Correlated optimized effective-potential treatment of the derivative discontinuity and of the highest occupied Kohn-Sham eigenvalue: A Janak-type theorem for the optimized effective-potential model

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A Janak theorem is derived for the correlated optimized effective-potential model of the Kohn-Sham exchange-correlation potential $v_{\rm xc}$. It is used to evaluate the derivative discontinuity (DD) and to show that the highest occupied Kohn-Sham eigenvalue, $\epsilon_{\rm H} \cong -I$, the negative of the ionization potential, when relaxation and correlation effects are included. This reconciles an apparent inconsistency between the ensemble theory and fractional occupation number approaches to noninteger particle number in density-functional theory. For finite systems, $\epsilon_{\rm H} = -I$ implies that $v_{\rm xc}^{\infty} = 0$ independent of particle number, and that the DD vanishes asymptotically as $1/r$. The difference in behavior of the DD in the bulk and asymptotic regions means that the DD affects the shape of $v_{\rm xc}$, even at fixed, integer particle number. [S0163-1829(99)04907-3]

I. INTRODUCTION

Hohenberg-Kohn-Sham density-functional theory[1,2] (DFT) is an important workhorse for electronic structure calculations in both physics and chemistry. Since the quality of the results is determined by the approximation used for the exchange-correlation functional, the development of improved practical, approximate functionals is of central importance in DFT. For example, the functionals widely used for molecular calculations yield exchange-correlation potentials $v_{\rm xc}$, whose asymptotic behavior is qualitatively incorrect. This is critical for the calculation of high-lying bound excitations from time-dependent DFT (Refs. 3 and 4) and is important for other properties that are sensitive to the outer part of the charge density, such as static and dynamic polarizabilities. Furthermore, the shortcomings of approximate functionals have meant that molecular first ionization potentials and band gaps in solids are, in practice, not computed from the Kohn-Sham eigenvalues but instead from total-energy-difference-based procedures and post-DFT Green-function approximations, respectively. Work on improving approximate functionals is often guided by properties demonstrated to hold for the exact functional.

The concept that the (exact) DFT exchange-correlation energy $E_{\rm xc}$ has a discontinuity in its derivative at integer particle (electron) number,

$$v_{\rm xc}^{+}(\mathbf{r}) \equiv \left(\frac{\delta E_{\rm xc}}{\delta \rho(\mathbf{r})} \right)_{N+0^+} \neq \left(\frac{\delta E_{\rm xc}}{\delta \rho(\mathbf{r})} \right)_{N-0^+} \equiv v_{\rm xc}^{-}(\mathbf{r}), \quad (1.1)$$

was originally introduced to explain the discrepancy between calculated and measured band gaps in solid-state physics[5,6] and the dissociation of diatomic molecules into neutral atoms.[7–9] In contrast to the well-established place of the derivative discontinuity (DD) in the theory for infinite systems, the problem of the DD in finite systems has often been regarded as abstruse, due to questions of consistency between different methods of introducing noninteger particle number into DFT, and as irrelevant for practical applications. However, several recent works suggest that the DD should be taken into account in designing functionals with the correct asymptotic behavior.[10,11,3,12,13] Indeed, the derivatives with respect to particle number are intimately connected to the relation between the highest occupied Kohn-Sham eigenvalue $\epsilon_{\rm H}$ and the ionization potential I and, hence, to the asymptotic value $v_{\rm xc}^{\infty} \equiv \lim_{r\to\infty} v_{\rm xc}(\mathbf{r})$ of the exchange-correlation potential. The proof of these latter relations has been the subject of recent controversy.[14,9,15] This paper reconciles the apparent inconsistencies in the DD obtained from different methods of handling noninteger particle number and gives an independent proof confirming that $\epsilon_{\rm H} = -I$. For finite systems, this means $v_{\rm xc}^{\infty} = 0$ and that the DD affects the shape of $v_{\rm xc}$. Thus, a proper consideration of the DD is important for the design of improved practical functionals.

