

Adiabatic Connection and the Kohn–Sham Variety of Potential–Functional Theory

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Abstract: In potential–functional theory the total electronic energy is expressed as a functional of the external potential. We discuss how approximations, $T_s^{\text{app}}[v]$, of the noninteracting kinetic energy functional can be exploited for interacting systems. Two possibilities are discussed: (a) Via an adiabatic connection formula, $T_s^{\text{app}}[v_0]$ can be used directly with the external potential v_0 of the interacting system, and (b) by employing the variational principle of density functional theory, the kinetic energy functional $T_s^{\text{app}}[v_s]$ is evaluated at the Kohn–Sham potential v_s , which, in turn, is determined by an iterative procedure. Advantages and disadvantages of the two approaches are discussed.

The Kohn–Sham equations of density functional theory (DFT) are the method of choice to calculate medium to large electronic systems of up to 10000–100000 electrons. The basic strategy of the Kohn–Sham method is to map the interacting electronic system of interest onto a system of noninteracting particles such that the latter has the same ground-state density as the interacting system. Solving the Kohn–Sham single-particle Schrödinger equations rather than the interacting many-body Schrödinger equation makes the problem numerically tractable. However, for larger systems, even the solution of the Kohn–Sham equations becomes too costly. Here, orbital-free DFT,¹ that is, the representation of the total energy as an explicit functional of the density, is the ultimate method. Alternatively, one may express the total energy as a functional of the external potential.² This alternative approach, called potential–functional theory (PFT), will be addressed in this communication. The approach has its roots in semiclassical Wigner–Kirkwood-type expansions.^{3–5} The design of more refined semiclassical approximations was outlined in the 1960s by Kohn and Sham⁶ in one-dimensional systems. Three-dimensional generalizations have also been formulated.⁷ On the basis of the work of Kohn and Sham, highly

accurate potential functionals in 1D have recently been developed by Elliot et al.⁸

We start from the many-body Hamiltonian

$$\hat{H}[v] = \sum_{i=1}^N v(\mathbf{r}_i) + \hat{T} + \hat{W}_{\text{ee}} \quad (1)$$

where \hat{T} is the kinetic energy and \hat{W}_{ee} is the Coulomb repulsion of the electrons. Restricting ourselves to potentials $v(\mathbf{r})$ having a nondegenerate ground state, the Schrödinger equation

$$\hat{H}[v]\Psi[v] = E[v]\Psi[v] \quad (2)$$

implies that the ground-state wave function $\Psi[v]$ is uniquely determined by the potential $v(\mathbf{r})$. Consequently, the ground-state density

$$\rho[v](\mathbf{r}) = \int d^3r_2 \dots \int d^3r_N |\Psi[v](\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 \quad (3)$$

is a unique functional of the potential, and so is the total energy

$$E[v] = T[v] + W[v] + \int \rho[v](\mathbf{r})v(\mathbf{r})d^3r \quad (4)$$

with

$$T[v] = \langle \Psi[v] | \hat{T} | \Psi[v] \rangle \quad (5)$$

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$$W[v] = \langle \Psi[v] | \hat{W}_{ee} | \Psi[v] \rangle \quad (6)$$

The basic idea of PFT is to find good approximations for $T[v]$ and $W[v]$ so that the total energy of a given system, characterized by the external potential $v_0(\mathbf{r})$, is obtained directly by plugging $v_0(\mathbf{r})$ in the functional (eq 4).

Most potential functionals known to date have been obtained by semiclassical considerations.^{3–6} Highly accurate approximations have recently been constructed⁸ for the kinetic energy and the density of noninteracting particles in one spatial dimension (1D). To use these approximations as part of the total energy functional of interacting systems, it appears desirable to have a coupling constant integration formula (or adiabatic connection) in PFT. We will deduce such a formula in the following. Consider the λ -dependent Hamiltonian

$$H_\lambda[v] = \hat{T} + \lambda \hat{W}_{ee} + \sum_{i=1}^N v(\mathbf{r}_i) \quad (7)$$

