Adiabatic connection for strictly correlated electrons

Zhen-Fei Liu[a)] and Kieron Burke

Department of Chemistry, University of California, Irvine, California 92697-2025, USA

Modern density functional theory (DFT) calculations employ the Kohn–Sham system of noninteracting electrons as a reference, with all complications buried in the exchange-correlation energy (E_{XC}). The adiabatic connection formula gives an exact expression for E_{XC}. We consider DFT calculations that instead employ a reference of strictly correlated electrons. We define a "decorrelation energy" that relates this reference to the real system, and derive the corresponding adiabatic connection formula. We illustrate this theory in three situations, namely, the uniform electron gas, Hooke's atom, and the stretched hydrogen molecule. The adiabatic connection for strictly correlated electrons provides an alternative perspective for understanding DFT and constructing approximate functionals. © *2009 American Institute of Physics.*
[doi:10.1063/1.3239472]

I. INTRODUCTION

For most modern calculations using density functional theory (DFT),[1] the accuracy of results depends only on approximations to the exchange-correlation functional, $E_{XC}[n]$. An exact expression for $E_{XC}[n]$ is given by the adiabatic connection formula,[2,3] in which E_{XC} is expressed as an integral over a coupling constant λ, which connects the reference [Kohn–Sham (KS) system, $\lambda=0$] and the real physical interacting system (ground state, $\lambda=1$), keeping the density $n(\mathbf{r})$ fixed. Study of the adiabatic connection integral has proven very useful for understanding approximate (hybrid) functionals,[4,5] and is an ongoing area of research.[6–8]

Almost all modern DFT calculations employ the KS system[9] as a reference. The KS system is defined as the unique fictitious system that has the same density as the real system, but consists of noninteracting electrons. The great practicality of KS DFT is due to the relative ease with which the noninteracting equations can be solved, with relatively crude approximations, giving KS DFT a useful balance between speed and accuracy.

However, DFT calculations could also be based on another fictitious system which is known as the strictly correlated (SC) system.[10] The SC system has the same density as the real system (as does the KS system), but the Hamiltonian consists of electron repulsion and external potential energy terms only. In recent years, the pioneering work of Seidl and co-workers[10–17] has led to substantial progress in solving this problem exactly and efficiently. The strictly correlated electrons (SCE) ansatz[14–17] has been shown to yield the density and energy of this system, going beyond the earlier point-charge-plus-continuum (PC) model.[12,13] They have achieved great success in calculating spherical symmetric systems with arbitrary number of electrons.[15]

In this article, we look to the future and assume that the SC limit of *any* system can be calculated with less difficulty than the original interacting problem, and all our successive

work is developed based on this reference. We derive a new version of the adiabatic connection formalism, which connects the SC system (fully interacting) and the physical system. We also introduce a new coupling constant μ, and a "decorrelation energy" E_{DC}, the counterpart of E_{XC} in KS DFT, which must be evaluated to extract the true ground-state energy from the calculation of the SC system. We argue that, as long as the SC system can be solved easily (just as the KS case), one can develop another version of DFT based on this system, a version that is better-suited to strongly localized electrons.

Throughout this paper, we use atomic units ($e^2 = \hbar = \mu = 1$), which means that if not particularly mentioned, all energies are in hartree, and all lengths are in Bohr radii, etc.

II. THEORY

In this section, we introduce the alternative adiabatic connection formula, and relate its quantities to more familiar ones. All results here are formally exact.