There are two main approaches for introducing noninteger particle number into DFT. In the fractional occupation number approach, the usual Kohn-Sham equation, which was derived only for integer occupation number, is used, but the orbital occupation numbers f_i entering into the total-energy expression

$$E = -\frac{1}{2}\sum_i f_i \langle \psi_i | \nabla^2 | \psi_i \rangle + \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\rm xc}[\rho] \quad (1.2)$$

through the kinetic energy and the charge density $\rho(\mathbf{r}) = \sum_j f_j |\psi_j(\mathbf{r})|^2$ are allowed to be fractional. In this formalism, Janak's theorem states that

$$\left(\frac{\partial E}{\partial f_i} \right)_v = \epsilon_i , \quad (1.3)$$

wherever the derivative exists.[16]

The fractional occupation number approach can be viewed as simply providing a well-defined smooth extension of the charge density and of the energy expression, which

were derived only for integer occupation number, to include the case of fractional occupation number. Note that both the charge density and the energy expressions are smooth functions of the f_i on the interval $0<f_i\leqslant 1$. Minimization of the energy expression (1.2) then yields a Kohn-Sham equation involving fractional occupation number. This is purely a mathematical device that allows properties of the functionals to be studied in the neighborhood of integer particle number, thereby giving useful information about the physical case of an integer number of particles. In this point of view, no physical reality is ascribed to the fractional particle number.

In the ensemble approach,[7] the orbital occupation numbers of the standard Kohn-Sham theory remain integer but an ensemble is introduced where a fraction $0\leqslant f\leqslant 1$ of the members have $N+1$ electrons while the rest have N electrons, where N is integer. The energy of a system with a noninteger number of electrons is then defined by

$$E[\rho_{N+f}]=fE[\rho_{N+1}]+(1-f)E[\rho_N], \tag{1.4}$$

$$\rho_{N+f}=f\rho_{N+1}+(1-f)\rho_N. \tag{1.5}$$

In a second step, a Kohn-Sham formalism is constructed for this ensemble energy and density, and a set of fictitious orbitals is introduced for the ensemble. Fractional electron number is handled by allowing partial occupation of the highest occupied Kohn-Sham orbital. The resultant formalism resembles the ''fractional occupation number approach'' discussed above but with the important difference that the exchange-correlation energy functional $E_{\rm xc}[\rho]$ need not be the same. In particular, $E_{\rm xc}[\rho]$ differs in its domain of definition (and hence in its functional derivatives) in the two approaches. In the fractional occupation number approach, $E_{\rm xc}[\rho]$ is defined (within the Levy-Lieb constrained search formalism) initially over the domain of densities that integrate to an integer number of electrons N and is then extended to fractional N. Whereas in the ensemble approach, $E_{\rm xc}[\rho]$ is defined over the larger domain of ensemble densities, including fractional N, from the outset. Although this might seem like a minor technicality, such differences in the domain of definition of the functional can, in fact, be important (see, e.g., Ref. 17).

While the ensemble approach is convenient for certain formal work, practical calculations making use of noninteger electron number (such as Slater's transition orbital method for calculating ionization potentials and excitation energies) typically use the fractional occupation number formalism. Consistency between results from the two is clearly desirable.

In both approaches, for finite systems it is useful to distinguish a ''bulk region,'' where the density is large enough that the effect on ρ of the addition or removal of a small fraction of an electron is insignificant, and an ''asymptotic region'' where only the most diffuse orbital contributes significantly to the density, which is small. (One would, of course, also expect a ''transition region'' in between, where the density is small but several orbitals still contribute.) In the bulk region, or in infinite systems, the DD must be a nonzero constant,[5,6]

$$\Delta_{\rm xc}=v_{\rm xc}^{+}(\mathbf{r})-v_{\rm xc}^{-}(\mathbf{r}). \tag{1.6}$$