where λ with $0 \leq \lambda \leq 1$ allows us to switch off the electron–electron interaction. The $v(\mathbf{r})$ is an external potential which, in contrast to the adiabatic connection of DFT, is independent of λ . For the time being, we restrict ourselves to systems where for each λ , the ground-state solution $\Psi_\lambda[v]$ of the Schrödinger equation

$$H_\lambda[v] \Psi_\lambda[v] = E_\lambda[v] \Psi_\lambda[v] \quad (8)$$

is nondegenerate. Evidently, the fully interacting ($\lambda = 1$) total energy can then be written as

$$E_{\lambda=1}[v] = E_{\lambda=0}[v] + \int_0^1 \frac{dE_\lambda[v]}{d\lambda} d\lambda \quad (9)$$

Let us first evaluate the total energy functional of noninteracting particles $E_{\lambda=0}[v]$. The (nondegenerate) ground-state wave function of noninteracting particles is the determinant

$$\Psi_s[v](\mathbf{r}_1 \dots \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \det\{\varphi_j[v](\mathbf{r}_k)\} \quad (10)$$

with orbitals satisfying the single-particle Schrödinger equation (atomic units are used)

$$\left(-\frac{\nabla^2}{2} + v(\mathbf{r})\right) \varphi_j[v](\mathbf{r}) = \epsilon_j[v] \varphi_j[v](\mathbf{r}) \quad (11)$$

The total energy of the noninteracting system then reads

$$E_{\lambda=0}[v] = T_s[v] + \int \rho_s[v](\mathbf{r}) v(\mathbf{r}) d^3r \quad (12)$$

with

$$T_s[v] = \sum_{j=1}^N \int d^3r \varphi_j^*[v](\mathbf{r}) \left(-\frac{\nabla^2}{2}\right) \varphi_j[v](\mathbf{r}) \quad (13)$$

$$\rho_s[v](\mathbf{r}) = \sum_{j=1}^N |\varphi_j[v](\mathbf{r})|^2 \quad (14)$$

The integrand of the coupling constant integral can be evaluated using the Hellmann–Feynman theorem

$$\begin{aligned} \frac{dE_\lambda[v]}{d\lambda} &= \left\langle \Psi_\lambda[v] \left| \frac{\partial \hat{H}_\lambda[v]}{\partial \lambda} \right| \Psi_\lambda[v] \right\rangle \\ &= \langle \Psi_\lambda[v] | \hat{W}_{ee} | \Psi_\lambda[v] \rangle \end{aligned} \quad (15)$$

Defining

$$W_\lambda[v] := \langle \Psi_\lambda[v] | \hat{W}_{ee} | \Psi_\lambda[v] \rangle \quad (16)$$

the total energy at full interaction can then be written as

$$E_{\lambda=1}[v] = T_s[v] + \int \rho_s[v](\mathbf{r}) v(\mathbf{r}) d^3r + \int_0^1 W_\lambda[v] d\lambda \quad (17)$$

This is the adiabatic connection formula of PFT. $T_s[v]$ and $\rho_s[v]$ are exactly the functionals for which highly accurate approximations have recently become available.⁸ $W_\lambda[v]$, on the one hand, can be approximated using standard many-body perturbation theory, that is, Feynman diagrams with

$$\hat{H}_s[v] = \hat{T} + \sum_{i=1}^N v(\mathbf{r}_i) \quad (18)$$

representing the unperturbed Hamiltonian. This leads to approximations of the form

$$W_\lambda[v] = W_\lambda[G_s[v]] \quad (19)$$

where $G_s[v](\mathbf{x}, \mathbf{x}')$ is the Green's function associated with the noninteracting Hamiltonian (eq 18). The functional $G_s[v]$, on the other hand, can be approximated very accurately, at least in 1D, using the semiclassical approach described in refs 6 and 8. Hence, the adiabatic connection formula of PFT can readily be used to evaluate the total energy of interacting systems without ever solving any interacting or noninteracting Schrödinger equation. Despite this attractive feature, the approach described so far has some drawbacks:

(i) In practice, evaluation of the functional $W_\lambda[G_s[v]]$ in eq 19 may be rather costly.

