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Development of exchange-correlation functionals with minimal many-electron self-interaction error

Aron J. Cohen, Paula Mori-Sánchez, and Weitao Yang
Department of Chemistry, Duke University, Durham, North Carolina 27708

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New exchange-correlation functionals that address the important issue of many-electron self-interaction are developed. This is carried out by considering the performance of the functional on systems with fractional numbers of electrons at the same time as more standard thermochemical tests. The inclusion of Coulomb-attenuated exchange in the functional is facilitated by use of the adiabatic connection coupled with a short-range and long-range splittings. The new functionals have a good performance on thermochemistry and a much improved description of the total energy versus number of electrons and henceforth a much smaller many-electron self-interaction error. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2741248]

One of the most important challenges in density-functional theory (DFT) is the proper description of fractional charge systems, relating to the self-interaction error (SIE). Traditionally, the SIE has been formulated as a one-electron problem,[1] which has been addressed in several recent functionals.[2,3] However, these recent one-electron SIE-free functionals, while greatly improving the description of thermochemistry and reaction barriers in general, still exhibit many of the same difficulties associated with SIE. Thus we have further introduced the concept of many-electron self-interaction error (N-SIE) in approximate density functionals.[4] Although it is difficult to define it in terms of electron density, N-SIE has been shown to be related to the exhibition of convexity in the curve of the total energy $E(N+\delta)$ as a function of the fractional number of electron δ.[4] Thus, functionals with N-SIE have too low energy for fractional charges. This problem has also attracted much recent attention.[5]

Functionals having SIE lead to many qualitative and quantitative failures. Compared to normal chemical systems with no fractional charge, SIE is much larger for systems with fractional charge.[6] SIE in general leads to too much charge delocalization and too low total energies. For the general dissociation of any molecule into two fragments, Zhang and Yang showed that when one of the fragments has an electron affinity similar to the ionization energy of the other fragment, SIE will make each fragment incorrectly have a fractional charge at large separation and too low total energy.[6] This occurs in one-electron systems and many-electron radicals,[6] and also in neutral molecules.[7,8] For the same reason, SIE also leads to too much binding energy in charge transfer complexes and too low barriers of chemical reactions. SIE has also been shown[9] to account for the overestimation of polarizabilities observed.[10]

The analysis of fractional charges offers a useful understanding of these problems. We examine this directly by incorporating the occupation numbers n_i in the density

$$\rho(\mathbf{r}) = \sum_i n_i|\phi_i(\mathbf{r})|^2, \quad n_i = \begin{cases} 0, & i > i_{\max} \\ \delta, & i = i_{\max} \\ 1, & i < i_{\max}, \end{cases} \tag{1}$$

where $0 \leqslant \delta \leqslant 1$ and $i_{\max}$ is the highest occupied molecular orbital (HOMO). We have also assumed no degeneracy in HOMO for simplicity. Equation (1) thus describes the ground state of a noninteracting system with a fractional charge.

The exact behavior of the energy versus number of electrons (E vs N) should be a straight line connecting the values at integers based on the ensemble argument.[11] The proof of the linearity has also been given within the ground-state wave function framework in the molecular dissociation limits, without using the grand canonical ensemble.[12] We have recently studied the fractional charge behavior of many approximate functionals.[4] All the standard local functionals (LDA, GGA, meta-GGA) have a very poor description, giving a smooth convex, almost parabolic, interpolation between the integers; Perdew-Zunger correction[1] applied to these functionals straightens the curve for fractional charges but significantly worsens the description of integers; Hartree-Fock (HF) has the opposite behavior, with a concave interpolation between the integers; and finally hybrid and adiabatic functionals which combine these two ingredients are still, in general, quite convex. We also found that the only class of functionals which showed signs of improvement in the description of fractional numbers of electrons are functionals which contain some Coulomb-attenuated exchange.[4]