Basic formal considerations yield[5]

$$\Delta_{\rm xc}=\left[\left(\frac{\partial E}{\partial N}\right)_v^{+}-\left(\frac{\partial E}{\partial N}\right)_v^{-}\right]-(\epsilon_{\rm L}-\epsilon_{\rm H}), \tag{1.7}$$

where H and L refer, respectively, to the highest occupied and lowest unoccupied molecular orbitals of the N-electron system, within a zero-temperature formalism where integer-N quantities are defined as the usual[6,8,9] limit from the electron-deficient side. The superscripts $(\pm)$ indicate that the derivative is evaluated at $N\pm 0^{+}$. The result (1.7) is independent of the method used to extend DFT to noninteger particle number. However, evaluating the derivatives in this expression requires the use of one method or the other, thus the values obtained cannot *a priori* be assumed to be independent of the choice of method.

In the ensemble theory, Eq. (1.4) gives

$$\left(\frac{\partial E}{\partial N}\right)_v^{-}=E_N-E_{N-1}=-I, \tag{1.8a}$$

$$\left(\frac{\partial E}{\partial N}\right)_v^{+}=E_{N+1}-E_N=-A, \tag{1.8b}$$

where I and A are, respectively, the ionization potential and electron affinity of the N-electron system. Thus

$$\Delta_{\rm xc}=(I-A)-(\epsilon_{\rm L}-\epsilon_{\rm H}). \tag{1.9}$$

Perdew and Levy[9] have recently shown, completely within their ensemble theory formalism, without recourse to Janak's theorem, that $\epsilon_{\rm H}=-I$. [An earlier proof[7,5] relied on combining Janak's theorem with the ensemble theory derivatives (1.8), which, in view of the differences in the two formalisms, was less clear.] Both these proofs have been contested by Kleinman.[14,15] An independent proof, within the fractional occupation number formalism, will be given in the present paper, thus confirming the result of Perdew, Levy, and co-workers.

In the fractional occupation number formalism, explicit evaluation of the derivatives in Eq. (1.7) can be carried out, given an orbital-dependent energy expression. Such an energy expression is provided by the optimized effective potential (OEP) method. The OEP exchange potential (OEPx) is that local potential $\tilde{v}_{\rm x}$ whose orbitals minimize the Hartree-Fock (HF) energy expression.[18,19] This $\tilde{v}_{\rm x}$ is identical to the Kohn-Sham exchange potential $v_{\rm x}$ within a linear-response approximation.[6] Krieger, Li, and Iafrate[20] extended the OEPx to include fractional occupation number and derived a Janak-type theorem

$$\left(\frac{\partial E}{\partial f_i}\right)_v=\epsilon_i^{\rm HF'}, \tag{1.10}$$

where $\epsilon_i^{\rm HF'}$ is the usual HF orbital energy expression evaluated using the OEPx orbitals. They thus obtain

$$\Delta_{\rm x}=(\epsilon_{\rm L}^{\rm HF'}-\epsilon_{\rm H}^{\rm HF'})-(\epsilon_{\rm L}-\epsilon_{\rm H}). \tag{1.11}$$

They further verified the existence of this nonzero DD by direct calculation.[20] Taken together, Eqs. (1.3) and (1.10)

imply that $\epsilon_{\rm H}=\epsilon_{\rm H}^{\rm HF'}$, in an exchange-only theory. Levy and Görling obtained the same result by using coordinate scaling for the external potential, within the coupling-constant approach.[21]

Although it neglects correlation and relaxation, the work of Krieger, Li, and Iafrate[20] was an important first step toward reconciling the fractional occupation number and ensemble theory results. The fractional occupation number result for $\Delta_{\rm x}$ [Eq. (1.11)] is consistent with the ensemble theory result for $\Delta_{\rm xc}$ [Eq. (1.9)] insofar as Koopmans's theorem gives the correct ionization potential and electron affinity. However, $-\epsilon_{\rm H}^{\rm HF}$ and $-\epsilon_{\rm L}^{\rm HF}$ are not the same as the I and A obtained as total-energy differences ΔE in HF, due to relaxation effects. Yet the ensemble theory clearly gives the total-energy difference quantities [Eqs. (1.8)]. This is a concrete illustration that, in the exchange-only case, the functional $E_{\rm xc}[\rho]$ must be different in the fractional occupation number and ensemble approaches, since otherwise the two approaches would agree. [This same difference in the functional is also seen from the difference between the Levy and Görling (exchange-only) result that $\epsilon_{\rm H}=\epsilon_{\rm H}^{\rm HF'}$ (which does not use ensemble theory) and the ensemble theory result[7,9] that $\epsilon_{\rm H}=-I$.] It has also been emphasized[22] that the ensemble theory assumes E to be a linear functional of ρ, whereas the fractional occupation number formalism does not.