(ii) In the context of DFT, the noninteracting kinetic energy functional, $T_s^D[\rho_{\text{int}}]$, evaluated at the interacting ground-state density ρ_{int} , represents a major contribution to the total energy. In PFT, an analogous role is played by the functional $T_s[v]$ (cf. eqs 13 and 17). The latter, however, has to be evaluated at the external potential, $v_0(\mathbf{r})$, that is, the bare nuclear Coulomb potential in the case of atoms, molecules, and solids. The density of noninteracting particles moving in the bare nuclear Coulomb potential is much more localized than the interacting density, $\rho_{\text{int}}(\mathbf{r})$, and consequently, $T_s[v_0]$ will be much larger than $T_s^D[\rho_{\text{int}}]$. It is expected that, in terms of numbers, $T_s^D[\rho_{\text{int}}]$ is much closer to the fully interacting kinetic energy, $T^D[\rho_{\text{int}}]$, than $T_s[v_0]$ is to $T[v_0]$. The difference, $T[v_0] - T_s[v_0]$, is of course accounted for by the coupling constant integral $\int_0^1 W_\lambda[v] d\lambda$. However, since $T[v_0] - T_s[v_0]$ is expected to be larger than $T^D[\rho_{\text{int}}] - T_s^D[\rho_{\text{int}}]$, one has to work harder to construct sufficiently accurate approximations for the potential functional $W_\lambda[v]$ than for the corresponding density functional $W_\lambda^D[\rho]$.

(iii) The approach described so far is not variational. In fact, a variational principle has been formulated as well.^{2,9} Employing the Rayleigh–Ritz principle, one simply minimizes the total energy functional

$$E_{v_0}[v] = \langle \Psi[v] | \hat{T} + \hat{W}_{\text{ee}} + \sum_{i=1}^N v_0(\mathbf{r}_i) | \Psi[v] \rangle \quad (20)$$

$$= T[v] + W[v] + \int \rho[v](\mathbf{r}) v_0(\mathbf{r}) d^3r$$

with respect to $v(\mathbf{r})$. Hence, for the exact functional, the following Euler–Lagrange equation is satisfied

$$\left. \frac{\delta E_{v_0}[v]}{\delta v(\mathbf{r})} \right|_{v_0} = 0 \quad (21)$$

In practice, however, this variational principle is not very useful. For an approximate functional, $E_{v_0}^{\text{app}}[v]$, the stationary point will generally be achieved at an approximate external potential, $v_0^{\text{app}}(\mathbf{r})$, which is the solution of the Euler equation

$$\left. \frac{\delta E_{v_0}^{\text{app}}[v]}{\delta v(\mathbf{r})} \right|_{v_0^{\text{app}}} = 0 \quad (22)$$

The variationally optimized external potential $v_0^{\text{app}}(\mathbf{r})$, however, is not really of interest because, after all, the true external potential, $v_0(\mathbf{r})$, is known. Furthermore, at the true external potential, $E_{v_0}^{\text{app}}[v_0]$ will usually not be stationary, which may cause difficulties, for example, in the calculation of vibrational spectra. However, the variational eq 22 may be useful as a quality check for the approximate functional $E_{v_0}^{\text{app}}[v]$. One may either compare $v_0(\mathbf{r})$ and $v_0^{\text{app}}(\mathbf{r})$ directly, or one may assess the difference $E_{v_0}^{\text{app}}[v_0] - E_{v_0}^{\text{app}}[v_0^{\text{app}}]$.

