Scaling the spin densities separately in density-functional theory

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Coordinate scaling of each spin density separately is considered in spin-density-functional theory. A virial theorem relates the spin-scaled correlation energy to the spin-scaled correlation potentials. An adiabatic connection formula expresses energies at different spin interaction strengths in terms of spin scaling. Several popular approximate functionals are evaluated on the spin-scaled densities of atoms and of the uniform electron gas. The differences between this and uniform scaling are discussed.

I. INTRODUCTION

Density-functional theory combines accuracy and celerity in a computational scheme which has long been used by solid state physicists and has become popular in quantum chemistry [1]. The Hohenberg-Kohn theorem [2] demonstrates that the electron density uniquely characterizes a ground-state electronic structure problem so that the total energy is a functional of the density. This idea suggests the computationally expedient Kohn-Sham scheme [3] where only one part of the total energy functional must be approximated. This is the exchange-correlation energy, E_{XC}, and the calculational accuracy of density-functional is limited by the accuracy of approximations to E_{XC}; therefore, improvements in this functional are of great importance.

Exact constraints limit the possible forms of approximations to E_{XC} and provide guidance for the construction of approximations [4]. For total electron density functionals, Levy and Perdew [5] discovered a set of important scaling and integral requirements that the exact functional must satisfy. They introduced the concept of uniform coordinate density scaling. This scaling takes a density $n(\mathbf{r})$ into

$$n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r}), \quad 0 \leq \gamma < \infty, \quad (1)$$

and is a natural way to explore the behavior of density functionals. Many properties of the exact functional have been found by studying its behavior under this scaling [6–8]. For example, the exchange energy changes as

$$E_X[n_\gamma] = \gamma E_X[n]. \quad (2)$$

All commonly used approximations such as the local density approximation (LDA), the generalized gradient approximation (GGA), and hybrids of GGA with exact exchange [9] satisfy this relation, some by construction. But for correlation, only inequalities can be derived,

$$E_C[n_\gamma] > \gamma E_C[n] \quad (\gamma > 1), \quad (3)$$

which some approximations satisfy [4,10] while others do not [11]. Levy and Perdew further showed that translational invariance implies virial theorems relating potentials to energies. An example is

$$E_X[n] = -\int d^3 r\, n(\mathbf{r})\mathbf{r} \cdot \boldsymbol{\nabla} v_X[n](\mathbf{r}) \quad (4)$$

with a more complicated corresponding relation for correlation. The virials have been used to construct energy densities directly from potentials [12]. Exact statements about exact functionals are nontrivial and extremely useful in the construction and analysis of approximate functionals. Functionals that violate these exact conditions are unlikely to give reliable and physical results when applied to wide ranges of materials.

On the other hand, modern density-functional calculations do not employ *density* functionals but rather use *spin*-density functionals. The basic idea is to replace $E_{XC}[n]$ with $E_{XC}[n_\uparrow, n_\downarrow]$ so that the universal functional depends explicitly on both the up and down spin electron densities. Formal justification for this scheme was first given by von Barth and Hedin [13] and later by Rajagopal and Calloway [14] although some fundamental questions remain [15]. There are several compelling reasons for using spin-density functionals instead of total electron-density functionals. Spin-density functionals can more accurately describe systems with odd numbers of electrons [16]. They also allow the treatment of electrons in collinear magnetic fields and yield magnetic response properties [17]. Accurate calculation of these properties would be far more difficult in total density-functional theory because a local spin-density functional is a nonlocal total density functional. One cannot exaggerate how useful spin-density-functional theory has been in accurately and efficiently calculating physical properties.

To help develop improved spin-density functionals, it would be of great interest to develop a formalism that probes the spin dependence of functionals and yields exact conditions about their spin-dependence. Here, we investigate whether scaling techniques developed for total density functionals can be generalized to spin-density-functional theory.

Towards this end, we generalize uniform coordinate scaling of the density, Eq. (1), to separate scaling of spin densities:

$$n_{\uparrow\alpha}(\mathbf{r}) = \alpha^3 n_\uparrow(\alpha\mathbf{r}), \quad 0 \leq \alpha < \infty,$$
$$n_{\downarrow\beta}(\mathbf{r}) = \beta^3 n_\downarrow(\beta\mathbf{r}), \quad 0 \leq \beta < \infty. \tag{5}$$

According to this scheme, a spin-unpolarized system becomes spin-polarized for $\alpha \neq \beta$. There are many other ways we could have chosen to alter the spin densities. For example, we could require that the total density remain constant while the polarization changes. However, such a transformation would require introduction of ensembles because fractions of electrons would be changing spin. The present scheme is simply the logical extension of coordinate scaling to separate spin densities.

A principal result of this work is that, under such a transformation, a spin-dependent virial theorem holds true. Previous work towards combining spin-density-functional theory and the virial relationship was done by Nagy [38]. She stressed that the spin virial theorem is a new quantum mechanical relationship and can be used to analyze existing spin-dependent functionals. Here, we will consider a spin virial theorem within the context of spin scaling. This theorem can be used to carefully check the convergence of spin-density-functional calculations. It also provides a method for calculating the exact dependence of the correlation energy on spin density for model systems for which accurate Kohn-Sham potentials have been found. Finally, it can be integrated over the scale factor α to give a new formal expression for the functional E_{XC}.