The idea behind these Coulomb-attenuated functionals (CAM) is a splitting up of the Coulomb operator into short-range and long-range pieces,

$$\frac{1}{r_{12}} = \underbrace{\frac{\operatorname{erfc}(\mu r_{12})}{r_{12}}}_{\text{short range}} + \underbrace{\frac{\operatorname{erf}(\mu r_{12})}{r_{12}}}_{\text{long range}}, \tag{2}$$

and to then treat the two pieces differently, generally one with DFT and the other with exact exchange. Some of the early work on this area is from Gill[13] and Savin.[14] More recently several functionals have been proposed using short-range DFT and long-range HF.[15–18] Also the opposite splitting has been used with long-range DFT and short-range HF, which may be a useful approach for solids.[19]

In this paper we investigate building functionals containing CAM HF and DFT components. We attempt to construct an exchange-correlation functional that is accurate for thermochemistry and other standard properties but with a much improved performance on the description of fractional numbers of electrons, and therefore N-SIE related problems.

The main theoretical tool we use for building functionals is the adiabatic connection.[20] There are several ways to attempt to include the CAM integrals in the adiabatic framework. One is to use a generalized adiabatic connection,[21] which has been used previously by Baer and Neuhauser to develop a functional.[22] The approach we take here is to use the Langreth-Perdew linear adiabatic connection, as we have done in previous work,[3] but to apply the CAM splitting to each of the integrals used in the construction of the functional.

We build the exchange-correlation functional

$$E_{xc}[\rho] = \int_0^1 W_\lambda[\rho] d\lambda - J[\rho] = \int_0^1 \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle d\lambda - J[\rho] \tag{3}$$

by constructing a [1,1] Padé model for W_λ

$$W_\lambda[\rho] = a + \frac{\lambda b}{1 + \lambda c}, \tag{4}$$

where a, b, and c are themselves functionals of electron density, and will be determined by three pieces of input information at the initial point (W_0), the initial slope (W_0'), and a chosen point along the adiabatic curve ($W_{\lambda_p}, 0 < \lambda_p < 1$). Then we simply have to solve a set of simultaneous equations as shown previously.[3]

We make use of the inverse relationship constructing adiabatic curve $W_\lambda[\rho]$ from the knowledge of the density functional $E_{xc}[\rho]$,[24,23]

$$W_\lambda[\rho] = \frac{d(\lambda^2 E_{xc}[\rho_{1/\lambda}])}{d\lambda} = 2\lambda E_{xc}[\rho_{1/\lambda}] + \lambda^2 \frac{dE_{xc}[\rho_{1/\lambda}]}{d\lambda}, \tag{5}$$

which was developed from coordinate scaling.[25] These pieces can be easily calculated for a density functional approximation (DFA) by making the substitution $\rho_{1/\lambda}(\mathbf{r}) = \rho(\mathbf{r}/\lambda)/\lambda^3$ and $\nabla\rho_{1/\lambda}(\mathbf{r}) = \nabla\rho(\mathbf{r}/\lambda)/\lambda^4$ and with the integration performed over $\mathbf{r}/\lambda$.

In previous work, we used normal DFT or Hartree-Fock ingredients for the input functionals.[3] Here we consider the effect of using the Coulomb-attenuated splitting for the functionals. For each of the pieces we apply the Coulomb attenuation only to exchange, and use DFA for the short-range part (SR) and HF for the long-range part (LR). For correlation a standard density functional and corresponding derivatives are used,

$$\begin{aligned} E_{xc}[\rho] &= E_x^{\mathrm{SR,DFA}}[\rho] + E_x^{\mathrm{LR,HF}}[\rho] + E_c^{\mathrm{DFA}}[\rho] \\ &= E_{xc}^{\mathrm{DFA}}[\rho] - E_x^{\mathrm{LR,DFA}}[\rho] + E_x^{\mathrm{LR,HF}}[\rho]. \end{aligned} \tag{6}$$