The three difficulties mentioned above can all be overcome by another flavor of PFT, namely, by representing the total energy as a functional of the Kohn–Sham potential, $v_s(\mathbf{r})$, rather than the external potential. This idea was recently proposed by Yang and co-workers.² The crucial point is to exploit the standard variational principle of DFT

$$\left. \frac{\delta E_{v_0}[\rho]}{\delta \rho(r)} \right|_{\rho_0} = 0 \quad (23)$$

where the total energy functional is given by

$$E_{v_0}[\rho] = T_s^{\text{D}}[\rho] + \int \rho(\mathbf{r}) v_0(\mathbf{r}) d^3r + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho] \quad (24)$$

where $v_0(r)$ is the fixed external potential of the system at hand and $E_{\text{H}}[\rho]$ and $E_{\text{xc}}[\rho]$ are the usual Hartree and exchange–correlation energy functionals of DFT. Assuming noninteracting v representability, the ground-state density $\rho(\mathbf{r})$ of an interacting system with external potential $v(\mathbf{r})$ can be represented as the ground-state density of noninteracting particles moving in the Kohn–Sham potential $v_s(\mathbf{r})$. The uniqueness of $v_s(\mathbf{r})$ follows from the Hohenberg–Kohn theorem, while the existence of $v_s(\mathbf{r})$ (i.e., v representability) has been demonstrated¹⁰ in the ensemble sense for systems on an arbitrarily fine but discrete real-space grid. Hence, we can represent the densities $\rho(\mathbf{r})$ as $\rho_s[v_s](\mathbf{r})$ with the functional $\rho_s[v]$ given by eq 14. Consequently, substituting $\rho_s[v_s](\mathbf{r})$ for $\rho(\mathbf{r})$ in eq 24, the variational principle (eq 23) of DFT can be recast in the form

$$\left. \frac{\delta E_{v_0}[v_s]}{\delta v_s(r)} \right|_{v_{s,0}} = 0 \quad (25)$$

with

$$E_{v_0}[v_s] := T_s^{\text{D}}[\rho_s[v_s]] + \int \rho_s[v_s](\mathbf{r}) v_0(\mathbf{r}) d^3r + E_{\text{H}}[\rho_s[v_s]] + E_{\text{xc}}[\rho_s[v_s]] \quad (26)$$

where $v_{s,0}$ is the Kohn–Sham potential corresponding to the interacting ground-state density $\rho_0(r)$ of the external potential $v_0(\mathbf{r})$

$$v_{s,0}(\mathbf{r}) = v_s[\rho_0](\mathbf{r}) \quad (27)$$

It is easy to see that

$$T_s^{\text{D}}[\rho_s[v_s]] = T_s[v_s] \quad (28)$$

with the potential functional $T_s[v]$ defined in eq 13. Hence, the total energy functional (eq 26) can be written as

$$E_{v_0}[v_s] = T_s[v_s] + \int \rho_s[v_s](\mathbf{r}) v_0(\mathbf{r}) d^3r + E_{\text{H}}[\rho_s[v_s]] + E_{\text{xc}}[\rho_s[v_s]] \quad (29)$$

As opposed to the external potential functional (eq 17), eq 29 has to be evaluated at the Kohn–Sham potential $v_{s,0}(\mathbf{r})$. The latter is determined from the variational principle (eq 25); using the exact definition (eq 13) of the functional $T_s[v]$, one immediately verifies that

$$\frac{\delta T_s[v_s]}{\delta v_s(\mathbf{r})} = - \int d^3r' v_s(\mathbf{r}') \frac{\delta \rho_s[v_s](\mathbf{r}')}{\delta v_s(\mathbf{r})} \quad (30)$$

and the variational principle (eq 25) yields the desired potential as

$$v_{s,0}(\mathbf{r}) = v_0(\mathbf{r}) + v_{\text{H}}[\rho_s[v_{s,0}]] + v_{\text{xc}}[\rho_s[v_{s,0}]] \quad (31)$$

where, as usual

$$v_{\text{H}}[\rho](\mathbf{r}) := \frac{\delta E_{\text{H}}[\rho]}{\delta \rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' \quad (32)$$

$$v_{\text{xc}}[\rho](\mathbf{r}) := \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})} \quad (33)$$