Considerable progress has been made in density-functional theory by writing E_{XC} as an integral over a coupling constant λ in what is called the adiabatic connection relationship [18,19]. For example, the success of hybrid functionals such as B3LYP [9,20] can be understood in terms of this adiabatic connection [21,22]. The adiabatic connection is simply related to uniform coordinate scaling [23,24]. By analogy, we relate spin scaling to a spin-coupling constant integration, and we define a suitable generalization for this definition with a coupling constant for each spin density.

We illustrate our formal results with several cases. For the uniform electron gas, we can perform this scaling essentially exactly. We show how this transformation relates energies to changes in spin polarization. In this case, considerable care must be taken to deal with the extended nature of the system. We also show the results of spin-scaling densities of small atoms using presently popular approximations. We close with a discussion of the fundamental difficulty underlying this spin-scaling approach.

Throughout, we use atomic units ($e^2 = \hbar = m_e = 1$) so that all energies are in Hartrees and all lengths are in Bohr radii. We demonstrate all scaling relationships by scaling the up spin densities. Results for scaling the down spin are obtained in a similar fashion. Just change the spin label.

II. SEPARATE SPIN-SCALING THEORY

The first interesting property of the spin-scaling transformation, Eq. (5), is that it conserves the total number of elec-

trons globally even though the scaled spin density might tend towards zero at any point. As α diminishes, the two spin densities occupy the same coordinate space, but on two very distinct length scales. Even when $\alpha \to 0$, the up electrons do not vanish, but are merely spread over a very large volume. The scaled density presumably then has a vanishingly small contribution to the correlation energy. For finite systems, we can consider this limit as the effective removal of one spin density to infinitely far way. We will discuss what this means for extended systems later when we treat the uniform gas.

Another interesting property of the spin-scaling transformation is that a scaling of one spin density can always be written as a total density scaling plus an inverse spin scaling of the other spin; that is,

$$E_{XC}[n_{\uparrow\alpha}, n_\downarrow] = E_{XC}[\{n_\uparrow, n_{\downarrow 1/\alpha}\}_\alpha], \tag{6}$$

where the parenthesis notation on the right indicates scaling the total density. Thus, without loss of generality, we need only scale one spin density.

To understand what happens when a single spin density is scaled, we first study exchange. Because the spin up and down Kohn-Sham orbitals are independent, the exchange energy functional can be split into two parts, one for each spin [25]. The scaling relationships for total density-functional theory generalize for each term independently. For an up spin scaling, we find

$$E_X[n_{\uparrow\alpha}, n_\downarrow] = \frac{1}{2} E_X[2n_{\uparrow\alpha}] + \frac{1}{2} E_X[2n_\downarrow] = \frac{\alpha}{2} E_X[2n_\uparrow]$$
$$+ \frac{1}{2} E_X[2n_\downarrow]. \tag{7}$$

When $\alpha \to 0$, we are left with only the down contribution to exchange. Separate spin scaling allows us to extract the contribution from each spin density separately, e.g., $dE_X[n_{\uparrow\alpha}, n_\downarrow]/d\alpha$ at $\alpha = 1$ is the contribution to the exchange energy from the up density. A plot of $E_X[n_{\uparrow\alpha}, n_\downarrow]$ versus α between 0 and 1 yields a straight line and is twice as negative at 1 as at 0.

Separate spin scaling of the correlation energy is more complicated. Unlike $E_X[n_\uparrow, n_\downarrow]$, $E_C[n_\uparrow, n_\downarrow]$ cannot trivially be split into up and down parts. The Levy method of scaling the exact ground-state wave function does not yield an inequality such as Eq. (3) because the spin-scaled wave function is not a ground state of another Coulomb-interacting Hamiltonian. Nor does it yield an equality as in the spin-scaled exchange case, Eq. (7), because the many-body wave function is not simply the product of two single spin wave functions. In both cases, the two spins are coupled by a term $1/|\mathbf{r} - \alpha\mathbf{r}'|$.

To obtain an exact spin-scaling relationship for E_{XC}, we take a different route. Consider a change in the energy due a small change in the up-spin density:

$$\delta E_{XC} = E_{XC}[n_\uparrow + \delta n_\uparrow, n_\downarrow] - E_{XC}[n_\uparrow, n_\downarrow]. \tag{8}$$

Use $v_{XC\uparrow}(\mathbf{r}) = \delta E_{XC}/\delta n_\uparrow(\mathbf{r})$ to rewrite δE_{XC} as

$$\delta E_{XC} = \int d^3r \, \delta n_\uparrow(\mathbf{r}) v_{XC\uparrow}[n_\uparrow, n_\downarrow](\mathbf{r}) \qquad (9)$$

to first order in $\delta n_\uparrow$. Now, consider this change as coming from the following scaling of the density, $n_{\uparrow\alpha}(\mathbf{r}) = \alpha^3 n_\uparrow(\alpha\mathbf{r})$, where α is arbitrarily close to one. The change in the density is related to the derivative of this scaled density:

$$\left.\frac{dn_{\uparrow\alpha}(\mathbf{r})}{d\alpha}\right|_{\alpha=1} = 3n_\uparrow(\mathbf{r}) + \mathbf{r}\cdot\nabla n_\uparrow(\mathbf{r}). \qquad (10)$$