A. KS adiabatic connection

In KS DFT, the total energy for the interacting ground state is expressed as

$$E[n] = T_S[n] + \int d^3r \, v_{ext}(\mathbf{r})n(\mathbf{r}) + U[n] + E_{XC}[n]. \quad (1)$$

In this equation, T_S is the noninteracting kinetic energy of KS orbitals $\{\varphi_i\}$ that are eigenfunctions of the noninteracting KS equation, $v_{ext}(\mathbf{r})$ is the external potential (nuclear attraction in the case of atoms and molecules), U is the Hartree energy defined as the "classical" Coulomb repulsion between two electron clouds, and E_{XC} is the exchange-correlation energy.[18] The adiabatic connection integral[2,3] then gives an exact expression for E_{XC}:

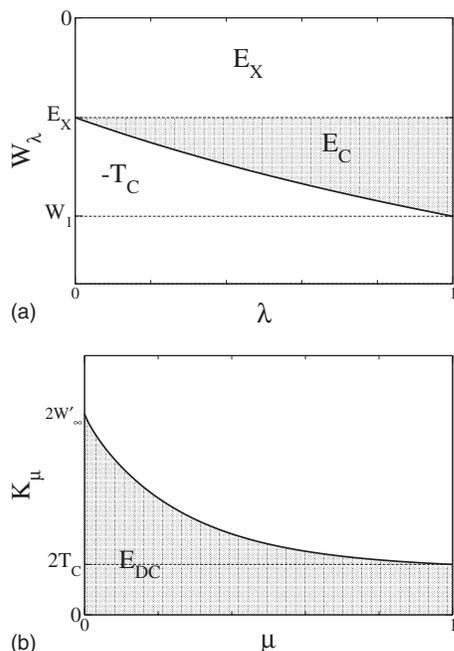---

a)Electronic mail: zhenfei.liu@uci.edu.

FIG. 1. Traditional (upper panel) and the new (lower panel) adiabatic connection curves.

$$E_{XC}[n] = \int_0^1 d\lambda\, W_\lambda[n], \tag{2}$$

where one can show that $W_\lambda = \langle \Psi^\lambda | \hat{V}_{ee} | \Psi^\lambda \rangle - U$, in which Ψ^λ is the wavefunction that minimizes $\hat{T} + \lambda \hat{V}_{ee}$ but has the same density as the real ground-state system.[19] At $\lambda = 0$, one recovers the KS system, and at $\lambda = 1$, one recovers the real interacting system. In this way, one connects the KS system with the real interacting system by changing λ from 0 to 1.

A cartoon of W_λ versus λ is shown in the upper panel of Fig. 1. By definition, we have $W_0 = E_X$ and the area under the curve is E_{XC}. We can also identify the kinetic correlation energy $T_C = E_{XC} - W_1$ in this graph.

B. SC reference system

The KS wavefunction can be defined as the wavefunction that minimizes the kinetic energy alone, but whose density matches that of the interacting system. Analogously, the SC wavefunction is found by minimizing the electron-electron repulsion energy alone, subject to reproducing the exact density. In practice, there might be multiple degeneracies, so it is best defined in the limit as the kinetic energy goes to zero.

Then, using the SC system as the reference, the energy of the true interacting ground state is

$$E[n] = U_{sc}[n] + \int d^3 r\, v_{ext}(\mathbf{r}) n(\mathbf{r}) + T_S[n] + E_{DC}[n], \tag{3}$$

where $U_{sc} = \langle \Psi^\infty | \hat{V}_{ee} | \Psi^\infty \rangle$. In KS DFT quantities, $U_{sc} = U + W_\infty$ [see Eq. (2)].

Just as we separate the Hartree energy from the total energy in KS DFT [Eq. (1)], here in Eq. (3) we separate $T_S[n]$ from the total energy in SC DFT. There are a variety of

algorithms that can be used to extract this quantity accurately for any given density, effectively by inverting the KS equations.[20] We label the remainder as the "decorrelation energy," $E_{DC}[n]$. The reason we call it decorrelation energy is that, if we consider the electrons in the reference system "strictly correlated," with energy $U_{sc}[n]$, the electrons in the real system are *less* correlated than in the reference system. We will see the physical meaning explicitly very soon.

So far, we have defined our reference, and next we deduce an exact expression for the newly defined decorrelation energy $E_{DC}[n]$ with the adiabatic connection formalism, just as one does for $E_{XC}[n]$ (Refs. 10 and 12) in the KS DFT [Eq. (2)].

