

Reconstruction of Density Functionals from Kohn–Sham Potentials by Integration along Density Scaling Paths

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Abstract: We demonstrate by specific examples that if a Kohn–Sham exchange–correlation potential is given explicitly in terms of the electron density and its derivatives, then one can easily reconstruct the parent density functional by evaluating analytically (or numerically with one-dimensional quadratures) the van Leeuwen–Baerends line integral (*Phys. Rev. A* **1995**, *51*, 170–178) along a path of (coordinate)-scaled densities. The choice of a density scaling path amounts to defining the gauge of the resultant exchange–correlation energy density. The well-known Levy–Perdew virial relation for exchange potentials can be viewed as an analytical line integral along the electron-number-conserving uniform density scaling path. Energies obtained from model exchange–correlation potentials should be interpreted with caution because the reconstructed density functional is unique (up to a gauge transformation) only if the model Kohn–Sham potential is a functional derivative.

1. Introduction

The exchange–correlation (xc) potential of Kohn–Sham density functional theory^{1–3} is formally defined as the functional derivative of the exchange–correlation energy functional $E_{xc}[\rho]$, that is

$$v_{xc}([\rho]; \mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \quad (1)$$

where $\rho(\mathbf{r})$ is the electron density found from Kohn–Sham orbitals as $\rho(\mathbf{r}) = 2 \sum_i^{\text{occ}} |\phi_i(\mathbf{r})|^2$. For simplicity, we will write all equations here for spin-compensated closed-shell systems, so that ϕ_i are the occupied Kohn–Sham orbitals of either one spin. The notation $v_{xc}([\rho]; \mathbf{r})$ emphasizes that v_{xc} is also a functional of ρ at each \mathbf{r} .

A functional $E_{xc}[\rho]$ that can be written in the form

$$E_{xc}[\rho] = \int d^3r f_{xc}(\mathbf{r}, \rho, \nabla \rho, \nabla^2 \rho, \dots) \quad (2)$$

where $d^3r \equiv dx dy dz$, is said to be an *explicit* density functional. The functional derivative of explicit functionals can be found directly by using a standard formula of the calculus of variations^{2,4} and cast in the form

$$v_{xc}([\rho]; \mathbf{r}) = \frac{\partial f_{xc}}{\partial \rho} - \nabla \cdot \left(\frac{\partial f_{xc}}{\partial \nabla \rho} \right) + \nabla^2 \left(\frac{\partial f_{xc}}{\partial \nabla^2 \rho} \right) - \dots \quad (3)$$

in which $\partial f_{xc} / \partial \nabla \rho$ is a shorthand for a vector with three components $\partial f_{xc} / \partial \rho'_\alpha$, where $\rho'_\alpha \equiv \partial \rho / \partial \alpha$ and $\alpha = x, y, z$. A functional of Kohn–Sham orbitals that cannot be reduced to the form of eq 2 is said to be *implicit* or orbital-dependent.⁵ The functional derivative of an implicit functional can be found indirectly as a solution of the optimized effective potential equation.^{5–7} Thus, given a density functional $E_{xc}[\rho]$, it is always possible to find the corresponding functional derivative $v_{xc}([\rho]; \mathbf{r})$.

An interesting and practically important question is whether it is possible to invert functional differentiation, that is, to reconstruct an exchange–correlation functional from a given Kohn–Sham potential. Clearly, the solution to the inverse problem is not unique because exchange–correlation energy density $f_{xc}(\mathbf{r})$ of eq 2 is defined only up to an arbitrary function that integrates to zero.^{8–13} Therefore, we will qualify the question: Given a functional derivative $v_{xc}([\rho]; \mathbf{r})$, is it possible to reconstruct its parent functional up to a gauge transformation of the energy density?

It is well-known that for exchange-only functionals, the functional differentiation can be inverted by the Levy–Perdew virial relation^{14,15}

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$$E_x[\rho] = - \int d^3r \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_x([\rho]; \mathbf{r}) \quad (4)$$

Less known is the fact that it is also possible to recover the entire exchange-correlation functional from the corresponding Kohn–Sham potential by the line-integral method of van Leeuwen and Baerends^{16–19}

$$E_{xc}[\rho] = \int_0^1 dt \int d^3r v_{xc}([\rho_t]; \mathbf{r}) \frac{\partial \rho_t(\mathbf{r})}{\partial t} \quad (5)$$

where $\rho_t(\mathbf{r})$ is a continuously parametrized density such that $E_{xc}[\rho_0] = 0$ and $\rho_1(\mathbf{r}) = \rho(\mathbf{r})$. Unlike exchange-only functionals, an exchange-correlation functional cannot be reconstructed from $v_{xc}([\rho]; \mathbf{r})$ at density $\rho(\mathbf{r})$ alone: eq 5 requires knowing the Kohn–Sham potential along a whole *path* of densities. It is essential, however, that the mapping from $\rho_t(\mathbf{r})$ to $v_{xc}([\rho_t]; \mathbf{r})$ does not have to be variational and that the resulting value of $E_{xc}[\rho]$ is path-independent.

The purpose of this work is to draw attention to the fact that if the exchange-correlation potential is given analytically in terms of $\rho(\mathbf{r})$, then the knowledge of the potential for all intermediate densities $\rho_t(\mathbf{r})$ is implicitly included. In such cases, the line integration in eq 5 can be carried out numerically or even analytically. We will demonstrate this by evaluating line integrals for several explicit exchange and correlation potentials along alternative density transformation paths to recover the corresponding parent functionals, often in unrecognizable disguise. We will also discuss what happens when one attempts to reconstruct a density functional from a potential $v_{xc}([\rho]; \mathbf{r})$ that is not a functional derivative.

2. Integration of Functional Derivatives

On the basis of eq 3, it is obvious that for any *local* exchange-correlation potential (that is, a potential that depends only on \mathbf{r} and ρ but not on $\nabla\rho$ or higher derivatives), the exchange-correlation energy density of the parent functional can be found simply as an indefinite integral (antiderivative) of v_{xc} with respect to ρ . This implies that any local $v_{xc}([\rho]; \mathbf{r})$ is a functional derivative of some $E_{xc}[\rho]$. For gradient-dependent potentials, a more general method is required, such as eq 5.

