Improved exchange-correlation potential for polarizability and dissociation in density functional theory

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(Received 23 March 2007; accepted 24 April 2007; published online 21 May 2007)

The authors propose a novel approach to the problem of polarizabilities and dissociation in electric fields from the static limit of the Vignale-Kohn (VK) functional. The response to the purely scalar part of the VK response potential is considered. This potential has ground-state properties that notably improve over the full VK response density and over usual (semi-)local functionals. The correct qualitative behavior of our potentials means that it is expected to work well for polarizabilities in cases such as the H_2 chain, and it will also correctly dissociate open-shell fragments in a field. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2741243]

Density functional theory[1–3] (DFT) has become the most popular electronic structure method in a wide range of problems in quantum chemistry, achieving an unprecedented balance between accuracy and efficiency. But in some applications there are fundamental problems with standard exchange-correlation (xc) approximations such as local density approximation (LDA) and generalized gradient approximation (GGA). The response to electric fields is severely overestimated for long-range molecules and for molecular chains.[4,5] Even for the simple H_2 molecule dissociating in an electric field, LDA and GGA yield unphysical fractional charges on each atom.[5,6] This is a problem in many topical applications, including molecular electronics[7,8] and nonlinear optics devices.[9,10]

It is now well known that the functionals in these cases must depend in an ultranonlocal way on the density.[5,11,12] There have been two approaches: The first is exact exchange (EXX). This has an implicit nonlocal density dependence through orbital dependence.[13] The second is Vignale-Kohn (VK) theory,[14] where a linear response calculation is performed within time-dependent current DFT (TDCDFT), a natural extension of time-dependent DFT.[15] VK uses functionals of the current density: the (time-integrated) current through a small volume in space contains information about the density response far from that volume, so functionals that are local in the current density are ultranonlocal in the density. Both EXX and VK have field-counteracting terms that decrease the response compared with LDA/GGA, and so yield improved static polarizabilities for many polymer chains. An exception is the hydrogen chain, for which VK performs almost as poorly as LDA.[11] Another problem that needs nonlocal functionals is the dissociation of simple diatomics in electric fields. As the molecule is pulled apart, a field-counteracting step develops in the exact Kohn-Sham (KS) potential midway between the atoms. In the limit of large separation, the step size approaches a constant that realigns the highest occupied molecular orbitals of the two atoms in the case of two open-shell fragments, and vanishes in the case of two closed-shell fragments. EXX captures the step in the latter, but until now, no density functional approximation has captured the step in the former case. VK has never before been applied to this problem.

The calculations in Ref. 11 utilize the zero-frequency limit of VK, which contains additional "dynamical" xc fields, on top of LDA.[16] The VK xc vector potential has both longitudinal as well as transverse components. Static response calculations are technically outside the realm of validity of VK,[14] but its success in many such cases suggest that such dynamical terms are also present in the true static functional and contain essential physics.[11,17]

The fact that a transverse xc field persists in the static limit of VK means that, in contrast to usual response methods, caution must be used when interpreting the zero-frequency limit as a ground-state perturbation. Satisfaction of the adiabatic theorem requires that the response in the static limit is representable by a scalar KS potential.[20] For a perturbation turned on slowly enough, the system remains arbitrarily close to the instantaneous ground state. Functionals in any time-dependent theory should reduce to ground-state DFT ones, where xc effects are contained in a scalar potential. However, a transverse field, with its nonzero curl, represents a nonconservative force, and so cannot correspond to a scalar potential underlying a conserved energy.

In this paper we reconsider the VK response to electric fields from a new perspective. We first generate the self-consistent xc vector potential from a full VK calculation in the static limit, but then discard its transverse component. Thereby we eliminate the non-conservative part of the force. We gauge transform the longitudinal part into a scalar potential which we view as a *ground-state xc response potential*. This approach is quite distinct from the previous use of VK,[11] where the key player is the *density response* of the VK potential, n_1^{VK}. This is not the ground-state density response of the scalar potential above, because n_1^{VK} is the full response

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to both the longitudinal and transverse fields of VK. Here, we consider the true ground-state response to just the scalar part of the VK potential. We show that this ground-state VK potential has desirable features arising from global field-counteracting terms. The dissociation limit of the electron-pair bond is correctly obtained, in contrast to the notorious fractional charges that result from all previous density functional approximations, including LDA, GGA, and EXX.[5,6,18] For cases where the VK response density has not performed well, e.g., hydrogen chains, features of this scalar VK potential suggest that our approach will perform very well. Dynamical terms that proved crucial in the usual VK approach to polarizabilities play an even more fundamental role here.