C. SC adiabatic connection formula

We denote Ψ^μ as the wavefunction minimizing $\hat{H}^\mu = \mu^2 \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}^\mu$ with density $n(\mathbf{r})$. For $\mu = 0$, we recover the SC system, and for $\mu = 1$, we recover the real system. For each value of μ, there is a corresponding unique external potential yielding the correct density, $v_{ext}^\mu(\mathbf{r})$. So we have

$$E^\mu = \langle \Psi^\mu | \mu^2 \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}^\mu | \Psi^\mu \rangle. \tag{4}$$

Using Hellmann–Feynman theorem,[21] we have

$$\frac{dE^\mu}{d\mu} = \langle \Psi^\mu | \frac{d\hat{H}^\mu}{d\mu} | \Psi^\mu \rangle = \langle \Psi^\mu | 2\mu \hat{T} + \frac{d\hat{V}_{ext}^\mu}{d\mu} | \Psi^\mu \rangle. \tag{5}$$

Integrating and canceling the external potential terms at both sides, we recognize the left hand side is just $T_S[n] + E_{DC}[n]$. Thus

$$E_{DC}[n] = \int_0^1 d\mu\, 2\mu \langle \Psi^\mu | \hat{T} | \Psi^\mu \rangle - T_S[n]. \tag{6}$$

This is our adiabatic connection formula for SC electrons. Finally, since $T_C[n] = T[n] - T_S[n]$, and $T_S[n]$ is independent of μ,

$$E_{DC}[n] = \int_0^1 d\mu\, K_\mu[n], \tag{7}$$

where

$$K_\mu[n] = 2\mu T_C^\mu[n]. \tag{8}$$

This is the SC doppelganger of Eq. (2). We plot a cartoon of the integrand K_μ versus μ in the lower panel of Fig. 1, identifying the area below the curve as E_{DC} and noting that $K_1 = 2T_C$.

D. Relation to KS DFT

From a formal viewpoint, what we derived here is not new, but simply another way to describe the real interacting system. Thus we can relate all quantities defined here, such as $E_{DC}[n]$ and $K_\mu[n]$, to quantities defined in the traditional KS DFT. Since both Eqs. (3) and (1) are exact for the real system, and if we use the expression of $U_{sc}[n]$ in KS language [see discussion below Eq. (3)], we find

$$E_{DC}[n] = E_{XC}[n] - W_\infty[n]. \tag{9}$$

Thus $E_{DC}[n]$ defined in our theory is just the difference between the usual exchange-correlation energy of the real system $E_{XC}[n]$ and the potential contribution to the exchange-correlation energy of the SC system, $W_\infty[n]$.

We can also deduce an expression for K_μ in terms of W_λ. Since Ψ^μ minimizes $\hat{H}^\mu = \mu^2 \hat{T} + \hat{V}_{ee}$, while yielding $n(\mathbf{r})$, and Ψ^λ minimizes $\hat{T} + \lambda \hat{V}_{ee}$, we deduce $\Psi^{1/\mu^2} = \Psi^\lambda$. Now, from the scaling properties of KS DFT,[22] we know

$$T_C^\lambda = E_C^\lambda - \lambda \frac{dE_C^\lambda}{d\lambda}. \tag{10}$$

If we write $E_C^\lambda = T_C^\lambda + U_C^\lambda$, i.e., U_C^λ is the potential contribution to E_C^λ, $U_C^\lambda = \lambda(W_\lambda - E_X)$, we have

$$\frac{dT_C^\lambda}{d\lambda} = \frac{U_C^\lambda}{\lambda} - \frac{dU_C^\lambda}{d\lambda}. \tag{11}$$

Integrating over λ from 0 to $1/\mu^2$, and using the definition of W_λ in Eq. (2) and that $E_X^\lambda = \lambda E_X$ by scaling,[22] we can express $T_C^\mu[n]$ in terms of $W_\lambda[n]$, we find

$$K_\mu[n] = 2\mu \int_0^{1/\mu^2} d\lambda (W_\lambda[n] - W_{1/\mu^2}[n]). \tag{12}$$

From this relation, we can generate the new adiabatic connection curve, as long as we know the integrand of the KS adiabatic connection, i.e., $W_\lambda[n]$ for $\lambda = 1$ to ∞.

