Discontinuous Nature of the Exchange-Correlation Functional in Strongly Correlated Systems

Paula Mori-Sánchez, Aron J. Cohen, and Weitao Yang

Department of Chemistry, Duke University, Durham, North Carolina 27708, USA

Standard approximations for the exchange-correlation functional have been found to give big errors for the linearity condition of fractional charges, leading to delocalization error, and the constancy condition of fractional spins, leading to static correlation error. These two conditions are now unified and extended to states with both fractional charge and fractional spin to give a much more stringent condition: the exact energy functional is a plane, linear along the fractional charge coordinate and constant along the fractional spin coordinate with a line of discontinuity at the integer. Violation of this condition underlies the failure of all known approximate functionals to describe the gaps in strongly correlated systems. It is shown that explicitly discontinuous functionals of the density or orbitals that go beyond these currently used smooth approximations is the key for the application of density functional theory to strongly correlated systems.

The great success of density functional theory (DFT) [1] is clouded by spectacular failures [2] that can manifest themselves in a variety of problems, from molecular bond stretching to magnetism and the band gap of materials. Some of these failures in practical calculations are even considered a breakdown of the theory itself, as exemplified by the concept of strong-correlation, which refers to the supposed qualitative collapse of the single particle picture and hence DFT. For example, the treatment of Mott insulators, such as transition-metal oxides, has demanded methods beyond the realm of DFT [3,4]. In this Letter, we reveal an important condition of the exact energy which is missing in currently used approximations that is vital for the application of DFT to strongly correlated systems, in particular, their band gaps.

The fundamental gap of a N-electron system with external potential $v(\mathbf{r})$ is given by the difference of the ionization energy, I, and electron affinity, A,

$$E_{\text{gap}}^{\text{integer}} = \{E_v(N-1) - E_v(N)\} - \{E_v(N) - E_v(N+1)\} \tag{1}$$

or, due to the straightline behavior of the exact functional [5], by a difference of derivatives at N

$$E_{\text{gap}}^{\text{deriv}} = \left.\frac{\partial E_v}{\partial N}\right|_+ - \left.\frac{\partial E_v}{\partial N}\right|_-. \tag{2}$$

Consider a prototypical example of a strongly correlated system, a stretched H_2 molecule. At its dissociation limit, there are two fractional spin hydrogen atoms each with half a spin up (α) electron and half a spin down (β) electron, $H[\frac{1}{2}, \frac{1}{2}]$. This is a one-electron system that is degenerate in energy [6] with the normal hydrogen atom with one α electron, $H[1,0]$, and therefore has the same $E_{\text{gap}}^{\text{integer}}(= 0.472E_h)$. However, $H[\frac{1}{2}, \frac{1}{2}]$ has identical α and β orbitals by symmetry, and hence all available functionals give $E_{\text{gap}}^{\text{deriv}} = 0$. Where is the gap? What is missing from

all available exchange-correlation functionals? In other words, what is the nature of the exact derivative discontinuity [7,8]?

In this Letter, we extend fractional charges and fractional spins to give a unified condition for the exact functional. This clarifies the behavior of the energy as the number of electrons passes through an integer and highlights an important discontinuity in the energy expression. An illustrative functional for the hydrogen atom is developed which clearly shows this discontinuous behavior and moreover how it manifests itself, with a discontinuous derivative.

We follow the methodology of Yang, Zhang and Ayers [9] and examine systems at their dissociation limit. First, we start with the simplest case. Consider the hydrogen molecular ion H_2^+, which has one electron, one proton at site R_1, and another proton infinitely far away at R_2. The one electron can be at either of the two sites, and it can be spin up ($m_s = \frac{1}{2}$) or spin down ($m_s = -\frac{1}{2}$). Thus, there are four degenerate electronic ground states, $\Psi_{m_s,l} = \Phi_{m_s}(R_l)$, where $\Phi_{m_s}(R_l)$ is the ground state of a hydrogen atom located at position R_l with the spin projection m_s and energy $E(H)$. Consider the equally weighted wave function

$$\bar{\Psi} = \sum_{m_s,l} \Psi_{m_s,l}/\sqrt{4}. \tag{3}$$

The electron density of this wave function is

$$\bar{\rho} = \sum_{l=1}^{2} \rho^l = \sum_{l=1}^{2} \sum_{m_s} \frac{1}{4} \rho_{m_s,l}, \tag{4}$$

where $\rho_{m_s,l}$ is the density of $\Psi_{m_s,l}$. The density $\bar{\rho}$ of Eq. (4) is simply the sum of two identical densities $\rho^l = \frac{1}{4} \times (\rho_{(1/2),l} + \rho_{-(1/2),l})$, $l = 1, 2$, separated from each other by an infinite distance. The energy of $\bar{\Psi}$ and $\bar{\rho}$ is $E(H)$. While the density $\bar{\rho}$ is v-representable, ρ^l is non-v-representable [10,11] and is the density of an isolated

subsystem inside the supermolecule described by the wave function of Eq. (3).

