Adiabatic connection in the low-density limit

Zhen-Fei Liu and Kieron Burke
Department of Chemistry, University of California, Irvine, California 92697-2025, USA
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In density-functional theory, the exchange-correlation functional can be exactly expressed by the adiabatic connection integral. It had been noticed that as $\lambda \to \infty$, the λ^{-1} term in the expansion of $W(\lambda)$ vanishes. We provide a simple derivation of this exact condition in this work. We propose a simple parametric form for the integrand, satisfying this condition, and show that it is highly accurate for weakly correlated two-electron systems.

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In density-functional theory (DFT) [1], the exchange-correlation functional $E_{\mathrm{XC}}[n]$ is exactly expressed by the adiabatic connection [2,3] formula

$$E_{\mathrm{XC}}[n] = \int_0^1 d\lambda W[n](\lambda), \tag{1}$$

where λ is a coupling constant that connects the Kohn-Sham system ($\lambda=0$) to the true system ($\lambda=1$), while keeping the density $n(\mathbf{r})$ fixed. The integrand, $W(\lambda)$, contains only potential contributions to E_{XC}. The shape of $W(\lambda)$ has been much studied in DFT [4]. For example, the success of hybrid functionals that mix some fraction of exact exchange with a generalized gradient approximation (GGA) can be understood this way [5]. There is ongoing research to use the low density ($\lambda \to \infty$) limit as information in construction of accurate models of $W(\lambda)$ [6–8]. Recently, the adiabatic connection formula has been used directly in functional construction [9].

The expansion of $W(\lambda)$ in the high-density (weak coupling) limit for finite systems is known to be [7]

$$W(\lambda) = W_0 + W_0'\lambda + \cdots \text{as } \lambda \to 0, \tag{2}$$

where $W_0' = 2E_{\mathrm{C}}^{\mathrm{GL2}}$, with $E_{\mathrm{C}}^{\mathrm{GL2}}$ the second-order coefficient in Görling-Levy perturbation theory [6,10,11]. The expansion in the low-density (strongly correlated) limit is believed to be [7,12]

$$W(\lambda) = W_\infty + W_\infty'\lambda^{-1/2} + \cdots \text{as } \lambda \to \infty, \tag{3}$$

where W_∞' is defined as the coefficient of $\lambda^{-1/2}$ in the expansion above, and W_∞ can be calculated from the strictly correlated electron (SCE) limit [13]. In addition to these expansions, by definition the exact $W[n](\lambda)$ is known to satisfy the following scaling property [7]:

$$W[n](\lambda) = \lambda W_1[n_{1/\lambda}], \tag{4}$$

where $n_{1/\lambda}(\mathbf{r})$ is the scaled density, defined by $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r})$, $0 < \gamma < \infty$. In the equations above, one can show that $W_0 = E_{\mathrm{X}}$, the exchange energy, and that W_∞ is finite [6]. The dependence on $\lambda^{-1/2}$ in the low-density limit is because correlation dominates here, and the Thomas-Fermi screening length is proportional to $\lambda_F^{-1/2}$.

In practical DFT calculations, $W(\lambda)$ must be approximated. However, any approximate $W(\lambda)$ should satisfy several exact conditions, such as Eqs. (2)–(4). In the erratum to Ref. [7], Seidl *et al.* concluded that for the interaction-strength interpolation (ISI) model (see below), the spurious $\lambda^2 \ln \lambda$ term in $E_{\mathrm{C}}[n_\lambda]$ is due to the λ^{-1} term in the expansion of $W(\lambda)$ as $\lambda \to \infty$ [Eq. (3)]. In a recent work [12], this was proved rigorously by calculating zero-point oscillations about the strictly correlated limit. In this Brief Report, we elaborate the statement in the erratum to Ref. [7], showing that a reasonable assumption about the scaling behavior of the correlation energy prohibits such spurious terms as $\lambda^2 \ln \lambda$. While this result is not new, we provide a simple derivation and show how this exact constraint affects approximate functionals. Throughout this Brief Report, we use atomic units ($e^2 = \hbar = \mu = 1$) everywhere, i.e., all energies are in Hartrees and all distances in Bohr radii.