Let us derive the van Leeuwen–Baerends formula. Consider an arbitrary exchange-correlation functional $E_{xc}[\rho]$. Following van Leeuwen and Baerends,¹⁶ we introduce a parametrized density $\rho_t(\mathbf{r})$, where t is a parameter varying in the range $A \leq t \leq B$. If $E_{xc}[\rho_t]$ is a continuous function of t in this interval, then we can write

$$E_{xc}[\rho_B] - E_{xc}[\rho_A] = \int_A^B dt \frac{dE_{xc}[\rho_t]}{dt} \quad (6)$$

As shown in the Appendix, the derivative in eq 6 can be rewritten as

$$\frac{dE_{xc}[\rho_t]}{dt} = \int d^3r \frac{\partial E_{xc}[\rho_t]}{\partial \rho_t(\mathbf{r})} \frac{\partial \rho_t(\mathbf{r})}{\partial t} \quad (7)$$

where the integral is over the entire real-space domain of the density $\rho(\mathbf{r})$. The functional derivative appearing in eq

7 is the Kohn–Sham potential written in terms of the parametrized density

$$\frac{\delta E_{xc}[\rho_t]}{\delta \rho_t(\mathbf{r})} \equiv v_{xc}([\rho_t]; \mathbf{r}) = v_{xc}([\rho]; \mathbf{r}) \Big|_{\rho=\rho_t} \quad (8)$$

Combining eqs 6–8 we obtain

$$E_{xc}[\rho_B] - E_{xc}[\rho_A] = \int_A^B dt \int d^3r v_{xc}([\rho_t]; \mathbf{r}) \frac{\partial \rho_t(\mathbf{r})}{\partial t} \quad (9)$$

which holds for an arbitrary path connecting ρ_A and ρ_B .¹⁶ Equation 9 is the most general form of the van Leeuwen–Baerends line integral. In particular, if $\rho_t(\mathbf{r})$ is parametrized in the range $0 \leq t \leq 1$ in such a way that $E_{xc}[\rho_0] = 0$ and $\rho_1(\mathbf{r}) = \rho(\mathbf{r})$, then eq 9 reduces to eq 5.

The standard interpretation¹⁶ of the van Leeuwen–Baerends formula is that it provides an “energy expression” for obtaining the value of $E_{xc}[\rho_B]$ when the value of $E_{xc}[\rho_A]$ is known (for numerical examples, see refs 20–22). Here we adopt a somewhat different view according to which eq 5 is a solution to the inverse problem of functional differentiation. To emphasize this, we will call an expression for $E_{xc}[\rho]$ obtained by eq 5 a *reconstruction* of the density functional. The fact that the integration path in eq 5 is arbitrary (except for the end points) suggests that there are many equivalent reconstructions from a given functional derivative.

3. Density Scaling Paths

In this work, we are concerned with reconstruction of density functionals from exchange-correlation potentials that are *explicit* functionals of the density. For such potentials, it is convenient to take $\rho_t(\mathbf{r})$ as a magnitude- or coordinate-scaled density. This allows one to have $v_{xc}([\rho_t]; \mathbf{r})$ in a closed form at any point along the integration path. We will employ the following three density scaling transformations:

(a) Linear scaling^{16,23–25}

$$\rho_q(\mathbf{r}) = q\rho(\mathbf{r}) \quad (10)$$

which we will call here the *q*-scaling. A line of *q*-scaled densities from $q = 0$ to $q = 1$ will be referred to as a *Q*-path.

(b) Uniform number-conserving coordinate scaling studied extensively by Levy²⁶

$$\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda \mathbf{r}) \quad (11)$$

or the λ -scaling. A line of λ -scaled densities from $\lambda = 0$ to $\lambda = 1$ will be called a Λ -path.

(c) Thomas–Fermi-inspired scaling introduced by Perdew and co-workers²⁷

$$\rho_\zeta(\mathbf{r}) = \zeta^2 \rho(\zeta^{1/3} \mathbf{r}) \quad (12)$$

which we will call the ζ -scaling. A line of ζ -scaled densities from $\zeta = 0$ to $\zeta = 1$ is termed a *Z*-path.

Among these paths, only the Λ -path conserves the electron number. The number of electrons along the *Q*- and *Z*-paths changes as qN and ζN , respectively, where N is the electron number at $\rho_1(\mathbf{r})$. Note that the condition $E_{xc}[\rho_0] = 0$ is trivially satisfied for the *Q*-path. For the Λ -path, $\rho_\lambda(\mathbf{r})$

becomes infinitely dilute (vanishes locally) as $\lambda \rightarrow 0$, so that $\lim_{\lambda \rightarrow 0} E_{xc}[\rho_\lambda] = 0$.^{17,26,28} For the Z-path, both $\rho_\xi(\mathbf{r})$ and $E_{xc}[\rho_\xi]$ vanish in the $\xi \rightarrow 0$ limit.

Partial derivatives of these scaled densities with respect to their scaling parameters are readily obtained by applying the chain rule of differentiation. For future reference, we write out the results

$$\frac{\partial \rho_q(\mathbf{r})}{\partial q} = \rho(\mathbf{r}) \quad (13)$$

$$\frac{\partial \rho_\lambda(\mathbf{r})}{\partial \lambda} = \lambda^2 [3\rho(\lambda\mathbf{r}) + (\lambda\mathbf{r}) \cdot \nabla_{\lambda\mathbf{r}} \rho(\lambda\mathbf{r})] \quad (14)$$

$$\frac{\partial \rho_\xi(\mathbf{r})}{\partial \xi} = \xi \left[2\rho(\xi^{1/3}\mathbf{r}) + \frac{\xi^{1/3}\mathbf{r}}{3} \cdot \nabla_{\xi^{1/3}\mathbf{r}} \rho(\xi^{1/3}\mathbf{r}) \right] \quad (15)$$

If $v_{xc}([\rho_t]; \mathbf{r})$ and $\partial \rho_t(\mathbf{r})/\partial t$ in eq 5 are piecewise-continuous functions of \mathbf{r} and t and if the real-space integral exists for every t , as can be expected for physical exchange-correlation potentials and reasonable scaling transformations of the density, then by Fubini's theorem²⁹ the order of integration over t and \mathbf{r} in eq 5 can be interchanged. We will exploit this property repeatedly in sections 4–6.