Use Eqs. (9) and (10), and integrate by parts to find

$$\left.\frac{dE_{XC}[n_{\uparrow\alpha}, n_\downarrow]}{d\alpha}\right|_{\alpha=1} = -\int d^3r \, n_\uparrow(\mathbf{r}) \mathbf{r}\cdot\nabla v_{XC\uparrow}[n_\uparrow, n_\downarrow](\mathbf{r}). \qquad (11)$$

Equation (11) is an exact result showing how $dE_{XC}/d\alpha|_{\alpha=1}$ can be extracted from the spin densities and potentials. For an initially unpolarized system, $n_\uparrow = n_\downarrow = n/2$, and $v_{XC\uparrow} = v_{XC\downarrow} = v_{XC}$. Thus the right-hand side of Eq. (11) becomes half the usual virial of the exchange-correlation potential. This virial is equal to $dE_{XC}[n_\alpha]/d\alpha|_{\alpha=1} = E_{XC} + T_C$. T_C is the kinetic contribution to the correlation energy [5]. Thus, for spin-unpolarized systems,

$$\left.\frac{dE_C[n_{\uparrow\alpha}, n_\downarrow]}{d\alpha}\right|_{\alpha=1} = \frac{1}{2}(E_C + T_C). \qquad (12)$$

For initially polarized systems, there is no simple relation between the two types of scaling.

To generalize Eq. (11) to finite scalings, simply replace $n_\uparrow$ on both sides by $n_{\uparrow\alpha}$, yielding

$$\frac{dE_{XC}[n_{\uparrow\alpha}, n_\downarrow]}{d\alpha} = -\frac{1}{\alpha}\int d^3r \, n_{\uparrow\alpha}(r) \mathbf{r}\cdot\nabla v_{XC\uparrow}[n_{\uparrow\alpha}, n_\downarrow](\mathbf{r}). \qquad (13)$$

We can then write the original spin-density functional as a scaling integral over this derivative:

$$E_{XC}[n_\uparrow, n_\downarrow] = \lim_{\alpha\to 0} E_C[n_{\uparrow\alpha}, n_\downarrow] + \int_0^1 d\alpha \frac{dE_{XC}[n_{\uparrow\alpha}, n_\downarrow]}{d\alpha}. \qquad (14)$$

This is a new expression for the exchange-correlation energy as an integral over separately spin-scaled densities where the spin-scaled density is scaled to the low-density limit. With some physically reasonable assumptions, we expect

$$\lim_{\alpha\to 0} E_C[n_{\uparrow\alpha}, n_\downarrow] = E_C[0, n_\downarrow]. \qquad (15)$$

For example, if the antiparallel correlation hole vanishes as rapidly with scale factor as the parallel-spin correlation hole of the scaled density, this result would be true. Numerical results indicate that this is the case for the approximate functionals used in this paper. Nevertheless, we have not proven Eq. (15) here.

A symmetric formula can be written down by scaling the up and down spins separately and averaging:

$$E_{XC}[n_\uparrow, n_\downarrow] = \frac{1}{2}\lim_{\alpha\to 0}(E_{XC}[n_{\uparrow\alpha}, n_\downarrow] + E_{XC}[n_\uparrow, n_{\downarrow\alpha}])$$

$$+ \frac{1}{2}\int_0^1 d\alpha \int d^3r \, n_{\uparrow\alpha}(\mathbf{r}) \mathbf{r}\cdot\nabla v_{XC\uparrow}[n_{\uparrow\alpha}, n_\downarrow](\mathbf{r})$$

$$+ \frac{1}{2}\int_0^1 d\beta \int d^3r \, n_{\downarrow\beta}(\mathbf{r}) \mathbf{r}\cdot\nabla v_{XC\downarrow}[n_\uparrow, n_{\downarrow\beta}](\mathbf{r}). \qquad (16)$$

This result is the spin-density functional generalization of spin-decomposition, coordinate scaling, and the virial theorem. Each of these ideas yields separate results for pure exchange or uniform coordinate scaling, but all are combined here. Notice that the potentials depend on both spins, one scaled and the other unscaled. This reflects the difficulty in separating up and down spin correlations.

The proof of Eq. (16) is true for exchange-correlation, but in taking the weakly correlated limit, the result also holds true for exchange. In the exchange case, Eq. (16) reduces to Eq. (7) with equal contributions from the limit terms and the virial contributions. To obtain this result, recall how E_X scales, Eq. (2). Since the energy contribution from each spin is separate and since the scaling law is linear, the limits in the first two terms of Eq. (16) are doable without any extra physical assumptions. The virial terms are a bit more difficult to handle as the exchange potentials change under scaling. In the end, the first two terms contribute half the exchange energy while the virial terms contribute the other half.

III. UNIFORM GAS

To illustrate the effect of spin scaling, we examine the uniform electron gas, a system for which we have essentially exact results. Great care must be taken to define quantities during separate spin scaling of extended systems. Begin with a spin-unpolarized uniform electron gas of density n and Wigner-Seitz radius $r_s = (3/4\pi n)^{1/3}$. When one spin density is scaled, the system becomes spin-polarized, and relative spin polarization is measured by

$$\zeta = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}. \qquad (17)$$

We assume that for a spin-polarized uniform system, the exchange-correlation energy per electron, $\epsilon_{XC}^{\text{unif}}(r_s, \zeta)$, is known exactly. We use the correlation energy parametrization of Perdew and Wang [10] to make our figures.

