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Extension to Negative Values of the Coupling Constant of Adiabatic Connection for Interaction-Strength Interpolation

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Abstract: A new exchange and correlation functional, called ISIN here, of the fifth rung of Jacob's ladder is presented. It is based on the explicit approximation of W_λ, the integrand in the adiabatic connection (AC) with λ representing the coupling constant. Besides utilizing the two leading terms of each asymptotic expansion of W_λ at $\lambda = 0$ and ∞, the ISIN extends the coupling constant λ to negative values (i.e., to attractive electron−electron interactions). For the simple system of two electrons on the surface of a sphere (2ESS), the correlation energies yielded by the ISIN are in excellent agreement with the exact values. However, the ISIN seriously fails to approximate W_λ when W_0, the slope at $\lambda = 0$, goes to $-\infty$, which leads to much more negative correlation energies for real systems.

1. Introduction

In recent years, density-functional theory (DFT)[1,2] has become one of the most frequently applied methods in many-body theory, largely due to the fact that the basic variable in DFT is the simple, non-negative particle density $n(\mathbf{r})$, instead of the complicated (correlated) N-particle wave function ψ. In principle, the exact ground-state energy of the interacting N-electron system, including the correlation energy missed in the Hartree−Fock (HF) theory, can be obtained by solving the Kohn−Sham (KS) single-particle equations of the auxiliary noninteracting system, given the exact density functional $E_{xc}[n]$ for the exchange-correlation energy. In practice, however, $E_{xc}[n]$ must be approximated, and the accuracy of the approximation therefore determines the success of KS DFT. Significant insight into this quantity is obtained from the adiabatic connection (AC),[3−10] which smoothly connects the KS noninteracting system to the interacting physical system.

With the aid of the adiabatic connection, $E_{xc}[n]$ is represented by the coupling-constant integral[3,4]

$$E_{xc}[n] = \int_0^1 d\lambda W_\lambda[n] \tag{1}$$

$$W_\lambda[n] = \langle \psi^\lambda | \hat{V}_{ee} | \psi^\lambda \rangle - U[n] \tag{2}$$

Here, $U[n]$ is the classical coulomb energy of a continuous charge distribution with density $n(\mathbf{r})$

$$U[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{3}$$

$\hat{V}_{ee} = ((e^2)/2)\sum_{i=1}^{N}\sum_{j(i\neq j)=1}^{N}|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|^{-1}$ is the two-particle Coulomb interaction operator for electrons. $\psi^\lambda[n]$ is that wave function which minimizes the expectation value $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$ for a fictive electron system with the kinetic-energy operator $\hat{T}$ and the interaction $\lambda \hat{V}_{ee}$, subject to the constraint that it has the ground-state density $n(\mathbf{r})$ of the real system with interaction $\hat{V}_{ee}(\lambda = 1)$.

When $\lambda = 0$, the wave function is the noninteracting Kohn−Sham single determinant $\psi^0[n]$, so $W_0[n] = \langle \psi^0[n] | \hat{V}_{ee} | \psi^0[n] \rangle - U[n] = E_x[n]$, where $E_x[n]$ is the exact orbital exchange energy evaluated using Kohn−Sham orbitals. The exact slope of W'_λ at $\lambda = 0$ is known exactly to be twice the second-order correlation energy from Goerling-Levy density functional perturbation theory (GL2),[11,12] $W'_0[n] = 2E_c^{GL2}[n]$. Therefore, in the weak interaction limit, we have

$$W_\lambda = W_0 + W'_0\lambda \quad \lambda \to 0 \tag{4}$$

When $\lambda = 1$, the wave function is the exact wave function of the interacting physical system, $\psi^1[n]$, so

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$$W_1[n] = \langle \psi^1[n] | \hat{V}_{ee} | \psi^1[n] \rangle - U[n] = V_{ee} - U[n] \quad (5)$$

which is the difference between the total electron−electron repulsion energy V_{ee} of the interacting physical system and the Coulomb energy.