In order to address the questions of consistency between the ensemble theory and fractional occupation number results for the DD, the inclusion of relaxation effects in the latter formalism, the relation between $\epsilon_{\rm H}$ and I, and the value of $v_{\rm xc}^{\infty}$, the general (correlated) OEP method,[23] which is based on many-body Green functions, will be used. Note that many-body Green-function theory includes relaxation effects. In particular, the negatives of the eigenvalues of Dyson's quasiparticle equation

$$[\hat{h}_H+\hat{\Sigma}_{\rm xc}(\omega_I)]\psi_I=\omega_I\psi_I, \tag{1.12}$$

where $\hat{h}_H$ is the Hartree operator and $\hat{\Sigma}_{\rm xc}$ is the exchange-correlation self-energy operator, are the ionization potentials and electron affinities. The first ionization potential and electron affinity solutions will be referred to as $\omega_{\rm H}$ and $\omega_{\rm L}$, respectively.

II. JANAK-TYPE THEOREM FOR THE OEP

In the (correlated) OEP method, the exchange-correlation potential $\tilde{v}_{\rm xc}$ is that potential, local in space and time, whose Green function makes a Klein-Luttinger-Ward-type energy expression stationary.[23] The resultant $\tilde{v}_{\rm xc}$ is identical to the exact $v_{\rm xc}$ of Kohn-Sham theory, within a linear-response approximation.[23] A similar energy expression was used by Sham and Schlüter in their original treatment of the DD;[6,24] however, they did not address the issue of noninteger particle number.

First, note that the OEP method can be extended to handle fractional occupation number by writing the OEP Green function in the form

$$\tilde{G}(\mathbf{r},\mathbf{r}';\omega)=\sum_i f_i\frac{\tilde{\psi}_i(\mathbf{r})\tilde{\psi}_i^*(\mathbf{r}')}{\omega-\tilde{\epsilon}_i-i\eta}+\sum_i (1-f_i)\frac{\tilde{\psi}_i(\mathbf{r})\tilde{\psi}_i^*(\mathbf{r}')}{\omega-\tilde{\epsilon}_i+i\eta}, \tag{2.1}$$

where the tilde indicates OEP quantities, $\eta=0^+$, and f_i may be noninteger. Combined with the OEP energy expression [Eq. (2.11) of Ref. 23], this provides an explicit formula for the ''exact'' exchange-correlation energy at fractional occupation number.

A Janak-type theorem for the OEP can now be derived. The notation of Ref. 23 will be used. The derivative to be evaluated is

$$\left(\frac{\partial\tilde{E}}{\partial f_i}\right)_v=\int\int\int\frac{\delta\tilde{E}}{\delta\tilde{G}(1,2;\omega)}\left(\frac{\partial\tilde{G}(1,2;\omega)}{\partial f_i}\right)_v d1\,d2\,d\omega. \tag{2.2}$$

Differentiating Eq. (2.1) gives

$$\left(\frac{\partial\tilde{G}(1,2;\omega)}{\partial f_i}\right)_v=\frac{\tilde{\psi}_i(1)\tilde{\psi}_i^*(2)}{\omega-\tilde{\epsilon}_i-i\eta}-\frac{\tilde{\psi}_i(1)\tilde{\psi}_i^*(2)}{\omega-\tilde{\epsilon}_i+i\eta}. \tag{2.3}$$