To perform separate spin scaling of this system, we focus on a region deep in the interior of any finite but large sample. A simple example is a jellium sphere of radius $R \gg r_s$. The correlation energy density deep in the interior will tend to that of the truly translationally invariant uniform gas as $R \to \infty$. At $\alpha = 1$, we have an unpolarized system with $n_\uparrow$
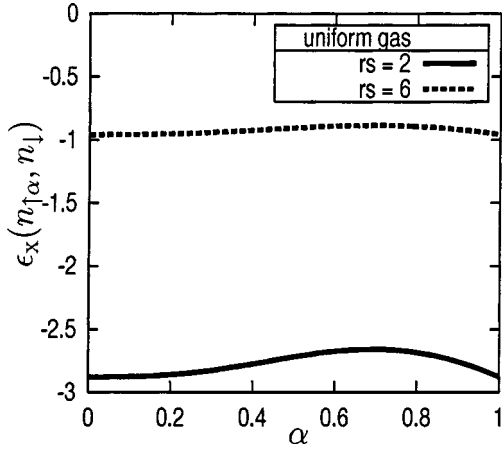
FIG. 1. Spin scaling of a uniform gas: exchange energy per particle Eq. (22), $\epsilon_X(n_{\uparrow\alpha},n_\downarrow)$, at $r_s=2$ (dotted line) and 6 (solid line). The spin-scaled exchange energy per particle is different than what one might naively expect from Eq. (7). This subtlety is discussed in Sec. IV.

$=n_\downarrow=n/2$. The up-spin scaling, $n_\uparrow=\alpha^3 n/2$, changes both the total density and the spin-polarization. Deep in the interior

$$r_s(\alpha)=r_s\left(\frac{2}{1+\alpha^3}\right)^{1/3}, \qquad (18)$$

where r_s is the Seitz radius of the original unpolarized gas, and

$$\zeta(\alpha)=\frac{\alpha^3-1}{\alpha^3+1}. \qquad (19)$$

The energy density here is then

$$e_{XC}(\alpha)=e_{XC}^{\text{unif}}(n_{\uparrow\alpha},n_\downarrow)=e_{XC}^{\text{unif}}[r_s(\alpha),\zeta(\alpha)], \qquad (20)$$

and the energy per particle is

$$\epsilon_{XC}(\alpha)=e_{XC}(\alpha)/n(\alpha), \qquad (21)$$

where $n(\alpha)$ is the interior density.

To illustrate the effects of this spin scaling, consider the simple exchange case. Deep in the interior, we have a uniform gas of density $n_{\uparrow\alpha}$ and $n_\downarrow$, and the energy densities of these two are given by Eq. (7), since the integrals provide simple volume factors. The Slater factor of $n^{4/3}$ in the exchange density of the uniform gas produces a factor of $(1+\alpha^4)$. When transforming to the energy per electron, there is another factor of $(1+\alpha^3)$ due to the density out front. Thus the exchange energy per electron is

$$\epsilon_X(\alpha)=\left(\frac{1+\alpha^4}{1+\alpha^3}\right)\epsilon_X^{unpol.}(n). \qquad (22)$$

This variation is shown in Fig. 1. This result may appear to disagree with Eq. (7), but it is valid deep in the interior only. To recover the total exchange energy, one must include those electrons in a shell between R and R/α with the full polar-
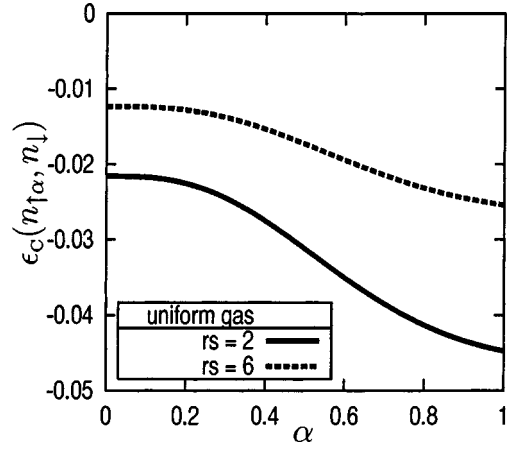

FIG. 2. Spin scaling of a uniform gas: correlation energy per particle, $\epsilon_C(n_{\uparrow\alpha},n_\downarrow)$, at $r_s=2$ (dotted line) and 6 (solid line). The energy per particle is different than what one might naively expect from Eq. (7). Section IV discusses this subtlety in detail.

ized uniform density $\alpha^3 n/2$. The exchange energy integral includes this contribution, and then agrees with Eq. (7).

Near $\alpha=1$, Eq. (22) yields $(1+\alpha)\epsilon_X^{unpol.}/2$, in agreement with a naive application of Eq. (7). This is because, in the construction of the energy from the energy per electron, the factor of the density accounts for changes in the number electrons to first order. So the derivative at $\alpha=1$ remains a good measure of the contribution to the total exchange energy from one spin density. On the other hand, as $\alpha\to 0$, the exchange energy per electron in the interior returns to that of the original unpolarized case. This reflects the fact that exchange applies to each spin separately, so that the exchange per electron of the down-spin density is independent of the presence of the up-spin density.

Figure 2 shows the uniform electron gas correlation energy per particle scaled from unpolarized ($\alpha=1$) to fully polarized limits ($\alpha=0$). Again, the curves become flat as $\alpha\to 0$, because for small α, there is very little contribution from the up-spins. Now, however, there is a dramatic reduction from $\alpha=1$ to $\alpha=0$ because of the difference in correlation between unpolarized and fully polarized gases. Note that the correlation changes tend to cancel the exchange variations.