Any λ dependence can always be expressed in terms of density scaling [14]. Using the fundamental relation of Levy-Perdew [15] one finds

$$W[n](\lambda) = E_{\mathrm{X}}[n] - \gamma^2 \frac{d}{d\gamma}\left(\frac{E_{\mathrm{C}}[n_\gamma]}{\gamma^2}\right), \tag{5}$$

and it is generally believed for nondegenerate Kohn-Sham systems [16] that $E_{\mathrm{C}}[n_\gamma]$ has the following expansion in the low-density limit ($\gamma \to 0$):

$$E_{\mathrm{C}}[n_\gamma] = \gamma(B_0[n] + \gamma^{1/2}B_1[n] + \gamma B_2[n] + \cdots), \tag{6}$$

where the $B_k[n]$'s ($k = 0, 1, 2\cdots$) are scale-invariant functionals. Substituting into Eq. (5), we find the expansion of $W(\lambda)$ for large λ

$$W(\lambda) = E_{\mathrm{X}}[n] + B_0[n] + \frac{1}{2}\lambda^{-1/2}B_1[n] - \frac{1}{2}\lambda^{-3/2}B_3[n] + \cdots, \tag{7}$$

i.e., the λ^{-1} term is missing, and $W(\lambda)$ is independent of $B_2[n]$.

Now we survey approximations to $W(\lambda)$ and see whether they have the correct low-density expansion [Eq. (7)]. There are several kinds of approximations, the most famous being the ISI model by Seidl and co-workers [6–8]:

$$W^{\mathrm{ISI}}[n](\lambda) = W_\infty[n] + \frac{X[n]}{\sqrt{1 + Y[n]\lambda} + Z[n]}, \tag{8}$$

where $X = xy^2/z^2$, $Y = xX/z^2$, and $Z = X/z - 1$, with $x = -2W_0'[n]$, $y = W_\infty'[n]$, and $z = E_{\mathrm{X}}[n] - W_\infty[n]$.

The ISI model uses the values of $W[n]$ and its derivatives

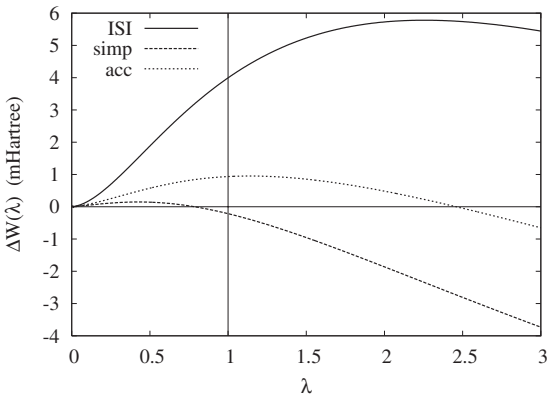

FIG. 1. Comparison of three different approximations to $W(\lambda)$ for Hooke's atom ($k=1/4$), plotted as $\Delta W = W^{\text{model}} - W^{\text{exact}}$. The exact curve (up to $\lambda=3$) is taken from Ref. [19].

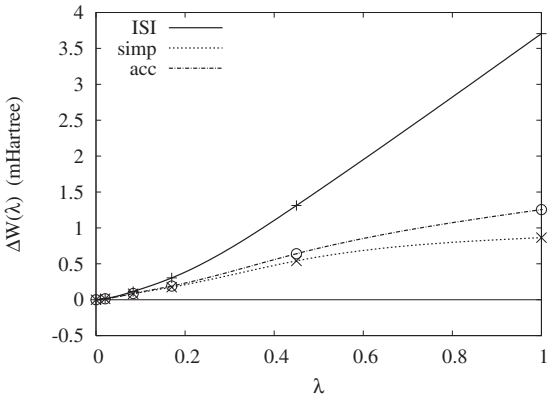

FIG. 2. Comparison of three different approximations to $W(\lambda)$ for helium atom, plotted as $\Delta W = W^{\text{model}} - W^{\text{exact}}$. The discrete values are shown, as well as fitting curves to aid the eyes. W^{exact} values (up to $\lambda=1$) are taken from Ref. [22].

at both the high-density ($\lambda \to 0$) and the low-density ($\lambda \to \infty$) limits, to produce an accurate curve for $W(\lambda)$, $0 \le \lambda \le 1$, to insert in Eq. (1) to get an approximation to E_{XC}. It gives very accurate results for the correlation energy [7] and meets several conditions. But if we expand W^{ISI} in the low-density limit

$$W^{\text{ISI}}(\lambda) = W_\infty + \frac{X}{\sqrt{Y}}\lambda^{-1/2} + \frac{XZ}{Y}\lambda^{-1} + \cdots, \tag{9}$$

we can see that its λ^{-1} term does not generally vanish, although it works very well numerically for E_{C} [17]. This wrong coefficient was already shown to produce a spurious term ($\lambda^2 \ln \lambda$) in the expansion of $E_{\text{C}}[n_\lambda]$ as $\lambda \to \infty$ [7].