In ref 2, the above variational approach was employed with the exact functional $T_s[v_s]$ to put the optimized effective potential method on a firm variational basis. Here, we exploit the variational approach with approximate functionals $T_s^{\text{app}}[v_s]$ and $\rho_s^{\text{app}}[v_s]$. We propose to determine the desired potential $v_{s,0}(\mathbf{r})$ by the following iteration

$$\rho^{n+1}(\mathbf{r}) = \rho_s^{\text{app}}[v_s^{(n)}](\mathbf{r}) \quad (34)$$

$$v_s^{(n+1)}(\mathbf{r}) = v_0(\mathbf{r}) + v_{\text{H}}[\rho^{n+1}](\mathbf{r}) + v_{\text{xc}}[\rho^{n+1}](\mathbf{r}) \quad (35)$$

Clearly, eqs 34 and 35 would represent the usual Kohn–Sham self-consistency loop if the new density ρ^{n+1} had to be evaluated from the exact functional (eq 14), that is, by solving the one-body Schrödinger equation with the potential $v_s^{(n)}(\mathbf{r})$. By using the approximate (but explicit) functional $\rho_s^{\text{app}}[v_s^{(n)}]$

in eq 34, the costly step of solving the Schrödinger equation is avoided. The charm of this procedure is that it only relies on the well-established time-proven approximations for the density functional $v_{xc}[\rho]$ and on the noninteracting potential functionals $\rho_s^{\text{app}}[v]$ and $T_s^{\text{app}}[v]$, both of which are accurately known within the recent semiclassical approximations.⁸

It should be noted that the above derivation of the variational eq 31 relies on the exact noninteracting functionals $T_s[v_s]$ and $\rho_s[v_s]$. For approximate functionals, $T_s^{\text{app}}[v_s]$ and $\rho_s^{\text{app}}[v_s]$, the Euler eq 25 takes the form

$$\left. \frac{\delta T_s^{\text{app}}[v_s]}{\delta v_s(\mathbf{r})} \right|_{v_{s,0}} = - \int d^3 r' (v_0(\mathbf{r}') + v_H[\rho_s^{\text{app}}[v_{s,0}]](\mathbf{r}') + v_{xc}[\rho_s^{\text{app}}[v_{s,0}]](\mathbf{r}')) \frac{\delta \rho_s^{\text{app}}[v_s](\mathbf{r}')}{\delta v_s(\mathbf{r})} \Big|_{v_{s,0}} \quad (36)$$

This general variational equation is, of course, much more complicated than eq 31. As a consequence, in each iterative step, the following nonlinear equation

$$\left. \frac{\delta T_s^{\text{app}}[v_s]}{\delta v_s(\mathbf{r})} \right|_{v_s^{(n+1)}} = - \int d^3 r' (v_0(\mathbf{r}') + v_H[\rho^{(n+1)}](\mathbf{r}') + v_{xc}[\rho^{(n+1)}](\mathbf{r}')) \frac{\delta \rho_s^{\text{app}}[v_s](\mathbf{r}')}{\delta v_s(\mathbf{r})} \Big|_{v_s^{(n+1)}} \quad (37)$$

has to be solved to obtain the new potential v_s^{n+1} . This raises the question whether, for certain approximations, the variational eq 36 still takes the simple form of eq 31. This is expected, if $T_s^{\text{app}}[v_s]$ and $\rho_s^{\text{app}}[v_s]$ come from the same semiclassical expansion for the one-body Green's function, $G_s^{\text{app}}[v_s](\mathbf{r})$. In the Appendix, we show explicitly that this is the case for two specific varieties of semiclassical Green's functions.

Employing the iteration (eqs 34 and 35) and plugging the resulting $v_{s,0}(\mathbf{r})$ in the functional of eq 29, the total energy of the interacting system is evaluated without ever solving the interacting or noninteracting Schrödinger equation. This procedure is clearly a very efficient way to exploit PFT for interacting particles. We expect the approach to become the method of choice for very large interacting many-body systems.

