

Density functionals that are one- and two- are not always many-electron self-interaction-free, as shown for H_2^+ , He_2^+ , LiH^+ , and Ne_2^+

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The common density functionals for the exchange-correlation energy make serious self-interaction errors in the molecular dissociation limit when real or spurious noninteger electron numbers N are found on the dissociation products. An “ M -electron self-interaction-free” functional for positive integer M is one that produces a realistic linear variation of total energy with N in the range of $M-1 < N \leq M$, and so can avoid these errors. This desideratum is a natural generalization to all M of the more familiar one of one-electron self-interaction freedom. The intent of this paper is not to advocate for any functional, but to understand what is required for a functional to be M -electron self-interaction-free and thus correct even for highly stretched bonds. The original Perdew-Zunger self-interaction correction (SIC) and our scaled-down variant of it are exactly one- and nearly two-electron self-interaction-free, but only the former is nearly so for atoms with $M > 2$. Thus all these SIC’s produce an exact binding energy curve for H_2^+ , and an accurate one for He_2^+ , but only the unscaled Perdew-Zunger SIC produces an accurate one for Ne_2^+ , where there are more than two electrons on each fragment $Ne^{+0.5}$. We also discuss LiH^+ , which is relatively free from self-interaction errors. We suggest that the ability of the original and unscaled Perdew-Zunger SIC to be nearly M -electron self-interaction-free for atoms of all M stems in part from its formal resemblance to the Hartree-Fock theory, with which it shares a sum rule on the exchange-correlation hole of an open system. © 2007 American Institute of Physics. [DOI: 10.1063/1.2566637]

I. INTRODUCTION AND DEFINITIONS

Kohn-Sham density functional theory^{1,2} is widely used in ground-state quantum chemistry and condensed matter physics because of the conceptual and computational simplicity of its self-consistent field form and because of the useful accuracy of its common semilocal approximations to the density functional for the exchange-correlation energy $E_{xc}[n_1, n_1]$. Of special utility are (in order of increasing accuracy and complexity) the local spin density approximation (LSDA), the generalized gradient approximation (GGA), the meta-GGA, and the hybrids of these with exact exchange. These functionals, especially at the higher levels, can be remarkably accurate for compact systems of integer electron number, such as isolated atoms and molecules near equilibrium, and for the binding energy curves of neutral symmetric diatomics X_2 . It is a well-known problem that none of these successful many-electron approximations is exact for all one-electron densities (although the first three have nonempirical constructions^{3–6}). By way of contrast, in the Hartree-Fock approximation the spurious fully nonlocal self-Hartree energy is canceled exactly by self-exchange, and no spurious self-correlation is present.

The self-interaction errors of common density functionals are believed to be responsible for their underestimation of

energy barriers to gas-phase chemical reactions and for their underestimation of many excitation energies within time-dependent density functional theory. While it is easy to define, quantify, and understand these errors in one-electron systems, it has not been so easy to do so in many-electron systems. That is the general problem we address here.

The self-interaction error of common density functionals is also believed to be responsible for several serious qualitative errors that can arise in the approach to the dissociation limit (1). The approximate binding energy curves of symmetric charged radicals X_2^+ (e.g., H_2^+ , He_2^+ , and Ne_2^+)^{7–12} display a spurious energy barrier at intermediate bond lengths R . When referenced to the integer-charge dissociation fragments (like $H^+ \cdots H^0$), the binding energies tend toward limits below zero as $R \rightarrow \infty$ (as shown, for example, in Figs. 1 and 2 of Ref. 13, and in several figures of the present work, including Fig. 1 for B_2^+). (2) Many asymmetric molecules (e.g., NaCl and CaO) are predicted to show spurious fractional-charge dissociation (e.g., $Na^{+0.4} \cdots Cl^{-0.4}$),^{14–19} with total energy below that of the proper integer-charge dissociation fragments (e.g., $Na^0 \cdots Cl^0$).