4. Levy–Perdew Virial Relation

The Levy–Perdew virial relation is a special case of the generalized virial theorem derived by Ghosh and Parr¹⁵ based on universal scaling properties of homogeneous density functionals. Here we would like to emphasize an even deeper generalization,¹⁶ according to which the Levy–Perdew relation is a special case of the line integral (eq 5) taken along the Λ -path. To see this, recall that the functional derivative of any valid exchange functional is homogeneous of degree one with respect to the uniform density scaling^{30,31}

$$v_x([\rho_\lambda]; \mathbf{r}) = \lambda v_x([\rho]; \lambda\mathbf{r}) \quad (16)$$

Using eqs 5, 14, and 16 we have

$$E_x[\rho] = \int_0^1 d\lambda \int d^3r \lambda v_x([\rho]; \lambda\mathbf{r}) \times \lambda^2 [3\rho(\lambda\mathbf{r}) + (\lambda\mathbf{r}) \cdot \nabla_{\lambda\mathbf{r}} \rho(\lambda\mathbf{r})] \quad (17)$$

The parameter λ in the second integral can be eliminated by the variable change $\lambda\mathbf{r} \rightarrow \mathbf{r}'$. The result is

$$E_x[\rho] = \int_0^1 d\lambda \int d^3r' v_x([\rho]; \mathbf{r}') [3\rho(\mathbf{r}') + \mathbf{r}' \cdot \nabla_{\mathbf{r}'} \rho(\mathbf{r}')] \quad (18)$$

where $d^3r' = d^3(\lambda\mathbf{r}) \equiv d(\lambda x)d(\lambda y)d(\lambda z)$. Switching back to \mathbf{r} and noting that the integral over λ is simply 1, we obtain

$$E_x[\rho] = \int d^3r v_x([\rho]; \mathbf{r}) [3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r})] \quad (19)$$

An additional integration by parts in the last equation gives eq 4. The two forms of the Levy–Perdew reconstruction given by eqs 4 and 19 differ only by a gauge transformation of the energy density.

5. Examples

We will now illustrate how eq 5 can be used to reconstruct exchange and correlation density functionals from the corresponding functional derivatives. For verification purposes, our examples deliberately employ potentials whose parent functionals are known from the outset. Of course, in real-life applications of the line integral method, parent functionals would be normally unknown *a priori*.

5.1. Local Density Approximation for Exchange. Consider the local density approximation (LDA) for exchange

$$E_x^{\text{LDA}}[\rho] = -C_x \int d^3r \rho^{4/3}(\mathbf{r}) \quad (20)$$

where $C_x = (3/4)(3/\pi)^{1/3}$. The functional derivative of the LDA functional is

$$v_x^{\text{LDA}}([\rho]; \mathbf{r}) = -\frac{4}{3} C_x \rho^{1/3}(\mathbf{r}) \quad (21)$$

Suppose we did *not* know what functional generated this potential. Let us employ the line integral method to reconstruct this “unknown” functional.

Under the q -scaling of the density, the LDA exchange potential transforms as

$$v_x^{\text{LDA}}([\rho_q]; \mathbf{r}) = q^{1/3} v_x^{\text{LDA}}([\rho]; \mathbf{r}) \quad (22)$$

Multiplying this potential by $\partial \rho_q(\mathbf{r})/\partial q = \rho(\mathbf{r})$ and integrating over q we obtain the Q-reconstruction

$$E_{x,Q}^{\text{LDA}}[\rho] = \frac{3}{4} \int d^3r \rho(\mathbf{r}) v_x^{\text{LDA}}([\rho]; \mathbf{r}) \quad (23)$$

which, in view of eq 21, is identical with $E_x^{\text{LDA}}[\rho]$.

Under the uniform density scaling, the LDA exchange potential transforms as

$$v_x^{\text{LDA}}([\rho_\lambda]; \mathbf{r}) = \lambda v_x^{\text{LDA}}([\rho]; \lambda\mathbf{r}) \quad (24)$$

Inserting the λ -scaled LDA potential into eq 5 (or directly into eq 19) we obtain the Λ -reconstruction

$$E_{x,\Lambda}^{\text{LDA}}[\rho] = \int d^3r v_x^{\text{LDA}}([\rho]; \mathbf{r}) [3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r})] \quad (25)$$

which is just the Levy–Perdew relation. It is not obvious, but can be proven by invoking the divergence theorem, that the value of $E_{x,\Lambda}^{\text{LDA}}[\rho]$ is equal to $E_{x,Q}^{\text{LDA}}[\rho]$ for any ρ vanishing at infinity. Numerical evaluation of the integrals of eqs 23 and 25 for test densities also confirms their equivalence.

The Q- and Λ -reconstructions of the LDA for exchange are well-known results. In fact, eqs 23 and 25 are special cases of the scaling identities for strictly local functionals derived by Parr et al.³² using the density functional expansion method.

Consider now the ξ -scaling of the LDA exchange potential

$$v_x^{\text{LDA}}([\rho_\xi]; \mathbf{r}) = \xi^{2/3} v_x^{\text{LDA}}([\rho]; \xi^{1/3}\mathbf{r}) \quad (26)$$

Substitution of the ξ -scaled LDA exchange potential into the line integral formula yields

$$E_{x,Z}^{\text{LDA}}[\rho] = \int_0^1 d\zeta \int d^3r \zeta^{2/3} v_x^{\text{LDA}}([\rho]; \zeta^{1/3} \mathbf{r}) \times \zeta \left[2\rho(\zeta^{1/3} \mathbf{r}) + \frac{\zeta^{1/3} \mathbf{r}}{3} \cdot \nabla_{\zeta^{1/3} \mathbf{r}} \rho(\zeta^{1/3} \mathbf{r}) \right] \quad (27)$$

After the substitution $\zeta^{1/3} \mathbf{r} \rightarrow \mathbf{r}$ and integration over ζ we obtain the Z-reconstruction of the LDA

$$E_{x,Z}^{\text{LDA}}[\rho] = \frac{3}{5} \int d^3r v_x^{\text{LDA}}([\rho]; \mathbf{r}) \left[2\rho(\mathbf{r}) + \frac{\mathbf{r}}{3} \cdot \nabla \rho(\mathbf{r}) \right] \quad (28)$$

This functional is actually a linear combination of the Q- and Λ -reconstructions, namely, $4/5 E_{x,Q}^{\text{LDA}}[\rho] + 1/5 E_{x,\Lambda}^{\text{LDA}}[\rho]$, as can be seen by combining eqs 23 and 25. Since each of the Q- and Λ -reconstructions is numerically equivalent to $E_x^{\text{LDA}}[\rho]$, the value of $E_{x,Z}^{\text{LDA}}[\rho]$ is also equal to $E_x^{\text{LDA}}[\rho]$. Thus, eqs 23, 25, and 28 are different but equivalent representations of the same functional.