The derivative $\delta\tilde{E}/\delta\tilde{G}$ is given in Eq. (2.16) of Ref. 23 [see also Eq. (2.21) of that reference],

$$\frac{\delta\tilde{E}}{\delta\tilde{G}(1,2;\omega)}=\frac{e^{i\eta\omega}}{2\pi i}[\Sigma'_{\rm xc}(2,1;\omega)-\tilde{v}_{\rm xc}(1)\delta(1-2)+\omega\delta(1-2)]. \tag{2.4}$$

Inserting Eqs. (2.3) and (2.4) into Eq. (2.2) and taking advantage of the fact that the factor $e^{i\eta\omega}$ allows us to close the contour in the upper-half complex ω plane gives

$$\left(\frac{\partial\tilde{E}}{\partial f_i}\right)_v=\frac{1}{2\pi i}\oint(\omega+\langle\tilde{\psi}_i|\hat{\Sigma}'_{\rm xc}(\omega)-\tilde{v}_{\rm xc}|\tilde{\psi}_i\rangle)\times[(\omega-\tilde{\epsilon}_i-i\eta)^{-1}-(\omega-\tilde{\epsilon}_i+i\eta)^{-1}]d\omega. \tag{2.5}$$

This integral is straightforward and evaluates to

$$\left(\frac{\partial\tilde{E}}{\partial f_i}\right)_v=\tilde{\epsilon}_i+\langle\tilde{\psi}_i|\hat{\Sigma}'_{\rm xc}(\tilde{\epsilon}_i)-\tilde{v}_{\rm xc}|\tilde{\psi}_i\rangle\equiv\epsilon_i^{\rm QP'}, \tag{2.6}$$

which is the usual quasiparticle energy expression evaluated using the OEP orbitals and orbital energies. ($\hat{\Sigma}'_{\rm xc}$ denotes $\hat{\Sigma}_{\rm xc}$ but constructed using the OEP orbitals and orbital energies.) Note that this is analogous to Janak's theorem. Note also that it reduces to the exchange-only Janak-type theorem (1.10) of Krieger, Li, and Iafrate when correlation is neglected.

Using the present OEP Janak theorem (2.6) to evaluate the derivatives in Eq. (1.7) gives

$$\Delta_{\rm xc}=(\epsilon_{\rm L}^{\rm QP'}-\epsilon_{\rm H}^{\rm QP'})-(\epsilon_{\rm L}-\epsilon_{\rm H}). \tag{2.7}$$

This is a positive quantity because $\epsilon_{\rm L}^{\rm QP'}$ is the orbital energy for an electron that is repeled by one more electron than is the case for $\epsilon_{\rm H}^{\rm QP'}$, while the Kohn-Sham orbital energies $\epsilon_{\rm L}$ and $\epsilon_{\rm H}$ are for orbitals that see the same effective potential.

Equation (2.7) is consistent with the result for $\Delta_{\rm xc}$ obtained from ensemble theory [Eq. (1.9)] because the quasiparticle energies $\epsilon_i^{\rm QP'}$ [Eq. (2.6)] provide first-order solutions to Dyson's equation (1.12). (See Ref. 25 for a discussion of the similarities and differences between OEP orbitals and Dyson orbitals.) In particular $\epsilon_{\rm H}^{\rm QP'}\cong -I$ and $\epsilon_{\rm L}^{\rm QP'}\cong -A$.

In the fractional occupation number formalism, many-body effects, including relaxation effects, are included through the self-energy. This can be seen explicitly at second order. Using the usual second-order approximation for the self-energy, the OEP energy expression is

$$\tilde{E}^{(2)}=E_{\rm HF'}+\frac{1}{4}\sum\frac{f_if_j(1-f_k)(1-f_l)|V'_{ij,kl}|^2}{\tilde{\epsilon}_i+\tilde{\epsilon}_j-\tilde{\epsilon}_k-\tilde{\epsilon}_l}, \quad (2.8)$$

where $V'_{ik,jl}$ is an electron repulsion integral involving the OEP orbitals. Straightforward differentiation gives, for the ionization potential out of orbital q,

