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Electronic states with fractional spins arise in systems with large static correlation (strongly correlated systems). Such fractional-spin states are shown to be ensembles of degenerate ground states with normal spins. It is proven here that the energy of the exact functional for fractional-spin states is a constant, equal to the energy of the comprising degenerate pure-spin states. Dramatic deviations from this exact constancy condition exist with all approximate functionals, leading to large static correlation errors for strongly correlated systems, such as chemical bond dissociation and band structure of Mott insulators. This is demonstrated with numerical calculations for several molecular systems. Approximating the constancy behavior for fractional spins should be a major aim in functional constructions and should open the frontier for density functional theory to describe strongly correlated systems. The key results are also shown to apply in reduced density-matrix functional theory. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2987202]

Density functional theory (DFT)[1,2] is a rigorous approach for describing the ground state of any electronic system. The success or failure of DFT is based on the quality of the density functional approximation (DFA). One of the dramatic failures[3] is in strongly correlated systems, characterized by the presence of degeneracy or near degeneracy,[4] having large static correlation. The simplest example is the dissociation of H_2 molecule[5–8] for which commonly used DFAs overestimate the energy by more than 50 kcal/mol. Closely related are the band structure of Mott insulators,[9] which are described as metallic by known DFAs, and problems in describing superconducting cuprates.[10]

The improvement in the DFA is, therefore, a major goal that critically depends on the underlying theoretical construction. One of the most useful developments is the extension of DFT to fractional charges developed by Perdew *et al.*[11] in a grand canonical ensemble, which was also established later in a pure state formulation.[12] For a system with fractional charges, the exact energy is a straight line interpolating the energies of the integer electron systems. The violation of this exact condition leads to two types of errors,[13] the delocalization error (DE) of most functionals such as local density approximation (LDA), generalized gradient approximation (GGA), and hybrids,[14–17] and the localization error of the Hartree–Fock (HF) functional. DE captures the tendency of commonly used functionals to bias toward a delocalized description of electrons with widespread implications[18,19] from molecular reactions to the band gap of solids. Addressing this error resulted in the construction of the MCY3 and rCAMB3LYP functionals,[20] which correct many of the errors of previous functionals. In particular they correctly predict the ionization energy and electron affinity from their single-electron eigenvalues and, hence, the energy gaps in molecules.[21]

In this Communication, we make an extension of DFT to fractional-spin systems and prove that the exact energy functional of a fractional-spin state is that of the comprising degenerate normal spin states. We show that states with fractional spins arise in systems with large static correlation (strongly correlated systems) and that the dramatic deviation from the proven exact condition accounts for large static correlation errors (SCEs). We also introduce a quantitative measure for SCE.

Our starting point is the exact result for an ensemble of degenerate densities derived by Yang *et al.*[12] For an N-electron system in the external potential $v(\mathbf{r})$ that has g-fold degenerate orthogonal ground state wave functions $(\Phi_i, i=1,2,\ldots,g)$ with corresponding densities $(\rho_i, i=1,2,\ldots,g)$ and ground state energy $E_v^0(N)$, the ensemble density is $\rho=\Sigma_{i=1}^g C_i\rho_i$, where $0\le C_i\le 1$ and $\Sigma_{i=1}^g C_i=1$. The exact energy functional satisfies the following equation:

$$E_v\left[\sum_{i=1}^g C_i\rho_i\right] = E_v[\rho_j] = E_v^0(N), \quad j=1\ldots g, \tag{1}$$

if $E_v^0(N)\le(E_v^0(N+1)+E_v^0(N-1))/2$. Note that in the derivation of Eq. (1) only pure states were used and the ensemble densities appear in the limit of large separation of fragments.[12]

We now examine the application of Eq. (1) to fractional-spin systems. Consider an N-electron atom or molecule that is a doublet, with total spin $S=\frac{1}{2}$, for example, the H atom with $N=1$. It has two degenerate spin states labeled with the z-component of the spin $m_s=\frac{1}{2}$ and $m_s=-\frac{1}{2}$. Now we construct $\rho_{\mathrm{fs}}(S,\gamma)$, an ensemble density with fractional spins as

$$\rho_{\mathrm{fs}}\left(\tfrac{1}{2},\gamma\right) = \left(\tfrac{1}{2}+\gamma\right)\rho\left(\tfrac{1}{2},\tfrac{1}{2}\right) + \left(\tfrac{1}{2}-\gamma\right)\rho\left(\tfrac{1}{2},-\tfrac{1}{2}\right), \tag{2}$$

where $\rho(S,m_s)$ is the ground state density with m_s and γ $(-\frac{1}{2}\le\gamma\le\frac{1}{2})$ is the net z-component of the spin in the fractional-spin state. $\rho_{\mathrm{fs}}(S,\gamma)$ represents many fractional-spin states. In particular, $\gamma=0$ represents a state that has half a spin-up electron and half a spin-down electron occupying the