5.2. Generalized Gradient Approximation for Exchange.

To illustrate how the line integral formalism works for gradient-dependent Kohn–Sham potentials, we will reconstruct the exchange functional of Gill³³

$$E_x^{\text{G96}}[\rho] = E_x^{\text{LDA}}[\rho] - \int d^3r \beta \rho^{4/3}(\mathbf{r}) s^{3/2}(\mathbf{r}) \quad (29)$$

where s is a dimensionless reduced gradient defined as

$$s = \frac{|\nabla \rho|}{\rho^{4/3}} \quad (30)$$

and $\beta = 2^{1/6}/137$ is a constant. The functional derivative of the Gill exchange can be written as

$$v_x^{\text{G96}}([\rho]; \mathbf{r}) = v_x^{\text{LDA}}([\rho]; \mathbf{r}) + w_x^{\text{G96}}([\rho]; \mathbf{r}) \quad (31)$$

where the first term is given by eq 21 and

$$w_x^{\text{G96}}([\rho]; \mathbf{r}) = \frac{2\beta}{3} \rho^{1/3} s^{3/2} + \nabla \cdot \left(\frac{3\beta}{2\rho^{4/3} s^{1/2}} \nabla \rho \right) \quad (32)$$

The last expression was obtained with the help of eq 3 and by using the identity $\partial s / \partial \nabla \rho = \rho^{-8/3} s^{-1} \nabla \rho$.

Under the q -scaling, $s_q(\mathbf{r}) = q^{-1/3} s(\mathbf{r})$, so the Gill potential becomes

$$v_x^{\text{G96}}([\rho_q]; \mathbf{r}) = q^{1/3} v_x^{\text{LDA}}([\rho]; \mathbf{r}) + q^{-1/6} w_x^{\text{G96}}([\rho]; \mathbf{r}) \quad (33)$$

The line integral of this potential along the Q-path is

$$E_{x,Q}^{\text{G96}}[\rho] = E_x^{\text{LDA}}[\rho] + \frac{6}{5} \int d^3r \rho(\mathbf{r}) w_x^{\text{G96}}([\rho]; \mathbf{r}) \quad (34)$$

where we have utilized eq 23. The integral in eq 34 can be simplified through integration by parts to give

$$\int d^3r \rho(\mathbf{r}) w_x^{\text{G96}}([\rho]; \mathbf{r}) = -\frac{5}{6} \int d^3r \beta \rho^{4/3} s^{3/2} \quad (35)$$

Inserting this result into eq 34 we obtain the right-hand side of eq 29. Thus, the line integral of the Gill exchange potential along the Q-path recovers the energy density of the parent functional in the original gauge.

Under the λ -scaling, the Gill exchange potential transforms just like any other exchange potential

$$v_x^{\text{G96}}([\rho_\lambda]; \mathbf{r}) = \lambda v_x^{\text{G96}}([\rho]; \lambda \mathbf{r}) \quad (36)$$

so the line integral along the Λ -path is simply the Levy–Perdew reconstruction

$$E_{x,\Lambda}^{\text{G96}}[\rho] = E_x^{\text{LDA}}[\rho] + \int d^3r w_x^{\text{G96}}([\rho]; \mathbf{r}) [3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r})] \quad (37)$$

Finally, under the ζ -scaling, $s_\zeta(\mathbf{r}) = \zeta^{-1/3} s(\zeta^{1/3} \mathbf{r})$, so

$$v_x^{\text{G96}}([\rho_\zeta]; \mathbf{r}) = \zeta^{2/3} v_x^{\text{LDA}}([\rho]; \zeta^{1/3} \mathbf{r}) + \zeta^{1/6} w_x^{\text{G96}}([\rho]; \zeta^{1/3} \mathbf{r}) \quad (38)$$

The line integral along the Z-path is then

$$E_{x,Z}^{\text{G96}}[\rho] = E_x^{\text{LDA}}[\rho] + \frac{6}{7} \int d^3r w_x^{\text{G96}}([\rho]; \mathbf{r}) \left[2\rho(\mathbf{r}) + \frac{\mathbf{r}}{3} \cdot \nabla \rho(\mathbf{r}) \right] \quad (39)$$

This functional is a linear combination of the Q- and Λ -reconstructions $E_{x,Q}^{\text{G96}}[\rho]$ and $E_{x,\Lambda}^{\text{G96}}[\rho]$ with the weights $5/7$ and $2/7$, respectively. Therefore, $E_{x,Z}^{\text{G96}}[\rho]$ is also numerically equivalent to the original $E_x^{\text{G96}}[\rho]$ up to a gauge transformation of the energy density.

It would be straightforward, although tedious, to carry out similar reconstructions for gradient-dependent exchange potentials derived from more complicated functionals such as Becke's 1988 exchange.³⁴ However, when the parent functional is known *a priori* in some gauge, such reconstructions are of interest only as ways of generating gauge-transformed energy densities.

5.3. Local Density Approximation for Correlation.

Consider now the Wigner correlation functional³⁵

$$E_c^{\text{W}}[\rho] = - \int d^3r \frac{a\rho}{b + r_s} \quad (40)$$

where $r_s = (3/4\pi\rho)^{1/3}$ and $a = 0.44$ and $b = 7.8$ are constants. The functional derivative of $E_c^{\text{W}}[\rho]$ is

$$v_c^{\text{W}}([\rho]; \mathbf{r}) = -a \frac{b + (4/3)r_s(\mathbf{r})}{[b + r_s(\mathbf{r})]^2} \quad (41)$$

where we have used the fact that $dr_s/d\rho = -r_s/3\rho$. Let us reconstruct the Wigner correlation functional from $v_c^{\text{W}}([\rho]; \mathbf{r})$ by using eq 5 and integrating the potential along three distinct density scaling paths.