Consider a system initially in its field-free ground state of density $n_0(\mathbf{r})$. In VK response theory, xc contributions to a perturbative time-dependent field are contained in a vector potential that is a local functional of the induced current density $\mathbf{j}(\mathbf{r}t)$,[14] $\mathbf{a}_{\mathrm{xc}}[\mathbf{j}](\mathbf{r}t)$. In the frequency domain (atomic units),

$$i\omega\mathbf{a}_{\mathrm{xc}}[\mathbf{j}](\mathbf{r},\omega) = \nabla v_{\mathrm{xc}}^{\mathrm{ALDA}}(\mathbf{r}) - \nabla\cdot\overleftrightarrow{\sigma}(\mathbf{r},\omega)/n_0(\mathbf{r}), \tag{1}$$

where, in the static limit, $\omega\to 0$,

$$\sigma_{ij} = -\frac{3}{4i\omega}n_0(\mathbf{r})^2 f_{\mathrm{xc}}^{\mathrm{dyn}}(\mathbf{r})\left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} - \frac{2}{3}\nabla\cdot\mathbf{u}\,\delta_{ij}\right), \tag{2}$$

with $\mathbf{u}(\mathbf{r})=\mathbf{j}(\mathbf{r})/n_0(\mathbf{r})$. Here $f_{\mathrm{xc}}^{\mathrm{dyn}}(\mathbf{r})$ is a dynamical correction to the static scalar xc kernel of the homogeneous electron gas $f_{\mathrm{xc}}^{\mathrm{hom}}$ in the long-wavelength limit, evaluated at the field-free density at $\mathbf{r}$, i.e.,

$$f_{\mathrm{xc}}^{\mathrm{dyn}}(\mathbf{r}) = \lim_{\omega\to 0} f_{\mathrm{xc}}^{\mathrm{hom}}(n_0(\mathbf{r})) - \left.\frac{d^2 e_{\mathrm{xc}}^{\mathrm{hom}}}{dn^2}\right|_{n_0(\mathbf{r})}. \tag{3}$$

The *static* xc response of the homogeneous electron gas is given by the second-derivative of the xc energy density $e_{\mathrm{xc}}^{\mathrm{hom}}$. This differs from the zero-frequency limit of the scalar kernel by $f_{\mathrm{xc}}^{\mathrm{dyn}}=4\mu_{\mathrm{xc}}^{\mathrm{dyn}}/3n^2$, where $\mu_{\mathrm{xc}}^{\mathrm{dyn}}$ is the elastic shear modulus at $\omega\to 0$.[19] Thus VK contains dynamical corrections to adiabatic LDA (ALDA) that persist all the way through $\omega\to 0$. The response kernels are defined in VK by taking the wave vector q of the perturbing field to zero before taking the static limit, and these limits do not commute.[14,16,17,19]

We now define a ground-state potential from the static limit of the VK response. Taking $\omega\to 0$, the longitudinal component of Eq. (1) is gauge transformed to a scalar potential, $v_{\mathrm{xc}}^{(1)}[n](\mathbf{r})$, a nonlocal functional of the density, $i\omega\mathbf{a}_{\mathrm{xc,L}}[\mathbf{j}](\mathbf{r}\omega)=\nabla v_{\mathrm{xc}}^{(1)}[n](\mathbf{r})$. We restrict now to cylindrically symmetric linear systems, and *approximate* this potential in the following way. We consider Eqs. (1) and (2) for a purely one-dimensional inhomogeneity,[8,16] so we effectively average over the transverse directions in our cases. We then obtain an approximate potential[8,16] for linear systems,