E. Exact conditions

Many of the well-established exact conditions on the correlation energy can be translated and applied to the decorrelation energy. In particular, the simple relations between scaling the density and altering the coupling constant all apply, i.e.,

$$E_C^\lambda[n] = \lambda^2 E_C[n_{1/\lambda}], \tag{13}$$

where $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma \mathbf{r})$. Thus, in terms of scaling

$$K_\mu[n] = \frac{2}{\mu^3} T_C[n_{\mu^2}]. \tag{14}$$

Note that, as $\mu \to \infty$, $K_\mu \to 0$, while $K_{\mu=0} = 2W_\infty'$, where W_∞' is defined in the expansion of W_λ as $\lambda \to \infty$ (Ref. 12)

$$W_\infty' = \lim_{\lambda \to \infty} \sqrt{\lambda}(W_\lambda - W_\infty). \tag{15}$$

Thus the SC energy is found from solving the SC system, while $K_{\mu=0}$ is determined by the zero-point oscillations around that solution. Both are currently calculable for spherical systems.[15,17]

The most general property known about the correlation energy[22] is that, under scaling toward lower densities, it must become more negative. In turn, this implies that W_λ is never positive. Using the definition of T_C^μ and changing variable $\lambda = 1/\mu^2$ in Eq. (11), we find

$$\frac{dT_C^\mu}{d\mu} = \frac{2}{\mu^5} \frac{dW_\lambda}{d\lambda} < 0, \tag{16}$$

then using $K_\mu = 2\mu T_C^\mu$ and the fact that $K_\mu > 0$, we find

$$\frac{d}{d\mu} \ln K_\mu < 0. \tag{17}$$

Also, because $T_C^\mu > 0$, so $K_\mu = 2\mu T_C^\mu > 0$, and E_{DC} as an integration of K_μ is always positive.

Based on these properties of K_μ, a crude approximation to K_μ can be a simple exponential parametrization, using K_0 and the derivative of $\ln K$ at $\mu=0$ as inputs:

$$K = K_0 e^{-\gamma \mu}, \quad \gamma = -\left. \frac{d}{d\mu} \ln K \right|_0. \tag{18}$$

III. ILLUSTRATIONS

In this section, we illustrate the theory developed above on three different systems, to show how K_μ behaves for very different systems, and where the adiabatic connection formula might be most usefully approximated.

A. Uniform electron gas

For a uniform electron gas, we assume we know the correlation energy per particle ϵ_C, accurately as a function of $r_s = (3/4\pi n)^{1/3}$. In order to apply Eq. (12) to calculate $K_\mu[n]$, we use $\epsilon_C^\lambda(r_s) = \lambda^2 \epsilon_C(\lambda r_s)$ (Ref. 22). Substituting into Eq. (10), changing variables $\lambda = 1/\mu^2$, and using $K_\mu = 2\mu T_C^\mu = N\kappa_\mu$, with N as the number of particles, we find

$$\kappa_\mu^{unif} = -\frac{2}{\mu^3} \frac{d}{dr_s} (r_s \epsilon_C(r_s))\big|_{r_s/\mu^2}. \tag{19}$$

Using Eq. (9) and the definition of W_∞, we find

$$\epsilon_{DC}^{unif} = \epsilon_C + \frac{d_0}{r_s}, \tag{20}$$

where d_0 is defined below and $d_0 = 0.433\ 521$. In the large-r_s limit or the low-density expansion[23]

$$\epsilon_C(r_s) = -\frac{d_0}{r_s} + \frac{d_1}{r_s^{3/2}} + \frac{d_2}{r_s^2} + \cdots, \tag{21}$$

where $d_2 = -3.661\ 51$ from data of Ref. 23. Substituting this expansion into Eq. (19), we find

$$\kappa_\mu^{unif} = \frac{d_1}{r_s^{3/2}} + 2\mu \frac{d_2}{r_s^2} + \cdots \quad \text{as} \ \mu \to 0. \tag{22}$$

Thus κ_μ is expected to have a well-behaved expansion in powers of μ for small μ.