The q -scaled Wigner correlation potential is

$$v_c^{\text{W}}([\rho_q]; \mathbf{r}) = -a \frac{b + (4/3)q^{-1/3}r_s(\mathbf{r})}{[b + q^{-1/3}r_s(\mathbf{r})]^2} \quad (42)$$

The Q-reconstruction is, therefore

$$\begin{aligned} E_{c,Q}^{\text{W}}[\rho] &= -a \int d^3r \rho(\mathbf{r}) \int_0^1 dq \frac{b + (4/3)q^{-1/3}r_s}{(b + q^{-1/3}r_s)^2} \\ &= - \int d^3r \frac{a\rho(\mathbf{r})}{b + r_s(\mathbf{r})} \end{aligned} \quad (43)$$

which is precisely the original functional $E_c^{\text{W}}[\rho]$.

Under the uniform density scaling, the Wigner correlation potential transforms as

$$v_c^W([\rho_\lambda]; \mathbf{r}) = -a \frac{b + (4/3)\lambda^{-1}r_s(\lambda\mathbf{r})}{[b + \lambda^{-1}r_s(\lambda\mathbf{r})]^2} \quad (44)$$

The line integral along the Λ -path can be written as

$$E_{c,\Lambda}^W[\rho] = -a \int_0^1 d\lambda \int \frac{d^3(\lambda\mathbf{r})}{\lambda} \frac{b + (4/3)\lambda^{-1}r_s(\lambda\mathbf{r})}{[b + \lambda^{-1}r_s(\lambda\mathbf{r})]^2} \times [3\rho(\lambda\mathbf{r}) + (\lambda\mathbf{r}) \cdot \nabla_{\lambda\mathbf{r}}\rho(\lambda\mathbf{r})] \quad (45)$$

Changing the real-space integration variable $\lambda\mathbf{r} \rightarrow \mathbf{r}$ and integrating over λ we obtain the Λ -reconstruction of the Wigner functional

$$E_{c,\Lambda}^W[\rho] = -a \int d^3r [3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla\rho(\mathbf{r})] \times \left[\frac{1}{b} \ln \frac{b + r_s}{r_s} + \frac{1}{3(b + r_s)} \right] \quad (46)$$

Similarly, we have derived the Z-reconstruction

$$E_{c,Z}^W[\rho] = -a \int d^3r \left[2\rho(\mathbf{r}) + \frac{\mathbf{r}}{3} \cdot \nabla\rho(\mathbf{r}) \right] \times \left[\frac{1 - r_s/b - (3/2)(r_s/b)^2}{b + r_s} + \frac{3r_s^{3/2}\tan^{-1}\sqrt{b/r_s}}{2b^{5/2}} \right] \quad (47)$$

which, unlike the exchange functionals above, does not appear to be a linear combination of the Q- and Λ -reconstructions.

We have implemented the functionals $E_{c,\Lambda}^W[\rho]$ and $E_{c,Z}^W[\rho]$ in a development version of the Gaussian program³⁶ and evaluated them numerically for a number of atoms and molecules using several Gaussian basis sets and large real-space grids. Our calculations confirm that, within submicroharte errors of the real-space integration, the correlation energies obtained by eqs 46 and 47 are exactly the same as those obtained by eq 40.

5.4. Generalized Gradient Approximation for Correlation. Consider the gradient-dependent Wilson–Levy correlation functional for spin-compensated systems³⁷

$$E_c^{\text{WL}}[\rho] = \int d^3r \frac{(a_0 + a_1s)\rho}{b_0 + b_1s + r_s} \quad (48)$$

where s is the dimensionless reduced density gradient given by eq 30 and $a_0 = -0.74860$, $a_1 = 0.06001$, $b_0 = 3.60073$, and $b_1 = 2^{4/3}b'_1$, where $b'_1 = 0.90000$ are constants. The functional derivative of this approximation can be written as

$$v_c^{\text{WL}}([\rho]; \mathbf{r}) = \frac{\partial f_c^{\text{WL}}}{\partial \rho} - \nabla \cdot \left(\frac{\partial f_c^{\text{WL}}}{\partial \nabla \rho} \right) \quad (49)$$

where

$$f_c^{\text{WL}} = \frac{(a_0 + a_1s)\rho}{b_0 + b_1s + r_s} \quad (50)$$

is the correlation energy density in the initial gauge and

$$\frac{\partial f_c^{\text{WL}}}{\partial \rho} = \frac{a_0 - a_1s/3}{b_0 + b_1s + r_s} - \frac{1}{3} \frac{(r_s - 4b_1s)(a_0 + a_1s)}{(b_0 + b_1s + r_s)^2} \quad (51)$$

$$\frac{\partial f_c^{\text{WL}}}{\partial \nabla \rho} = \left[\frac{a_1s\rho^{-5/3}}{b_0 + b_1s + r_s} - \frac{(a_0 + a_1s)b_1\rho^{-8/3}}{(b_0 + b_1s + r_s)^2} \right] \nabla \rho \quad (52)$$

Rewriting eq 49 in terms of ρ_q and substituting the result into eq 5 we obtain for the Q-reconstruction

$$E_{c,Q}^{\text{WL}}[\rho] = \int d^3r \rho(\mathbf{r}) \tilde{v}_{c,Q}^{\text{WL}}([\rho]; \mathbf{r}) \quad (53)$$

where $\tilde{v}_{c,Q}^{\text{WL}}$ is the *hypercorrelated*⁹ potential defined by

$$\tilde{v}_{c,Q}^{\text{WL}}([\rho]; \mathbf{r}) = \int_0^1 dq v_c^{\text{WL}}([\rho_q]; \mathbf{r}) \quad (54)$$

which can be evaluated analytically. Alternatively, one can first simplify the Hessian-dependent term in eq 53 through integration by parts and then integrate the result over q . In the latter case, the Q-reconstructed energy density is identical with the f_c^{WL} of eq 50.

Before proceeding further, we point out that analytical integration over the density scaling parameter can be too complicated to be worth pursuing. In such cases, it is much more efficient to evaluate the line integral *numerically* for each real-space grid point \mathbf{r} using a one-dimensional Gauss–Legendre quadrature³⁸ with a sufficient number of nodes. After the numerical integration over the density scaling parameter at each \mathbf{r} is completed, the real-space integration is performed as usual using standard three-dimensional quadratures. The overhead cost associated with the numerical integration over a density scaling parameter is actually quite small. As a test, we have implemented a 64-point Gauss–Legendre quadrature over q in eq 53 (after it was simplified by real-space integration by parts) and used it for a number of atomic and molecular densities. The agreement between the total correlation energies obtained by analytical and numerical integration over q is excellent.

