Coordinate scaling and adiabatic-connection formulation in density-functional theory

Yan Alexander Wang
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599
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Five theorems and one lemma, regarding the limits of density functionals as one or several of the coordinate-scaling parameters go to zero or infinity, are proved. A unified description of the coordinate-scaling method and the adiabatic-connection formulation is also introduced. [S1050-2947(97)03308-8]

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Modern density-functional theory (DFT) [1] has benefited much from the coordinate-scaling method [2] and the adiabatic-connection formulation [3], which have been used extensively in checking and developing density functionals [1–4]. In the following, a unified formalism of these two theoretical techniques is introduced within the framework of DFT.

Via the constrained-search formulation [5], the Hohenberg-Kohn (HK) universal functional [6] \( F_N[\rho_{abz}] \), defined within an extended domain

\[
F_N[\rho_{abz}] = \langle \Psi^N[\rho_{abz}] | \hat{T} + \lambda \hat{V}_{\text{xc}} + \lambda \hat{V}_{\text{ext}} | \Psi^N[\rho_{abz}] \rangle,
\]

(1)

always has a minimum [7] for an antisymmetric \( N \)-electron wave function \( \Psi^N[\rho_{abz}] \), with a specific non-negative interelectron interaction coupling constant \( \alpha, \beta, \zeta \). Here, \( \Psi^N[\rho_{abz}] \) generates a coordinate-scaled \( N \)-representable electron density \( \rho_{abz}(r) \), which relates to the original unscalled \( v \)-representable electron density \( \rho(r) \) via [8–12]

\[
\rho_{abz}(x,y,z) = \alpha \beta \zeta \rho(ax,by,\zeta z).
\]

(2)

It can be shown [1,13] that \( \Psi^N[\rho_{abz}] \) is an eigenstate (not necessarily the ground state) of the coupled Hamiltonian

\[
\hat{H}_\lambda = \hat{T} + \lambda \hat{V}_{\text{xc}} + \lambda \hat{V}_{\text{ext}},
\]

(3)

where \( \hat{T}, \hat{V}_{\text{xc}}, \text{and} \hat{V}_{\text{ext}} \) are the kinetic-energy, the interelectron Coulomb repulsion, and the external potential operators, respectively. Using arguments presented earlier [1,9–12], one can further show that

\[
F_N[\rho_{abz}] = \langle \Psi_{abz}^{\lambda} | \hat{T} + \lambda \hat{V}_{\text{xc}} + \lambda \hat{V}_{\text{ext}} | \Psi_{abz}^{\lambda} \rangle,
\]

(4)

where \( \Psi_{abz}^{\lambda} \) generates \( \rho(r) \) directly, minimizes

\[
\langle \Psi_{abz}^{\lambda} | \hat{T} + \lambda \hat{V}_{\text{xc}} + \lambda \hat{V}_{\text{ext}} | \Psi \rangle,
\]

(5)

and is an eigenstate of the coordinate-scaled coupled Hamiltonian

\[
\hat{H}_\lambda = \hat{T} + \lambda \hat{V} + \lambda \hat{V}_{\text{ext}}.
\]

(6)

Here \( \rho_{abz}^{\lambda} \), \( \lambda \hat{V}_{\text{xc}} \), and \( \lambda \hat{V}_{\text{ext}} \), are coordinate scaled as

\[
\rho_{abz}^{\lambda}(x,y,z) = \frac{1}{N} \sum_{i>j} \left[ \alpha^2 \frac{\partial^2}{\partial x_i^2} + \beta^2 \frac{\partial^2}{\partial y_i^2} + \zeta^2 \frac{\partial^2}{\partial z_i^2} \right],
\]

(7)

\[
\rho_{abz}^{\lambda}(x,y,z) = \frac{1}{N} \sum_{i>j} \left[ \frac{x_i^2}{\alpha^2} + \frac{y_j^2}{\beta^2} + \frac{z_{ij}^2}{\zeta^2} \right]^{1/2},
\]

(8)

with \( x_i = x_i - x_j, y_j = y_j - y_i \), and \( z_{ij} = z_i - z_j \).

