful approximations to the exact v^{SP}, and we argue this point both with model calculations, in this section, and later by comparing experimental photoemission data with the density-of-states (DOS) of Koopmans-compliant functionals. For the model calculations, we consider the self-Hartree correction (H-SIC) [the Hartree part of the PZ correction, given by the first term in the last expression of Eq. (15)], and show that not only it trivially provides a good approximation to the nonlocal HF exchange operator when calculated in a localized representation, but that in particular its potentials match qualitatively and quantitatively the exact (numerical) SP-SSE ones.

Due to the unitary invariance of $\Sigma = v_{\mathrm{x}}^{\mathrm{HF}}$, we can choose for the HF Hamiltonian a representation in which the orbitals are as localized (and nonoverlapping) as possible. The full exchange potential can then be approximated by the H-SIC (which provides localized orbitals) just by neglecting the off-diagonal contributions:

$$\langle \mathbf{r}|v_{\mathrm{x}}^{\mathrm{HF}}|\phi_i\rangle = -\sum_{j}^{\mathrm{occ}} \int d\mathbf{r}_1 \frac{\langle \mathbf{r}|\phi_j\rangle\langle\phi_j|\mathbf{r}_1\rangle}{|\mathbf{r}-\mathbf{r}_1|}\langle\mathbf{r}_1|\phi_i\rangle$$
$$\simeq -v_{\mathrm{H}}(\mathbf{r};[\rho_i])\langle\mathbf{r}|\phi_i\rangle. \qquad (15)$$

The eigenvalues of the ODD Λ matrix obtained from Eqs. (3) and (5) reproduce very closely the HF eigenvalues, as can be seen by examining the HF and H-SIC DOS in Fig. 1.

We next compare the H-SIC ODD potentials with the exact spectral potentials obtained for this HF model. We show the H-SIC canonical potentials (i.e., those corresponding to the canonical orbitals, obtained by diagonalizing the Λ matrix, as opposed to those corresponding to the variational orbitals, obtained by minimizing the ODD functional) in Fig. 2. These display very similar features to the exact ones, and, most importantly, when multiplied by the corresponding wave functions (the product of the two is the only relevant quantity for the calculations) show a remarkable qualitative and quantitative agreement. These findings highlight how potentials derived from ODD functionals can approximate accurately exact spectral potentials, a statement that will also be supported in the last section by the study of photoemission spectra in realistic cases.

V. DERIVATIVE DISCONTINUITY

As is also apparent from the numerical example of Fig. 1, while the KS-HOMO energy level correctly reproduces the HF target, this is not the case for the KS-LUMO, nor in general for all other orbitals. This behavior of the KS theory is well known and arises from the requirement of an exchange-correlation (XC) derivative discontinuity in the exact KS potential [4,36,37]; the addition of an infinitesimal fraction of an electron to a system may generate a finite discontinuity in the KS potential, so that the new infinitesimally filled HOMO is positioned correctly. Such discontinuity Δ_{xc} is the quantity to be added to the exact KS gap to retrieve the exact fundamental (transport) gap (since the position of the HOMO is correct in exact DFT, Δ_{xc} restores the physical position for the LUMO).

Recently, an expression for Δ_{xc} has been derived by Hellgren and Gross [38] using the Klein functional E_{K} [39] and the resulting linearized SSE for the KS potential [Eq. (A1) in Appendix A]. Across the discontinuity, the KS potential varies as

$$v^{\mathrm{KS}+}(\mathbf{r}) = v^{\mathrm{KS}-}(\mathbf{r}) + \Delta_{\mathrm{xc}}, \qquad (16)$$

where the indexes ± refer to a number of particles $N \pm 0^+$. The derivative discontinuity is then given by

$$\Delta_{\mathrm{xc}} = \langle\phi_L|\Sigma^+(\epsilon_L^+)|\phi_L\rangle - \langle\phi_L|v^{\mathrm{KS}-}|\phi_L\rangle. \qquad (17)$$

Here, ϕ_L is the lowest unoccupied orbital that changes with continuity upon charge addition and removal, and ϵ_L is its (discontinuous) KS eigenvalue. Σ has also a discontinuity at integer particle numbers because in the linearized SSE we have $\Sigma = \Sigma[G^{\mathrm{KS}}]$. Inspecting Eq. (17) one can immediately see that Δ_{xc} accounts for the shift between the exact KS LUMO and the physical LUMO.