$$\begin{aligned} v_{\mathrm{xc}}^{(1)}(z) = {} & f_{\mathrm{xc}}^{\mathrm{hom}}(z)n_1(z) - \frac{n_0'(z)}{n_0(z)}f_{\mathrm{xc}}^{\mathrm{dyn}}(z)\int_{-\infty}^{z} dz' n_1(z') \\ & - \int_{z}^{\infty} dz' \frac{n_0'(z')}{n_0(z')} f_{\mathrm{xc}}^{\mathrm{dyn}}(z')n_1(z') \\ & + \int_{z}^{\infty} dz' \left(\frac{n_0'(z')}{n_0(z')}\right)^2 f_{\mathrm{xc}}^{\mathrm{dyn}}(z')\int_{-\infty}^{z'} dz'' n_1(z''). \end{aligned} \tag{4}$$

Here $n_0'(z)=dn_0(\mathbf{r})/dz$ [where $\mathbf{r}=(0,0,z)$ is along the bond axis] and $n_1(\mathbf{r})=\nabla\cdot\mathbf{j}/(i\omega)$ is the system's density response, which is taken in the zero-frequency limit. This potential consists of four terms: the first is the LDA response, local in the density response. The second term is directly proportional to the local current-density response. The third and fourth display global behavior across the molecule, and are the key terms for the purposes of this paper. It follows from the structure of the fourth term that any polarization of the density, be it local or of charge-transfer nature, yields field-counteracting behavior. The third term tends to align along the field, but is generally smaller than the fourth.

The first step is to run a zero-frequency VK response calculation on the chosen system in a weak external field Ez placed along the bond axis z. We utilize the ADF program package[21] with the TDCDFT extension; see Ref. 11 for implementation details. In the second step, the resulting density response is inserted in Eq. (4) to define our ground-state potential. We study three classes of systems that are challenging for usual semilocal density functionals: (i) dissociation of the electron-pair bond (ii) a dimer composed of two closed-shell fragments at large but finite separation, and (iii) a molecular chain. Atomic units are used throughout.

(i) Dissociation of the electron-pair bond: H_2*-like systems*. The step that forms in the exact KS potential when a molecule composed of open-shell units dissociates in an electric field prevents dissociation to fractionally charged species, and is consistent with the physical picture of two locally polarized species.[5] An analogous step occurs in field-free dissociation of a heteroatomic molecule composed of open-shell units.[6,22–25] Its origin is static correlation, and it is particularly difficult for approximations to capture, eluding not only LDA/GGA but also EXX. Reference 18 has a density-matrix solution for this.

The lower left panel of Fig. 1 shows the field-free density (scaled by 0.01), the exact density response within bound-state perturbation theory, and the VK density response n_1^{VK} for H_2 at bond length 10 a.u. in a field of 0.001 a.u. The exact response demonstrates local polarization with no charge transfer, as expected. However, this is not true for the VK (or LDA) response density, which yields fractionally charged atoms. Correspondingly, the VK polarizability is grossly overestimated, as it is in the LDA. The top panel of this same figure shows the exact xc response potential $v_{\mathrm{xc}}^{(1)}$ (within bound-state perturbation theory) and the VK and LDA xc response potentials (i.e., subtracting the field-free potential). The exact was obtained by numerically inverting the KS equation, for the exact KS bonding orbital composed of polarized atomic orbitals. The salient feature of the exact $v_{\mathrm{xc}}^{(1)}$ is the field-counteracting step which compensates for the

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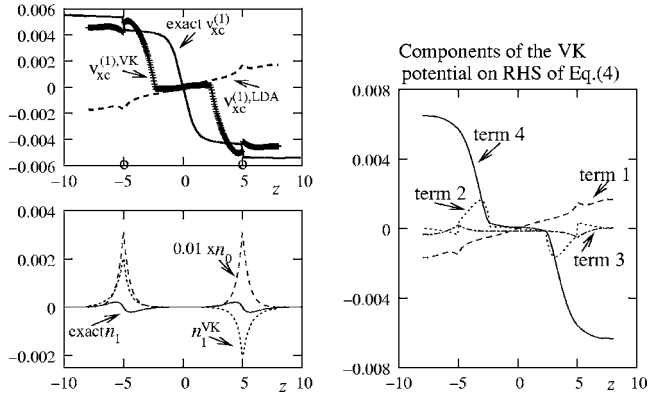

FIG. 1. H_2 at bond length 10 a.u., in a field of 0.001 a.u. The circles on the z axis in the top panel represent the position of the atoms, as in all subsequent figures. A similar field-compensating behavior was observed in other diatomics composed of open-shell fragments, e.g., Li_2.