There were several attempts to overcome this problem [correctly omitting the λ^{-1} term but including all the other (integer and half-integer powers) terms] in the literature [18,12] by modifying the ISI model, but they are less simple: one requires W_0'' [the next order in Eq. (2)] [18] and the other is not a direct model to W_λ [12]. Consider instead the following four parameter interpolation model

$$W^{\text{acc}}(\lambda) = a + by + dy^4, \quad y = \frac{1}{\sqrt{1+c\lambda}}, \tag{10}$$

where a, b, c, and d are scale-invariant functionals. We use the same inputs as those for the ISI model, i.e., W_0, W_0', W_∞, and W_∞' to fit the parameters. Generally there are no analytical expressions in compact form for the parameters, and one has to solve for them numerically. The 4th power in y is the lowest that can be added while satisfying the exact conditions, but producing an expansion with nonzero λ^{-n} terms ($n \in \mathbb{Z}, n > 1$). We recommend use of this W^{acc} to replace the ISI model because it is numerically accurate and avoids the λ^{-1} term in the low-density limit. One can show that W^{acc} obeys the scaling property [Eq. (4)], provided that $W_0[n_\gamma] = \gamma W_0[n]$, $W_0'[n_\gamma] = W_0'[n]$, $W_\infty[n_\gamma] = \gamma W_\infty[n]$, and $W_\infty'[n_\gamma] = \gamma^{3/2} W_\infty'[n]$, as they should. If we integrate $W^{\text{acc}}(\lambda)$ over λ from 0 to 1, we find a simple expression for the exchange-correlation energy

$$E_{\text{XC}}^{\text{acc}} = a + \frac{d}{1+c} + 2b(-1 + \sqrt{1+c})/c. \tag{11}$$

We compare the performance of the new model and ISI on Hooke's atom, two electrons in a spherical harmonic well, with force-constant $k=1/4$. We show below that for this system, our W^{acc} works as a highly accurate interpolation, even more accurate than the ISI model.

Magyar *et al.* [19] calculated the $W(\lambda)$ curve for $0 \le \lambda \le 4$ for Hooke's atom ($k=1/4$) using $W_0 = E_{\text{X}} = -0.515$ and $W_0' = -0.101$ as inputs. They confirmed that $W_\infty = -0.743$, consistent with the SCE ansatz [6]. They also found $W_\infty' = 0.235$, but this was based on a fit that violated our condition, so we discount this result. Gori-Giorgi [20] calculated $W_\infty' = 0.208$ based on the SCE model [6,12], which we consider exact. We apply these inputs (W_0, W_0', W_∞, and W_∞') to our W^{acc} and the ISI model (W^{acc} generates two sets of solu-

TABLE I. Comparison of several quantities for three different approximations to $W(\lambda)$ for Hooke's atom ($k=1/4$). The exact values are taken from Ref. [19] except for W_∞' (Ref. [20]). All energies are in mHartrees.

	exact	ISI	simp	acc
W_1	−583	−579	−583	−582
W_1'	−44	−41	−45	−44
E_{C}	−39	−37	−38	−38
$E_{\text{C}}+T_{\text{C}}$	−10	−10	−9	−9

TABLE II. Comparison of several quantities for three different approximations to $W(\lambda)$ for helium atom. The exact values are taken from Ref. [22]. All energies are in mHartrees.

	exact	ISI	simp	acc
W_1	−1104	−1100	−1103	−1103
W_1'	−64	−60	−64	−63
E_{C}	−42	−40	−42	−41
$E_{\text{C}}+T_{\text{C}}$	−6	−6	−5	−5

TABLE III. Comparison of W^{simp} and W^{ISI} on systems with more than two electrons. E_{X}, W_0' and W_∞ are taken from Ref. [13], and W_∞' is taken from Ref. [12]. All energies are in Hartrees.

	E_{X}	W_0'	W_∞^{SCE}	$W_\infty'^{\mathrm{SCE}}$	$E_{\mathrm{C}}^{\mathrm{ISI}}$	$E_{\mathrm{C}}^{\mathrm{simp}}$	$E_{\mathrm{C}}^{\mathrm{exact}}$
Be	−2.67	−0.250	−4.02	2.59	−0.104	−0.110	−0.096
Ne	−12.1	−0.938	−20.0	22.0	−0.410	−0.432	−0.394

tions for a, b, c, and d, but we select the one with d closest to b, for it can be reduced to W^{simp} as below). We plot the differences between these models and the exact curve (taken from Ref. [19]) in Fig. 1. One can see that our W^{acc} works very well between $\lambda=0$ and 1, which is the range of interest. Its predictions for W_1', E_{C}, and $E_{\mathrm{C}}+T_{\mathrm{C}}$ are excellent, with T_{C} being the correlation energy from the kinetic part, as listed in Table I. With these exact inputs, we found that, as $\lambda\to\infty$, $W^{\mathrm{ISI}}\to -0.743+0.208\lambda^{-1/2}+0.068\lambda^{-1}+\cdots$, which shows that although the coefficient of λ^{-1} is small, it does not vanish.