Now we consider the behavior of the exact energy functional, $E_v[\rho]$, for this density. $E_v[\rho]$ possesses the following properties: (A) $E_v[\rho]$ is exact for any (pure-state) v-representable density. Hence, for the total density in Eq. (4), we have $E_v[\bar{\rho}] = E(H)$. (B) $E_v[\rho]$ is size extensive. Therefore, $E_v[\bar{\rho}] = \sum_{l=1}^{2} E_v[\rho^l]$. (C) $E_v[\rho]$ is translationally invariant. Therefore, $E_v[\rho^1] = E_v[\rho^2]$. From (A), (B), and (C), it follows that

$$E_v[\rho^1] = \frac{1}{2} E(H). \qquad (5)$$

Thus, the exact energy for the non-v-representable density $\rho^1 = \frac{1}{4}(\rho_{(1/2),1} + \rho_{-(1/2),1})$ is $\frac{1}{2} E(H)$. This density has a fractional charge of $\frac{1}{2}$ and fractional spins of $\frac{1}{4}$ up spin and $\frac{1}{4}$ down spin. Its energy is $\frac{1}{2} E(H)$, the average of hydrogen atoms with 1 and 0 electrons, independent of the fractional spins. Thus, in this specific case, we obtain a condition for the exact functional for a density with fractional charge and spins, which extends the previous results of fractional charge [5] and fractional spin [6].

We now generalize our result of Eq. (5) to include general fractional charge and fractional spins. We also extend the discussion to general degeneracies, instead of just a degeneracy because of spin symmetry. Consider an external potential $v(\mathbf{r})$ that has two sets of degenerate grounds states: N-electron degenerate ground states with energy $E_v(N)$, wave functions and densities $(\Phi_{N,i}, \rho_{N,i}; i = 1, 2, ..., g_N)$, and $(N + 1)$-electron degenerate ground states with energy $E_v(N + 1)$, wave functions and densities $(\Phi_{N+1,j}, \rho_{N+1,j}; j = 1, 2, ..., g_{N+1})$. For the density $\rho = \frac{1}{q} \sum_{i=1}^{g_N} c_i \rho_{N,i} + \frac{1}{q} \sum_{j=1}^{g_{N+1}} d_j \rho_{N+1,j}$ where $\{c_i\}$ and $\{d_j\}$ are positive and finite integers, the exact energy functional satisfies the following equation,

$$E_v\left[\frac{1}{q} \sum_{i=1}^{g_N} c_i \rho_{N,i} + \frac{1}{q} \sum_{j=1}^{g_{N+1}} d_j \rho_{N+1,j}\right] = \frac{q - p}{q} E_v(N)$$
$$+ \frac{p}{q} E_v(N + 1), \qquad (6)$$

where $q = \sum_{i=1}^{g_N} c_i + \sum_{j=1}^{g_{N+1}} d_j$, $p = \sum_{j=1}^{g_{N+1}} d_j$, and $q - p = \sum_{i=1}^{g_N} c_i$. Equation (5) is a special case of the general result, Eq. (6), and the proof is given in [12]. Equation (6) is also valid in first-order reduced density-matrix functional theory.

We analyze the simple case of a hydrogen atom with general spin up and spin down occupations, $H[n_\alpha, n_\beta]$, to illustrate the scenario of fractional charges and fractional spins combined. This is of key importance for the consideration of strongly correlated systems and more especially the band-gap of Mott insulators in the nonmagnetic phase. We focus on the simple strongly correlated system $H[\frac{1}{2}, \frac{1}{2}]$, which can be viewed as the infinitely stretched limit of H_2 [6] or as the infinitely expanded limit of a lattice of hydrogen atoms [13] but with zero spin density everywhere. We

now address the very interesting question: Is there a gap for $H[\frac{1}{2}, \frac{1}{2}]$?