IV. FINITE SYSTEMS

Next, we examine the behavior of finite systems under separate-spin scaling. We choose the He and Li atoms to demonstrate the effects on the simplest nontrivial unpolarized and spin-polarized cases. For each system, we solve the Kohn-Sham equations using a specific density-functional approximation. The resulting self-consistent densities are then spin scaled and the approximate energies evaluated on the scaled densities using that same functional. Since these are approximate functionals, neither the densities nor the energies are exact. We are unaware of any system, aside from the uniform gas, for which exact spin-scaled plots are easily obtainable. For now, we must compare plots generated from approximate functionals. Even the simple atomic calcula-
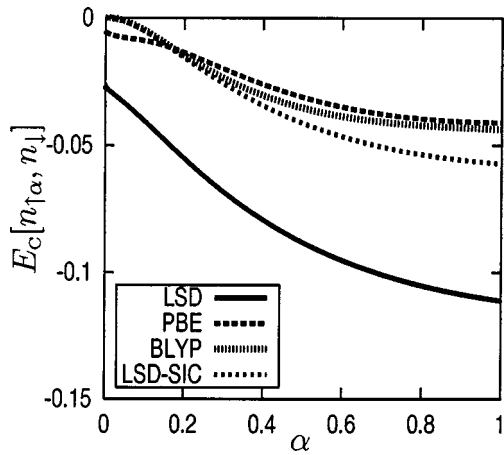
FIG. 3. Spin scaling of the He atom density using various approximate functionals for E_C: local spin-density approximation (solid line), generalized gradient approximation (PBE, dashed line), BLYP (bars), and self-interaction corrected LSD (short dashes).

FIG. 4. Up-spin scaling of the Li atom density using various approximate functionals for E_C: local spin-density approximation (solid line), generalized gradient approximation (PBE, dashed line), and BLYP (bars).

tions presented here were rather demanding since, especially for very small spin-scaling parameters, integrals containing densities on two extremely distinct length scales are needed.

The He atom (Fig. 3) is spin unpolarized at $\alpha = 1$. Scaling either spin density gives the same results. The local spin-density (LSD) curve gives far too much correlation and does not vanish as $\alpha \rightarrow 0$. In the fully scaled limit, we expect, as we have argued in Sec. II, that the correlation energy should vanish. This is because the two electrons are now on very different length scales and so should not interact with each other. The residual value at $\alpha \rightarrow 0$ reflects the self-interaction error in LSD for the remaining (unscaled) one-electron density. The Perdew-Burke-Ernzerhof GGA (PBE) curve is on the right scale but also has a residual self-interaction error as $\alpha \rightarrow 0$. The Becker-Lee-Yang-Parr GGA (BLYP) functional [11,26] is popular in quantum chemistry and gets both limits correct. However, the functional's lack of self-interaction error is because the correlation energy vanishes for *any* fully polarized system. This vanishing is incorrect for any atom other than H or He. Finally, the self-interaction corrected local spin-density (LSD-SIC) curve [27] is probably the most accurate in shape (if not quantitatively) since this functional handles the self-interaction error appropriately. We further observe that the curves appear quite different from those of the uniform gas. The atomic curves are much flatter near $\alpha \rightarrow 1$ and have appreciable slope near $\alpha \rightarrow 0$. This is because

these energies are integrated over the entire system, including the contribution from the entire spin-scaled density, whereas the energy densities in the uniform gas case were only those in the interior.

Quantitative results are listed in Table I. The exact He values, including the derivative at $\alpha = 1$, using Eq. (12), were taken from Refs. [28,29]. Note that PBE yields the most accurate value for this derivative. The BLYP correlation energy is too flat as a function of the scale parameter. BLYP produces too small a value for T_C leading to a lack of cancellation with E_C and a subsequent overestimate of the derivative at $\alpha = 1$. LSD-SIC has a similar problem. The LSD value, while far too large, is about 8% of the LSD correlation energy, close to the same fraction for PBE, and not far from exact. However, the important point here is that results from separate spin scaling are a new tool for examining the accuracy of the treatment of spin dependence in approximate spin-density functionals.

TABLE I. He atom energies, both exactly and within several approximations. All energies in Hartrees; all functionals evaluated on self-consistent densities.

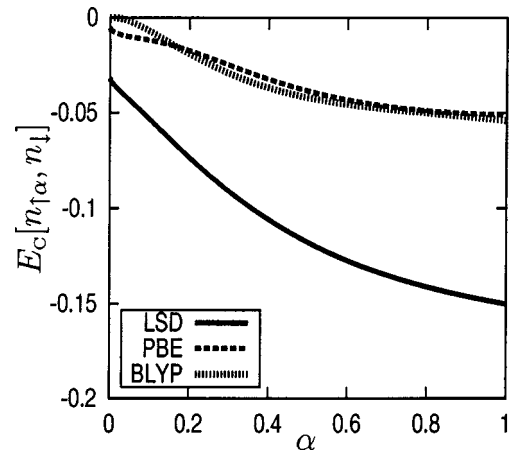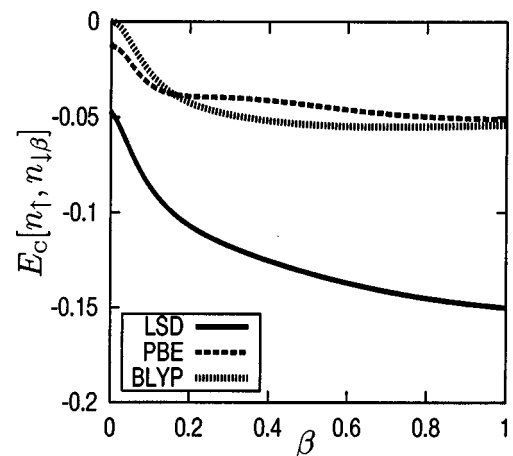| Approximation	E_X	E_C	$E_C[n_\uparrow,0]$	$dE_C/d\alpha$
LSD	-0.862	-0.111	-0.027	-0.022
PBE	-1.005	-0.041	-0.005	-0.002
SIC	-1.031	-0.058	0.000	-0.011
BLYP	-1.018	-0.044	0.000	-0.005
exact	-1.026	-0.042	0.000	-0.003