The presence of such derivative discontinuity is also at the origin [9,10,38,40–43] of the formation of steps and peaks in the KS potential of donor-acceptor (D-A) systems undergoing dissociation. This is in particular the case when the KS-HOMO level of one of the subsystems is higher in energy than the KS-LUMO of the other, and the potential step can prevent an incorrect D-A charge transfer.

We show here that spectral potentials do not require these derivative discontinuities, and do not express them, making them much better conditioned and easier to approximate than the exact KS potential. For this, we again solve numerically a model 1D dimer with eight electrons, but heteroatomic and with a different parametrization (M2, see Appendix B) to target the challenge of charge transfer discussed above. We address in Fig. 3(a) the KS-EXX potential for this asymmetric double well at two different distances; the emergence of a potential step (at 10 a.u.) for the almost-dissociated distance of 16 a.u. between the two atoms is clearly evident. In Fig. 3(c) we show the DOS for the isolated subunits (D and A) and for the complete system (D-A) at $d = 16$ a.u., corresponding to the solid curve in Fig. 3(a). We also highlight the derivative discontinuity term ($\Delta^A_{\rm xc}$) corresponding to the A subsystem. The potential step δ in Fig. 3(a) is needed to avert a spurious charge transfer from D to A since, at variance with HF, the KS-EXX LUMO of the isolated A system is lower than the HOMO of the D system. This is in qualitative agreement with existing literature [38]. The different local potentials for each orbital (coming from the QP approximation to SP-SSE) allow us instead to describe the entire DOS correctly.

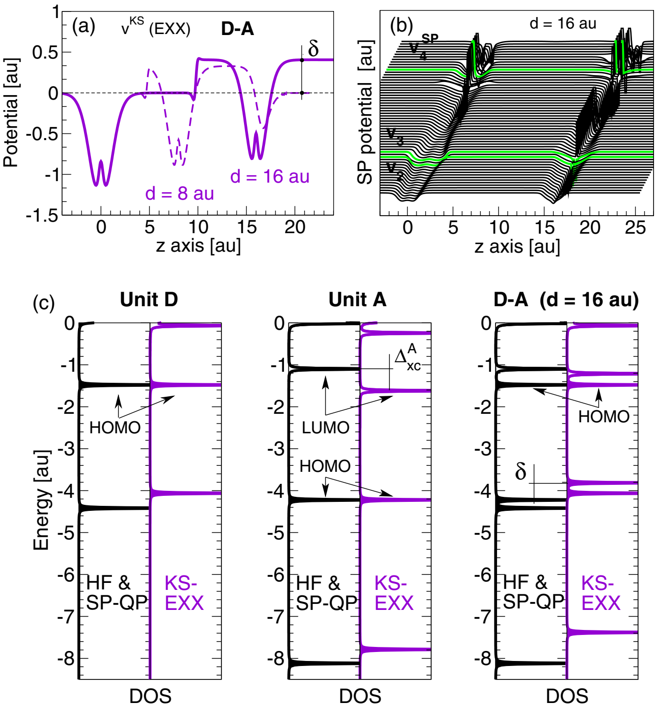

FIG. 3. (Color online) Dissociation of an eight-electron, spin-unpolarized one-dimensional heteroatomic dimer (M2, discussed in Appendix B); the interacting electronic structure is calculated at the HF level. (a) shows the KS-SSE (EXX) potentials $v^{\rm KS}(\mathbf{r})$ for the two atomic distances of 8 a.u. (dashed line) and 16 a.u. (solid line). The latter distance corresponds to an almost dissociated dimer and the finite step (δ) duly arising in the exact potential is highlighted. (b) shows the local spectral potential $v^{\rm SP}(\mathbf{r},\omega)$ as a function of frequency, calculated for this dissociation nuclear distance of 16 a.u., highlighting how no discontinuity is present at any frequency. The potentials corresponding to the HF eigenvalue energies are reported in green. (c): HF and KS-EXX energy levels of the full system (D-A) at the distance of 16 a.u. and those of the isolated D and A subunits, showing that the KS LUMO of the acceptor is below the KS HOMO of the donor. For the case of Unit A, the derivative discontinuity shift of the KS potential is highlighted ($\Delta^A_{\rm xc}$). As usual, results from a QP approximation to SP-SSE (SP-QP) are found to be virtually identical to the HF target.