In the spirit of the Kohn-Sham (KS) theory [14], \( F_N[\rho_{abz}] \) is partitioned into three main pieces:

\[
F_N[\rho_{abz}] = T_1[\rho_{abz}] + \lambda J[\rho_{abz}] + \lambda E_{\text{xc}}[\rho_{abz}],
\]

(9)

where \( T_1[\rho_{abz}] \) is the coordinate-scaled noninteracting \( \lambda = 0 \) kinetic-energy functional, \( J[\rho_{abz}] \) is the coordinate-scaled classical interelectron Coulomb repulsion functional, and \( E_{\text{xc}}[\rho_{abz}] \) is the coordinate-scaled exchange-correlation functional. Following an earlier work by Levy and Perdew [8], one can decompose \( E_{\text{xc}}[\rho_{abz}] \) into two components:

\[
E_{\text{xc}}[\rho_{abz}] = E_s[\rho_{abz}] + E_c[\rho_{abz}],
\]

(10)

namely, the \( \lambda \)-dependent coordinate-scaled exchange functional \( E_s[\rho_{abz}] \),

\[
E_s[\rho_{abz}] = \langle \Psi_{abz}^{\lambda} | \hat{T} + \lambda \hat{V}_{\text{xc}} + \lambda \hat{V}_{\text{ext}} | \Psi_{abz}^{\lambda} \rangle + J[\rho_{abz}^{\lambda}] - J[\rho_{abz}^{\lambda=0}] \]

(11)

and the \( \lambda \)-independent coordinate-scaled correlation functional \( E_c[\rho_{abz}] \),

\[
E_c[\rho_{abz}] = (1/\lambda) T_1[\rho_{abz}] + \lambda E_{\text{xc}}[\rho_{abz}],
\]

(12)

where

\[
T_1[\rho_{abz}] = \langle \Psi_{abz}^{\lambda} | \hat{T} + \lambda \hat{V}_{\text{xc}} + \lambda \hat{V}_{\text{ext}} | \Psi_{abz}^{\lambda} \rangle
\]

(13)

and

\[
T_{\lambda}[\rho_{abz}] = \langle \Psi_{abz}^{\lambda=0} | \hat{T} + \lambda \hat{V}_{\text{xc}} + \lambda \hat{V}_{\text{ext}} | \Psi_{abz}^{\lambda=0} \rangle
\]

(14)

\[
= T[\rho_{abz}] - T_1[\rho_{abz}] \]
\[ V_c^{\lambda} [\rho_{ab}] = V_c^{\lambda} [\rho_{ab}] - V_c^{\lambda} [\rho_{ab}] = V_c^{\lambda} [\rho_{ab}] - V_c^{\lambda} [\rho_{ab}] . \] (15)

At \( \lambda = 0 \), \( F_{\lambda = 0} [\rho_{ab}] \) reduces to \( T_a [\rho_{ab}] \), \( x_{y z} \Phi_{xy}^{\lambda} \) becomes a single Slater determinant \( x_{y z} \Phi^{\lambda} \) made from the first- \( N \) KS orbitals \( \{ \psi_{ab} \} \), and \( x_{y z} \Phi^{\lambda} \) turns into the KS effective potential \( x_{y z} \Phi^{\lambda} \) [14].

Without loss of generality, the coordinate-scaling parameters \( \{ \beta, \xi \} \) will be assumed to be analytic functions of \( \alpha \).

Lemma: If an analytic function of \( \{ \beta, \xi \} \) is assumed to be zero, then it also satisfies

\[ V_c^{\lambda} [\rho_{ab}] = V_c^{\lambda} [\rho_{ab}] = V_c^{\lambda} [\rho_{ab}] . \] (16)

Using Eqs. (13) and (16), one arrives at a lemma.