FIG. 5. Down-spin scaling of the Li atom density using various approximate functionals for E_C: local spin-density approximation (solid line), generalized gradient approximation (PBE, dashed line), and BLYP (bars).

TABLE II. Li atom energies, both exactly and within several approximations. All energies are in Hartrees, all functionals are evaluated on self-consistent densities.

Approximation	E_X	E_C	$E_C[n_\uparrow,0]$	$dE_C/d\alpha$	$E_C[0,n_\downarrow]$	$dE_C/d\beta$
LSD	-1.514	-0.150	-0.047	-0.037	-0.032	-0.019
PBE	-1.751	-0.051	-0.012	-0.004	-0.005	-0.001
BLYP	-1.771	-0.054	-0.054	-0.020	0.000	-0.005
Exact	-1.781	-0.046			0.000	

The Li atom (Figs. 4 and 5) is the smallest nontrivial odd-electron atom. We choose the up-spin density to have occupation $1s2s$. As the up spin is scaled away, as in Fig. 4, we find a curve very similar to that of He, Fig. 3. The primary difference is the greater correlation energy for $\alpha=1$. On the other hand, scaling away the down-density gives a very different picture, Fig. 5. The most dramatic changes in the correlation energy now occur at small α. Near $\alpha \to 1$, the system energy is quite insensitive to spin-scaling, especially in GGA. This is exactly opposite to what we have seen for the uniform gas. It is an open question whether this would be observed with the exact functional. For up-spin scaling, we expect the correlation energy to vanish as $\alpha \to 0$. But for down-spin scaling one expects a finite correlation energy in the limit $\beta \to 0$. The two spin-up electrons remain and are still correlated. In this case, the BLYP functional errs noticeably since it predicts no correlation energy for the remaining two electrons.

Quantitative results for Li are given in Table II. The exact result for E_X is the E_X of a self-consistent OEP calculation. Using the highly accurate energy prediction from [30], we deduce the exact $E_C = E_T - E_{T,OEP}$. The other exact results are not extractable from the literature here, but could be calculated from known exact potentials and densities [31]. Even in this simple case, an SIC calculation is difficult. For the up-spin density, one would need to find the $1s$ and $2s$ orbitals for each value of α that yield the spin-scaled densities.

V. SPIN ADIABATIC CONNECTION

Here, we define an analog of the adiabatic connection within the spin-scaling formalism. Traditionally, we think of λ as a parameter in the Hamiltonian, but this way of thinking becomes prohibitively complicated in spin-density functional theory. We would have to define three coupling constants: $\lambda_\uparrow$, $\lambda_\downarrow$, and $\lambda_{\uparrow\downarrow}$. Even if we did that, it would be nontrivial to relate changes in these coupling constants to changes in the electron density. Instead, we *define* a relationship between spin-scaling and a spin-dependent *coupling parameter*. For total density scaling, the relationship between scaling and evaluating a functional at a different coupling constant is [5,23]

$$E_{XC}^\lambda[n] = \lambda^2 E_{XC}[n_{1/\lambda}]. \qquad (23)$$

The adiabatic connection formula is

$$E_{XC} = \int_0^1 d\lambda \frac{dE_{XC}^\lambda}{d\lambda} = \int_0^1 d\lambda\, U_{XC}(\lambda). \qquad (24)$$

By virtue of the Hellmann-Feynman theorem, $U_{XC}(\lambda)$ can be identified as the potential contribution to exchange-correlation at coupling constant λ. The integrand $U_{XC}(\lambda)$ can be plotted both exactly and within density-functional approximations, and its behavior lends insight into deficiencies of functionals [32]. For separate spin scaling, we apply the same ideas but now to

$$\Delta E_{XC}[n_\uparrow,n_\downarrow] = E_{XC}[n_\uparrow,n_\downarrow] - E_{XC}[0,n_\downarrow], \qquad (25)$$

the exchange-correlation energy difference between the physical system and the system with one spin density removed while keeping the remaining spin-density fixed. For polarized systems, this quantity depends on which spin density is removed. We define

$$\Delta E_{XC}^{\lambda_\uparrow} = \lambda_\uparrow^2 \Delta E_{XC}[n_{1/\lambda_\uparrow},n_\downarrow] \qquad (26)$$

and

$$\Delta U_{XC}(\lambda_\uparrow) = d\Delta E_{XC}^{\lambda_\uparrow}/d\lambda_\uparrow, \qquad (27)$$

so that

$$\Delta E_{XC} = \int_0^1 d\lambda_\uparrow \Delta U_{XC}(\lambda_\uparrow). \qquad (28)$$

This produces a spin-dependent decomposition of the exchange-correlation energy, related to separate spin scaling rather than total density scaling, with the integral now including the high-density limit. As $\lambda_\uparrow \to 0$, exchange dominates, and $U_{XC}(\lambda_\uparrow) \to U_X(\lambda_\uparrow)$ which is just $E_X[2n_\uparrow]/2$ according to the simple results for exchange in Sec. I. Furthermore, in the absence of correlation, $U_{XC}(\lambda_\uparrow)$ is independent of $\lambda_\uparrow$. This is not true if one uses a naive generalization of Eq. (23).