Using Perdew and Wang's[23] parametrization of the correlation energy of the uniform gas, we plot κ_μ versus μ for $r_s = 1$ in Fig. 2, and find $\epsilon_{DC} = 0.374$ at $r_s = 1$.

Using the exact curve for $r_s = 1$ in the simple exponential parametrization [Eq. (18)], we find $\kappa_0 = 1.440\ 73$ and $\gamma = 5.0826$. We plot the exponential parametrization in Fig. 2 and we can see that it decays much faster than the exact curve, producing a ϵ_{DC} that is too small by about 25%, which means about 150% larger in $|\epsilon_C|$ [see Eq. (9)].
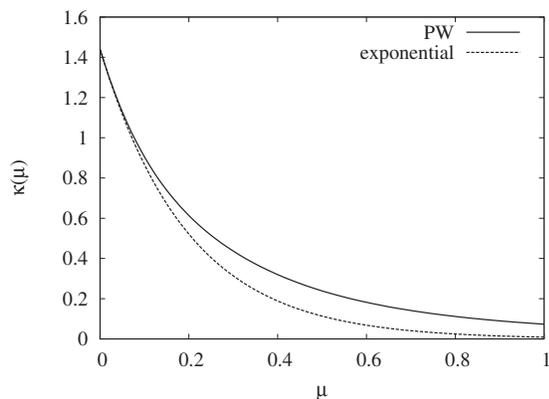
FIG. 2. Exact adiabatic connection curve κ_μ for uniform electron gas ($r_s=1$) and a simple exponential parametrization.

We calculated $\epsilon_{DC}/|\epsilon_C|$ for different values of r_s and plot the curve in Fig. 3. At small r_s, $\epsilon_{DC} \gg |\epsilon_C|$, which suggests that the KS reference system is a better starting point, as a smaller contribution to the energy needs to be approximated. At large r_s, $|\epsilon_C| > \epsilon_{DC}$ so ϵ_{DC} is a smaller quantity and may be better approximated. Under such circumstances, the SC system might serve as a better reference. For the uniform gas, the switch-over occurs at about $r_s=16$, which is at densities much lower than those relevant to typical processes of chemical and physical interest. However, as we show below, for systems with static correlation, this regime can occur much more easily.

B. Hooke's atom

As we pointed out, as long as we have an approximate $W_\lambda[n]$ for λ between 1 and ∞, we can substitute it into Eq. (12) to get the new adiabatic connection formula for the decorrelation energy. Of course, most such formulas focus on the shape between 0 and 1, since only that section is needed for the regular correlation energy. However, any such approximate formula can be equally applied to K_μ, yielding an approximation for the decorrelation energy. Peach *et al.*[5] analyze various parametrizations for W_λ and the same forms can be used as well to parametrize K_μ, based on the similar shape of W_λ and K_μ curves. In general, application to K_μ will yield a distinct approximation to the ground-state energy, with quite different properties.
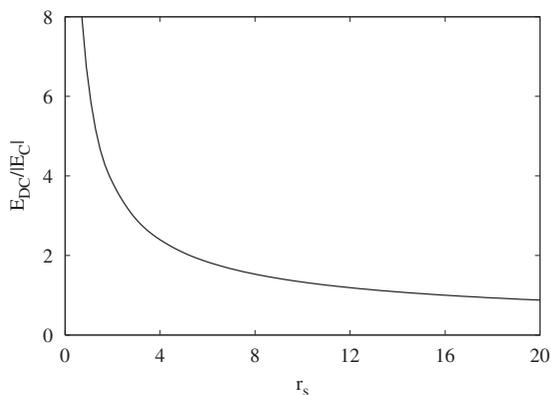

FIG. 3. $\epsilon_{DC}/|\epsilon_C|$ for different r_s for uniform electron gas.