**Lemma**: If an analytic function of \( \alpha \), \( f_{\alpha}(\alpha) \), satisfies

\[ \lim_{\alpha \to 0} f_{\alpha}(\alpha) V_c^{\lambda} [\rho_{ab}] = 0. \] (17)

then it also satisfies

\[ \lim_{\alpha \to 0} f_{\alpha}(\alpha) G_c^{\lambda} [\rho_{ab}] = 0. \] (18)

Similarly, if an analytic function of \( \alpha \), \( f_{\alpha}(\alpha) \), satisfies

\[ \lim_{\alpha \to 0} f_{\alpha}(\alpha) V_c^{\lambda} [\rho_{ab}] = \text{const.} \] (19)

then it also satisfies

\[ \lim_{\alpha \to 0} f_{\alpha}(\alpha) G_c^{\lambda} [\rho_{ab}] = \text{const.} \] (20)

In principle, for an analytic function \( f_{\alpha}(\alpha) \), \( \lim_{\alpha \to 0} f_{\alpha}(\alpha) E_c^{\lambda} [\rho_{ab}] \) can be zero, a finite constant, or infinity when \( \lim_{\alpha \to 0} f_{\alpha}(\alpha) T_a [\rho_{ab}] \) and \( \lim_{\alpha \to 0} f_{\alpha}(\alpha) V_c^{\lambda} [\rho_{ab}] \) diverge. However, there is a great chance practically for them all to be divergent at the same time. This lemma suggests that one only need to pay attention to the limit of \( f_{\alpha}(\alpha) V_c^{\lambda} [\rho_{ab}] \) in order to figure out the limits of \( f_{\alpha}(\alpha) E_c^{\lambda} [\rho_{ab}] \) and \( f_{\alpha}(\alpha) T_a [\rho_{ab}] \) for an analytic function \( f(\alpha) \). The two special cases \( \alpha \to 0 \) and \( \alpha \to \infty \) will be considered below.

First, as \( \alpha \to 0 \), \( \{ \alpha, \beta, \xi \} \) are assumed to be \( \alpha \approx \beta \approx \xi \), and \( \xi = (\alpha / \xi)^2 \) is assumed to be 0:

\[ \lim_{\alpha \to 0} \xi = 0. \] (21)

Then the interelectron Coulomb interaction operator in Eq. (8),

\[ x_{y z} \Phi^{\lambda} \] (22)

can be treated as a perturbation to the kinetic-energy operator in Eq. (7),

\[ x_{y z} \Phi^{\lambda} T = -\frac{1}{2} \sum_{i=1}^{N} \left( \hat{\xi}^2 + \beta^2 \hat{\xi}^2 \right) + \frac{\alpha^2 \hat{\xi}^2}{\hat{x}^2 + \hat{z}^2} . \] (23)

Also, physical intuition indicates that \( x_{y z} \Phi^{\lambda} \) converges to \( x_{y z} \Phi^{\lambda} \) as \( O(\xi^2 \hat{\xi}) \); otherwise, either \( x_{y z} \Phi^{\lambda} \) would have a nonphysical residue for a virtually zero \( x_{y z} \Phi^{\lambda} \), or \( x_{y z} \Phi^{\lambda} \) would have a nonphysical residue for an almost converged \( x_{y z} \Phi^{\lambda} \). Thus one can expand \( x_{y z} \Phi^{\lambda} \) as a power series from \( x_{y z} \Phi^{\lambda} \) with the parameter \( \xi \),

\[ x_{y z} \Phi^{\lambda} = x_{y z} \Phi^{\lambda} + \sum_{n=1}^{\infty} (x_{y z} \Phi^{\lambda})^n \xi^n . \] (24)

where \( x_{y z} \Phi^{\lambda} \) is the \( n \)-th order wave function. Inserting Eq. (24) into Eq. (15) yields

\[ V_c^{\lambda} [\rho_{ab}] = \alpha \sum_{n=1}^{\infty} V_c^{\lambda} [\rho_{ab}] \xi^n . \] (25)

where \( V_c^{\lambda} [\rho_{ab}] \) is the \( n \)-th order correlation potential energy. From Eq. (25) and the lemma, one arrives at the following theorem.