There have been a number of attempts to construct exchange-correlation functionals by explicitly approximating W_λ. By linearly interpolating W_0 and W_1, where the latter is approximated by the local spin-density approximation (LSDA), Becke first introduced the so-called hybrid exchange-correlation functional.[13] With different assumptions for the λ dependence in the range of [0, 1] and local or semilocal exchange-correlation functionals to approximate W_1, many other constructions have been proposed, including nonempirical PBE0,[6] the [1/1]-Pade-based form of Ernzerhof,[14] the two-legged representation of Burke et al.,[15] and the MCY proposed by Mori-Sanchez, Cohen, and Yang.[16] The MCY also adds the information of W'_0, approximated by a modified Tao-Perdew-Staroverov-Scuseria[17] (TPSS) slope to avoid the computational expense of W'_0. Instead of W_1, Seidl et al.[18,19] used information from the strong interaction limit $\lambda \to \infty$, where W_λ approaches asymptotically a finite value W_∞

$$W_\lambda = W_\infty + W'_\infty \lambda^{-1/2} \quad \lambda \to \infty \quad (6)$$

The so-called interaction strength interpolation (ISI) functional interpolates the weak and strong interaction limits with W_∞ and W'_∞ approximated in the point-charge-plus-continuum (PC) model. Due to their nonlinearity in terms of $W_0[n]$, $W'_0[n]$, $W_\infty[n]$, and $W'_\infty[n]$, the [1/1]-Pade-based form of Ernzerhof,[14] the MCY,[16] and the ISI[18,19] are not size consistent, which is an important property of the exact $E_{xc}[n]$: $E_{xc}[n_1 + n_2] = E_{xc}[n_1] + E_{xc}[n_2]$ for two well separated densities n_1 and n_2.

Despite these attempts, the exact dependence W_λ is known only for the uniform electron gas (UEG) and for some relatively simple systems.[15,20,21] One of these systems is two electrons on the surface of a sphere (2ESS), which recently has been solved numerically for $\lambda \in [-\infty,\infty]$ by Seidl.[21] The extension of λ to negative values for this simple system then naturally brings up questions: does W_λ with negative λ exist for every system? If so, what is the asymptotical form as $\lambda \to -\infty$? Although the exchange-correlation energy is only an integral over $\lambda \in [0,1]$, the asymptotical form at limit $\lambda \to \infty$ still provides much information concerning W_λ, especially as a function of λ. On the contrary, at $\lambda = 1$, there is not an exact general form available for W_λ. Furthermore, with such information built in, the ISI[18,19] obtains accuracy comparable to the [1/1]-Pade-based form of Ernzerhof[14] and the MCY,[16] much better than the GL2 where only the weak interaction ($\lambda \to 0$) limit is used. Therefore, it is suspected that the construction of an exchange-correlation functional might benefit from the information at $\lambda \to -\infty$ too, to the extent that this limit is known.

In this paper, it is assumed that for every system W_λ exists for negative λ. An exchange-correlation functional triggered almost by the solution of 2ESS is then proposed in section 2 by approximating W_λ with λ extending to negative values. Results for 2ESS and some simple atoms are presented in section 3, followed by conclusions and future work discussed in section 4.

2. Interaction Strength Interpolation Extended to Negative λ (ISIN)

In ref 21, Seidl introduced an extra term to the ISI to recover the third leading term in the weak ($\lambda \to 0$) and strong ($\lambda \to \infty$) interaction limit, respectively, which led to a new functional, ISI3, and increased the accuracy of the correlation energy for 2ESS. However, this improvement was bought at a high price since the third leading term in the weak ($\lambda \to 0$) interaction limit, W''_∞, is the third-order of the GL perturbation expansion, although the third leading term in the strong ($\lambda \to \infty$) interaction limit, W''_∞, is 0.[18]

By extending to negative λ and using two leading terms in the weak ($\lambda \to 0$) and strong ($\lambda \to \infty$) interaction limit, respectively, I propose

$$W_\lambda^{ISIN} = a + b\lambda \, arcctg(c\lambda) + \frac{d}{(1 + e^2\lambda^2)^{1/4}} \quad (7)$$

where $a = W_0 - f(W_0 - W_\infty)$, $b = (2)/(\pi)W'_0$, $c = (2)/(\pi)(W'_0)/((W_\infty - W_0)(1 - f))$, $d = f(W_0 - W_\infty)$, and $e = ((f(W_0 - W_\infty))/(W'_\infty))^2$.