Long-range DFT exchange is given by the expression used in Ref. 15,

$$\begin{aligned} E_x^{\mathrm{LR,DFA}}[\rho] = \frac{1}{2}\sum_\sigma \int \rho_\sigma^{4/3} K_\sigma^{\mathrm{DFA}} \Bigg(\frac{8}{3} a_\sigma \Bigg[\sqrt{\pi}\, \mathrm{erf}\left(\frac{1}{2a_\sigma}\right) \\ + 2a_\sigma (b_\sigma - c_\sigma) \Bigg] \Bigg) d\mathbf{r}, \end{aligned} \tag{7}$$

with a_σ, b_σ, and c_σ and K_σ^{DFA} (with GGA as a specific case of DFA) as defined in Ref. 15. The long-range HF is

$$\begin{aligned} E_x^{\mathrm{LR,HF}}[\rho] = -\frac{1}{2}\sum_{i \geqslant j} \int \int \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1) \frac{\mathrm{erf}(\mu r_{12})}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ \times \phi_i(\mathbf{r}_2)\phi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \end{aligned} \tag{8}$$

where μ is a parameter which determines the splitting into SR and LR parts.

If we apply the CAM splitting to each of the input functionals we find that the initial point of the adiabatic connection is

$$\begin{aligned} W_0[\rho] = \lim_{\lambda=0} \Bigg(2\lambda (E_x^{\mathrm{LR}}[\rho_{1/\lambda}] + E_x^{\mathrm{SR}}[\rho_{1/\lambda}]) \\ + \lambda^2 \frac{d(E_x^{\mathrm{LR}}[\rho_{1/\lambda}] + E_x^{SR}[\rho_{1/\lambda}])}{d\lambda} \Bigg) = E_x^{\mathrm{HF}}[\rho], \end{aligned} \tag{9}$$

where the separation into short-range and long-range pieces has no effect. CAM splitting of the initial slope gives

$$W_0'[\rho] = 2E_c^{\mathrm{DFA}}[\rho_\infty] - 2E_x^{\mathrm{LR,DFA}}[\rho_\infty] + 2E_x^{\mathrm{LR,HF}}[\rho_\infty]. \tag{10}$$

The HF contribution to the slope is

$$\begin{aligned} E_x^{\mathrm{LR,HF}}[\rho_\infty] &= -\frac{1}{2} \lim_{\lambda \to 0} \sum_{i \geqslant j} \int \int \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1) \frac{\mathrm{erf}(\mu\lambda r_{12})}{\lambda|\mathbf{r}_1 - \mathbf{r}_2|} \\ &\quad \times \phi_i(\mathbf{r}_2)\phi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= -\frac{\mu}{\sqrt{\pi}} \sum_{i \geqslant j} \int \int \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2)\phi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= -\frac{\mu}{\sqrt{\pi}} N, \end{aligned} \tag{11}$$

where N is the number of electrons. CAM splitting of the functional for the point λ along the adiabatic curve is

$$W_\lambda[\rho] = W_\lambda^{\mathrm{DFA}}[\rho] - W_\lambda^{\mathrm{LR,DFA}}[\rho] + W_\lambda^{\mathrm{LR,HF}}[\rho], \tag{12}$$

where the DFT pieces are simply Eq. (5) for the appropriate DFA and

$$
\begin{aligned}
W_{\lambda}^{\mathrm{LR,HF}}[\rho] &= E_x^{\mathrm{LR,HF}}[\rho_{1/\lambda}] + \lambda^2 \frac{\partial E_x^{\mathrm{LR,HF}}[\rho_{1/\lambda}]}{\partial \lambda} \\
&= -\frac{1}{2}\sum_{i\geqslant j} \int\int \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1) \\
&\quad \times \frac{\mathrm{erf}(\mu\lambda r_{12})}{|\mathbf{r}_1-\mathbf{r}_2|}\phi_i(\mathbf{r}_2)\phi_j(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \\
&\quad - \frac{\mu\lambda}{2}\sum_{i\geqslant j}\int\int \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1) \\
&\quad \times \exp(-\mu^2\lambda^2 r_{12}^2)\phi_i(\mathbf{r}_2)\phi_j(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2, \qquad (13)
\end{aligned}
$$

including the CAM integral and also a second two-electron integral, encountered previously in consideration of the *erf-gau* interaction.[26] In this way, we introduce the CAM and related functionals into the adiabatic connection. There are many other ways to do this with variation on these ideas, which we hope to investigate in future work.