The nonanalytic features of the exact KS potential make it challenging to approximate, even more so because they can appear exactly where the charge density goes to zero. In contrast, this is not the case for the $v^{\rm SP}(\mathbf{r},\omega)$ potential, where a derivative discontinuity is neither expected nor needed, as numerically confirmed in Fig. 3(b) where the spectral-function potential and its QP approximations are shown.

VI. COMPARISON WITH UPS DATA

Having established that canonical ODD potentials $\bar{v}^{\rm OD}_{{\rm xc},m}(\mathbf{r})$ can represent a QP approximation to the contraction $v^{\rm SP}(\mathbf{r},\omega)$ of a self-energy operator $\Sigma(\mathbf{r},\mathbf{r}',\omega)$ [note that $v^{\rm SP}(\mathbf{r},\omega)$ differs from $\Sigma(\mathbf{r},\mathbf{r},\omega)$, see Eq. (13)], it remains to exploit the analytical freedom offered by this generalized formulation to propose explicit ODD functionals able to capture QP properties. To derive explicit $v^{\rm OD}_{{\rm xc},i}(\mathbf{r})$, one could ideally proceed by applying the SP-SSE to existing approximations for Σ. Although this direct approach is appealing theoretically, it has to cope with the complexity involved in realistic cases. A very successful alternative has emerged [11,14] that purifies approximate KS functionals with orbital-dependent terms restoring desirable physical constraints, and in particular piecewise linearity, as suggested in Refs. [5–7] building on the ideas of Perdew and coworkers [4]. Following this route, one can impose a generalized Koopmans' condition, crucial for the interpretation of electronic spectra as ionization energies, to DFT approximations, thereby obtaining the ODD Koopmans-compliant functionals [11,14,17,23]. Even in their simplest screened form, namely the K_0[LDA] correction, orbital energies improve drastically. We note that similar approaches have also been recently proposed [12,51–53]. To illustrate this, we compare K_0[LDA] and LDA results to recent accurate photoemission data for thiophene, pentacene, and fullerene [44,46–48].

The comparative assessment of Fig. 4 highlights salient trends. First, we observe that LDA (purple empty triangles) does not accurately capture the onset of photoemission, with an overestimation of the first peak energy of several eV. Similarly, LUMO levels are typically found to be too low in LDA (this would be the case also for the exact KS functional, because of the missing derivative discontinuity term). At variance with LDA, K_0[LDA] reduces the error for the highest orbital to less than a few tenths of an eV. Moreover, K_0[LDA] photoemission peaks are found to be in excellent quantitative agreement with experiments, without requiring any shift to align the orbitals. The overall accuracy of Koopmans-compliant functionals on molecular orbital energies is found to be comparable and to

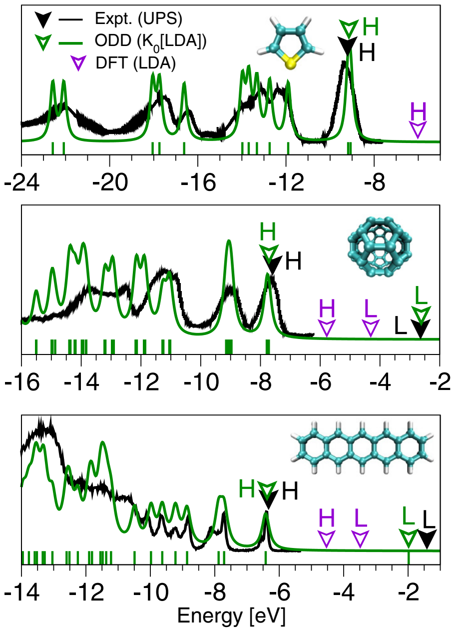

FIG. 4. (Color online) ODD (K_0[LDA]) density of states (thick green line) compared to ultraviolet photoemission experiments (thick black line) for (a) thiophene [44], (b) C_{60}, [45], and (c) pentacene [46–48]. Filled (black) and empty triangles indicate respectively the experimental [49,50] and theoretical (LDA, purple, and K_0[LDA], green) HOMO, LUMO levels. The K_0[LDA] and LDA levels have not been aligned to any experimental data.

improve on even highly accurate methods, such as the GW approximation, at a fraction of the cost (see Ref. [11] for organic photovoltaics, and Ref. [33] for the G2 set). The above computational benchmark lends weight to the practical benefit of simple inexpensive ODD functionals for the reliable description of photoemission spectra [11].