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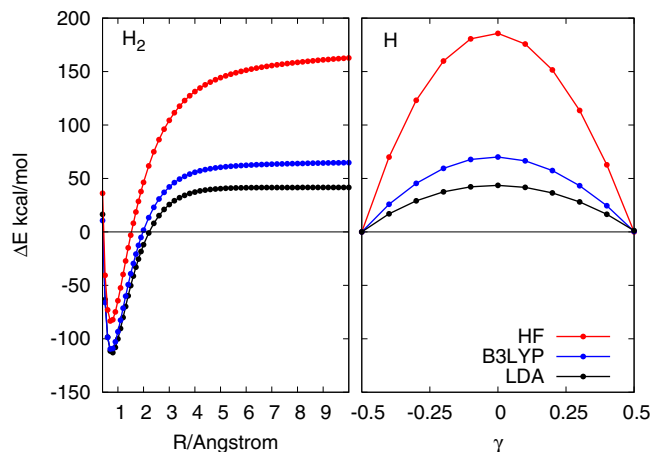[a)]Electronic mail: yang@chem.duke.edu.

FIG. 1. (Color online) Binding curve of H_2 calculated with spin-restricted KS and fractional spins of H atom calculated with spin-unrestricted KS (multiplied by 2). $\gamma=0$ is a H atom with half an α electron and half a β electron, which is the dissociation limit of H_2. All calculations are self-consistent using a cc-pVQZ basis set.

same spatial orbital, its total spin density being equal to zero everywhere. Applying Eq. (1) leads to

$$E_v\left[\rho_{\text{fs}}\left(\tfrac{1}{2},\gamma\right)\right]=E_v\left[\rho\left(\tfrac{1}{2},\tfrac{1}{2}\right)\right]=E_v\left[\rho\left(\tfrac{1}{2},-\tfrac{1}{2}\right)\right], \qquad (3)$$

which shows that for the exact density functional, all the fractional-spin densities $\rho_{\text{fs}}\left(\tfrac{1}{2},\gamma\right)$ have the same degenerate energy. This may seem to be a trivial result for the exact functional but it has very important consequences for the application of DFT. All known DFAs fail dramatically and give much too high an energy for $E_v\left[\rho_{\text{fs}}\left(\tfrac{1}{2},\gamma\right)\right]$, as illustrated in the right-hand side of Fig. 1. In the self-consistent spin-unrestricted Kohn–Sham (KS) calculations, we use the spin densities $\rho_{\text{fs}}^\sigma(S,\gamma)$ ($\sigma=\alpha,\beta$), which are represented by a non-interacting system with fractional occupation numbers,

$$\rho_{\text{fs}}^\sigma(S,\gamma)=\sum_i^{\text{HOMO}} n_i^\sigma|\phi_i^\sigma|^2, \qquad (4)$$

where only the highest occupied molecular orbital (HOMO) for each spin is fractionally occupied, with $n_{\text{HOMO}}^\alpha=\tfrac{1}{2}+\gamma$ and $n_{\text{HOMO}}^\beta=\tfrac{1}{2}-\gamma$. At $\gamma=0$, the ground state is spin unpolarized with $\rho_{\text{fs}}^\alpha\left(\tfrac{1}{2},0\right)=\rho_{\text{fs}}^\beta\left(\tfrac{1}{2},0\right)$ everywhere, and the deviation of the constancy requirement [Eq. (3)] reaches its maximum for DFAs.

In carrying out KS calculations with Eq. (4), we have used the following variational principle:

$$E_v[\rho_{\text{fs}}]=\lim_{\tilde{\rho}_{\text{fs}}} E_v[\tilde{\rho}_{\text{fs}}], \qquad (5)$$

where the domain of variation for $\tilde{\rho}_{\text{fs}}$ is all the ensemble densities constructed from Eq. (2) but with arbitrary spin densities $\rho\left(\tfrac{1}{2},\tfrac{1}{2}\right)$ and $\rho\left(\tfrac{1}{2},-\tfrac{1}{2}\right)$. We have assumed that such ensemble densities can be represented by an ensemble of noninteracting densities that come from the same potential and have the same set of orbitals. Then we can represent the ensemble with a noninteracting system with fractional occupations as in Eq. (4). Details of the proof for Eq. (5) can be found in Ref. 22.