The answer to this problem in terms of the total energy can be understood from Eq. (6). Figure 1 shows the behavior of the exact energy functional for the hydrogen atom with $0 \leq n_\alpha \leq 1$, $0 \leq n_\beta \leq 1$, and $0 \leq n \leq 2$ ($n = n_\alpha + n_\beta$). The exact functional has flat plane behavior, linear along the fractional charge coordinate and constant along the fractional spin coordinate. This gives two flat planes, one for $0 \leq n \leq 1$ and other for $1 < n \leq 2$, that intersect with a discontinuity at $n = 1$. The simple fractional charge states correspond to the edge lines connecting $[0, 0]$ with $[1, 0]$ or $[0, 1]$ and then with $[1, 1]$, and the question of the gap in $H[\frac{1}{2}, \frac{1}{2}]$ is highlighted by the line connecting $[0, 0]$ with $[\frac{1}{2}, \frac{1}{2}]$ and then with $[1, 1]$. If we now analyze this problem from a total energy perspective, it is clear that the energy of $H[\frac{1}{2}, \frac{1}{2}]$ is degenerate with the normal $H[1, 0]$ atom, and also upon addition and removal of an electron (or any infinitesimal amount of an electron) the energy change is again exactly the same as the normal atom. This means that $H[\frac{1}{2}, \frac{1}{2}]$ has an energy and derivatives, $\frac{\partial E}{\partial N}|_\pm$, and therefore gap, that are exactly the same as $H[1, 0]$.

It can be seen that the simple combination of fractional charges (the 4 edge lines) and fractional spin (the line across the middle at $n = 1$) only give five lines of Fig. 1. Equation (6) greatly extends this to cover the whole plane, which is a much more stringent set of conditions, for example, the highlighted $n_\alpha = n_\beta$ line in Fig. 1, and it is this that is essential for the understanding of the gap of strongly correlated systems.

To gain more insight, examine the behavior of several approximate functionals for the energy of $H[n_\alpha, n_\beta]$ shown in Fig. 2. If we first consider the fractional charge behavior, Hartree-Fock (HF) shows the exact straightline behavior between $[0, 0]$ and $[1, 0]$ as HF is exact for one orbital systems. However, it exhibits an incorrect gap for $H[1, 0]$ due to concave curvature for $1 < n \leq 2$, further characterized as localization error [14], and incorrect energy of $H[1, 1]$. The behavior of semilocal functionals is exemplified by BLYP in Fig. 2(b). They have an incorrect convex behavior for fractional charges which usually leads to the
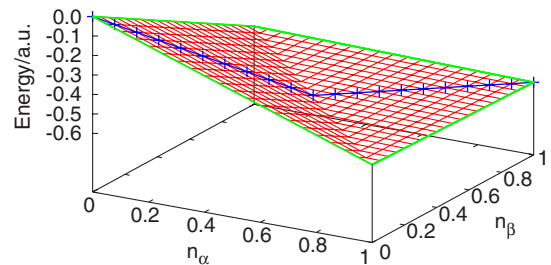

FIG. 1 (color online). Exact energy (a.u.) for densities with fractional charges and fractional spins in $H[n_\alpha, n_\beta]$. Fractional charges occur along the edge lines and fractional spins arise at the intersection $n_\alpha + n_\beta = 1$. The line for $n_\alpha = n_\beta$ is highlighted.
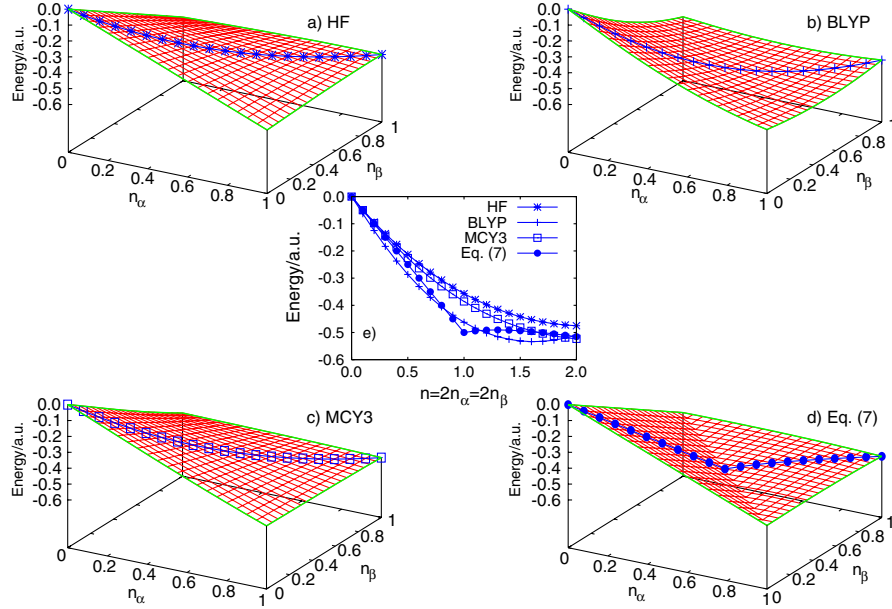
FIG. 2 (color online).   The same as Fig. 1 for approximate functionals. All calculations are self-consistent using a cc-pVQZ basis set.