The procedure we undertake to develop a functional is to have the basic form determined by the adiabatic connection and to introduce some parameters which are determined to improve the behavior on certain criteria. Usually this is thermochemical performance (e.g., 93 set,[27] 407 set,[28] or G3 set[29] of molecules). However we can in principle fit to other criteria. In the present study, we include the behavior of $\mathrm{C}^+ \rightarrow \mathrm{C} \rightarrow \mathrm{C}^-$ as a measure of the performance for fractional systems.

In this work we fit to the 93 set[27] of total energies the ionization energies and atomization energies used in the development of many previous functionals. To include N-SIE in our functional construction, we define the following measure of the deviation from the correct fractional charge behavior:

$$\mathcal{E}_{\mathrm{frac}}(M) = E(M) - E_{\mathrm{PL}}(M), \qquad (14)$$

where $E(M)$ is the total energy of a system given by the approximate functional for any fractional number of electrons M, and E_{PL} is the piecewise-linear interpolation of the energies at integer numbers of electrons given by the same approximate functional. For example, $E_{\mathrm{PL}}(N+\delta)=(1-\delta)E(N)+\delta E(N+1)$ for N an integer and $0\leqslant\delta\leqslant 1$. When the error in fractional behavior $\mathcal{E}_{\mathrm{frac}}(M)$ is negative, the $E(M)$ curve is convex and the functional has N-SIE; when $\mathcal{E}_{\mathrm{frac}}(M)$ is positive, the $E(M)$ curve is concave, which is also a deviation from the correct fractional charge behavior. We use the following positive definite measure in our functional construction:

$$\Delta_{\mathrm{frac}}(M_1,M_2) = \int_{M_1}^{M_2} dM(\mathcal{E}_{\mathrm{frac}}(M))^2. \qquad (15)$$

We thus included $\Delta_{\mathrm{frac}}(5,7)$ for the carbon atom and evaluated the integral over the electron number in Eq. (15) using a trapezoidal rule with a step size of 0.1 electron.

Upon including parameters in the above form for the three ingredients W_0, W_0', and W_{λ_p} we found that not all the integrals were necessary to achieve the aim of a good performance on thermochemistry and E vs N. In fact for the slope no normal $E_c[\rho_\infty]$ is necessary and the simple LR HF is all that is needed. In the fitting, post-BLYP calculations with a cc-pVQZspd basis set (cc-pVQZ with only *s*, *p*, and *d* functions) were carried out on all the systems using a modified version of CADPAC.[30] We minimized $Q=\mathrm{MAE}_{93}+w_{\mathrm{frac}}\Delta_{\mathrm{frac}}$ (where MAE_{93} is the mean absolute error for the 93 set and w_{frac} is a weighting factor chosen to be 100) for several different values of λ_p and μ and we found the optimum functionals to be

$$W_0 = E_x^{\mathrm{HF}}, \qquad (16)$$

$$W_0' = -c_1\frac{2\mu}{\sqrt{\pi}}N, \qquad (17)$$

$$W_{\lambda_p} = W_{\lambda_p}^{\mathrm{BLYP}} - c_2 W_{\lambda_p}^{\mathrm{LR,B88}} + c_3 W_{\lambda_p}^{\mathrm{LR,HF}}, \qquad (18)$$

with the long-range parameter $\mu=0.2$ and the chosen point on the adiabatic curve $\lambda_p=0.71$ and other parameters $c_1=0.23163$ and $c_2=1+a$, $c_3=1-a$ with $a=0.05601$. The overall energy expression is the same as in our previous MCY functionals[3] but with the above modified components,

$$E_{xc}^{\mathrm{MCY3}}[\rho] = W_0 + W_0'\left(\frac{\{(W_{\lambda_p}-\lambda_p W_0' - W_0)/[\lambda_p(W_0 - W_{\lambda_p})]\} - \log\{1+[(W_{\lambda_p}-\lambda_p W_0' - W_0)/[\lambda_p(W_0-W_{\lambda_p})]]\}}{\{(W_{\lambda_p}-\lambda_p W_0' - W_0)/[\lambda_p(W_0-W_{\lambda_p})]\}^2}\right). \qquad (19)$$