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Appendix

Semiclassical Approximations in PFT. An alternative expression for the noninteracting kinetic energy functional as given by eq 13 is the following

$$T_s[v] = \int d^3 x t_s[v](\mathbf{x}) \quad (A1)$$

with

$$t_s[v](\mathbf{x}) = \frac{1}{2\pi i} \oint_C d\varepsilon [\varepsilon - v(\mathbf{x})] G_s[v](\mathbf{x}, \varepsilon) \quad (A2)$$

The integration in eq A2 is in the complex ε -plane, along any closed contour C which encloses the occupied energy levels.⁶ $G_s[v](\mathbf{x}, \varepsilon)$ is the diagonal of the noninteracting one-body Green function, which is the solution of

$$\left[-\frac{1}{2} \nabla^2 + v(\mathbf{x}) - \varepsilon \right] G_s(\mathbf{x}, \mathbf{x}', \varepsilon) = \delta(\mathbf{x} - \mathbf{x}') \quad (A3)$$

Throughout this appendix, we use the shorthand notation $G_s[v](\mathbf{x}, \varepsilon) \equiv G_s[v](\mathbf{x}, \mathbf{x}, \varepsilon)$. The density can be expressed as a contour integral as well

$$\rho_s[v](\mathbf{x}) = \frac{1}{2\pi i} \oint_C d\varepsilon G_s[v](\mathbf{x}, \varepsilon) \quad (A4)$$

Taking the functional derivative of eq A1 with respect to $v(\mathbf{y})$, we obtain the identity

$$\frac{\delta T_s[v]}{\delta v(\mathbf{y})} = -\rho_s[v](\mathbf{y}) + \int d^3 x \oint_C \frac{\varepsilon d\varepsilon}{2\pi i} \frac{\delta G_s[v](\mathbf{x}, \varepsilon)}{\delta v(\mathbf{y})} - \int d^3 x v(\mathbf{x}) \frac{\delta \rho_s[v](\mathbf{x})}{\delta v(\mathbf{y})} \quad (A5)$$

Equation A5 is valid both for the exact, $G_s[v](\mathbf{x}, \varepsilon)$, and for approximate, $G_s^{\text{app}}[v](\mathbf{x}, \varepsilon)$, Green's functions. In the former case, comparison with the result of eq 30 reveals that for consistency between both expressions, the first and second terms on the right-hand side of eq A5 should cancel each other. In the following, we will show that this cancellation also holds for approximate Green's functions, provided that $G_s^{\text{app}}[v](\mathbf{x}, \varepsilon)$ satisfies two conditions. The first one

$$G_s^{\text{app}}[v](\mathbf{x}, \varepsilon) = G_s^{\text{app}}[k(v(\mathbf{x}), \varepsilon)] \quad (A6)$$

requires that $G_s^{\text{app}}[v](\mathbf{x}, \varepsilon)$ depends on v and ε exclusively through its functional dependence on $k(v(\mathbf{x}), \varepsilon) = [2(\varepsilon - v(\mathbf{x}))]^{1/2} \equiv k(\mathbf{x})$. This condition is obviously satisfied for all semiclassical approximations.

The second condition

$$\frac{\delta G_s^{\text{app}}[v](\mathbf{x}, \varepsilon)}{\delta v(\mathbf{y})} = \frac{\delta G_s^{\text{app}}[v](\mathbf{y}, \varepsilon)}{\delta v(\mathbf{x})} \quad (A7)$$

requires symmetry under exchange of coordinates. This condition is obviously satisfied for local Thomas–Fermi–von-Weizsäcker-type approximations

$$G_s^{\text{app}}[k(\mathbf{x})] = g(k(\mathbf{x}), \nabla k(\mathbf{x}), \nabla^2 k(\mathbf{x}), \dots) \quad (A8)$$

It is straightforward to verify that the symmetry condition (eq A7) also holds for the exact Green's function. To prove

the cancellation of the first two terms on the right-hand side of eq A5 under these conditions, we first realize that

$$\begin{aligned} \int d^3x \frac{\delta G_s^{\text{app}}[v](\mathbf{x}, \varepsilon)}{\delta v(\mathbf{y})} &= \int d^3x \frac{\delta G_s^{\text{app}}[v](\mathbf{y}, \varepsilon)}{\delta v(\mathbf{x})} \\ &= \int d^3x \int d^3z \frac{\delta G_s^{\text{app}}[v](\mathbf{y}, \varepsilon)}{\delta k(\mathbf{z})} \frac{\delta k(\mathbf{z})}{\delta v(\mathbf{x})} \\ &= - \int d^3x \int d^3z \frac{\delta G_s^{\text{app}}[v](\mathbf{y}, \varepsilon)}{\delta k(\mathbf{z})} \frac{1}{k(\mathbf{z})} \delta(\mathbf{x} - \mathbf{z}) \quad (\text{A9}) \end{aligned}$$