**Theorem 1**: Assume that as \( \alpha \to 0 \), \( \alpha \xi \approx \beta \approx \xi \), and \( \lim_{\alpha \to 0} \xi = 0 \). If an analytic function of \( \alpha \), \( f_{\alpha}(\alpha) \), satisfies

\[ \lim_{\alpha \to 0} f_{\alpha}(\alpha) \alpha \xi = 0, \] (26)

then it also satisfies

\[ \lim_{\alpha \to 0} f_{\alpha}(\alpha) \alpha \xi = 0. \] (27)

Similarly, if an analytic function of \( \alpha \), \( f_{\alpha}(\alpha) \), satisfies

\[ \lim_{\alpha \to 0} f_{\alpha}(\alpha) \alpha \xi = \text{const.} \] (28)

then it also satisfies

\[ \lim_{\alpha \to 0} f_{\alpha}(\alpha) \alpha \xi = \text{const.} \] (29)

A simple choice for \( f_{\alpha}(\alpha) \) in Eq. (28) is just \( 1/(\alpha \xi) \).

When Eq. (21) is invalid, the interelectron Coulomb interaction operator in Eq. (22) can no longer be treated as a perturbation to the kinetic-energy operator in Eq. (23), and hence Eqs. (24) and (25) are also invalid. However, one can still rely on the lemma, and conclude the following theorem, since this time, \( V_c^{\lambda} [\rho_{ab}] \) is simply \( O(\alpha) \).

**Theorem 2**: Assume that as \( \alpha \to 0 \), \( \alpha \approx \beta \approx \xi \), and \( \lim_{\alpha \to 0} \xi = 0 \). If an analytic function of \( \alpha \), \( f_{\alpha}(\alpha) \), satisfies

\[ \lim_{\alpha \to 0} f_{\alpha}(\alpha) \alpha \xi = 0, \] (30)

then it also satisfies

\[ \lim_{\alpha \to 0} f_{\alpha}(\alpha) \alpha \xi = 0. \] (31)
Similarly, if an analytic function of \( \alpha, f_1(\alpha) \), satisfies
\[
\lim_{a \to 0} (f_1(\alpha) a) = \text{const},
\]
then it also satisfies
\[
\lim_{a \to 0} (f_1(\alpha) G_{\alpha}^{\alpha'}(p_{a\beta\xi})) = \text{const}.
\]

Second, as \( a \to \infty \), \( \{\alpha, \beta, \xi\} \) are assumed to be \( \alpha \geq \beta \equiv \xi \), and \( \eta = (\xi/\alpha^2) \) is always 0:
\[
\lim_{a \to \infty} \eta = 0.
\]

Then the interelectron Coulomb interaction operator in Eq. (8),
\[
\hat{V}_{\alpha\beta\xi} = \alpha^2 \eta \sum_{i,j=1}^{N} \left( \frac{z_{ij}^2 + \beta^2 y_{ij}^2 + \xi^2 x_{ij}^2}{\alpha^2} \right)^{1/2},
\]
can be regarded as a perturbation to the kinetic-energy operator in Eq. (7),
\[
\hat{T}_{\alpha\beta\xi} = -\frac{1}{\alpha^2} \sum_{i=1}^{N} \left( \frac{\beta^2}{\alpha^2} x_i^2 + \frac{\xi^2}{\alpha^2} y_i^2 + \frac{\xi^2}{\alpha^2} z_i^2 \right).
\]