We also found that if we attempt to refit normal GGA and standard hybrid forms that it is very difficult to achieve a straight line for fractional numbers of electrons. Even if it is possible to get a straight line then the performance on thermochemistry gets considerably worse; for example, if we refit B3LYP and the Δ_{frac} reduces to around 0.2 then the error on the 93 set is more than 10 kcal/mol. If we try to fit functionals which include the CAM integrals then we can find a much improved performance for the E vs N curve and a good performance for thermochemistry. Hence we give a functional, rCAM-B3LYP, very similar to CAM-B3LYP (Ref. 16) (with different parameters) which gives a much improved performance for E vs N,

$$
\begin{aligned}
E_{xc}^{\mathrm{rCAM\text{-}B3LYP}} &= \alpha E_x^{\mathrm{HF}} + (1-\alpha)E_x^{\mathrm{Slater}} + c^{\mathrm{B88}}\Delta E_x^{\mathrm{B88}} \\
&\quad + \beta(E_x^{\mathrm{LR,HF}} - E_x^{\mathrm{LR,B88}}) + E_c^{LYP}, \qquad (20)
\end{aligned}
$$

with $\mu=0.33$, $\alpha=0.183\,52$, $\beta=0.949\,79$, and $c^{\mathrm{B88}}=0.952\,38$.

TABLE I. Performance of different functionals for thermochemistry (mean absolute error in kcal/mol) and fractional number of electrons (Δ_{frac} in $1000E_h^2$). All calculations are self-consistent using the cc-pVQZspd basis set.

	93	G3	Barrier	Δ_{frac}
BLYP	4.23	9.96	8.23	22.48
LC-BLYP	8.62	31.44	5.78	1.37
B3LYP	3.30	7.37	4.65	12.80
CAM-B3LYP	3.37	3.62	2.96	4.09
rCAM-B3LYP	3.52	5.59	2.73	0.21
MCY2	2.14	3.39	1.93	10.67
MCY3	2.44	6.53	2.75	0.20

For comparison the original CAM-B3LYP parameters are $\mu=0.33$, $\alpha=0.19$, $\beta=0.46$, and $c^{\text{B88}}=0.81$; also the correlation functional was $E_c=0.81E_c^{\text{LYP}}+0.19E_c^{\text{VWN(5)}}$.

All the above functionals have been implemented self-consistently in a modified version of CADPAC,[30] with the new two-electron integrals implemented following Ref. 26.

In Table I we present the performance of several functionals upon four sets of molecules: (1) the standard set of 93 atoms and molecules which was used in the development of MCY3 and rCAM-B3LYP functionals (the parameters in CAM-B3LYP and B3LYP were also determined from fitting to this set), (2) the 227 heats of formation in the G3 set,[29] (3) the BH42/04 set of Truhlar *et al.*[31] of 42 hydrogen-transfer energy barriers, and (4) carbon with fractional numbers of electrons, Δ_{frac}.

For the new functionals MCY3 and rCAM-B3LYP we see a very reasonable performance on thermochemistry comparable to standard functionals such as B3LYP. This is not only true for the 93 set, for which the functionals were fitted to, but also to the much larger G3 set. Also the performance of MCY3 and rCAM-B3LYP for the hydrogen-transfer barriers is an improvement over normal GGA and hybrid functionals, though the improvement is not as much as seen for the MCY2 functional. The main difference of the new functionals is in the performance on fractional systems with a marked improvement in Δ_{frac} over other functionals. This can be seen more clearly in Fig. 1 where we plot the energy of carbon with fractional numbers of electrons for the different functionals. We also see very similar straight line behavior for many other atoms and molecules with fractional numbers of electrons with the new functionals.[32]