VII. CONCLUSIONS

In conclusion, we have shown how nonunitary-invariant orbital-density-dependent functionals and potentials can be interpreted within the framework of many-body dynamical methods, where the orbital dependency originates from a suitable quasiparticle approximation. This feature has been linked to the local dynamical potentials introduced in Ref. [27], showing that orbital dependency can be used to reproduce spectral properties. This picture leads to ODD potentials that are more general than local KS potentials and have the flexibility to describe both total energies and orbital energies. They naturally incorporate features that otherwise require a derivative discontinuity in the Kohn-Sham theory and act as an intermediate framework between density-functional theory and many-body formulations.

ACKNOWLEDGMENTS

We wish to thank S. Baroni, K. Burke, S. de Gironcoli, M. Gatti, R. Godby, and L. Reining for very useful discussions and comments about the KS- and SP-SSE. We also thank A. B. Trofimov, M. G. Betti, and C. Mariani for sharing their experimental data. We acknowledge partial support from: Italian MIUR FIRB-RBFR08FOAL_001 (A.F.); French National Research Agency, Grant No. ANR 12-BS04-0001 PANELS (I.D.); and US NSF Career award DMR 1151738 (M.C.).

APPENDIX A: VARIATIONAL DERIVATION OF SP-SSE

In this Appendix we derive a variational formulation of the linearized SP-SSE [27], as is usually done in the context of the OEP method for KS-DFT. Though similar formulations based on the spectral density exist [28], here an energy functional corresponding to the linearized SP-SSE is obtained.

As is well known [32], the linearized version of the SSE [Eq. (14)]

$$\int \frac{d\omega}{2\pi i} e^{i\omega 0^+} \left[G^{\mathrm{KS}} v^{\mathrm{KS}} G^{\mathrm{KS}}\right]_{\mathbf{r},\mathbf{r}} = \int \frac{d\omega}{2\pi i}\, e^{i\omega 0^+} \left[G^{\mathrm{KS}} \Sigma[G^{\mathrm{KS}}] G^{\mathrm{KS}}\right]_{\mathbf{r},\mathbf{r}}$$

can be obtained by making the Klein functional $E_{\mathrm{K}}[G^{\mathrm{KS}}]$ [39] stationary with respect to variations of the local potential $v^{\mathrm{KS}}(\mathbf{r})$ used to build $G^{\mathrm{KS}} = G[v^{\mathrm{KS}}]$:

$$\frac{\delta\, E_{\mathrm{K}}[G^{\mathrm{KS}}]}{\delta\, v^{\mathrm{KS}}(\mathbf{r})} = 0. \tag{A1}$$

This is the proper generalization of the OEP technique to cases involving a dynamical Φ-derivable self-energy. Instead of the exact KS-SSE of Eq. (14), the above procedure leads to its linearized version because the domain of the Klein functional has been restricted to those GF's coming from a local and static potential.

In a similar way, we can take the variation of the Klein functional with respect to a local and dynamical potential $\mathrm{v}(\mathbf{r},\omega)$ used to construct the GF G_{v} in $E_{\mathrm{K}}[G_{\mathrm{v}}]$. Here G_{v} is assumed to belong to the domain of E_{K}. The variation gives:

$$\frac{\delta E_{\mathrm{K}}}{\delta\, \mathrm{v}(\mathbf{r},\omega)} = \int d\omega'\, d\mathbf{r}_1 d\mathbf{r}_2\, \frac{\delta E_{\mathrm{K}}}{\delta\, G_{\mathrm{v}}(\mathbf{r}_1,\mathbf{r}_2,\omega')} \frac{\delta G_{\mathrm{v}}(\mathbf{r}_1,\mathbf{r}_2,\omega')}{\delta\, \mathrm{v}(\mathbf{r},\omega)} = \frac{1}{2\pi i}\, [G_{\mathrm{v}}\, (\Sigma - \mathrm{v})\, G_{\mathrm{v}}]_{\mathbf{r},\mathbf{r},\omega}, \tag{A2}$$