This formalism is particularly interesting because the fractional-spin density $\rho_{\text{fs}}^\sigma\left(\tfrac{1}{2},0\right)$ describes the dissociation limit of a single chemical bond. For example, at the dissociation limit of the H_2 molecule, a singlet system ($S=0$) is obtained, which consists of two fractional-spin H atoms separated by a large distance.[23] This system can be properly described by multiconfigurational wave function methods. However in DFT, spin-restricted KS calculations, having the correct spin state ($S=0$), give much too high an energy, with DFAs. The overestimation in the energy for the dissociation of H_2 matches exactly the overestimation for the H atom with fractional-spin density $\rho_{\text{fs}}^\sigma\left(\tfrac{1}{2},0\right)$.

Figure 1 illustrates the performance of three commonly used functionals: LDA, B3LYP, and HF. The left-hand side shows the spin-restricted binding curve of the H_2 molecule from the ground state unrestricted atoms [with integer spins, i.e., one α electron and zero β electrons or vice versa, corresponding to $\rho_{\text{fs}}^\sigma\left(\tfrac{1}{2},\pm\tfrac{1}{2}\right)$] and the right-hand side shows the difference in energy of the H atom with fractional spins, $\rho_{\text{fs}}^\sigma\left(\tfrac{1}{2},\gamma\right)$, from the energy of the same ground state unrestricted atom (multiplied by 2 for direct comparison with the binding curve). The energy should be constant with the change in γ but all the energy functionals have a very large error, ranging from 30 to 170 kcal/mol for the midpoint, $\gamma=0$. HF has the largest error and LDA has the smallest error, but both functionals overestimate the energy for fractional-spin states. B3LYP, as expected, has a behavior in between LDA and HF. Other functionals also suffer from large errors,[22] with GGA functionals performing roughly the same as LDA and other hybrid functionals somewhere in between LDA and HF (this also includes Coulomb attenuated functionals with reduced DE). This suggests that the calculation of strongly correlated systems, where this error is important, will qualitatively fail if any of the above functionals are used. There are many attempts in literature to circumvent this error, for example, breaking the spin symmetry, which gives reasonable energies but wrong spin densities.

Our discussion for the single bond dissociation can be extended to multiple bond dissociation. Using the notation in Eq. (2), for a system with total spin S, we can construct the fractional-spin density $\rho_{\text{fs}}(S,\gamma)$ from the two degenerate spin states with maximum $|m_s|=S$,

$$\rho_{\text{fs}}(S,\gamma)=\left(\frac{1}{2}+\frac{\gamma}{2S}\right)\rho(S,S)+\left(\frac{1}{2}-\frac{\gamma}{2S}\right)\rho(S,-S), \qquad (6)$$