This spin adiabatic connection formula should prove useful for the improvement of present-day functionals in the same way that the adiabatic connection formula has been useful for improving total density functionals. For example, it might be possible to perform Görling-Levy perturbation theory [33] in this parameter ($\lambda_\uparrow$) or to extract a correlation contribution to kinetic energy [34]. We show the spin adiabatic connection for the He atom in Fig. 6. In generating each adiabatic connection plot, we now take the scaled spin density to the high density limit. The area under each curve is precisely ΔE_{XC} for a particular approximation. To get $E_{XC}[n_\uparrow,n_\downarrow]$, we must add the contribution from the unscaled spin, $E_{XC}[0,n_\downarrow]$. The spin adiabatic connection curve looks
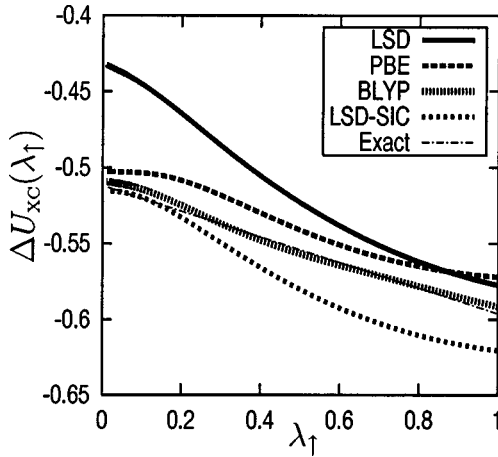
FIG. 6. Single spin adiabatic connection for a He atom: local spin-density approximation (solid line), generalized gradient approximation (PBE, dashed line), BLYP (bars), self-interaction corrected LSD (short dashes), and exact (fancy dashes).

quite similar to the regular adiabatic connection curve: for the He atom, $\Delta U_{XC}(\lambda_\uparrow)$ becomes more negative with λ everywhere and is close to linear. This suggests that the spin-correlation effects are weak for this system, just as the correlation effects are.

To better understand how popular approximations perform, we would like to compare with the exact curve. In principle, this requires a sophisticated wave-function calculation designed to reproduce the spin-scaled densities at every point in the adiabatic connection curve. Here, we use a simple interpolation that should be highly accurate. Analytic formulas give exact limits for $\Delta U_{XC}(\lambda_\uparrow)$. At the small $\lambda_\uparrow$ limit, exchange dominates, and we are left with the exchange contribution from the scaled spin to the total energy:

$$\Delta U_{XC}(\lambda_\uparrow=0)=\frac{1}{2}E_X[n]. \quad (29)$$

At the other end,

$$\Delta U_{XC}(\lambda_\uparrow=1)=2E_{XC}[n_\uparrow,n_\downarrow]-2E_{XC}[0,n_\downarrow]$$
$$-dE_{XC}[n_{\uparrow\alpha},n_\downarrow]/d\alpha|_{\alpha=1}. \quad (30)$$

For a spin-unpolarized two electron system like the He atom, this becomes

$$\Delta U_{XC}(\lambda_\uparrow=1)=E_X/2+2E_C-(E_C+T_C)/2$$

$$(2 \text{ electrons, unpolarized}). \quad (31)$$

TABLE III. Spin adiabatic connection $\Delta U_{XC}(\lambda_\uparrow)$ for a He atom, both exactly and in several approximations.

	LSD	PBE	SIC	BLYP	Exact
$\Delta U_{XC}(0)$	-0.43	-0.50	-0.53	-0.51	-0.51
$\Delta U_{XC}(1)$	-0.58	-0.57	-0.62	-0.59	-0.60
ΔE_{XC}	-0.54	-0.54	-0.57	-0.55	-0.56

For He at $\lambda_\uparrow=1$, $\Delta U_{XC}(\lambda_\uparrow)=-0.60$. To approximate the exact curve, we use a $(1,1)$ Padé approximant. The values $\Delta U_{XC}(0)$, $\Delta U_{XC}(1)$, and ΔE_{XC} fix the three unknown parameters. This Padé approximation turns out to be nearly a straight line.

Table III shows the exact limits and the limits given by several popular functionals. BLYP reproduces both limits most accurately and is mostly linear. This should come as no surprise as BLYP yields good energies and accounts for He's self-interaction error (if a bit serendipitously). However, we do not expect such good results from BLYP when using it on Li. For Li, as we have see in Sec. IV, BLYP predicts no correlation energy when only one electron is scaled away. BLYP will fail noticeably and uncontrollably in this case. The LSD functional dramatically underestimates the single spin exchange energy and, therefore, gets the small $\lambda_\uparrow$ limit quite wrong. This reflects the usual error for LDA exchange. But notice how well LSD performs at $\lambda_\uparrow=1$. The value here is only a 3% overestimate of the exact value, much better than the 9% overestimate for the exchange-correlation energy. Furthermore, the LSD derivative as $\lambda_\uparrow \to 1$ is almost exact. PBE and LDA-SIC are qualitatively similar, the greater error in LSD-SIC being due to the errors in LSD. Both show a flattening of the curve as $\lambda_\uparrow \to 0$, much more than BLYP. Our *exact* curve is too crudely constructed to indicate which behavior is more accurate.