To give just one example, one of the earliest sensible smooth parametrizations is the [1,1] Pade of Ernzerhof[24]

$$W_\lambda = a\left(\frac{1+b\lambda}{1+c\lambda}\right). \tag{23}$$

One can imagine applying it with inputs of, e.g., E_X, W_0' given by Görling–Levy perturbation theory, and W_∞ from the SC limit. It yields a sensible approximation to W_λ in the 0–1 range, but because it was not designed with the SC limit in mind, the formula itself is not immediately applicable to the decorrelation energy, since, e.g., $K_{\mu=0}$ vanishes. However, much more sensible is to make the same approximation directly for K_μ instead, if one is doing an SC calculation, i.e.,

$$K_\mu = \tilde{a}\left(\frac{1+\tilde{b}\mu}{1+\tilde{c}\mu}\right), \tag{24}$$

whose inputs could be K_0, K_0', and, e.g., a generalized gradient approximation for $K_{\mu=1}$. This is then a very different approximation from the same idea applied to the usual adiabatic connection formula.

On the other hand, there are several approximations designed to span the entire range of λ, the most famous being interaction strength interpolation (ISI) model developed by Seidl *et al.*[13] This model uses the values and the derivatives of W_λ at two limits, namely, the high-density limit (KS system, $\lambda=0$) and the low-density limit (SC system, $\lambda \to \infty$), to make an interpolation. Another approximation to W_λ is developed in our previous work,[25] which employs W_0, W_∞ and W_0' as inputs. We compare the approximate K_μ's obtained from the two models.

Hooke's atom is a two-electron system (i.e., with Coulomb repulsion) in a spherical harmonic well.[26] Using the accurate values $W_0=-0.515$, $W_\infty=-0.743$, $W_0'=-0.101$,[8] and $W_\infty'=0.208$,[27] we find

$$K_\mu^{ISI} = -0.947\mu + 1.029A\mu - \frac{0.336}{\mu B} + 0.270\mu \ln B, \tag{25}$$

where $A=\sqrt{1+0.653/\mu^2}$ and $B=A-0.263$. With the same data substituted in W^{simp} (Ref. 25), we find

$$K_\mu^{simp} = -\frac{0.228}{\alpha^4 \mu}(\alpha^3 - \alpha^2 + 1) + 1.287\mu(\alpha-1), \tag{26}$$

where $\alpha=\sqrt{1+0.354/\mu^2}$. We plot the two forms of K_μ in Fig. 4. The exact curve (down to $\mu=0.5$) is taken from Ref. 8. We compare three quantities in Table I. Although K_μ^{ISI} contains a spurious $\mu \ln \mu$ term as $\mu \to 0$,[15,17,25] it nonetheless yields accurate results. The simple model, applied with the usual inputs, is less accurate pointwise, but integrates to an accurate value.

We can try the simple exponential parametrization Eq. (18) for K_μ again for Hooke's atom. Because we do not know the value of $d/d\mu \ln K_\mu$ at $\mu=0$ exactly, instead we do an exponential fitting using the method of least-squares, with the exact K_μ values (between $\mu=0.5$ and 1) taken from Ref. 8. We plot K_μ versus μ in Fig. 4 and compare several quantities in Table I.
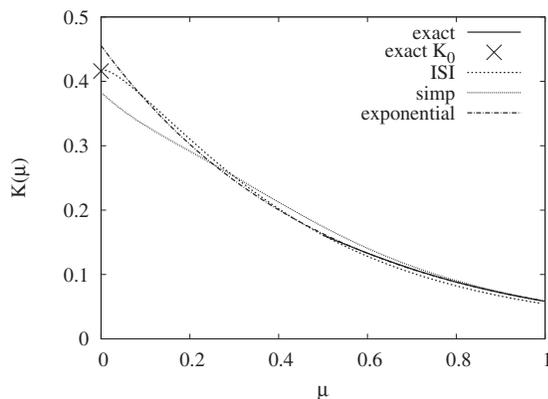
FIG. 4. Adiabatic connection curves for Hooke's atom. The exact curve (down to $\mu = 0.5$) is taken from Ref. 8.