We can also apply our W^{acc} to the helium atom. Here $W_0=E_{\mathrm{X}}=-1.025$, $W_0'=-0.095$ [21], and $W_\infty=-1.500$ [6], $W_\infty'=0.621$ [12] from the SCE model [6,12]. We plot the differences between these models and the exact curve (taken from Ref. [22]) in Fig. 2 and compare several key quantities in Table II.

One can see that our model here works fairly well, and W^{simp} (see below) is even a little better than W^{acc}. ISI does not satisfy the exact condition we derived in this work [Eq. (7)]: as $\lambda\to\infty$, $W^{\mathrm{ISI}}\to -1.500+0.621\lambda^{-1/2}+0.376\lambda^{-1}+\cdots$, so the λ^{-1} coefficient is not even small.

Now, we propose a simpler version of W^{acc}, which cannot be used in typical cases, as the exact value of W_∞' is not known in general. A simpler model is constructed by setting $d=b$, to yield

$$W^{\mathrm{simp}}(\lambda)=a+b(y+y^4),\quad y=\frac{1}{\sqrt{1+c\lambda}},\tag{12}$$

with a, b and c being scale-invariant functionals. We have found (see results for Hooke's atom and helium atom) that although there is one parameter less, the above form produces usefully accurate results, especially between $\lambda=0$ and 1. In a word, W^{acc} acts as an accurate interpolation to the whole adiabatic connection curve, while W^{simp} is more convenient and practical to use, without losing accuracy. It yields $W_\infty'=0.191$ for Hooke's atom and 0.594 for helium.

We use W_0, W_∞, and W_0' to construct the explicit form of $W^{\mathrm{simp}}(\lambda)$, and find

$$a=W_\infty,\quad b=\frac{W_0-W_\infty}{2},\quad c=\frac{4W_0'}{5(W_\infty-W_0)}.\tag{13}$$

Thus a and b set the end points, while c is a measure of the curvature. Substituting Eq. (13) into Eq. (12), we get the explicit form of $W(\lambda)$ in terms of W_0, W_∞, and W_0'. One can show that it has the correct expansion in both limits, and it obeys the scaling property [Eq. (4)]. Setting $d=b$ in Eq. (11) and subtracting exchange, it yields

$$E_{\mathrm{C}}^{\mathrm{simp}}=2b[f(c)-1],\quad f(c)=\left[\sqrt{1+c}-\frac{1+c/2}{1+c}\right]/c,\tag{14}$$

with b and c defined in Eq. (13). $E_{\mathrm{C}}^{\mathrm{simp}}$ correctly recovers GL2 in the weakly correlated limit ($W_\infty\to-\infty$, keeping W_0 and W_0' fixed, such as in the $Z\to\infty$ limit of two-electron ions) and $E_{\mathrm{XC}}^{\mathrm{simp}}$ correctly reduces to W_∞ for strong static correlation ($W_0'\to-\infty$, keeping W_0 and W_∞ fixed, such as for stretched H_2). We can calculate the kinetic correlation energy T_{C}

$$T_{\mathrm{C}}=b[2f(c)-z-z^4],\tag{15}$$

with $f(c)$ defined in Eq. (14) and $z=1/\sqrt{1+c}$, showing that the curvature $\beta=T_{\mathrm{C}}/|E_{\mathrm{C}}-T_{\mathrm{C}}|$ [23] is a function of c alone. We strongly urge $E_{\mathrm{XC}}^{\mathrm{simp}}$ be applied whenever its inputs are accurately known.

We can further test our W^{simp} in systems with more than two electrons, but only those for which all inputs are known, with results listed in Table III. One can see that W^{simp} predicts E_{C} fairly accurately, but is less accurate than W^{ISI}. This is perhaps due to lack of W_∞' in W^{simp}.

In fact, in their first paper on the ISI model, Seidl *et al.* proposed a similar model [6], which yields results numerically very close to those of ISI, but without the y^4 term. But their model contains no $\lambda^{-n}(n>1)$ contributions. Note that none of these models work for the uniform electron gas, because $W_0'=-\infty$ [17], so both the model developed by Seidl *et al.* [6] and W^{simp} reduce to $W(\lambda)=W_\infty$.

After the bulk of this work was completed, we received a preprint of Ref. [12], containing a detailed theory of the leading corrections to $W(\lambda)$ as $\lambda\to\infty$, consistent with the much simpler arguments given here. Also, we use their W_∞' value for helium (see text) to replace the old one predicted by point-charge-plus-continuum (PC) model [7].

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