underestimation of I and the overestimation of A from the derivatives [15] and a delocalization error in larger systems [14]. The MCY3 functional has been developed to give improved behavior for fractional charges [16], so it greatly improves the edge lines in Fig. 2(c) and hence the gap from the derivatives for H[1, 0]. For all of the above functionals, there is a failure to correctly predict the energy of H[$\frac{1}{2}$, $\frac{1}{2}$] associated with the static correlation error of fractional spins [6]. However, much more interesting is the gap of this system. This is most clearly illustrated in Fig. 2(e) where only the energy of the line $n_\alpha = n_\beta$ is shown for $0 \leq n \leq 2$. H[$\frac{1}{2}$, $\frac{1}{2}$] is in the middle at $n = 1$ and the derivative gap is given by the difference between the slope to the left and the slope to the right. It is clear that HF, BLYP, and MCY3 all have a massive failure as they incorrectly have no gap for this system. This is a direct consequence of the smooth continuous behavior of all these different exchange-correlation functionals in terms of the orbitals.

To understand the discontinuous behavior that is needed to give the correct gap, a simple illustrative functional is built to attempt to describe the whole two plane behavior of H[n_α, n_β] using a linear exchange term, a linear correlation term, and the challenging linear correction of the quadratic Coulomb term,

$$E_{xc}[n_\sigma, \rho_\sigma] = \sum_\sigma n_\sigma E_x[\rho_\sigma] + f_c E_c[\rho_\alpha, \rho_\beta]$$
$$+ (n_{\text{high}} - n) J[\rho_\alpha^{n_{\text{low}}}, \rho_\beta^{n_{\text{low}}}]$$
$$+ (n - n_{\text{low}}) J[\rho_\alpha^{n_{\text{high}}}, \rho_\beta^{n_{\text{high}}}] - J[n_\alpha \rho_\alpha, n_\beta \rho_\beta],$$
$$(7)$$

with the general repulsion $J[\rho_a, \rho_b] = \frac{1}{2} \iint [\rho_a(\mathbf{r}) +$

$\rho_b(\mathbf{r})][\rho_a(\mathbf{r}') + \rho_b(\mathbf{r}')]/|\mathbf{r} - \mathbf{r}'| d\mathbf{r} d\mathbf{r}'$. There is an explicit discontinuity in the correlation and Coulomb correction terms such that if $n \leq 1$; $f_c = 0$, $n_{\text{low}} = 0$, $\rho_\sigma^{n_{\text{low}}} = 0$, $n_{\text{high}} = 1$, $\rho_\sigma^{n_{\text{high}}} = n_\sigma \rho_\sigma/n$, and if $n > 1$; $f_c = (n - 1)$, $n_{\text{low}} = 1$, $\rho_\sigma^{n_{\text{low}}} = (1 - n_{\sigma'})\rho_\sigma/(2 - n)$, $n_{\text{high}} = 2$, $\rho_\sigma^{n_{\text{high}}} = \rho_\sigma$, where $\sigma = \{\alpha, \beta\}$ and σ' is the spin orientation opposite to σ. We use HF for $E_x[\rho_\sigma]$ and LYP for $E_c[\rho_\alpha, \rho_\beta]$. Note that irrespective of the form used for E_c, it gives exactly zero correlation energy for any one-electron system due to the prefactor, f_c. Equation (7) is a functional of the orbitals and occupation numbers and can be viewed within reduced-density-matrix functional theory, which has also been used to tackle strongly correlated systems [17], but in this work, we only consider optimization of the orbitals as in standard DFT. This idea can be generalized and placed much more clearly within DFT if the normalization of the exact-exchange hole [18,19] is used instead of the occupation number. The performance of this functional in Fig. 2(d) shows a qualitative improvement over normal functionals and now resembles the exact functional of Fig. 1. It recovers the overall feature of two intersecting planes with a completely flat plane between $0 \leq n \leq 1$ and an almost flat plane between $1 < n \leq 2$, though slightly curved due to the approximate nature of the dynamic correlation.