Based on a reason similar to that above, \( \hat{V}_{\alpha\beta\xi} \) converges to \( \hat{T}_{\alpha\beta\xi} \) as \( \eta \to 0 \). Thus one can expand \( \hat{V}_{\alpha\beta\xi} \) as a power series from \( \hat{\Phi}_{\alpha\beta\xi} \) with the parameter \( \eta \).
\[
\hat{V}_{\alpha\beta\xi} = \hat{T}_{\alpha\beta\xi} + \sum_{n=1}^{\infty} \left( \hat{\Phi}_{\alpha\beta\xi}^{n} \right) \eta^n,
\]
where \( \hat{\Phi}_{\alpha\beta\xi}^{n} \) is the \( n \)-th order wave function. Inserting Eq. (37) into Eq. (15) yields
\[
\hat{V}_{\alpha}^{\alpha'}(\rho_{a\beta\xi}) = \xi \sum_{i=1}^{N} \left[ \hat{\rho}_{a\beta\xi}^{\alpha'} \right] \eta^n,
\]
where \( \hat{\rho}_{a\beta\xi}^{\alpha'} \) is the \( n \)-th order correlation potential energy. From Eq. (38) and the lemma, one arrives at the following theorem.

**Theorem 3:** Assume that as \( a \to \infty \), \( \alpha \geq \beta \equiv \xi \), and \( \lim_{a \to \infty} \eta = 0 \). If an analytic function of \( \alpha, g_0(\alpha) \), satisfies
\[
\lim_{a \to \infty} (g_0(\alpha) \xi) = 0,
\]
then it also satisfies
\[
\lim_{a \to \infty} (g_0(\alpha) G_{\alpha}^{\alpha'}(p_{a\beta\xi})) = 0.
\]

Similarly, if an analytic function of \( \alpha, g_1(\alpha) \), satisfies
\[
\lim_{a \to \infty} (g_1(\alpha) \xi) = \text{const},
\]
then it also satisfies
\[
\lim_{a \to \infty} (g_1(\alpha) G_{\alpha}^{\alpha'}(p_{a\beta\xi})) = \text{const}.
\]

### Table I. Some popular choices for \( \{\alpha, \beta, \xi\} \) and their associated \( f_0(\alpha), f_1(\alpha), g_0(\alpha), \) and \( g_1(\alpha) \) functions in theorems 1–3.

<table>
<thead>
<tr>
<th>( {\alpha, \beta, \xi} )</th>
<th>( f_0(\alpha) )</th>
<th>( f_1(\alpha) )</th>
<th>( g_0(\alpha) )</th>
<th>( g_1(\alpha) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha^k, \alpha^k, \alpha^k )</td>
<td>( \alpha^{-p} ) (p&lt;( k ))</td>
<td>( \alpha^{-k} )</td>
<td>( \alpha^p ) (p&lt;( 0 ))</td>
<td>( \alpha^q )</td>
</tr>
<tr>
<td>( \alpha^k, \alpha^k, \alpha^k )</td>
<td>( \alpha^{-p} ) (p&lt;( q ))</td>
<td>( \alpha^{-q} )</td>
<td>( \alpha^p ) (p&lt;( q ))</td>
<td>( \alpha^q )</td>
</tr>
</tbody>
</table>

aSome of these cases can be found in Refs. [2, 8–10], but with \( \lambda = 1 \).

bThe coordinate-scaling parameters \( \{\alpha, \beta, \xi\} \) are assumed as \( \{\alpha^k, \alpha^k, \alpha^k\} \), such that \( k \equiv m \equiv n \) and \( q = 2(k-n) > 0 \).

cThese \( f_0(\alpha), f_1(\alpha), g_0(\alpha), \) and \( g_1(\alpha) \) functions are taken as simple powers of \( \alpha \).

A simple choice for \( g_1(\alpha) \) in Eq. (41) is just \( 1/\alpha \).