In both examples above, the problems arise for noninteger electron number on a separated compact subsystem or dissociation fragment. Perdew *et al.*¹⁵ showed how noninteger electron number N can appear as an average of fluctuat-

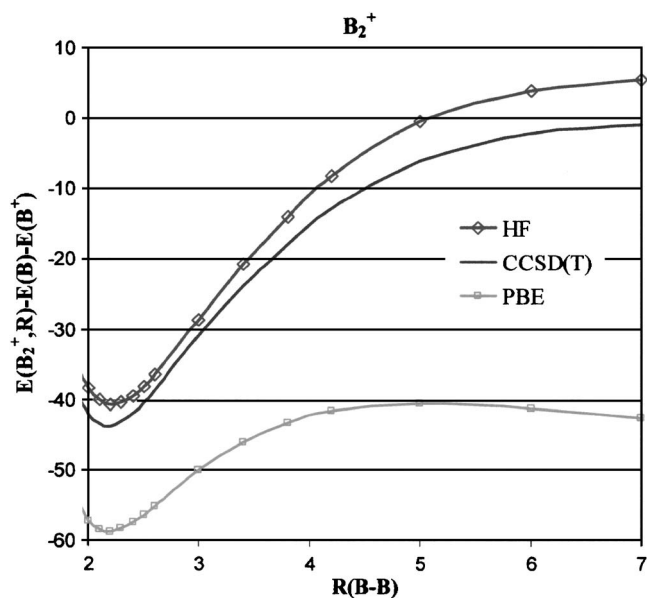


FIG. 1. $E(B_2^+, R) - E(B) - E(B^+)$ symmetric dissociation curves (kcal/mol) calculated with HF, PBE GGA, and CCSD(T)=full using the 6-311G(*d*) basis set. The interatomic distances are in Å. B_2^+ has almost a one-electron bond, cf. the HF and CCSD(T) curves. The oppositely signed HF and PBE GGA errors for $R \rightarrow \infty$ are explained by Fig. 2. (1 hartree=627.5 kcal/mol and 1 bohr=0.5292 Å).

ing integer electron numbers and argued that the exact ground-level energy for an isolated subsystem with a fixed external potential must vary linearly with N between any two adjacent integers ($M-1 < N \leq M$). (The relevance of this work to molecules X_2^+ was pointed out by Zhang and Yang.²⁰) A closed system with fixed electron number can be composed of two isolated open systems of fluctuating electron number, and then a fully correlated wave function description of the closed system is equivalent to an ensemble description of each open system (as shown in Sec. 2 A of Ref. 16). Exact density functionals can be defined by energy minimizing searches over wave functions or ensembles of a given electron density.

The dissociation limit of the one-electron system H_2^+ is the symmetric one $H^{+0.5} \cdots H^{+0.5}$ (which for the exact density functional becomes degenerate with $H^{+q} \cdots H^{1-q}$ for $0 \leq q \leq 1$ as the bond length R tends to infinity). In this case the noninteger electron number on $H^{+0.5}$ is not spurious, and the energy error of common functionals arises unambiguously from their failure to be exact for all one-electron densities. The LSDA dissociation limit of NaCl, $Na^{+0.4} \cdots Cl^{-0.4}$, is of course spurious.^{16,18,19} In either case, the common functionals make the energy for noninteger electron number relatively too low in comparison with that for integer electron number.²⁰ The reason for this can be seen directly from Fig. 1 for B_2^+ and Fig. 2 for the B atom. Alternatively, it can be traced back to a sum rule on the exchange-correlation hole density [Eq. 84 of Ref. 16]. Over a separated compact subsystem or dissociation fragment (e.g., $H^{+0.5}$ in stretched H_2^+), the hole that underlies the common functionals integrates to -1 . The exact hole integrates to -1 for integer electron number on the compact subsystem, but to a less negative value for noninteger electron number. This sum rule is discussed further in Sec. V.