We have also implemented a Λ -path reconstruction of the Wilson–Levy correlation functional using 16-, 32-, and 64-node Gauss–Legendre quadratures for the integral over λ . Provided that a large basis set is used (e.g., the universal Gaussian basis set of ref 39), the agreement between the Λ -reconstruction of the Wilson–Levy functional and its conventional implementation can be made better than 1 microharte.

We have not evaluated the line integral of the Wilson–Levy correlation potential along the Z-path, but it would not be difficult to do so using numerical quadratures.

5.5. Functionals Other Than Exchange–Correlation. So far, we have dealt exclusively with exchange–correlation functionals and potentials. However, the line integration technique is very general in that it applies to functionals of any other type. We shall illustrate this with examples involving the Coulomb repulsion and the von Weizsäcker kinetic energy functionals.

The Coulomb repulsion functional is

$$J[\rho] = \frac{1}{2} \int d^3r \int d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (55)$$

and has the following functional derivative

$$v_J([\rho]; \mathbf{r}) = \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (56)$$

The q -scaled Coulomb potential is

$$v_J([\rho_q]; \mathbf{r}) = qv_J([\rho]; \mathbf{r}) \quad (57)$$

The line integral along the Q-path recovers the Coulomb energy density in the original gauge

$$J_Q[\rho] = \frac{1}{2} \int d^3r \rho(\mathbf{r}) v_J([\rho]; \mathbf{r}) = J[\rho] \quad (58)$$

In contrast, line integrals of the Coulomb potential along the Λ - and Z-paths result in gauge-transformed Coulomb energy densities. Specifically, under the λ -scaling

$$v_J([\rho_\lambda]; \mathbf{r}) = \lambda v_J([\rho]; \lambda \mathbf{r}) \quad (59)$$

so the line integral is

$$J_\Lambda[\rho] = \int d^3r v_J([\rho]; \mathbf{r}) [3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r})] \quad (60)$$

This functional is numerically equivalent to $J[\rho]$ because it has the same value for an arbitrary density (which can be verified numerically). Similarly, under the ξ -scaling

$$v_J([\rho_\xi]; \mathbf{r}) = \xi^{4/3} v_J([\rho]; \xi^{1/3} \mathbf{r}) \quad (61)$$

so the Z-reconstruction of the Coulomb repulsion is

$$J_Z[\rho] = \frac{3}{7} \int d^3r v_J([\rho]; \mathbf{r}) \left[2\rho(\mathbf{r}) + \frac{\mathbf{r}}{3} \cdot \nabla \rho(\mathbf{r}) \right] \quad (62)$$

This functional is a linear combination of the functionals $J_Q[\rho]$ and $J_\Lambda[\rho]$ with coefficients $6/7$ and $1/7$, respectively. Therefore, $J_Z[\rho] = J[\rho]$ for an arbitrary ρ .

Next consider the von Weizsäcker kinetic energy functional which is defined by

$$T_W[\rho] = \int d^3r t_W(\mathbf{r}) = \int d^3r \frac{1}{8} \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \quad (63)$$

Using eq 3, we obtain the functional derivative

$$v_W([\rho]; \mathbf{r}) = \frac{t_W}{\rho} - \frac{1}{4} \frac{\nabla^2 \rho}{\rho} \quad (64)$$

Under the q -scaling

$$v_W([\rho_q]; \mathbf{r}) = \frac{t_W(\mathbf{r})}{\rho(\mathbf{r})} - \frac{1}{4} \frac{\nabla^2 \rho(\mathbf{r})}{\rho(\mathbf{r})} = v_W([\rho]; \mathbf{r}) \quad (65)$$

so the Q-path reconstruction yields

$$\begin{aligned} T_W^Q[\rho] &= \int d^3r v_W([\rho]; \mathbf{r}) \rho(\mathbf{r}) \\ &= \int d^3r \left[t_W(\mathbf{r}) - \frac{1}{4} \nabla^2 \rho(\mathbf{r}) \right] \end{aligned} \quad (66)$$

which equals $T_W[\rho]$ because the Laplacian of $\rho(\mathbf{r})$ integrates to zero.

Under the uniform density scaling

$$v_W([\rho_\lambda]; \mathbf{r}) = \lambda^2 v_W([\rho]; \lambda \mathbf{r}) \quad (67)$$

so the line integral along the Λ -path is

$$T_W^\Lambda[\rho] = \frac{1}{2} \int d^3r v_W([\rho]; \mathbf{r}) [3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r})] \quad (68)$$

Finally, under the ξ -scaling we have

$$v_W([\rho_\xi]; \mathbf{r}) = \xi^{2/3} v_W([\rho]; \xi^{1/3} \mathbf{r}) \quad (69)$$

and the line integral along the Z-path yields

$$T_W^Z[\rho] = \frac{3}{5} \int d^3r v_W([\rho]; \mathbf{r}) \left[2\rho(\mathbf{r}) + \frac{\mathbf{r}}{3} \cdot \nabla \rho(\mathbf{r}) \right] \quad (70)$$

This functional is the sum of $3/5 T_W^Q[\rho]$ and $2/5 T_W^\Lambda[\rho]$. Hence, $T_W^Z[\rho] = T_W[\rho]$.

An example of a reconstruction of the noninteracting kinetic energy functional $T_s[\rho]$ from the exact kinetic potential via the generalized Ghosh–Parr virial relation¹⁵ has been given by King and Handy.⁴⁰ We remark here that their method is equivalent to performing a Λ -reconstruction of the $T_s[\rho]$ functional.