In the first equality above, we have used the condition in eq A7. In the second equality, eq A6 was used. In the third line, we have used $\delta k(\mathbf{z})/\delta v(\mathbf{x}) = -\delta(\mathbf{x} - \mathbf{z})/k(\mathbf{z})$. Proceeding from eq A9 and noting now that $1/k(\mathbf{z}) = \partial k(\mathbf{z})/\partial \varepsilon$, we obtain

$$\begin{aligned} \int d^3x \frac{\delta G_s^{\text{app}}[v](\mathbf{x}, \varepsilon)}{\delta v(\mathbf{y})} &= - \int d^3x \int d^3z \frac{\delta G_s^{\text{app}}[v](\mathbf{y}, \varepsilon)}{\delta k(\mathbf{z})} \frac{\partial k(\mathbf{z})}{\partial \varepsilon} \delta(\mathbf{x} - \mathbf{z}) \\ &= - \int d^3x \frac{\delta G_s^{\text{app}}[v](\mathbf{y}, \varepsilon)}{\delta k(\mathbf{x})} \frac{\partial k(\mathbf{x})}{\partial \varepsilon} \\ &= - \frac{\partial G_s^{\text{app}}[v](\mathbf{y}, \varepsilon)}{\partial \varepsilon} \quad (\text{A10}) \end{aligned}$$

Inserting this into the second term on the right-hand side of eq A5, we obtain

$$\begin{aligned} \oint_C \frac{\varepsilon d\varepsilon}{2\pi i} \int d^3x \frac{\delta G_s^{\text{app}}[v](\mathbf{x}, \varepsilon)}{\delta v(\mathbf{y})} &= - \oint_C \frac{\varepsilon d\varepsilon}{2\pi i} \frac{\partial G_s^{\text{app}}[v](\mathbf{y}, \varepsilon)}{\partial \varepsilon} \\ &= + \oint_C \frac{d\varepsilon}{2\pi i} G_s^{\text{app}}[v](\mathbf{y}, \varepsilon) \\ &= \rho_s^{\text{app}}[v](\mathbf{y}) \text{ q.e.d.} \quad (\text{A11}) \end{aligned}$$

The second equality above follows from partial integration in the complex plane, with the “boundary” contribution of the contour integral being zero. Through this cancellation, eq A5 reduces to eq 30, with $T_s[v]$ replaced by $T_s^{\text{app}}[v]$ and $\rho_s[v](\mathbf{x})$ by $\rho_s^{\text{app}}[v](\mathbf{x})$. In turn, this implies that the general variational eq 36 reduces to

$$v_{s,0}(\mathbf{x}) = v_0(\mathbf{x}) + v_H[\rho_s^{\text{app}}[v_{s,0}]](\mathbf{x}) + v_{xc}[\rho_s^{\text{app}}[v_{s,0}]](\mathbf{x}) \quad (\text{A12})$$

provided that the approximate functionals $T_s^{\text{app}}[v]$ and $\rho_s^{\text{app}}[v]$ come from approximate Green’s functions $G_s^{\text{app}}[v]$ satisfying the conditions in eqs A7 and A8.

