Adiabatic connection in the low-density limit

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In density-functional theory, the exchange-correlation functional can be exactly expressed by the adiabatic connection [2,3] formula

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

where \( \lambda \) is a coupling constant that connects the Kohn-Sham system (\( \lambda=0 \)) to the true system (\( \lambda=1 \)), while keeping the density \( n(r) \) fixed. The integrand, \( W(\lambda) \), contains only potential contributions to \( E_{\text{XC}} \). 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 (\( \lambda \rightarrow -\infty \)) 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]

\[ W(\lambda) = W_0 + W_0 \lambda + \cdots \quad \text{as} \quad \lambda \rightarrow 0, \]  

where \( W_0 = 2E_{\text{G}}^{\text{G2.1}} \), with \( E_{\text{G}}^{\text{G2.1}} \) 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]

\[ W(\lambda) = W_{\infty} + W_{\infty} \lambda^{-1/2} + \cdots \quad \text{as} \quad \lambda \rightarrow -\infty, \]  

where \( W_{\infty} \) is defined as the coefficient of \( \lambda^{-1/2} \) in the expansion above, and \( W_{\infty} \) 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]:

\[ W[n](\lambda) = \lambda W[n](\lambda), \]  

where \( n_{1/\lambda}(r) \) is the scaled density, defined by \( n_{1/\lambda}(r) = \gamma n(r), \gamma < \lambda < \infty \). In the equations above, one can show that \( W_0 = E_X \), the exchange energy, and that \( W_{\infty} \) 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 \( \lambda^{-1/2} \).

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 \( E_{\text{ISI}}[n] \) is due to the \( \lambda^{-1} \) term in the expansion of \( W(\lambda) \) as \( \lambda \rightarrow -\infty \) [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 keeping \( \lambda \) fixed. The integrand, satisfying this condition, and show that it is highly accurate for weakly correlated two-electron systems.

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at both the high-density ($\lambda \to 0$) and the low-density ($\lambda \to \infty$) limits, to produce an accurate curve for $W(\lambda)$, $0 \leq \lambda \leq 1$, 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 $W^{\text{SI}}$ in the low-density limit

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

we can see that its $\lambda^{-1}$ 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 ($\lambda^{3} \ln \lambda$) in the expansion of $E_{C}[n_{\lambda}]$ as $\lambda \to \infty$ [7].

There were several attempts to overcome this problem [correctly omitting the $\lambda^{-1}$ 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 $W_{\lambda}$ [12]. Consider instead the following four parameter interpolation model

$$W^{\text{acc}}(\lambda) = a + b \lambda + d \lambda^{4}, \quad y = \frac{1}{\sqrt{1 + c \lambda}},$$

where $a$, $b$, $c$, and $d$ are scale-invariant functionals. We use the same inputs as those for the ISI model, i.e., $W_{0}$, $W_{\lambda}$, $W_{acc}$, and $W_{0}$ 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 $\lambda^{-n}$ terms ($n \in \mathbb{Z}, n > 1$). We recommend use of this $W^{\text{acc}}$ to replace the ISI model because it is numerically accurate and avoids the $\lambda^{-1}$ term in the low-density limit. One can show that $W^{\text{acc}}$ obeys the scaling property [Eq. (4)], provided that $W_{0}[n_{\lambda}] = y W_{0}[n]$, $W_{\lambda}[n_{\lambda}] = W_{\lambda}[n]$, $W_{C}[n] = y W_{C}[n]$, and $W_{acc}[n_{\lambda}] = y^{3/2} W_{acc}[n]$, as they should. If we integrate $W^{\text{acc}}(\lambda)$ over $\lambda$ from 0 to 1, we find a simple expression for the exchange-correlation energy

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

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 $W^{\text{acc}}$ works as a highly accurate interpolation, even more accurate than the ISI model.

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

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tions for $a$, $b$, $c$, and $d$, but we select the one with $d$ closest to $b$, for it can be reduced to $W_{\text{simp}}$ as before). We plot the differences between these models and the exact curve (taken from Ref. [19]) in Fig. 1. One can see that our $W_{\text{acc}}$ works very well between $\lambda=0$ and 1, which is the range of interest. Its predictions for $W^0_1$, $E_C$, and $E_C+T_C$ 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 $\lambda \to \infty$, $W_{\text{SCE}} \to -0.743+0.208\lambda^{-1/2}+0.068\lambda^{-1}+\cdots$, which shows that although the coefficient of $\lambda^{-1}$ is small, it does not vanish.

We can also apply our $W_{\text{acc}}$ to the helium atom. Here $W_{0}=E_X=-1.025$, $W_{0}=-0.095$ [21], and $W_{0}=-1.500$ [6], $W_{0}=0.621$ [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 $W_{\text{simp}}$ (see below) is even a little better than $W_{\text{acc}}$. ISI does not satisfy the exact condition we derived in this work [Eq. (7)]; as $\lambda \to \infty$, $W_{\text{SCE}} \to -1.500+0.621\lambda^{-1/2}+0.376\lambda^{-1}+\cdots$, so the $\lambda^{-1}$ coefficient is not even small.

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

$$W_{\text{simp}}(\lambda)=a+b(y+y^4), \quad y=\frac{1}{\sqrt{1+c\lambda}},$$

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 useful but accurate results, especially between $\lambda=0$ and 1. In a word, $W_{\text{acc}}$ acts as an accurate interpolation to the whole adiabatic connection curve, while $W_{\text{simp}}$ is more convenient and practical to use, without losing accuracy. It yields $W_{\text{simp}}=0.191$ for Hooke’s atom and 0.594 for helium.

We use $W_0$, $W_{\text{acc}}$, and $W_0$ to construct the explicit form of $W_{\text{simp}}(\lambda)$, and find

$$a = W_{\text{acc}}, \quad b = \frac{W_0-W_{\text{acc}}}{2}, \quad c = \frac{4W_0}{5(W_{\text{acc}}-W_0)}.$$

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 $W_0$, $W_{\text{acc}}$, 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

$$E_C^{\text{simp}} = 2b[f(c)-1], \quad f(c) = \left[\sqrt{1+c} - \frac{1+c/2}{1+c}\right]/c,$$

with $b$ and $c$ defined in Eq. (13). $E_C^{\text{simp}}$ correctly recovers GL2 in the weakly correlated limit ($W_{0} \to \infty$, keeping $W_0$ and $W_{\text{acc}}$ fixed, such as in the $Z \to \infty$ limit of two-electron ions) and $E_{\text{X}}^{\text{SCE}}$ correctly reduces to $W_0$ for strong static correlation ($W_{0} \to \infty$, keeping $W_0$ and $W_{\text{acc}}$ fixed, such as for stretched H$_2$). We can calculate the kinetic correlation energy $T_C$

$$T_C = b[2f(c)-z-z^2],$$

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

We can further test our $W_{\text{simp}}$ 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 $W_{\text{simp}}$ predicts $E_C$ fairly accurately, but is less accurate than $W_{\text{SCE}}$. This is perhaps due to lack of $W_{\text{acc}}$ in $W_{\text{simp}}$.

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 $W_{\text{simp}}(\infty) \neq W_{\text{SCE}}(\infty)$.

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 $W_{\text{acc}}$ value for helium (see text) to replace the old one predicted by point-charge-plus-continuum (PC) model [7].

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<th>$E_X$</th>
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<th>$W_{\text{SCE}}$</th>
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<th>$E_{\text{simp}}$</th>
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<td>$-20.0$</td>
<td>$22.0$</td>
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