With f chosen to be 0.5 without fitting to any data, surprisingly, it gives remarkably good results for 2ESS as shown in Figure 1 and Table 1. Actually, the value for f is between 0.5 and 0.51 if we vary f to search for the most nearly exact energy of 2ESS at $R = 1$. And the variation of the energy is negligible with f from 0.5 to 0.51. $f = 0.5$ is used in this article. It is not guaranteed that, for all cases, W_λ^{ISIN} is a monotonically decreasing function over $\lambda \in [-\infty,\infty]$, as shown in eq 9 later. However, it is indeed so guaranteed for $\lambda \geq 0$. As $\lambda \to -\infty$, W_λ^{ISIN} is linearly dependent on λ, which matches the exact solution of 2ESS although the coefficients at this limit are different.[21] Note that the constraint of W''_∞ being 0 is fulfilled automatically in ISIN.

The exchange-correlation energy of ISIN is obtained by analytical integration, according to eq 1, of eq 7

$$E_{xc}^{ISIN} = a + \frac{b}{2c^2}[(1 + c^2) arcctg(c) + c - \pi/2] + \frac{2d}{(1 + e^2)^{1/4}} + \frac{\sqrt{2}d}{e}\left[F\left(\alpha, \frac{1}{\sqrt{2}}\right) - 2E\left(\alpha, \frac{1}{\sqrt{2}}\right)\right] \quad (8)$$

where $\alpha = \arccos[(1 + e^2)^{-1/4}]$. $F(\alpha,k)$ and $E(\alpha,k)$ are the first- and second-kind incomplete elliptic integrals with the modulus $k = 1/\sqrt{2}$. An interesting point is that eq 8 gives the exact value for the H atom, where $W_0 = W_\infty = -0.3125$ Ha and $W'_0 = W'_\infty = 0$. Even if we use the PC model value of $W_\infty^{PC} = -0.313$ Ha and $W'^{PC}_\infty = 0.043$ Ha for the H atom, the correlation energy is still negligible, about 0.5×10^{-10} Ha.

Because the inputs $W_0[n]$, $W'_0[n]$, $W_\infty[n]$, *and* $W'_\infty[n]$ are size consistent, so is $W_\lambda^{ISIN}[n]$ in the weak- and strong-interaction limits. However, due to its nonlinearity, $E_c^{ISIN}[n]$ is not generally size consistent.