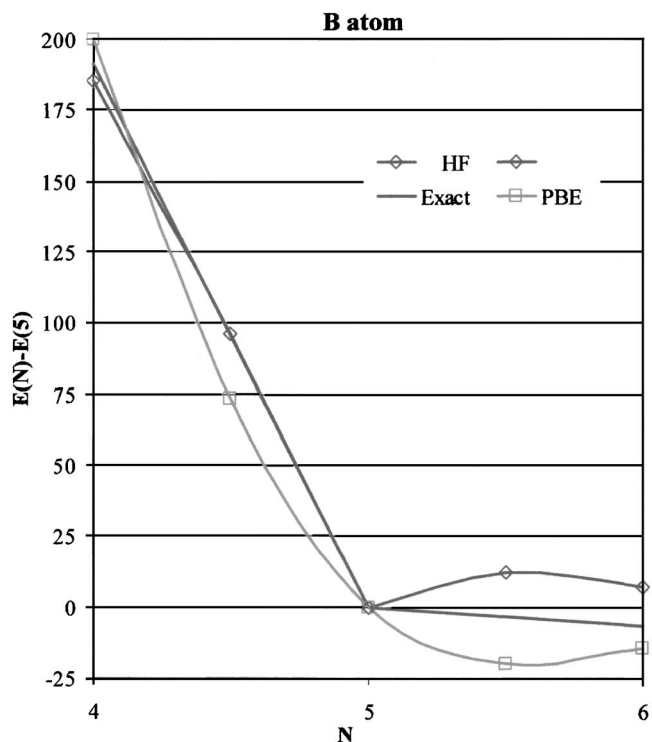


FIG. 2. The total ground-level energy difference $E(N) - E(5)$ (kcal/mol) of the B atom ($Z=5$) as a function of the number N of electrons bound to it. The exact energy is a linkage of straight lines between integers $M-1$ and M . The semilocal density functional approximation (e.g., PBE GGA) total energy difference is more parabolic and lower for noninteger N . The Hartree-Fock energy difference can even curve downward, although the curvature for $4 < N < 5$ (addition of the first $2p$ electron) is not large. Note that electron correlation is important to stabilize the anion, and the energy is sensitive to the basis set. The total energies for $N=4.5$ and 5.5 were taken to be half those of stretched B_2^+ and B_2^- , respectively, at bond lengths of 90 Å. The results were obtained with the aug-cc-pV5Z(*f*) basis set. The curves are simple interpolations over calculated values at $N=M-1$, $M-0.5$, and M .

Here and in Refs. 19 and 21, we have confirmed what we have long suspected. To avoid these self-interaction errors, it is not sufficient that the approximate functional be exact for all one-electron densities. A universally useful approximate functional must be nearly M -electron self-interaction-free for all positive integer M , not just for $M=1$. As defined in Ref. 19, a density functional is (nearly) “ M -electron self-interaction-free” if, for any given external potential and electron number N in the range of $M-1 < N \leq M$, the energy has (nearly) a realistic linear variation with N . Note that there are two components of this definition: (a) linearity of total energy with electron number N between adjacent integers and (b) realism of the energy at integer values of N . To satisfy condition (b), the total energies or at least the energy differences between adjacent integer particle numbers must be close to exact, leading to realistic slopes for the straight line connections. This desideratum is a natural extension to all M of the familiar one of the one-electron self-interaction freedom. The exact density functional¹⁵ is of course exactly M -electron self-interaction-free, but common approximations are not. The semilocal approximations tend roughly to satisfy (b) but not (a), while the Hartree-Fock approximation (or the energetically almost-equivalent Kohn-Sham exact-exchange approximation) satisfies (a) only for

one- and two-electron densities (see Fig. 2 and the end of Sec. IV) and fails to satisfy (b) because of the missing correlation energy.

Since the i th Kohn-Sham orbital energy,

$$\varepsilon_i = \partial E / \partial f_i, \quad (1)$$

is the derivative of the total energy with respect to the occupation number f_i ($0 < f_i \leq 1$) in exact or approximate density functional theory,²² it follows that the exact highest-occupied or partly occupied orbital energy ε^{HO} in the ground state is independent of N in the range of $M-1 < N \leq M$ and equal to minus the electron removal energy from the ground state of the M -electron system. (This removal energy is zero if the system cannot bind M electrons, and in that case the unbound electrons go into the bottom of the free-electron continuum).