Ideally, we would compare approximations to the exact adiabatic plot for this and other systems such as the Li atom. The plots are not easy to generate. But even so, analysis of the exact limits is sufficient to garner a deeper understanding of how functionals treat and mistreat spin densities.

VI. CONCLUSIONS

Both scaling and the adiabatic decomposition formula have proven extremely useful in studying and constructing total density functionals. We have suggested the possibility of scaling spin densities separately, derived a virial theorem, given exact results for the He atom, and pointed out the difficulties of deducing exact theorems from this decomposition. While exact calculations are difficult to perform and exact results appear difficult to prove within this approach, any results would be very useful and likely to improve spin-density-functional theory's treatment of magnetic properties.

We close with a significant challenge to developing separate spin scaling. In the total density scaling of Eq. (1), the density is both squeezed (or spread) and is also translated. The squeezing is independent of the choice of origin, but the translation is not. This origin-dependence should not affect the exchange-correlation energy because space is translationally invariant. However, when an individual spin density is scaled, the remaining spin density remains fixed in space. This means the resulting density depends on the choice of origin for the separate spin scaling. So while $E_C[n_{\uparrow\alpha},n_\downarrow]$ is a spin-density functional of $n_{\uparrow\alpha}$ and $n_\downarrow$, it is *not* a pure spin-density functional of the original spin densities because of this origin dependence. Most likely, a method of transforming away this origin dependence, as found for virial energy densities in Ref. [35], will be needed to make this spin-

scaling technique more physical and useful. For atoms, we made the obvious choice of origin at the center of the nucleus. Origin dependence will become acute in applications to molecules and even worse for solids. On the other hand, the nonuniform coordinate scaling of Görling and Levy [36] suffers from the same difficulties for nonspherical densities but has still produced useful limits for approximate density functionals [37].

However, it is important to stress that the spin virial relationship is unaffected by this challenge. For α arbitrarily close to 1, the spin-scaled energies are independent of the choice of origin, and these difficulties are irrelevant. The spin virial relationship is an exact constraint and gives us a useful measure of how the correlation energy is affected by small changes in the spin densities. It also leads to a natural decomposition of energy changes due to separate spin densities. It should be useful in determining whether calculations are self-consistent for each spin density separately. This might be useful, for example, in systems where small differences between spin densities are important to calculate properly.

[1] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).

[2] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

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

[4] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396(E) (1997).

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

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

[7] Q. Zhao, M. Levy, and R. Parr, Phys. Rev. A **47**, 918 (1993).

[8] M. Levy and A. Görling, Int. J. Quantum Chem. **56**, 385 (1995).

[9] A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).

[10] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).

[11] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[12] F. G. Cruz, K. C. Lam, and K. Burke, J. Phys. Chem. A **102**, 4911 (1998).

[13] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[14] A. K. Rajagopal and J. Calloway, Phys. Rev. B **7**, 1912 (1973).

[15] K. Capelle and G. Vignale, Phys. Rev. Lett. **86**, 5546 (2001).

[16] B. G. Johnson, P. M. W. Gill, and J. A. Pople, J. Chem. Phys. **98**, 5612 (1993).

[17] S. Matar and A. Mavromaras, J. Solid State Chem. **149**, 449 (2000).

[18] D. C. Langreth and J. P. Perdew, Solid State Commun. **17**, 1425 (1975).

[19] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[20] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

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

[22] J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).

[23] Y. A. Wang, Phys. Rev. A **56**, 1646 (1997).

[24] K. Burke, in *Electronic Density Functional Theory: Recent Progress and New Directions*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1997), p. 19.

[25] J. P. Perdew and S. Kurth, in *Density Functionals: Theory and Applications*, edited by D. Joubert (Springer, Berlin, 1998).

[26] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[27] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[28] C. J. Umrigar and X. Gonze, Phys. Rev. A **50**, 3827 (1994).

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

[30] E. Davidson, S. Hagstrom, S. Chakravorty, V. Umar, and F. Fischer, Phys. Rev. A **44**, 7071 (1991).

[31] R. Morrison and Q. Zhao, Phys. Rev. A **51**, 1980 (1995).

[32] K. Burke, J. P. Perdew, and M. Ernzerhof, in *Electronic Density Functional Theory: Recent Progress and New Directions* (Ref. [24]), p. 57.

[33] A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994).

[34] P. Süle, Chem. Phys. Lett. **259**, 69 (1996).

[35] K. Burke, F. G. Cruz, and K. C. Lam, J. Chem. Phys. **109**, 8161 (1998).

[36] A. Görling and M. Levy, Phys. Rev. A **45**, 1509 (1992).

[37] K. Burke, J. P. Perdew, and M. Levy, in *Modern Density Functional Theory: A Tool for Chemistry*, edited by J. M. Seminario and P. Politzer (Elsevier, Amsterdam, 1995).

[38] A. Nagy, Int. J. Quantum Chem. **49**, 353 (1994).