where $-S\le\gamma\le S$. Applying Eq. (1) leads to

$$E_v[\rho_{\text{fs}}(S,\gamma)]=E_v[\rho(S,S)]=E_v[\rho(S,-S)]. \qquad (7)$$

As in the case of $S=\tfrac{1}{2}$ where the fractional-spin state $\rho_{\text{fs}}\left(\tfrac{1}{2},0\right)$ describes the dissociation limit of a single chemical bond, the fractional-spin state $\rho_{\text{fs}}(S,0)$ describes the dissociation limit of a multiple chemical bond. This is demonstrated in Fig. 2 for the dissociation of a double bond, C_2, a triple bond, N_2, and a sextuple bond, Cr_2, into two $S=1$, $S=\tfrac{3}{2}$, and $S=3$ fractional-spin atoms, respectively. For the molecules we perform spin-restricted KS calculations and show the binding curve with respect to the spin-unrestricted ground state atoms calculated with no fractional spin ($m_s=S$). On the right-
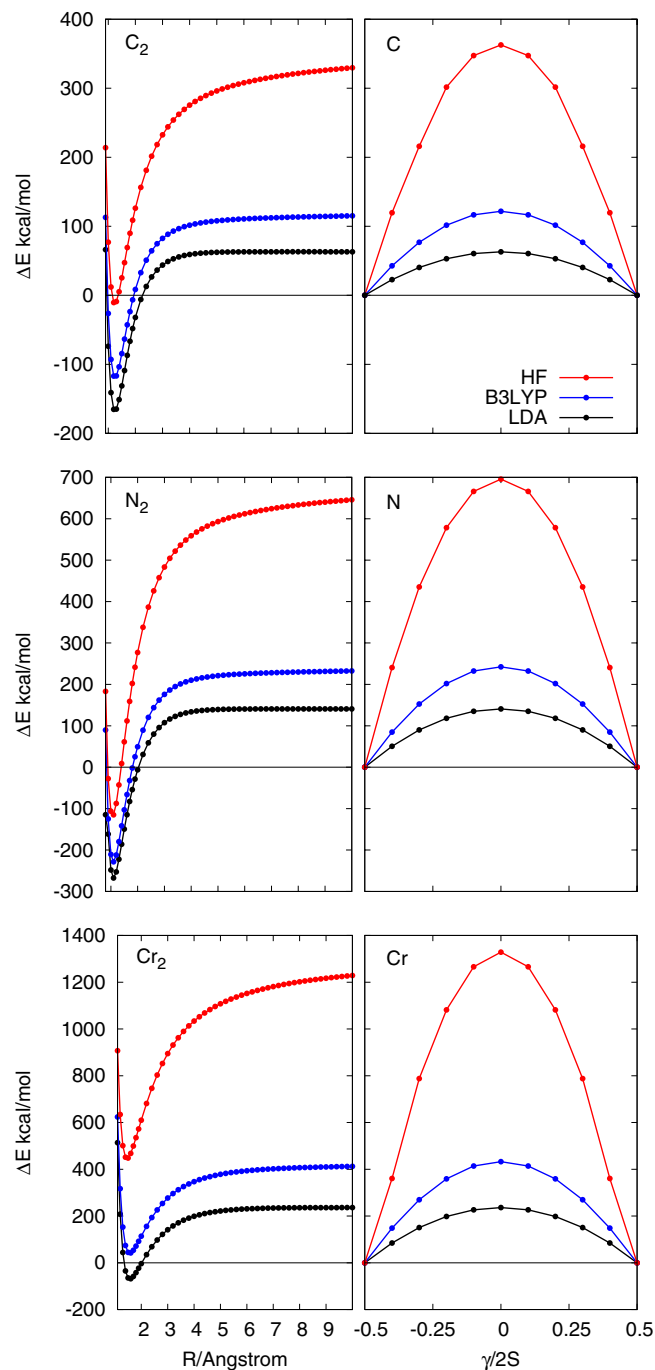
FIG. 2. (Color online) The same as in Fig. 1 but for top, C_2 (double bond), middle, N_2 (triple bond), and bottom, Cr_2 (sextuple bond).

hand side of Fig. 2 we show spin-unrestricted calculations on the atoms with fractional spins also relative to the normal ($m_s=S$) spin-unrestricted atoms. The expression for the density, $\rho_{fs}(S,\gamma)$, is exactly the same as Eq. (4) but with fractional occupation, $n^\alpha_{HOMO}=\frac{1}{2}+\frac{\gamma}{2S}$ and $n^\beta_{HOMO}=\frac{1}{2}-\frac{\gamma}{2S}$, for the top $2S$ multiple HOMOs [e.g., the N atom, $\rho_{fs}\left(\frac{3}{2},0\right)$ has half an α electron and half a β electron in the top three $2p$ orbitals]. To compare to molecular dissociation the two densities mixed in Eq. (7) must have the same symmetry. All DFAs violate the constancy condition [Eq. (7)]. The overestimation in the energy for molecular dissociation matches exactly the overestimation for the dissociating atoms with fractional-spin density $\rho^\sigma_{fs}(S,0)$.

The error in the energy for molecular dissociation is normally attributed to the lack of static correlation, which is remarkably captured by the violation of the constancy condition for the fractional-spin states of the dissociating atoms. It is thus natural to define a quantitative measure of the SCE for approximate density functionals as

$$SCE = E_v[\rho_{fs}(S,0)] - E_v[\rho(S,S)]. \tag{8}$$

Static correlation can be described with the use of a few Slater determinants for small molecules. However, for large and bulk systems, this becomes impractical. It is now clear that SCE is an inconsistency in the commonly used DFAs.

The errors are massive and increase with the number of bonds. It is also very significant to see that the error at the dissociation limit dominates at finite bond lengths and can even determine the behavior close to the bonding region, making the limiting behavior analysis of $E[\rho_{fs}(S,0)]$ broadly relevant. For Cr_2, SCE make HF and B3LYP fail to describe bound molecules and LDA has a very small range of bonding. Note that these cases are not only challenges for DFT but also for single reference wave function methods. The cases considered here are homonuclear diatomics but the same arguments apply to the dissociation of heteronuclear diatomics and more complicated molecules. The above discussion is extremely parallel to the case of fractional charges,[11,12] where the infinite dissociation limit is extremely important to understand the DE that is actually seen in real systems.