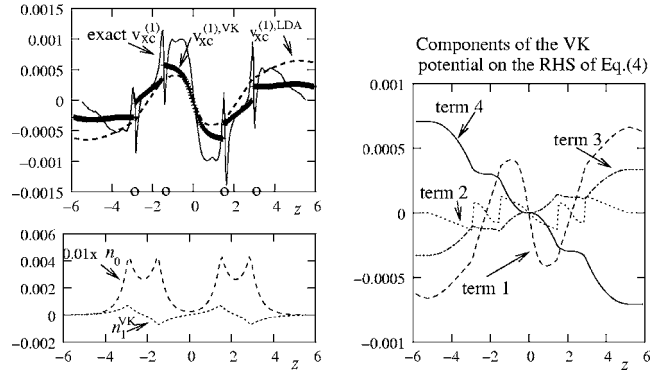

FIG. 2. The H_2 dimer, with H_2–H_2 distance of 3 a.u. and "intramolecular" H–H bond length of 1.4 a.u., in a 0.001 a.u. field.

difference in potential at the two separated atoms, and thus realigns them when the total potential is considered. This step is missed by the LDA which has an along-field component, strengthening the applied field. The step is also missing in EXX (not shown), as the potential there is simply minus half the Hartree. The VK potential does capture the step. In the right panel we see that the fourth term in Eq. (4) is responsible for this. The VK potential falls a little short of the exact step, but once the Hartree response potential (field counteracting[5]) is added to the VK xc potential, we expect that the total step completely compensates the change in potential created by the external field.

The VK potential realigns the two atoms, and so the ground state of this system would certainly not involve any charge transfer across the system, like in the exact case, in contrast to the VK density response (see Fig. 1). Indeed, as the bond length R increases, one finds that the VK density globally polarizes even more, while the VK step size increases as ER, maintaining the atoms at the same level. As the molecule dissociates, stretched H_2 has the metalliclike feature that its HOMO-LOMO gap vanishes. This may underlie the reason why VK exactly captures the step, since VK is based on the response of a metallic system, the weakly inhomogeneous electron gas.

It is important that the VK potential be evaluated on the "wrong" density response to the full VK fields. If evaluated on the exact response density, the field-counteracting term is reduced by a factor of about 20.

(ii) Dimer of two closed-shell units. Field-counteracting behavior also arises from the exchange interaction between closed shells, as explained in Refs. 5 and 26. In contrast to the step of (i), EXX methods can retrieve this step.[5] In Fig. 2 we see that the step is also nicely reproduced by the VK potential, shown in the top panel. Also shown there is the exact xc response potential, calculated from highly accurate wave function techniques in Ref. 5. Although details of the exact potential are missing in the VK response potential, the step is clearly captured, with the correct magnitude of drop in the potential between the up- and down-field molecules. In contrast, the LDA or any GGA has no net drop.

The right panel shows that the net step in the VK potential is a result of competition between the third and fourth terms. Note that in this case there is largely local polarization in the molecules, with small charge transfer (hardly discernable in the lower left panel).

The VK density response and polarizability are again very close to the LDA ones, both overestimating the exact polarizability. However, the ground-state response using the VK potential shown is expected to yield polarizabilities much closer to the exact one because of the field-counteracting behavior.

The magnitude of the exact step between two closed-shell units decreases as the intermolecular separation increases.[5] This is *not* the case for the VK step asymptotically. Essentially, the VK step arises from integrals over the current density [fourth term in Eq. (4)]. This integral persists at large separation, due to the local polarization.