where the integration over spatial coordinates is left implicit and we have used the relation $G_{\mathrm{v}} G_{\mathrm{v}}^{-1} = I$ to derive

$$\frac{\delta G_{\mathrm{v}}(\mathbf{r}_1,\mathbf{r}_2,\omega')}{\delta\, \mathrm{v}(\mathbf{r},\omega)} = G_{\mathrm{v}}(\mathbf{r}_1,\mathbf{r},\omega) G_{\mathrm{v}}(\mathbf{r},\mathbf{r}_2,\omega)\, \delta(\omega - \omega'). \tag{A3}$$

Setting $\frac{\delta E_{\mathrm{K}}}{\delta\, \mathrm{v}(\mathbf{r},\omega)} = 0$ we obtain a SP-SSE expression for $\mathrm{v}(\mathbf{r},\omega)$:

$$\int d\mathbf{r}_1 \mathrm{v}(\mathbf{r}_1,\omega)\big[G_{\mathrm{v}}(\mathbf{r},\mathbf{r}_1,\omega) G_{\mathrm{v}}(\mathbf{r}_1,\mathbf{r},\omega)\big] = \big[G_{\mathrm{v}} \Sigma[G_{\mathrm{v}}] G_{\mathrm{v}}\big]_{\mathbf{r},\mathbf{r}}. \tag{A4}$$

If the potential $\mathrm{v}(\mathbf{r},\omega)$ in Eq. (A2) is real, the derivative of E_{K} with respect to such a potential may become complex. This means that the $E_{\mathrm{K}}[G]$ functional may be complex when G is built from a real $\mathrm{v}(\mathbf{r},\omega)$ potential. In order to circumvent this problem, when restricting the potential $\mathrm{v}(\mathbf{r},\omega)$ to be real we work with a modified version of the Klein functional, $\widetilde{E}_{\mathrm{K}} = \mathrm{Re} E_{\mathrm{K}}$. By using this expression and the derivative in Eq. (A2) we can finally obtain the linearized version of the SP-SSE [Eq. (13)]. This completes the proof of the variationality of Eq. (13). The reason for having derived the linearized version of the equation instead of the full one is due, as for the case of KS-OEP, to the fact that the GF has been obtained by using a local dynamical potential [$v^{\mathrm{SP}}(\mathbf{r},\omega)$].

APPENDIX B: TECHNICAL DETAILS

1. Numerical models

Model M1. The external potential is the superposition of two soft-core ions [10] of the form $v(r) = v_0/\cosh^2(\beta r)$. We have used $v_0 = 9.0$ a.u. for both ions. The ion-ion distance has been set to 2.5 a.u. The electron-electron interaction is modeled by the same potential form, but using $v_0 = 1.5$ a.u. The parameter β is set to be 1.0 a.u. in all cases. The system contains eight interacting, spin-unpolarized electrons and is represented on a real-space grid of 600 points spanning 30 a.u.

Model M2. As above but heteroatomic and using a different parametrization of the external potential to discuss derivative discontinuity effects. We have set $v_0 = 9.0$ and 13.5 a.u. The dimer bond length d has been varied in the range 6–16 a.u. (only two distances shown in Fig. 3). The real-space grid is made of 700 points spanning 35 a.u.

HF and Sham-Schlüter equation. The HF and Sham-Schlüter problems are solved on a real-space grid. The kinetic energy operator is expressed by finite differences. All calculations are spin unpolarized. A symmetric and diagonal preconditioning of the linear systems has been used for both KS- and SP-SSE. The SP-SSE has been solved on a frequency grid of 180 (250) points in the range $[-6.0,0.2]$ a.u. ($[-8.5,0.2]$ a.u.), for M1 and M2 respectively.

In order to compute the Green's functions, a finite $i\delta$ term (0.05 au) is added to the denominators to shift the poles off of the real axis, thereby leading to a Lorentzian broadening of the spectral functions. We note that the size of the spikes in the $v^{\mathrm{SP}}(\mathbf{r},\omega)$ potential depends on the smearing scheme adopted. Nevertheless, such a dependency is not a numerical instability. In fact it is related to the fact that the local spectral function itself changes in shape when a different smearing scheme is adopted. All the SSE calculations reported have been performed without linearization (but no relevant differences have been found during testing).