For the fractional-spin states $\rho_{fs}(S,\gamma)$, we have only explored the consequence of the two-state ensemble, which leads to an understanding of static correlation. There are, however, more general fractional-spin states,

$$\rho_{fs}(S,\{C_{m_s}\}) = \sum_{m_s=-S}^{S} C_{m_s}\rho(S,m_s), \tag{9}$$

where $0 \le C_{m_s} \le 1$ and $\Sigma^S_{m_s=-S}C_{m_s}=1$. Based on Eq. (1) the fractional-spin constancy relation is

$$E_v[\rho_{fs}(S,\{C_{m_s}\})] = E_v[\rho(S,m_s)], \tag{10}$$

which will also have important consequence for molecules and solids. What may hinder the exploration of Eq. (9) is the difficulty with which DFT deals with $\rho(S,m_s)$ for $|m_s|<S$. Usually only the state $\rho(S,S)$ is calculated, as it can be constructed easily from a KS determinant. It is difficult, if not impossible, in general, to construct a KS determinant for other states $\rho(S,m_s)$ with $|m_s|<S$.

It is also possible to have fractional-spin states arising from an ensemble of states, which are degenerate because of other symmetries (e.g., spatial),

$$\rho_{fs}(S,\{C_{i,m_s}\}) = \sum_{i=1}^{g}\sum_{m_s=-S}^{S} C_{i,m_s}\rho_i(S,m_s), \tag{11}$$

for a g-fold degenerate system. The exact energy functional gives constant energy for all $\{C_{i,m_s}\}$. For example, a spherical atom density given by $\Sigma^L_{i=-L}1/(2L+1)\rho_i(S,S)$ has α fractional-spin occupation of the spatially degenerate states. If we consider the case of the B atom, which is threefold
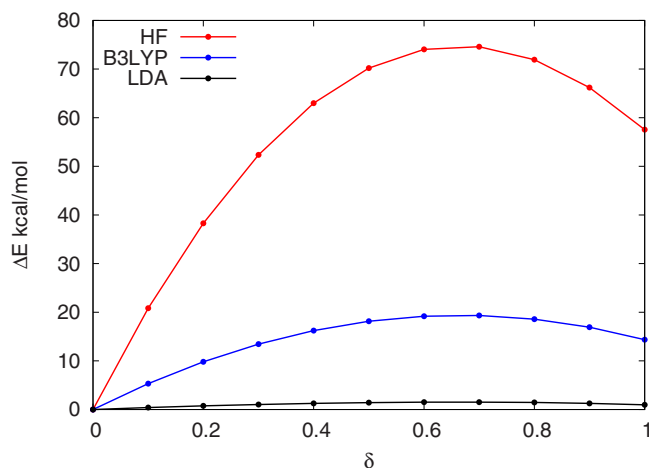
FIG. 3. (Color online) B atom with fractional α spins $\delta = \frac{2}{3}$ corresponds to the spherical B atom.

degenerate, the lowest energy state predicted by DFAs is given by a nonspherical density. We now examine the energy of $\rho_{fs}(S,\{C_\delta\}) = \delta/2[\rho_1(S,S) + \rho_2(S,S)] + (1-\delta)\rho_3(S,S)$ such that at $\rho_{fs}(S,\{C_0\})$ corresponds to the normal ground state nonspherical atom and $\rho_{fs}(S,\{C_{2/3}\})$ corresponds to the spherical B atom. The energy of the fractional-spin states relative to the ground state of the B atom is plotted in Fig. 3, and shows again the violation of the constancy relation for DFAs. The error of HF is similar to the case for $\rho_{fs}(S,\gamma)$ but with pure DFT the error is much smaller (only $\approx 1-2$ kcal/mol for LDA).

Equation (1) is also valid[12] for energy functionals of the first-order reduced density matrix (e.g., Ref. 5); therefore, our discussion and main results [Eqs. (7) and (10)] hold in reduced density-matrix functional theory.

In summary this Communication highlights a basic error of DFAs for degeneracy problems, which are also applicable to the case of near degeneracy. These situations can be described within DFT by fractional-spin states that are ensembles of degenerate pure-spin states. This is a simpler concept than the multiconfiguration view, which places any solution outside the realm of normal KS DFT. It is now clear that the error is solely in the exchange-correlation functional. The exact constancy relation for the energy derived from this Communication quantifies the SCE of functionals and shows the basic error that needs to be addressed for the proper description of strongly correlated systems, such as magnetic molecules and solids, band structures of superconductors and Mott insulators. Satisfying a similar straight line condition for fractional charges has been very important in addressing the DE of functionals,[20] and we expect the exact condition of constancy of $E[\rho_{fs}]$ to offer a new challenge for $E_{xc}[\rho]$ and open new frontiers of DFT for strongly correlated systems.

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