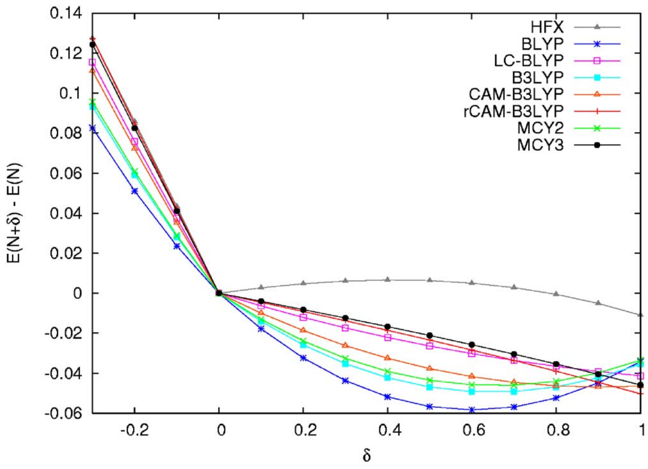

FIG. 1. Energy of carbon with fractional number of electrons relative to the neutral atom from unrestricted self-consistent calculations using the cc-pVQZspd basis set.

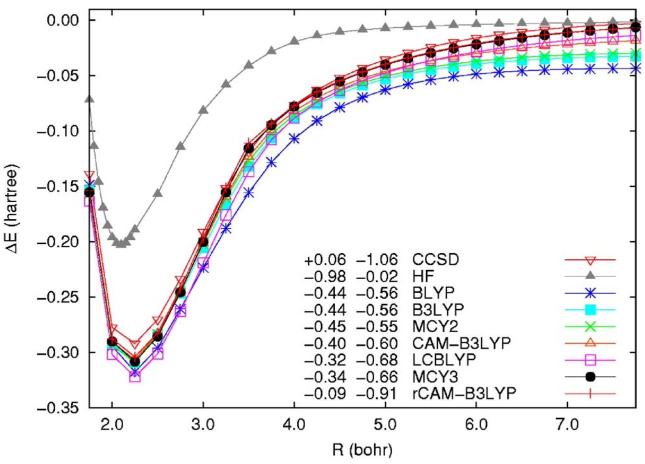

FIG. 2. Dissociation curve of CO^- from unrestricted self-consistent calculations using the aug-cc-pVQZ basis set.

We have also tested the new functionals for the SIE tests on dissociation of CO^- and polarizability of hydrogen chains outlined in our previous paper.[4] As expected we see an improvement in the description of these systems. For MCY3 and rCAM-B3LYP we find an energy difference at 8 bohrs of CO^- to be only 0.016 and 0.013 E_h; the corresponding values for HF, B3LYP, and CAM-B3LYP are 0.017, 0.046, and 0.030 E_h. The corresponding values for the self-consistent polarizability of $(H_2)_{14}$ are only 50 and 48 a.u. per oligomer for MCY3 and rCAM-B3LYP and the corresponding values for HF, B3LYP, and CAM-B3LYP are 40, 69, and 57 a.u. per oligomer. In Fig. 2 we show the full curve for CO^- dissociation and we see a similar trend in the energy for both MCY3 and rCAM-B3LYP which are much closer to the CCSD curve. Also we show the charges at 7.5 a_0 and see that there is a difference in the charges in MCY3 and rCAM-B3LYP from those of CCSD. However we do not believe that the charge differences are as important as the energy: the exact energy will be degenerate for any charge distribution in the molecular dissociation limit when the ionization energy of one fragment is equal to the electron affinity of the other fragment.[6] For example, in a homonuclear diatomic ion (e.g., H_2^+) dissociating with the exact functional, it is degenerate in energy no matter what are the charges ($H+H^+$ has the same energy as $H^{0.5+}+H^{0.5+}$).

In conclusion we have developed new exchange-correlation functionals which have a much improved description of systems with fractional numbers of electrons while performing well on normal thermochemical tests. Previously other functionals which had an improved description of fractional numbers of electrons performed markedly worse on these thermochemical tests. There are two important ingredients in the present functional development: (1) the use of the deviation from the correct fractional charge behavior as defined by $\mathcal{E}_{\text{frac}}$ and Δ_{frac} of Eqs. (14) and (15) and (2) the Coulomb-attenuated exchange integrals. We now have simple density functionals with an improved description of many-electron self-interaction and we hope to investigate these for more complicated tests in the future.

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[32] See EPAPS Document No. JCPSA6-126-313720 for additional information on the behavior of systems with fractional numbers of electrons and other SIE tests. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps. html).