(iii) Long-chain molecules. Polarizabilities and hyperpolarizabilities of long-chain polymers are notoriously overestimated in LDA/GGA calculations. Recent work has shed much light on the role of ultranonlocal density dependence in these systems. It has been demonstrated that orbital functionals such as EXX within OEP can significantly improve the polarizabilities,[5,9,12] due to field-counteracting behavior in the exchange potential. Approximate exchange methods such as KLI Ref. 27 also give corrections over LDA, although not as strongly as full exchange.[9] For example, for the hydrogen chain in Fig. 3, the LDA, KLI, and OEP polarizabilities are 114.6, 90.6, and 84.2 a.u., respectively. The VK functional was also applied[11] and gave 110.20 a.u., hardly an improvement over LDA; in contrast to its dramatic improvement for many other molecular chains. Again, the scalar VK *potential* has field-counteracting behavior, as shown in Fig. 3. This potential will give improved results (comparable to KLI) when used in a computation of ground-state response and polarizabilities.

In Ref. 9, the importance of intermolecular barriers in the *field-free* ground-state potential was stressed: these are lacking in LDA, underestimated in KLI, but captured well in OEP. Although formal arguments point to LDA as the correct field-free potential to be used in conjunction with the VK response potential, it will be interesting to compare polarizabilities using the VK response potential on top of a field-free OEP potential.

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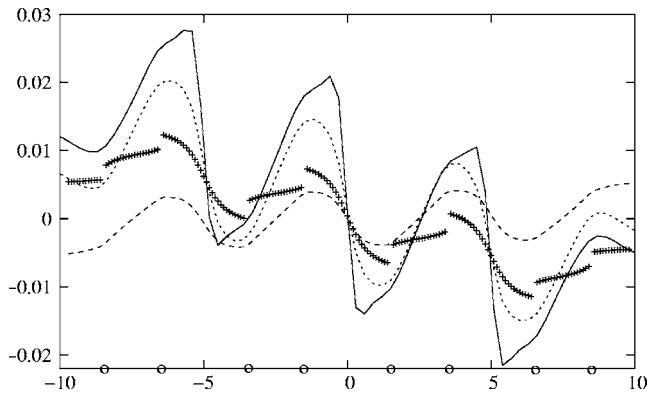

FIG. 3. H_2 chain in a field of 0.005 a.u. OEP (solid), KLI (dotted), LDA (dashed), and VK potentials (+). The H–H distances alternate between 2 and 3 a.u.

In summary, we have shown that the scalar part of the VK response potential contains crucial field-counteracting terms making it a good candidate for response properties of effectively one-dimensional systems in electric fields. It is the first approximation that captures the step in a molecule composed of open-shell fragments dissociating in an electric field. It captures field-counteracting terms in systems of two or more closed-shell units, and is promising for long chains, being numerically less intensive than EXX methods which also have been successful for these problems. The scalar VK potential works well even when the full VK response does not! In all cases studied, n_1^{VK} is very close to the LDA response, suggesting that the effects of the transverse VK and dynamical-longitudinal fields somewhat cancel. Satisfaction of the adiabatic theorem means that the transverse component of the response field should vanish in the static limit, suggesting that VK should be corrected by dropping its transverse part. This supports our results, where the ground-state response to the longitudinal component was considered. An alternative choice is to discard the transverse field from the start, and consider the self-consistent response to the purely longitudinal field. The results are not as good. The field-counteracting nature of Eq. (4) is most effective when evaluated on the full (wrong) density response n_1^{VK} rather than that obtained self-consistently. The non-self-consistent aspect of our present approach is somewhat dissatisfying from a rigorous viewpoint. On the other hand, there are many other situations in DFT where such post-self-consistent approaches have been successful, e.g., Ref. 28.

Finally, we note that the VK response potential smears over some local details of the true response potential (see, e.g., Fig. 2). Work is underway to investigate if this has a significant effect on the global polarizability.

The authors thank S. Kümmel for his OEP and KLI data on the H_2 chain, and K. Burke and G. Vignale for fruitful discussions. This work is financially supported by the American Chemical Society's Petroleum Research Fund and National Science Foundation Career No. CHE-0547913.

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