6. Potentials That Are Not Functional Derivatives

Not every analytical expression constructed from $\rho(\mathbf{r})$, $\nabla \rho(\mathbf{r})$, and $\nabla^2 \rho(\mathbf{r})$ is a functional derivative of some generalized gradient approximation with respect to $\rho(\mathbf{r})$. In order for a model potential $v_M([\rho]; \mathbf{r})$ to be a functional derivative of some density functional, it must satisfy the condition^{16,31}

$$\frac{\delta v_M([\rho]; \mathbf{r})}{\delta \rho(\mathbf{r}')} = \frac{\delta v_M([\rho]; \mathbf{r}')}{\delta \rho(\mathbf{r})} \quad (71)$$

A model potential $v_M([\rho]; \mathbf{r})$ that does not have a parent density functional from which it can be derived by eq 1 will be called here a *stray* potential. Existence of stray potentials adds an interesting dimension to the density functional reconstruction problem because the line integral evaluated for a stray potential is path-dependent.¹⁶ This principle can be used as a test for stray potentials.

Consider, for example, the following problem:⁴¹ Does there exist a density functional for which the expression

$$v_M([\rho]; \mathbf{r}) = \frac{|\nabla \rho(\mathbf{r})|}{\rho(\mathbf{r})} \quad (72)$$

is a functional derivative? We will show that the answer to this question is negative.

Under the q -scaling, this “potential” is unchanged

$$v_M([\rho_q]; \mathbf{r}) = \frac{|\nabla \rho_q|}{\rho_q} = v_M([\rho]; \mathbf{r}) \quad (73)$$

Therefore, the line integral along the Q-path is

$$I_Q = \int_0^1 dq \int d^3r v_M([\rho_q]; \mathbf{r}) \frac{\partial \rho_q(\mathbf{r})}{\partial q} = \int d^3r |\nabla \rho(\mathbf{r})| \quad (74)$$

Under the uniform density scaling

$$v_M([\rho_\lambda]; \mathbf{r}) = \frac{|\nabla \rho_\lambda|}{\rho_\lambda} = \lambda v_M([\rho]; \lambda \mathbf{r}) \quad (75)$$

so the line integral along the Λ -path is

$$I_{\Lambda} = \int_0^1 d\lambda \int d^3r v_M([\rho_{\lambda}]; \mathbf{r}) \frac{\partial \rho_{\lambda}(\mathbf{r})}{\partial \lambda} \\ = \int d^3r \frac{|\nabla \rho(\mathbf{r})|}{\rho(\mathbf{r})} [3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r})] \quad (76)$$

Finally, under the ξ -scaling

$$v_M([\rho_{\xi}]; \mathbf{r}) = \frac{|\nabla \rho_{\xi}(\mathbf{r})|}{\rho_{\xi}(\mathbf{r})} = \xi^{1/3} v_M([\rho]; \xi^{1/3} \mathbf{r}) \quad (77)$$

and the line integral along the Z-path is

$$I_Z = \int_0^1 d\xi \int d^3r v_M([\rho_{\xi}]; \mathbf{r}) \frac{\partial \rho_{\xi}(\mathbf{r})}{\partial \xi} \\ = \frac{3}{4} \int d^3r \frac{|\nabla \rho(\mathbf{r})|}{\rho(\mathbf{r})} \left[2\rho(\mathbf{r}) + \frac{\mathbf{r}}{3} \cdot \nabla \rho(\mathbf{r}) \right] \quad (78)$$

It is easy to see that the three reconstructions are related to each other by the equation $I_Z = {}^{3/4}I_Q + {}^{1/4}I_{\Lambda}$.

We have evaluated numerically the three integrals given by eqs 74, 76, and 78 for a number of atoms and molecules and, for each system, obtained three different values. For example, using the Hartree–Fock densities of the Ne atom obtained in the universal Gaussian basis set of ref 39, we found (in atomic units) $I_Q = 62.227$, $I_{\Lambda} = 22.424$, and $I_Z = 52.276$. Therefore, the quantity defined by eq 72 is not a functional derivative of any density functional with respect to $\rho(\mathbf{r})$.

Many of the model Kohn–Sham potentials for exact exchange proposed in the literature^{42–51} are probably stray. For example, Levy–Perdew virial energies obtained from several such approximations deviate by up to a few hartrees from the correct exact-exchange values.⁵²

7. Discussion

The significance of the van Leeuwen–Baerends method for computational density functional theory is not difficult to appreciate. Since line integrals of analytical potentials can be evaluated efficiently, one can turn the Kohn–Sham scheme inside out and model the Kohn–Sham exchange–correlation potential directly^{42–51} instead of approximating the density functional. This is possible because only the potential is required in principle to solve the Kohn–Sham equations, while the energy is an add-on that can be evaluated only when needed (e.g., to distinguish the true solution from false minima).

Generally, when a model Kohn–Sham potential has a simple behavior under some scaling transformation of the density, it is possible to evaluate the line integral analytically to obtain a closed-form expression that relates the unscaled potential directly to the energy. The Levy–Perdew–Ghosh–Parr virial relation can be viewed as a special case of line integrals for potentials that are homogeneous under uniform density scaling. Exchange, Coulomb repulsion, and noninteracting kinetic energy functionals all fall into this category. By contrast, the exact correlation potential and

realistic approximations to it are not homogeneous with respect to any simple density scaling transformation.

It is pertinent to note that the exact and even some approximate exchange–correlation potentials jump by a constant when the electron number in a partially filled electronic shell or subshell crosses an integer.^{53–55} Discontinuous changes of $v_{xc}([\rho_t]; \mathbf{r})$ along a number-nonconserving integration path would certainly complicate the line integral method.^{16,17} Fortunately, no discontinuities arise at any point of the number-nonconserving Q- and Z-paths for the local and semilocal approximations considered in this work, not least because the q -scaling and ξ -scaling are very different from the consecutive (Aufbau) filling of Kohn–Sham orbitals.