QP approximation to v^{SP}. Once $v^{\mathrm{SP}}(\mathbf{r},\omega)$ has been computed for each frequency, we select the frequencies ω_m (here $m = 1,\dots,4$) corresponding to the (occupied) spectrum to be described. For each $v^{\mathrm{SP}}_m = v^{\mathrm{SP}}(\omega_m)$ we compute the eigenvalues and eigenvectors and select the orbital whose energy matches best the original ω_m eigenvalue. We then compute the overlap matrix of the orbitals coming from different potentials (in principle not orthogonal) and build the SP-QP Green's function as:

$$G^{\mathrm{SP-QP}}(\omega) = \sum_i \frac{|\psi_i\rangle\langle\psi^i|}{\omega - \epsilon_i - i\delta}. \tag{B1}$$

A suitable extension to include also empty states can be formulated along the same lines.

2. Koopmans-compliant calculations

ODD Koopmans-corrected calculations have been performed at the K_0[LDA] level, according to Refs. [11,14] (referred there as $\alpha\mathrm{NK}_0$). We have implemented the method in the plane-wave code CP.X, from the QUANTUM-ESPRESSO distribution [54]. Standard norm-conserving pseudopotentials have been used and a kinetic energy cutoff of 40 Ry has been adopted. Periodic replica have been separated by at least 9 Å of vacuum and regularizing functions have been used to avoid the singularities in the reciprocal space summation of electrostatic terms [55]. Damped electronic dynamics has been used to optimize the electronic degrees of freedom. The scaling factor α has been computed self-consistently and nonempirically by imposing the HOMO energies for the neutral molecules to match the LUMO energies for the cations [14] (Koopmans' condition).

[1] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).

[2] S. Kümmel and L. Kronik, Rev. Mod. Phys. **80**, 3 (2008).

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

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

[5] M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005).

[6] H. J. Kulik, M. Cococcioni, D. A. Scherlis, and N. Marzari, Phys. Rev. Lett. **97**, 103001 (2006).

[7] A. Cohen, P. Mori-Sanchez, and W. Yang, Science **321**, 792 (2008).

[8] P. H.-L. Sit, M. Cococcioni, and N. Marzari, Phys. Rev. Lett. **97**, 028303 (2006).

[9] D. G. Tempel, T. J. Martínez, and N. T. Maitra, J. Chem. Theory Comput. **5**, 770 (2009).

[10] N. Helbig, I. V. Tokatly, and A. Rubio, J. Chem. Phys. **131**, 224105 (2009).

[11] I. Dabo, A. Ferretti, C.-H. Park, N. Poilvert, Y. Li, M. Cococcioni, and N. Marzari, Phys Chem Chem Phys **15**, 685 (2013).

[12] E. Kraisler and L. Kronik, Phys. Rev. Lett. **110**, 126403 (2013).

[13] U. Lundin and O. Eriksson, Int. J. Quantum Chem. **81**, 247 (2001).

[14] I. Dabo, A. Ferretti, N. Poilvert, Y. Li, N. Marzari, and M. Cococcioni, Phys. Rev. B **82**, 115121 (2010).

[15] I. Dabo, M. Cococcioni, and N. Marzari, arXiv:0901.2637 [cond-mat.mtrl-sci] (2009).

[16] S. Klupfel, P. Klupfel, and H. Jonsson, Phys. Rev. A **84**, 050501 (2011).

[17] I. Dabo, A. Ferretti, and N. Marzari, in *Topics in Current Chemistry*, Vol. 347 (Springer, Berlin, Heidelberg, 2014).

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

[19] M. Pederson, R. Heaton, and C. Lin, J. Chem. Phys. **80**, 1972 (1984).

[20] S. Goedecker and C. J. Umrigar, Phys. Rev. A **55**, 1765 (1997).

[21] M. Stengel and N. A. Spaldin, Phys. Rev. B **77**, 155106 (2008).

[22] T. Körzdörfer, S. Kümmel, and M. Mundt, J. Chem. Phys. **129**, 014110 (2008).