$$\left(\frac{\partial\tilde{E}^{(2)}}{\partial f_q}\right)_{f_q=1}=\epsilon_q^{\rm HF'}-\sum\frac{f_j(1-f_l)|V'_{qj,ql}|^2}{\tilde{\epsilon}_j-\tilde{\epsilon}_l}+\frac{1}{2}\sum\frac{f_j(1-f_k)(1-f_l)|V'_{qj,kl}|^2}{\tilde{\epsilon}_q+\tilde{\epsilon}_j-\tilde{\epsilon}_k-\tilde{\epsilon}_l}-\frac{1}{2}\sum_{i,j\neq q}\frac{f_if_j(1-f_l)|V'_{ij,ql}|^2}{\tilde{\epsilon}_i+\tilde{\epsilon}_j-\tilde{\epsilon}_q-\tilde{\epsilon}_l}. \quad (2.9)$$

Physically, the terms on the right-hand side represent, respectively (from left to right), the Koopmans's theorem value, relaxation, pair-correlation with orbital q, and correlation changes due to electron reorganization, and there is an analogous formula and interpretation for the electron affinity.[26] This makes it clear how relaxation (and some other) effects are in fact included, providing a sufficiently accurate model of $v_{\rm xc}$ is used. Note also that $\tilde{E}$ is a nonlinear function of the f_q, but that it is approximately linear.

III. RELATION BETWEEN $\epsilon_{\rm H}$ AND THE IONIZATION POTENTIAL

The Janak theorems for the OEP and Kohn-Sham theories can now be used together to relate $\epsilon_{\rm H}$ to I. Kohn-Sham theory gives the exact ground-state total energy. This is also true of the OEP theory, within the linear-response approximation used there. Thus, $E^{\rm KS}=\tilde{E}$. Applying the respective Janak theorems [Eqs. (1.3) and (2.6)] gives $\epsilon_{\rm H}=\epsilon_{\rm H}^{\rm QP'}$, which, as noted above, gives to first order

$$\epsilon_{\rm H}=\omega_{\rm H}, \quad (3.1)$$

which equals $-I$ in the limit of the exact self-energy $\hat{\Sigma}_{\rm xc}$. Note that the restriction to the ground-state energy means that Eq. (3.1) applies only to the highest occupied molecular-orbital energy. This is the same as the result obtained by Perdew, Levy, and co-workers within their ensemble theory formalism.[7,9] The present proof, within the fractional occupation number formalism, is completely independent of theirs and thus confirms their result. Note that no requirement has been imposed to fix the arbitrary additive constant in $\tilde{v}_{\rm xc}$, and it remains undetermined.

IV. ASYMPTOTIC BEHAVIOR OF $v_{\rm xc}$

For finite systems, one of the important implications of the result (3.1) is that, taken together with the known asymptotic form of $v_{\rm xc}$,[27] it determines the value of $v_{\rm xc}^{\infty}$, as has been shown by Levy, Perdew, and Sahni.[28,9] This is shown again here in order to resolve questions[22,14] surrounding the effect of neglecting relaxation effects, or other approximations, on the value of $v_{\rm xc}^{\infty}$.

Subtracting the Dyson equation from the Kohn-Sham equation in the asymptotic region, and noting that $\psi_{\rm H}$ in the two equations must be the same in the asymptotic region since ρ is necessarily the same, gives[27]

$$v_{\rm xc}(\mathbf{r})\rightarrow\frac{\psi_{\rm H}^*(\mathbf{r})\hat{\Sigma}_{\rm xc}(\omega_{\rm H})\psi_{\rm H}(\mathbf{r})}{|\psi_{\rm H}(\mathbf{r})|^2}+(\epsilon_{\rm H}-\omega_{\rm H})\rightarrow-\frac{f_{\rm H}}{r}+(\epsilon_{\rm H}-\omega_{\rm H}), \quad (4.1)$$

for the exact $v_{\rm xc}$, in the asymptotic region. In the limit $r\rightarrow\infty$,

$$v_{\rm xc}^{\infty}=\epsilon_{\rm H}-\omega_{\rm H}=\epsilon_{\rm H}+I. \quad (4.2)$$

Thus, Eq. (3.1) implies $v_{\rm xc}^{\infty}=0$.