We have seen that the line integral method generally recovers the parent density functional $E_{xc}[\rho]$ from a functional derivative $v_{xc}([\rho_t]; \mathbf{r})$ only up to a gauge transformation of the energy density. Drawing on the idea of Burke and co-workers,^{8–11} we can define the hypercorrelated exchange–correlation energy density

$$\tilde{f}_{xc}(\mathbf{r}) = \int_0^1 dt v_{xc}([\rho_t]; \mathbf{r}) \frac{\partial \rho_t(\mathbf{r})}{\partial t} \quad (79)$$

Then a choice of the density scaling path in eq 79 amounts to defining a gauge transformation for the exchange–correlation energy density. In particular, integration along the Λ -path yields the virial energy density of refs 16 and 8–11

$$\tilde{f}_{xc}^{\Lambda}(\mathbf{r}) = \int_0^1 \frac{d\lambda}{\lambda} v_{xc}([\rho_{\lambda}]; \frac{\mathbf{r}}{\lambda}) [3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r})] \quad (80)$$

where we have made the substitution $\lambda \mathbf{r} \rightarrow \mathbf{r}$ to avoid the appearance of λ on the left-hand side. The line integral along the Q-path formally defines the energy density

$$\tilde{f}_{xc}^Q(\mathbf{r}) = \rho(\mathbf{r}) \int_0^1 dq v_{xc}([\rho_q]; \mathbf{r}) \quad (81)$$

which, in contrast to the virial energy density of eq 80, does not depend on the choice of origin and is constant within a finite volume of a uniform electron gas. For purely local approximations, where $v_{xc}([\rho]; \mathbf{r}) = \partial f_{xc}/\partial \rho$, one can show that $\tilde{f}_{xc}^Q(\mathbf{r}) = f_{xc}(\mathbf{r})$, which explains the coincidences noted after eqs 23 and 43. Integration along the Z-path gives a third energy density

$$\tilde{f}_{xc}^Z(\mathbf{r}) = \int_0^1 d\xi v_{xc}([\rho_{\xi}]; \frac{\mathbf{r}}{\xi^{1/3}}) \left[2\rho(\mathbf{r}) + \frac{\mathbf{r}}{3} \cdot \nabla \rho(\mathbf{r}) \right] \quad (82)$$

where we have made the replacement $\xi^{1/3} \mathbf{r} \rightarrow \mathbf{r}$.

When $v_{xc}([\rho]; \mathbf{r})$ is a functional derivative, the total exchange–correlation energies obtained by integrating the energy densities of eqs 80–82 may not coincide exactly in finite basis sets, but these discrepancies disappear in the complete basis set limit.

8. Conclusions

We have demonstrated that it is relatively easy to reconstruct an exchange–correlation density functional from the corresponding functional derivative $v_{xc}([\rho]; \mathbf{r})$ if the latter is

known explicitly in terms of the density. This requires evaluating the van Leeuwen–Baerends line integral along some path of parametrized densities. The linear density scaling path (Q-path) and the uniform density scaling path (Λ -path) are two convenient choices. When $v_{xc}([\rho]; \mathbf{r})$ is homogeneous with respect to the chosen density scaling, the line integration can be completed analytically to give a closed-form expression similar to the generalized Ghosh–Parr virial relation. The choice of the density transformation path determines the gauge of the reconstructed exchange–correlation energy density.

If the potential $v_{xc}([\rho]; \mathbf{r})$ is stray, that is, not a functional derivative of some density functional, then a) the line integral is path-dependent and b) the Kohn–Sham equations do not represent a solution to a variational energy minimization problem. This implies that exchange–correlation energies assigned to stray potentials are somewhat arbitrary and, hence, should be interpreted with caution. Most semilocal exchange–correlation potentials modeled from Kohn–Sham orbitals are probably stray because an arbitrary combination of $\rho(\mathbf{r})$ and its derivatives is very unlikely to be a functional derivative of some density functional.⁵⁶ Nevertheless, a line integral energy expression obtained for a stray potential may still be used to *define* a new density functional approximation.

We conclude by reiterating Mel Levy’s yet unfulfilled prediction¹⁹ that the line integral method will play an increasingly prominent role in future developments of density functional theory.

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Appendix: Differentiation of a Functional with Respect to Parameter of the Function

The chain rule for differentiation of a functional of a parametrized density with respect to the parameter (eq 7) follows directly from eq A.33 of ref 2. Here we will give an alternative derivation of this formula. As in ref 2, we will consider the case of a one-dimensional density $\rho(x)$ and a functional that depends on x , $\rho(x)$, and $\rho'(x) \equiv d\rho/dx$ only. Generalizations of the following proof to three dimensions and higher derivatives are straightforward.

Consider a general density functional of the form

$$E[\rho_t] = \int_{-\infty}^{\infty} f(x, \rho_t, \rho'_t) dx \quad (83)$$

where $\rho_t(x)$ is a parametrized density and $\rho'_t \equiv d\rho_t(x)/dx$. Let us treat the scaling parameter t as an argument of ρ , that is, $\rho_t(x) \equiv \rho(x, t)$. Then $\rho'_t = \partial\rho(x, t)/\partial x$. Differentiation of eq 83 with respect to t gives

$$\frac{dE[\rho_t]}{dt} = \int_{-\infty}^{\infty} \left(\frac{\partial f}{\partial \rho_t} \frac{\partial \rho_t}{\partial t} + \frac{\partial f}{\partial \rho'_t} \frac{\partial \rho'_t}{\partial t} \right) dx \quad (84)$$

Since $\partial \rho'_t / \partial t = \partial^2 \rho(x, t) / \partial x \partial t$, we can integrate the second term in the parentheses by parts. Assuming that the product

$(\partial f / \partial \rho'_t) \partial \rho(x, t) / \partial t$ vanishes as $x \rightarrow \pm\infty$ (as it should in any finite system), we obtain

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{\partial f}{\partial \rho'_t} \frac{\partial \rho'_t}{\partial t} dx &= \int_{-\infty}^{\infty} \frac{\partial f}{\partial \rho'_t} \frac{\partial^2 \rho(x, t)}{\partial x \partial t} dx \\ &= - \int_{-\infty}^{\infty} \left(\frac{d}{dx} \frac{\partial f}{\partial \rho'_t} \right) \frac{\partial \rho(x, t)}{\partial t} dx \end{aligned} \quad (85)$$

Substitution of this result into eq 84 yields

$$\frac{dE[\rho_t]}{dt} = \int_{-\infty}^{\infty} \left(\frac{\partial f}{\partial \rho_t} - \frac{d}{dx} \frac{\partial f}{\partial \rho'_t} \right) \frac{\partial \rho_t}{\partial t} dx \quad (86)$$

The expression in parentheses is the functional derivative of $E[\rho_t]$ with respect to ρ_t .⁴ Thus, we can write

$$\frac{dE[\rho_t]}{dt} = \int_{-\infty}^{\infty} \frac{\delta E[\rho_t]}{\delta \rho_t} \frac{\partial \rho_t}{\partial t} dx \quad (87)$$

which completes the proof.

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