[23] I. Dabo, A. Ferretti, G. Borghi, N. L. Nguyen, N. Poilvert, C. H. Park, M. Cococcioni, and N. Marzari, Psi-k Newsletter **119** (2013), http://www.psi-k.org/newsletters/News_119/Highlight_119.pdf

[24] O. Vydrov, G. Scuseria, and J. Perdew, J. Chem. Phys. **126**, 154109 (2007).

[25] A. L. Fetter and J. D. Walecka, *Quantum theory of many-particle systems* (McGraw-Hill, New York, 1971).

[26] B. Farid, Philos Mag B **79**, 1097 (1999).

[27] M. Gatti, V. Olevano, L. Reining, and I. V. Tokatly, Phys. Rev. Lett. **99**, 057401 (2007).

[28] S. Y. Savrasov and G. Kotliar, Phys. Rev. B **69**, 245101 (2004).

[29] D. Chong, O. Gritsenko, and E. Baerends, J. Chem. Phys. **116**, 1760 (2002).

[30] L. J. Sham and M. Schlüter, Phys. Rev. B **32**, 3883 (1985).

[31] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986).

[32] M. E. Casida, Phys. Rev. A **51**, 2005 (1995).

[33] G. Borghi, A. Ferretti, N. L. Nguyen, I. Dabo, and N. Marzari, arXiv:1405.4635 [cond-mat.mtrl-sci] (2014).

[34] J. P. Perdew and M. Levy, Phys. Rev. B **56**, 16021 (1997).

[35] M. Gatti, Ph.D. thesis, École Polytechnique, Palaiseau, 2007, http://etsf.polytechnique.fr/sites/default/files/users/matteo/matteo_thesis.pdf

[36] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).

[37] L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).

[38] M. Hellgren and E. K. U. Gross, Phys. Rev. A **85**, 022514 (2012).

[39] A. Klein, Phys. Rev. **121**, 950 (1961).

[40] N. Maitra, J. Chem. Phys. **122**, 234104 (2005).

[41] O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends, Phys. Rev. A **52**, 1870 (1995).

[42] O. V. Gritsenko and E. J. Baerends, Phys. Rev. A **54**, 1957 (1996).

[43] A. Makmal, S. Kümmel, and L. Kronik, Phys. Rev. A **83**, 062512 (2011).

[44] A. B. Trofimov, I. L. Zaitseva, T. E. Moskovskaya, and N. M. Vitkovskaya, Chem Heterocyc Compd **44**, 1101 (2008).

[45] D. L. Lichtenberger, K. W. Nebesny, C. D. Ray, D. R. Huffman, and L. D. Lamb, Chem. Phys. Lett. **176**, 203 (1991).

[46] C. Baldacchini, Ph.D. thesis, University of Rome "La Sapienza", 2005.

[47] A. Ferretti, C. Baldacchini, A. Calzolari, R. Di Felice, A. Ruini, E. Molinari, and M. G. Betti, Phys. Rev. Lett. **99**, 046802 (2007).

[48] C. Baldacchini, C. Mariani, M. G. Betti, I. Vobornik, J. Fujii, E. Annese, G. Rossi, A. Ferretti, A. Calzolari, R. Di Felice, A. Ruini, and E. Molinari, Phys. Rev. B **76**, 245430 (2007).

[49] M. L. Tiago, P. R. C. Kent, R. Q. Hood, and F. A. Reboredo, J. Chem. Phys. **129**, 084311 (2008).

[50] L. Crocker, T. Wang, and P. Kebarle, J. Am. Chem. Soc. **115**, 7818 (1993).

[51] S. Lany and A. Zunger, Phys. Rev. B **81**, 205209 (2010).

[52] S. Refaely-Abramson, R. Baer, and L. Kronik, Phys. Rev. B **84**, 075144 (2011).

[53] S. Refaely-Abramson, S. Sharifzadeh, N. Govind, J. Autschbach, J. B. Neaton, R. Baer, and L. Kronik, Phys. Rev. Lett. **109**, 226405 (2012).

[54] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys.: Condens. Matter **21**, 395502 (2009).

[55] Y. Li and I. Dabo, Phys. Rev. B **84**, 155127 (2011).