C. H_2 bond dissociation

Bond dissociation of the H_2 molecule produces a well-known dilemma in computational chemistry.[28–31] In the exact case, as the bond length $R \to \infty$, the hydrogen molecule should dissociate to two free hydrogen atoms, with the ground state always a singlet and spin-unpolarized. However, spin-restricted, e.g., restricted Hartree–Fock or restricted KS DFT, give the correct spin multiplicity, i.e., the wavefunction is an eigenfunction of $\hat{S}^2$, but produce an overestimated total energy, much higher than that of two free hydrogen atoms. Spin-unrestricted, e.g., unrestricted Hartree–Fock or unrestricted KS DFT, give a fairly good total energy, but the wavefunction is spin-contaminated, i.e., the deviation of $\langle \hat{S}^2 \rangle$ from the exact value is significant. This is known as "symmetry breaking" in H_2 bond dissociation.

Fuchs *et al.*[32] argued that DFT within random phase approximation (RPA) gives a correct picture of the H_2 bond dissociation within the spin-restricted KS scheme. They also gave highly accurate adiabatic connection curves for ground-state H_2 at bond length $R = 1.4$ Å and stretched H_2 at bond length $R = 5$ Å. The curves were interpolated particularly between $\lambda = 0$ and 1, shown as the difference of the integrand ΔW_λ between the stretched H_2 molecule and two free H atoms (Figs. 1 and 3 of Ref. 32).

For $R = 1.4$ Å and $R = 5$ Å, if we use an interpolation (see Ref. 63 in Fuchs paper[32]) to estimate ΔW_λ, we find reasonable values $\Delta W_\infty = -7.00$ and $\Delta W_\infty = 0.13$, respectively. Using Eq. (9), we find $\Delta E_{DC} = 4.96$ and $\Delta E_{DC} = 0.69$, respectively. We compare ΔE_{DC} and ΔE_C values in Table II. The comparison shows a physical example where the SC system is a better starting point in the calculation.

We can see that at the equilibrium bond length $|\Delta E_C|$ is much smaller than ΔE_{DC}, presumably making it easier to approximate the ground-state energy starting from the KS reference system. This is typical at equilibrium. However for stretched bonds, ΔE_{DC} is much smaller than $|\Delta E_C|$, and so ΔE_{DC} instead may be better accurately approximated in the calculation and the SC system should be a better reference. Molecules with strong static correlation, such as Cr_2 and O_3, might fall somewhere in between.

IV. CONCLUSION

In this paper, we constructed an adiabatic connection formalism for the SC system. We found that this adiabatic connection formula and curve can be well defined with respect to this new reference. Our formula connects the SC system and the real system, by Eq. (7). We also defined the quantity for this new integral as "decorrelation energy" and related this with the usual KS adiabatic connection. We illustrated how the decorrelation energy behaves, using the uniform electron gas, Hooke's atom, and stretched H_2 as examples.

We emphasize again that a real application of this theory is only possible when the reference, i.e., the SC system, can be routinely calculated. At present, one can calculate quantities such as U_{sc} exactly only for spherical symmetric systems.[14] However, nonempirical approximations to E_{XC} of KS theory can be employed to estimate W_∞ with useful accuracy.[33] The computation of this quantity may become much easier in the future.[34] If this is so, then based on the properties discussed here, the SC reference may be preferable in cases that are difficult for standard KS DFT calculations with standard approximations to E_{XC}. In fact, a recent work[34] independently shows progress using exactly the formalism discussed here and suggests approximations to E_{DC}. In any event, the advent of SC calculations opens up a whole new alternative approach to DFT calculations of electronic structure, and only experience can show how and when this will prove more fruitful than the traditional (KS) scheme.

TABLE I. Comparison of several quantities for three approximations to K_μ. Note: ISI uses K_0 as an input. The exact values are taken from Ref. 8.

	Exact	ISI	simp	Exponential
K_0	0.416	0.416	0.383	0.456
K_1	0.058	0.054	0.059	0.058
E_{DC}	0.189	0.191	0.190	0.193

TABLE II. Comparison of several quantities for stretched H_2 at different bond lengths. The values for ΔE_X and ΔE_{XC} are taken from Ref. 32. All values are in eV.