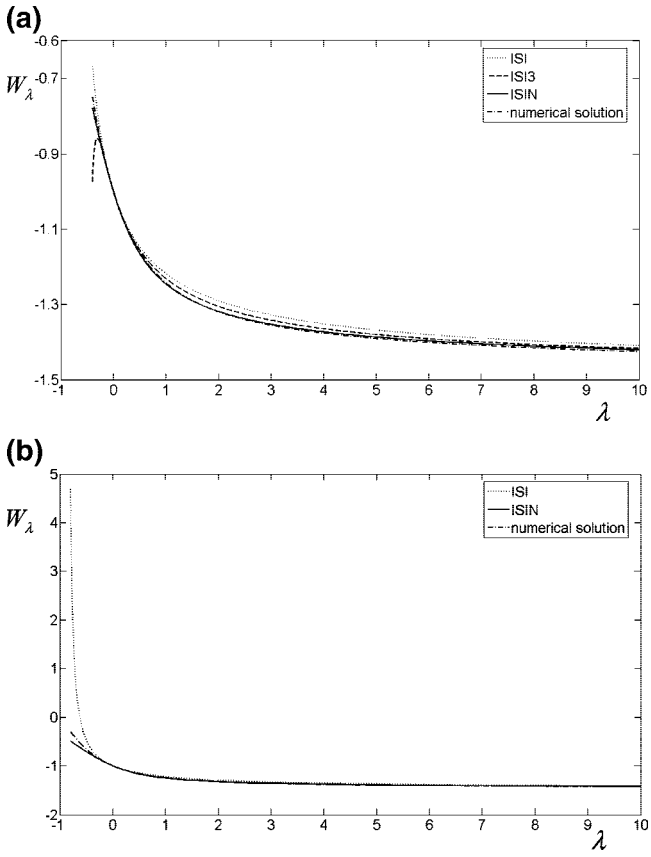

Figure 1. The coupling constant integrand W_λ of different approximations compared to the numerical solution for the singlet system of 2ESS. (a) $\lambda \in (-0.4,10)$; (b) $\lambda \in (-0.8,10)$, ISI3 is not shown in this figure since it has a singularity in this range. Here 2ESS means two electrons on the surface of a sphere of radius $R = 1$ Bohr.

Table 1. Correlation Energies $E_c[R]$ of the Singlet System of 2ESS[a]

R	ISI[b]	ISI3[b]	ISIN	exact[b]
0.1	−0.2118	−0.2157	−0.2183	−0.2175
0.2	−0.1985	−0.2045	−0.2094	−0.2064
0.5	−0.1679	−0.176	−0.1844	−0.1796
1	−0.1349	−0.1426	−0.1511	−0.1473
2	−0.0984	−0.104	−0.1098	−0.1081
5	−0.0562	−0.0587	−0.0608	−0.0605
10	−0.0337	−0.0348	−0.0355	−0.0355
M.E	0.007643	0.002657	−0.00206	
M.A.E	0.007643	0.002657	0.00206	

[a] The unit is Hartree. Here 2ESS means two electrons on the surface of a sphere of radius R =1 bohr. [b] Values are from ref 21.

3. Results and Discussions

In the 2ESS system, the electrons, distributing uniformly, are confined to the 2D surface of a sphere with radius R, variation of which can result in different density of the charge. The limit of $R\rightarrow\infty$ ($R\rightarrow 0$) corresponds to the low density (high density), i.e. the strong interaction (weak interaction). With W_0, W'_0, W_∞, and W'_∞ given in eqs 38 and 39 in ref 21 for the singlet system of 2ESS, Figure 1(a) plots W_λ vs λ with $\lambda \in [-0.4,10]$ for $R = 1$ Bohr. By recovering the additional third leading term in the strong and weak interaction limit, respectively, ISI3 shows significant improvement over ISI, while ISIN, by extending to negative λ with correct linear dependence as $\lambda \rightarrow -\infty$ (although the coefficient for this limit is not recovered) and recovering W'_∞ automatically, is slightly closer to the numerical solution. This observation is corroborated by Table 1, the correlation energies $E_c[R]$ for different R, where the mean absolute error drops from 0.007643 Ha of ISI largely to 0.002657 Ha of ISI3, then slightly to 0.00206 Ha of ISIN. Figure 1(b) shows that W_λ^{ISIN} deviates from the numerical solution very much for $\lambda < -0.5$ due to the inconsistency of the coefficient at $\lambda \rightarrow -\infty$, which is, however, still better than the other two, namely ISI and ISI3, obviously.

Table 2. Correlation Energies E_c of Atoms[a]

system	ISI[b]	ISIN	exact[b]
He	−0.041	−0.044	−0.042
Exp.	−0.034	−0.038	−0.037
Be	−0.1	−0.112	−0.096
Ne	−0.405	−0.439	−0.394

[a] Exp. is the two-electron system with exponential density $n(\mathbf{r}) = 2\exp(-2r)/\pi$. W_∞ and W'_∞, evaluated in the PC model, along with W_0 and W'_0, are given in Table 3 of ref 18. The unit is Hartree. [b] Values are from ref 18.

