

Supplemental Material to “Fractional Spins and Static Correlation Error in Density Functional Theory”

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The variational principle for the fractional spin ensemble density is proven here. Additional calculations, with several functionals, are presented for the H atom with fractional spins.

I. FRACTIONAL SPIN VARIATIONAL PRINCIPLE AND ITS GENERALIZATION

Our starting point is the exact result for an ensemble of degenerate densities derived by Yang, Zhang and Ayers (YZA) [1]: For a N -electron system in the external potential $v(\mathbf{r})$ that has g -fold degenerate orthogonal ground state wavefunctions $(\Phi_i, i = 1, 2, \dots, g)$ with corresponding densities $(\rho_i, i = 1, 2, \dots, g)$ and ground state energy $E_v^0(N)$, the ensemble density is

$$\rho = \sum_{i=1}^g C_i \rho_i, \quad (1)$$

where $0 \leq C_i \leq 1$ and $\sum_{i=1}^g C_i = 1$. The exact energy functional satisfies the following equation

$$E_v \left[\sum_{i=1}^g C_i \rho_i \right] = E_v[\rho] = E_v^0(N), \quad (2)$$

if $E_v^0(N) \leq (E_v^0(N+1) + E_v^0(N-1))/2$.

In deriving Eq. (2), YZA used only pure states and the three requirements on the density functional: (1) correct for each degenerate orthogonal ground state $(\rho_i, i = 1, 2, \dots, g)$, (2) translationally invariant and (3) size-consistent. The ensemble densities thus appear in the limit of large separation of fragments [1]. In this sense, we see that with density functional theory (DFT) and density matrix functional theory, we are forced to define functionals of ensemble densities.

To construct the functional of ensemble densities of the type of Eq. (1), we consider the following trial ensemble density matrix

$$\tilde{\Gamma} = \sum_{i=1}^g C_i \tilde{\Gamma}_i, \quad (3)$$

where $0 \leq C_i \leq 1$ and $\sum_{i=1}^g C_i = 1$. The density matrix $\tilde{\Gamma}_i$ is for a pure state corresponding to i th degenerate state (in terms of spin, symmetry), but not necessarily the ground state. Then we can use the constrained search [2, 3] and define the functional for the trial ensemble density $\tilde{\rho}$ as

$$F[\tilde{\rho}] = \min_{\tilde{\Gamma} \rightarrow \tilde{\rho}} \text{Tr} \left(\tilde{\Gamma} (\hat{T} + \hat{V}_{ee}) \right). \quad (4)$$

The total energy functional is then

$$E_v[\tilde{\rho}] = F[\tilde{\rho}] + \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}. \quad (5)$$

The minimum of $E_v[\tilde{\rho}]$ is the ground state energy

$$E_v^0(N) = \min_{\tilde{\rho}} E_v[\tilde{\rho}], \quad (6)$$

independent of the mixing coefficients $\{C_i\}$, because the trial ensemble density matrix, Eq. (3), cannot have an energy lower than the ground state energy. This is the general variational principle used in the text for the particular fractional spin systems.

While it may appear as a direct consequence of ensemble DFT, the variational principle of Eq. (6), unlike a general ensemble DFT theory, connects directly to normal pure-state DFT calculations without ensembles. The key is the following: the particular trial ensemble density of Eq. (1), which consists of densities from orthogonal degenerate ground states, arises directly as the dissociation limit of normal pure systems [1]. Such pure states are calculated with normal pure-state DFT with one KS determinant, making the YZA analysis and our variational principle of Eq. (6) directly relevant.

In carrying out corresponding self-consistent KS calculations, we have also assumed that such trial ensemble densities $\tilde{\rho}$ can be represented by a noninteracting systems with fractional occupation. This parallels the development in the self-consistent KS calculations of fractional charge systems [4] where the fractional charge ensemble is also represented by a noninteracting system with fractional occupation.

While the validity of such a KS representation has not been mathematically established here, just as in the case of the KS representation for normal pure state densities, the most important justification is that such fractional occupation KS calculations reveal important features in the functionals for fractional spin ensembles as reported in this work and fractional charge ensembles as reported earlier [4]. These important failures of density functionals are observed in normal DFT calculations without using fractional charge nor spin. When they are analyzed in terms of the fractional occupation KS calculations, they become transparent as a clear violation of the fundamental equalities: linearity in the fractional charge case and constancy in the fractional spin case.