Bond length	1.4 Å	5 Å	∞
ΔE_X	−0.98	5.85	8.5
ΔE_{XC}	−2.04	0.82	0.0
ΔW_∞	−7.00	0.13	0.0
ΔE_C	−1.06	−5.03	−8.5
ΔE_{DC}	4.96	0.69	0.0

[1] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).
[2] D. C. Langreth and J. P. Perdew, Solid State Commun. **17**, 1425 (1975).
[3] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).
[4] P. Mori-Sánchez, A. J. Cohen, and W. Yang, J. Chem. Phys. **124**, 091102 (2006).

[5] M. J. G. Peach, A. M. Miller, A. M. Teale, and D. J. Tozer, J. Chem. Phys. **129**, 064105 (2008).

[6] K. Burke, M. Ernzerhof, and J. P. Perdew, Chem. Phys. Lett. **265**, 115 (1997).

[7] D. Frydel, W. M. Terilla, and K. Burke, J. Chem. Phys. **112**, 5292 (2000).

[8] R. J. Magyar, W. Terilla, and K. Burke, J. Chem. Phys. **119**, 696 (2003).

[9] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[10] M. Seidl, J. P. Perdew, and M. Levy, Phys. Rev. A **59**, 51 (1999).

[11] M. Seidl, Phys. Rev. A **60**, 4387 (1999).

[12] M. Seidl, J. P. Perdew, and S. Kurth, Phys. Rev. A **62**, 012502 (2000); **72**, 029904(E) (2005).

[13] M. Seidl, J. P. Perdew, and S. Kurth, Phys. Rev. Lett. **84**, 5070 (2000).

[14] M. Seidl, P. Gori-Giorgi, and A. Savin, Phys. Rev. A **75**, 042511 (2007).

[15] M. Seidl, Phys. Rev. A **75**, 062506 (2007).

[16] P. Gori-Giorgi, M. Seidl, and A. Savin, Phys. Chem. Chem. Phys. **10**, 3440 (2008).

[17] P. Gori-Giorgi, G. Vignale, and M. Seidl, J. Chem. Theory Comput. **5**, 743 (2009).

[18] *A Primer in Density Functional Theory*, edited by C. Fiolhais, F. Nogueira, and M. Marques (Springer-Verlag, Berlin, 2003).

[19] W. Yang, in *Density Matrices and Density Functionals*, edited by R. Erdahl and V. H. Smith, Jr. (Reidel, Dordrecht, 1987).

[20] K. Peirs, D. Van Neck, and M. Waroquier, Phys. Rev. A **67**, 012505 (2003).

[21] M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).

[22] M. Levy, Phys. Rev. A **43**, 4637 (1991).

[23] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[24] M. Ernzerhof, Chem. Phys. Lett. **263**, 499 (1996).

[25] Z.-F. Liu and K. Burke, Phys. Rev. A **79**, 064503 (2009).

[26] M. Taut, J. Phys. A **27**, 1045 (1994).

[27] P. Gori-Giorgi, private conmmunication (2009).

[28] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory* (Wiley-VCH, Weinheim, 2001).

[29] J. P. Perdew, A. Savin, and K. Burke, Phys. Rev. A **51**, 4531 (1995).

[30] E. J. Baerends, Phys. Rev. Lett. **87**, 133004 (2001).

[31] A. J. Cohen, P. Mori-Sanchez, and W. Yang, Science **321**, 792 (2008).

[32] M. Fuchs, Y.-M. Niquet, X. Gonze, and K. Burke, J. Chem. Phys. **122**, 094116 (2005).

[33] J. P. Perdew, J. Tao, V. N. Staroverov, and G. E. Scuseria, J. Chem. Phys. **120**, 6898 (2004).

[34] P. Gori-Giorgi, M. Seidl, and G. Vignale, e-print arXiv:0908.0669, to be published in Phys. Rev. Lett.