Adiabatic Connection in the Low-Density Limit

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

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

where \( \lambda \) is a coupling constant that connects the Kohn-Sham system \((\lambda = 0)\) to the true system \((\lambda = 1)\), while keeping the density \(n(\mathbf{r})\) 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 \((\lambda \rightarrow \infty)\) limit as information in construction of accurate models of \(W(\lambda)\) \([6, 7, 8]\). 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 \([7]\):

\[
W(\lambda) = W_0 + W'_0 \lambda + \cdots \text{as } \lambda \rightarrow 0,
\]

where \(W_0 = 2E_{SCL}^{\text{GL2}}\), with \(E_{SCL}^{\text{GL2}}\) the second-order coefficient in G{"o}rling-Levy perturbation theory \([6, 10, 11]\). The expansion in the low-density (strongly correlated) limit is believed to be \([7, 12]\):

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

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 \([7]\):

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

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 \(W_0 = E_X\), 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. \((2), (3)\), and \((4)\). In the erratum to Ref. \([7]\), Seidl et al. concluded that for the ISI model (see below), the spurious \(\lambda^2 \ln \lambda\) term in \(E_C[n_\lambda]\) 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, but only by calculating zero-point oscillations about the strictly-correlated limit. In this paper, we provide a simple derivation and how this exact constraint affects approximate functionals. Throughout this paper, we use atomic units \((\varepsilon^2 = \hbar = \mu = 1)\) everywhere, i.e. all energies are in Hartrees and all distances in Bohr radii.

Any \(\lambda\)-dependence can always be expressed in terms of density scaling. Using the fundamental relation of Levy-Perdew equation \([14]\), one finds:

\[
W[n](\lambda) = E_X[n] - \gamma^2 \frac{d}{d\gamma} \left( \frac{E_C[n_\gamma]}{\gamma^2} \right),
\]

and it is generally believed for nondegenerate Kohn-Sham systems \([15]\) that \(E_C[n_\gamma]\) has the following expansion in the low density limit \((\gamma \rightarrow 0)\):

\[
E_C[n_\gamma] = \gamma \left( B_0[n] + \gamma^{1/2} B_1[n] + \gamma B_2[n] + \cdots \right),
\]

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 \(\lambda\):

\[
W(\lambda) = E_X[n] + B_0[n] + \frac{1}{2} \lambda^{-1/2} B_1[n] - \frac{1}{2} \lambda^{-3/2} B_2[n] + \cdots,
\]

i.e. the \(\lambda^{-1}\) 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 (interaction-strength interpolation) model by Seidl et al \([6, 7, 8]\):

\[
W^{\text{ISI}}[n](\lambda) = W_\infty[n] + \frac{X[n]}{\sqrt{1 - Y[n] \lambda + Z[n]}},
\]

where \(X = x y^2 / z^2\), \(Y = x X / z^2\), \(Z = X / z - 1\), with \(x = -2W'_0[n]\), \(y = W'_\infty[n]\), and \(z = E_X[n] - W_\infty[n]\).

The ISI model uses the values of \(W[n]\) and its derivatives at both the high-density \((\lambda \rightarrow 0)\) and the low-density \((\lambda \rightarrow \infty)\) 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 \cite{17} and meets several conditions. But if we expand $W_{\text{ISI}}$ in the low-density limit:

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

we can see that its $\lambda^{-1}$ term does not generally vanish, although it works very well numerically for $E_c$ \cite{16}. This wrong coefficient was already shown to produce a spurious term ($\lambda^2 \ln \lambda$) in the expansion of $E_c[n\lambda]$ as $\lambda \to \infty$ \cite{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 \cite{12, 17} by modifying the ISI model, but they are less simple: one requires $W''_0$ [the next order in Eq. (2)] \cite{17} and the other is not a direct model to $W_a$ \cite{12}. Consider instead the following 4-parameter interpolation model:

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

where $a, b, c$, and $d$ are scale-invariant functionals. We use the same inputs as those for the ISI model, i.e. $W_0, W'_0, W_\infty$, and $W'_\infty$, 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 non-zero $\lambda^{-n}$ 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. (11)], provided that $W_0[n] = \gamma W_0[n], W'_0[n] = \gamma W'_0[n], W_\infty[n] = \gamma W_\infty[n]$, and $W'_\infty[n] = \gamma^{3/2} W'_\infty[n]$, 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:

$$E_{xc} = a + \frac{d}{1 + c} + 2b(-1 + \sqrt{1 + c})/c. \quad (11)$$

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

Magyar et al. \cite{18} calculated the $W(\lambda)$ curve for $0 \leq \lambda \leq 4$ for Hooke’s atom ($k = 1/4$) using $W_0 = E_x = -0.515$ and $W'_0 = -0.101$ as inputs. They confirmed that $W_\infty = -0.743$, consistent with the SCE ansatz [3]. 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 \cite{19} calculated $W'_\infty = 0.208$ based on the SCE model [6, 12], which we consider exact. We apply these inputs ($W_0, W'_0, W_\infty$, and $W'_\infty$) to our $W_{\text{acc}}$ and the ISI model ($W_{\text{acc}}$ generates two sets of solutions 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 below). We plot the differences between these models and the exact curve (taken from Ref. \cite{18}) 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 $W'_0, E_c$, 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 $\lambda \to \infty$, $W_{\text{ISI}} \to -0.743 + 0.208 \lambda^{-1/2} + 0.068 \lambda^{-1} + \cdots$, which shows that although the coefficient of $\lambda^{-1}$ is small, it does not vanish.

![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. \cite{18}.](image)

| $W_1$ | $W'_0$ | $E_c$ | $E_c + T_c$ |
|-------|--------|-------|-------------|
| -583  | -44    | -30   | -10         |
| -579  | -41    | -37   | -10         |
| -583  | -45    | -38   | -9          |

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. \cite{18} except for $W'_\infty$ \cite{19}. All energies are in mHartrees.

We can also apply our $W_{\text{acc}}$ to the helium atom. Here $W_0 = E_x = -1.025$, $W'_0 = -0.095$ [20], and $W_\infty = -1.500$ [6], $W'_\infty = 0.621$ \cite{12} from the SCE model [6, 12]. We plot the differences between these models and the exact curve (taken from Ref. \cite{21}) 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
Setting $d = b$ in Eq. (11) and subtracting exchange, it yields:

$$E_C^{\text{simp}} = 2b[f(c) - 1], \quad f(c) = [\sqrt{1 + c} - 1 + c/2]/c,$$  \hspace{1cm} (14)

with $b$ and $c$ defined in Eq. (13). $E_C^{\text{simp}}$ 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 $E_C^{\text{simp}}$ correctly reduces to $W_\infty$ for strong static correlation ($W'_0 \to -\infty$, keeping $W_0$ and $W_\infty$ fixed, such as for stretched H2). We can calculate the kinetic correlation energy $T_C$:

$$T_C = b[2f(c) - z - z^4],$$  \hspace{1cm} (15)

with $f(c)$ defined in Eq. (14) and $z = 1/\sqrt{1 + c}$, showing that the curvature $\beta = T_C/E_C - T_C$ \hspace{1cm} (22) is a function of $c$ alone. We strongly urge $E_C^{\text{simp}}$ 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 $W^{\text{ISI}}$. This is perhaps due to lack of $W'_0$ in $W^{\text{simp}}$.

In fact, in their first paper on the ISI model, Seidl et al. proposed a similar model \hspace{1cm} [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 $W'_0 = -\infty$ \hspace{1cm} [13], so both the model developed by Seidl et al. \hspace{1cm} [6] and $W^{\text{simp}}$ reduce to $W(\lambda) = W_\infty$.

After the bulk of this work was completed, we received a preprint of Ref. \hspace{1cm} [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 $W'_\infty$ value for helium (see text) to replace the old one predicted by point-charge-plus-continuum (PC) model \cite{7}.

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