Many requirements for \( E_{\alpha}^{\alpha'}(\rho_{a\beta\xi}) \) obtained earlier [2, 8–10] are applications of these three theorems. Specifically, at \( \lambda = 1 \), the constants in Eqs. (36b) and (43b) of Ref. [10] are identified as zero:
\[
\lim_{a \to \infty} (\alpha E_{\alpha}^{\alpha'}(\rho_{a\beta\xi})) = \lim_{a \to \infty} (E_{\alpha}^{\alpha'}(\rho_{a\beta\xi}))/\alpha^2 = 0.
\]

Following the description of the lemma and theorems 1–3, one can easily carry out the same analysis for more complex cases as those collected in Table I. It is also necessary to emphasize that the present discussion differs from different works [2, 8–10] in two ways: first, Eq. (16) and the lemma have been observed throughout the derivation, and, second, the convergence property of \( \hat{V}_{\alpha\beta\xi}^{\alpha'} \) has been taken into consideration in the perturbation expansions of Eqs. (24).
\[
\lim_{a \to 0} (h(a) a) = C_{ha},
\]
then it also satisfies
\[
\lim_{a \to 0} h(a) H[\rho_{a b}] = C_{ha} H[\rho_{ab}],
\]

**Theorem 5:** Assume that as \(a \to \infty\), \(a \geq \beta \geq \zeta\),
\[
\lim_{a \to \infty} (a/\beta) = C_{a\beta} \quad \text{and} \quad \lim_{a \to \infty} (a/\zeta) = C_{a\zeta}.
\]
If an analytic function of \(a, k(a)\), satisfies
\[
\lim_{a \to \infty} (k(a)/\zeta) = C_{k\zeta},
\]
then it also satisfies
\[
\lim_{a \to \infty} (k(a) H[\rho_{a b}] = C_{k\zeta} H[\rho_{a b}].
\]

The proofs of theorems 4 and 5 from Eqs. (44) and (46) are elementary, and hence are omitted here. Also, Eqs. (49) and (52) automatically satisfy the general inequality in Eq. (46). With these five theorems and the lemma, one can then easily discuss the limits of \(f(a) E_{c, l}[\rho_{a b}]\) for any analytic function \(f(a)\).

Finally, it is worthwhile to point out the intrinsic equivalence [16,17] between the uniform coordinate scaling [2,8] and the adiabatic-connection formulation [3]. In Eqs. (1) and (4), after setting \(a = \beta = \zeta\), one has an identity
\[
F_{\lambda}[\rho_{aaa}] = \alpha^2 F_{\lambda/a}[\rho].
\]
From Eqs. (10)–(15) and (53), one can further derive the following identities:
\[
T_{\lambda}[\rho_{aaa}] = \alpha^2 T_{\lambda}[\rho], \quad H[\rho_{aaa}] = \alpha H[\rho],
\]

\[
K[\rho_{aaa}] = \alpha^2 K[\rho], \quad L[\rho_{aaa}] = \alpha L[\rho],
\]
where the dummy functional \(K[\rho_{aaa}]\) denotes \(T_{\lambda}[\rho_{aaa}]\) or \(T[\rho_{aaa}]\), and the dummy functional \(L[\rho_{aaa}]\) denotes \(E_{\lambda}[\rho_{aaa}]\), \(E_{\lambda}[\rho_{aaa}]\), \(V_{\lambda}[\rho_{aaa}]\) or \(V[\rho_{aaa}]\). In Eq. (54), the first two identities were first introduced in Ref. [8], and the identity for \(E_{\lambda}[\rho_{aaa}]\) was derived in Ref. [16,17]. Further, the general identity for \(E_{\lambda}[\rho_{aaa}]\) in Eq. (54) has been used to generalize [18] the original Levy-Perdew equation (8,17) to
\[
T_{\lambda}[\rho] = -\lambda E_{\lambda}[\rho] + \lambda \left( \frac{\partial E_{\lambda}[\rho]}{\partial \lambda} \right)_{\lambda=1},
\]
from the identity [19]
\[
T_{\lambda}[\rho] = -\lambda^2 \frac{d E_{\lambda}[\rho]}{d \lambda}.
\]

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