As a further example for the validity of the variational result of eq 31 for approximate functionals of $T_s[v]$ and $\rho_s[v]$, we now discuss the recently developed semiclassical approximations of Elliot et al.⁸ Adding and subtracting NE_F , eqs A1 and A2 can be written in the more convenient form

$$\begin{aligned} T_s[v] &= \int dx [E_F - v(x)] \rho_s[v](x) + \\ &\quad \int dx \oint_C d\varepsilon (\varepsilon - E_F) \frac{G_s[v](x, \varepsilon)}{2\pi i} \quad (\text{A13}) \end{aligned}$$

where, in order to make contact with the work of Elliot et al., we restrict ourselves to the 1D case. Taking again the functional derivative with respect to $\delta v(y)$, we obtain

$$\begin{aligned} \frac{\delta T_s[v]}{\delta v(y)} &= -\rho_s[v](y) + \int dx [E_F - v(x)] \frac{\delta \rho_s[v](x)}{\delta v(y)} + \\ &\quad \int dx \oint_C d\varepsilon \frac{(\varepsilon - E_F)}{2\pi i} \frac{\delta G_s[v](x, \varepsilon)}{\delta v(y)} \quad (\text{A14}) \end{aligned}$$

The particular model studied by Elliot et al.⁸ consists of a one-dimensional box with potential $v(x)$, $0 \leq x \leq L$, and $E_F > v(x)$ everywhere. Hard-wall boundary conditions were imposed at $x = 0$ and L . The corresponding $G_s^{\text{semi}}[v](x, \varepsilon)$ is given by

$$G_s^{\text{semi}}[v](x, \varepsilon) = \frac{f(\Theta)}{k(x)} \quad (\text{A15})$$

with $f(\Theta) = \{\cos \Theta(L) - \cos[2\Theta(x) - \Theta(L)]\}/\sin \Theta(L)$, $k(x) = [2(\varepsilon - v(x))]^{1/2}$, and $\Theta(x) = \int_0^x dx' k(x')$. One easily verifies that $G_s^{\text{semi}}[v](0, \varepsilon) = G_s^{\text{semi}}[v](L, \varepsilon) = 0$. Inserting $G_s^{\text{semi}}[v](x, \varepsilon)$ from eq A15 into the 1D version of eq A4, the semiclassical expression for the density is⁸

$$\rho_s^{\text{semi}}[v](x) = \frac{k_F(x)}{\pi} - \frac{\sin 2\Theta_F(x)}{2T_F k_F(x) \sin \alpha(x)} \quad (\text{A16})$$

where $\alpha(x) = \pi \tau_F(x)/T_F$, $\tau_F(x) = \int_0^x dx' /k_F(x')$, and $T_F = \tau_F(L)$; also, $k_F(x) = [2(E_F - v(x))]^{1/2}$. The first term on the right-hand side of eq A16 is the 1D analogue of the 3D Thomas–Fermi density; the second term, which is of the same order in \hbar as the first, ensures satisfaction of the hard-wall boundary condition $\rho_s^{\text{semi}}[v](0) = \rho_s^{\text{semi}}[v](L) = 0$. Considering that, from eq A15

$$\frac{\delta G_s^{\text{semi}}[v](x, \varepsilon)}{\delta v(y)} = \delta(x - y) \frac{f(\Theta)}{k^3(x)} + \frac{1}{k(x)} \frac{\delta f(\Theta)}{\delta v(y)} \quad (\text{A17})$$

and inserting the first term on the right-hand side of eq A17 in the last term on the right-hand side of eq A14, we obtain

$$\begin{aligned} \int dx \delta(x - y) \oint_C \frac{d\varepsilon}{2\pi i} (\varepsilon - E_F) \frac{f(\Theta)}{k^3(x)} &= \frac{\rho_s^{\text{semi}}[v](y)}{2} - \\ &\quad [E_F - v(y)] \oint_C \frac{d\varepsilon}{2\pi i} \frac{f(\Theta)}{k^3(y)} \quad (\text{A18}) \end{aligned}$$

Following the same steps as those in ref 8, the last contribution in eq A18 is found to be another half of $\rho_s^{\text{semi}}[v](x)$. As the contribution from the second term in the right-hand side of eq A17 to eq A14 can be proved to be null, we obtain again the desired result

$$\frac{\delta T_s^{\text{semi}}[v]}{\delta v(y)} = \int dx [E_F - v(x)] \frac{\delta \rho_s^{\text{semi}}(x)}{\delta v(y)} \quad (\text{A19})$$

which translates also in this case to a variational equation of the type of eq A12, with the label “app” replaced by “semi”.

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