To examine the gap of Eq. (2), consider the derivatives of the energy expression,

$$E_{\text{gap}}^{\text{deriv}} = \left.\frac{\partial E_v}{\partial N}\right|_+ - \left.\frac{\partial E_v}{\partial N}\right|_- = \Delta \epsilon^{\text{KS}} + \Delta_{xc} + \mathcal{D}_{xc}$$
$$= \Delta \epsilon^{\text{GKS}} + \mathcal{D}_{xc} \qquad (8)$$

where $\Delta \epsilon^{\text{GKS}}$ is the difference in the generalized Kohn-Sham frontier eigenvalues and incorporates all the discon-

TABLE I. Energy gap (a.u.) from the derivatives [Eq. (8)].

		BLYP	HF	MCY3	Eq. (7)	Expt.
H[1,0]	*I-A*	0.250	0.546	0.425	0.576	0.472
	I	0.272	0.500	0.448	0.500	0.500
	A	0.022	−0.046	0.023	−0.076	0.028
H[$\frac{1}{2}$, $\frac{1}{2}$]	*I-A*	0	0	0	0.576	0.472
	I	0.239	0.227	0.252	0.500	0.500
	A	0.239	0.227	0.252	−0.076	0.028

tinuity due to a change of orbitals [15], including the smooth part, Δ_{xc}, of an orbital dependent exchange-correlation term. Furthermore, $\mathcal{D}_{xc}$ represents only the explicit discontinuity of the exchange-correlation term, and hence goes beyond previous work [15,20]. To understand the nature of the exact derivative discontinuity [7,8], both Δ_{xc} and $\mathcal{D}_{xc}$ have to be considered. The HF, BLYP, MCY3 and all known approximations are only smooth functionals of the orbitals, and therefore $\mathcal{D}_{xc}$ is zero. Only some methods based on the Hubbard model have a nonzero $\mathcal{D}_{xc}$ [21]. The new functional, Eq. (7) has an explicit derivative discontinuity at $n = 1$

$$\mathcal{D}_{xc}^{\mathrm{Eq.(7)}} = -2J[\rho_\alpha^1, \rho_\beta^1] + J[\rho_\alpha^2, \rho_\beta^2] + E_c^{\mathrm{LYP}}[\rho_\alpha^2, \rho_\beta^2]. \quad (9)$$

Table I shows I, A, and the gap from the derivatives. The gap of H[1, 0] is underpredicted by BLYP due to its convex behavior and overpredicted by HF due to its concave behavior and bad endpoint, while MCY3 improves in this case due to its straightline behavior. However, none of these normal functionals offer a gap for H[$\frac{1}{2}$, $\frac{1}{2}$] due to a lack of $\mathcal{D}_{xc}$. The functional in Eq. (7) reveals the correct picture with a reasonable gap that is the same for both H[$\frac{1}{2}$, $\frac{1}{2}$] and H[1,0], although A is slightly underpredicted due to the concave nature for $1 < n \leq 2$. Moreover, these two gaps are both due to the explicit discontinuity of the functional, $\mathcal{D}_{xc}$, and there is no contribution from the orbital discontinuity, as the α and β orbitals from the self-consistent solution of Eq. (7) are always degenerate at $n = 1$. This raises an interesting question about normal functionals which erroneously break this degeneracy for $n = 1$ when $n_\alpha \neq n_\beta$. They give a gap that is therefore of the wrong nature, due to a discontinuity because of the orbital dependence, which only mimics the correct explicit discontinuity with degenerate orbitals. This erroneous behavior of normal functionals must no doubt contribute to the incorrect prediction of quantities related to these orbitals such as hyperfine, spin, and magnetic properties.

In this Letter, an exact condition for the energy functional is derived that shows the combined behavior for fractional charge and spins. It shows a discontinuous behavior when passing through the integer that reveals the explicitly discontinuous nature of the derivative of the

exchange-correlation functional. This is most clearly highlighted by the gap of H[$\frac{1}{2}$, $\frac{1}{2}$]. A gap for this system only appears if the exchange-correlation functional has an explicit discontinuity because the orbitals are degenerate and give no contribution. For Mott insulators, the unit cell has fractional spins corresponding to different magnetic phases, and the correct gap prediction critically depends on this explicit discontinuity. For the future, it is crucial to develop better approximations that go beyond smooth orbital functionals by including an explicit discontinuity, along the line suggested by Eq. (7). This is essential for the advancement of DFT towards the calculation of strongly correlated systems.

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