Table 3. Atomization Energies of 18 Molecules (in Units of 1 kcal/mol), in Second-Order Goerling-Levy Perturbation Theory (GL2),[14] in ISI,[18,19] in ISIN, and from Experiment (as in ref 22)

mol.	GL2[c]	ISI[c]	ISIN	expt
H2	114	107.3	109.2	109.5
LiH	70	58.8	61.4	57.8
Li2	39	22.5	24.6	24.4
LiF	193	142.7	157.9	138.9
Be2	22	5.7	8.6	3
CH4	454	423.4	433.3	419.3
NH3	340	300.9	313.2	297.4
OH	128	108.6	114.5	106.4
H2O	274	235.7	248.4	232.2
HF	173	143.7	153.2	140.8
B2	190	68.1	88.4	71
CN	335	188.1	220.5	178.5
CO	355	265.9	292.1	259.3
N2	342	234.6	262	228.5
NO	265	157.9	184.2	152.9
O2	230	123.6	149.6	120.5
O3	407	136.8	187.1	148.2
F2	134	34	51.2	38.5
ME	74	1.7	18.5	
MAE	74	4.3	18.5	

[c] Values are from ref 19.

Although ISIN works well in this simple 2ESS model, it turns out that it is inferior to ISI when applied to the real system, as shown in Table 2. The inferiority might be due to the fact that, while ISI does not break down completely for metals and systems with large static correlation, W_λ^{ISIN} does when $W'_0 \rightarrow -\infty$

$$\lim_{W'_0\rightarrow-\infty} W_\lambda^{ISIN} = W_\infty + \frac{d}{(1+e^2\lambda^2)^{1/4}} \tag{9}$$

As $W'_0 \rightarrow -\infty$, the second term in the right-hand side of eq 7 becomes discontinuous at $\lambda = 0$, jumping from 0 to b/c, which then leads to $\lim_{\lambda\rightarrow 0^+} \lim_{W'_0\rightarrow-\infty} W_\lambda^{ISIN} = (W_0 + W_\infty)/2$, more negative to the supposed W_0. This discontinuity implies that W_λ^{ISIN} biases toward W_∞ and thus results in more

negative correlation energies, as shown in Tables 1 and 2. This is also corroborated by the calculation of the atomization energies of 18 small molecules, using the idea and data given in refs 14, 18, and 19. In Table 3, ISIN overbinds these molecules with the mean absolute error (MAE) of 18.5 kcal/mol, compared to 4.3 kcal/mol of ISI, due to the fact that the molecules have much larger W_0' because of static correlation, therefore, much more spurious negative correlation energies, than their component atoms. However, ISIN is still better than GL2, which gave a MAE of 74 kcal/mol.[14]

4. Conclusion and Future Work

With the coupling constant λ extending to negative values, the ISIN explicitly approximates W_λ, covering the two leading terms of the asymptotic expansion of W_λ at $\lambda = 0$ and ∞, respectively. For the simple system of 2ESS, ISIN works well, even better than ISI3. The mean absolute error of the correlation energies $E_c[R]$ for different R yielded by the ISIN is 0.00206 Ha, slightly better than 0.002657 Ha by ISI3 and much better than 0.007643 Ha by ISI. However, due to the discontinuity of W_λ^{ISIN} at $\lambda = 0$ as $W_\lambda' \to -\infty$, W_λ^{ISIN} breaks down completely with W_λ^{ISIN} biasing toward W_∞, resulting in much more negative correlation energies and overbinding of molecules for real systems.

Although the ISIN proposed in this article fails to give accurate correlation energies for real systems, the future work on this subject might be to find one which recovers the behavior of ISI as $W_0' \to -\infty$, meanwhile extending λ to negative values.

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