Now, note that Eq. (4.1) applies to any self-energy approximation whose correlation part falls off more rapidly than the exchange part. (This is the case for nearly all systems of interest except superconductors.) The exact $v_{\rm xc}$ is determined by the exact $\hat{\Sigma}_{\rm xc}$, via the Sham-Schlüter equation.[6] Similarly, for any self-energy approximation there is a corresponding approximate $v_{\rm xc}$, which is exact within the model defined by the self-energy approximation. In the case of an approximate self-energy, $\omega_{\rm H}$ in Eq. (4.1) is the quasiparticle eigenvalue for whatever approximate $\hat{\Sigma}_{\rm xc}$ was used. For example, in the exchange-only case, $\omega_{\rm H}=\epsilon_{\rm H}^{\rm HF}$. This means that in Eq. (4.2), I should be interpreted as $-\omega_{\rm H}$, not as ΔE, when these are different. Thus neglect of relaxation (or other) effects in $\hat{\Sigma}_{\rm xc}$ resulting in $-\omega_{\rm H}\neq\Delta E$ does not affect the asymptotic value of the corresponding $v_{\rm xc}$, contrary to a previous argument.[22,14]

Since the conclusion that $v_{\rm xc}^{\infty}=0$ is based on the Janak theorems, it holds independent of particle number. Thus, the DD must go to zero at infinity. In the asymptotic region, Eq. (4.1) gives

$$v_{\rm xc}^{-}(\mathbf{r})\rightarrow-\frac{1}{r}, \quad v_{\rm xc}^{+}(\mathbf{r})\rightarrow-\frac{\delta}{r}, \quad (4.3)$$

upon addition or removal of a small fraction δ of an electron. Thus, the DD vanishes as $1/r$ in the asymptotic region. This is the same as the exchange-only result of Krieger, Li, and Iafrate[20] for the asymptotic behavior of the DD, since only $\hat{\Sigma}_{\rm x}$ contributes at large r.

V. CONCLUSION

This paper has presented a Janak-type theorem based on the full (correlated) OEP model. This was used to evaluate the DD. The resulting value of Δ_{xc} [Eq. (2.7)] is consistent with the ensemble theory result of Perdew and Levy[5] [Eq. (1.9)] and reduces to the exchange-only result of Krieger, Li, and Iafrate[20] [Eq. (1.11)] when correlation is neglected. The present correlated OEP treatment makes it clear that the main apparent differences[22,14] between the ensemble and fractional occupation number results, such as the inclusion of relaxation effects, are resolved when a sufficiently accurate model of v_{xc} is used. The present OEP-Janak theorem is also used to show that $\epsilon_H = -I$, thus confirming the widely known but recently contested[14,15] theorem of Perdew, Levy, and co-workers.[7,9] For finite systems this implies $v_{xc}^{\infty}=0$, independent of particle number, and thus that the DD vanishes as $1/r$ in the asymptotic region.

The difference between the effect of the DD on v_{xc} in the bulk and asymptotic regions means that the DD affects the *shape* of v_{xc}, even at fixed, integer particle number. The development of improved practical approximations of v_{xc} is important, and especially so for the calculation of high-lying discrete excitations and properties sensitive to the ''large-r'' region. Now that a full OEP treatment has been given, and the ensemble theory and fractional occupation number results for the DD have been shown to be consistent, the challenge will be to develop approximate functionals that incorporate the essential features of the DD. As a step in this direction, we have shown how the effect of the DD on the shape of v_{xc} can be mimicked through an asymptotic correction scheme involving a shifted local-density approximation (or gradient corrected) v_{xc} and that this does indeed yield a significant improvement in high-lying discrete excitation energies from time-dependent DFT.[12,13]

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