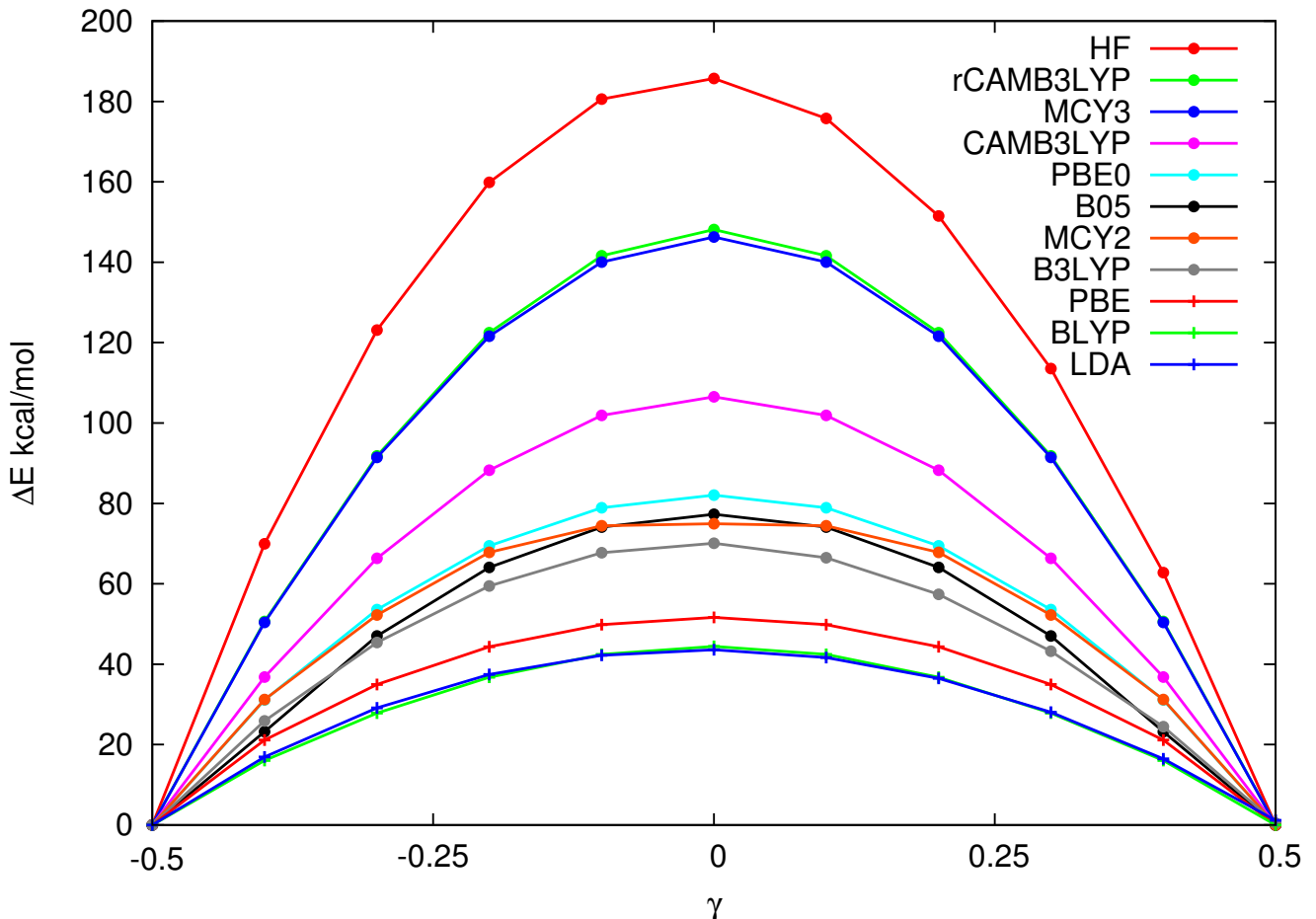


Figure 1: Spin-unrestricted KS calculations, using several different functionals, on the H atom with fractional spins (multiplied by 2). $\gamma = 0$ is a H atom with half an α electron and half a β electron, which is the dissociation limit of H_2 . All calculations are self-consistent using a cc-pVQZ basis set.

II. RESULTS FOR THE H ATOM

The performance of several different functionals is shown in Fig. 1 for the fractional spin H atom. The smallest error is seen for LDA and GGA functionals [5–7] with hybrid functionals B3LYP [8], MCY2 [9], B05 [10] and PBE0[11] all having very similar performance

despite their varied forms. Functionals with improved behaviour on delocalization error, such as MCY3 and rCAMB3LYP [12], which have a much straighter line for fractional charges, have a very poor performance for this fractional spin problem. Note also that functionals which are exact for the integer spin H atom such as HF, MCY2 and B05 have large errors for fractional spin.

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