The Perdew-Zunger self-interaction-corrected (SIC) LSDA (Ref. 23) is exactly one-electron self-interaction-free. As shown, for example, in Fig. 6 of Ref. 16, it is also nearly M -electron self-interaction-free ($M > 1$) for atoms. It eliminates or greatly reduces fractional-charge errors, as shown in Refs. 16, 17, 19, and 23–26, and here, but worsens the equilibrium properties of molecules.^{27–31} By scaling down this correction in many-electron regions³¹ (Sec. III), we improve the equilibrium properties. The scaled-down SIC is exactly one-electron self-interaction-free, and as shown in Sec. III, it is nearly two-electron self-interaction-free. But, as shown in Ref. 19 and here, it fails to be M -electron self-interaction-free for $M > 2$. Moreover, as shown in Ref. 31, the exchange-correlation potential of the scaled-down SIC has the correct long-range $-1/r$ behavior only for $N \leq 2$; however, as shown in Ref. 21, the correct $-1/r$ asymptote for all M does not guarantee M -electron self-interaction freedom.

As shown in Ref. 19, scaling down the SIC brings back part of the spurious fractional-charge dissociation error. We will show here that it also brings back part of the error of the binding energy curve for Ne_2^+ . However, it does not bring back any part of the error for He_2^+ , because in this three-electron system each dissociation fragment $\text{He}^{+0.5}$ has 1.5 (i.e., less than 2) electrons.

We will also investigate the performance of SIC and scaled-down SIC for LiH^+ , a three-electron system which properly dissociates to integer-charge fragments ($\text{Li}^+ \cdots \text{H}$) even without SIC.¹³

II. COMPUTATIONAL DETAILS

The common functionals to which we apply SIC are nonempirical semilocal ones:³² the Vosko-Wilk-Nusair⁴ (VWN5) LSDA, the Perdew-Burke-Ernzerhof⁵ (PBE) GGA, and the Tao-Perdew-Staroverov-Scuseria⁶ (TPSS) meta-GGA. Some binding energy curves for these common functionals without SIC have been compared and evaluated in our earlier work.¹³ TPSS is by construction one-electron self-correlation-free, so only its exchange part gets a self-interaction correction.

All our calculations used the developmental version of the GAUSSIAN 03 molecular code.³³ Our density functional and SIC calculations were spin unrestricted and employed

the triple-zeta basis sets, 6-311G(d,p) and 6-311+G(3 df,p). SIC was implemented as in Refs. 29 and 30. Because we avoid approximations made in the original Perdew-Zunger²³ SIC solutions for atoms (neglect of off-diagonal Lagrange multipliers and spherical averaging of orbital densities), and because the original solutions are only for LSDA SIC, conclusions based upon them may be only qualitatively applicable to ours.

It was found that the SIC-DFT (density functional theory) energy is more sensitive to the grid size than the regular Kohn-Sham DFT and small grids can even lead to convergence problems.²⁹ Thus, for the SIC calculations, we used the large unpruned (99 590) grid that gave equivalent results compared to the larger (120 770) grid proposed earlier.²⁹ For the Ne^+ ion, the initial guess of SIC orbitals was prepared by solving the Kohn-Sham equations with the restriction of spherical density followed by localization.²⁹ For the Ne_2^+ radical, we found self-consistent field (SCF) convergence problems with the usual direct inversion on iterative subspace (DIIS) SCF convergence acceleration procedure, so we used the “SCF=QC” keyword (quadratic convergence) instead. For Ne_2^+ SIC ($k=0$) calculations, we were able to find a low-energy asymmetric dissociation curve starting from the Hartree-Fock (HF) guess at large interatomic distances.

III. SELF-INTERACTION CORRECTION

Let $E_{\text{xc}}^{\text{DFA}}[n_{\uparrow}, n_{\downarrow}]$ be any density functional approximation for the exchange-correlation energy. We can construct a self-interaction-corrected version of it,

$$E_{\text{xc}}^{\text{DFA-SIC}} = E_{\text{xc}}^{\text{DFA}}[n_{\uparrow}, n_{\downarrow}] - \sum_i \chi_i \{E_{\text{xc}}[n_i, 0] + U[n_i]\}, \quad (2)$$

that is exact for any fully spin-polarized one-electron density. Here $n(\mathbf{r}) = \sum_i n_i(\mathbf{r})$ is a sum of occupied orbital densities [$n_i(\mathbf{r}) = f_i \cdot |\psi_i(\mathbf{r})|^2$, where f_i is an occupation number ($0 \leq f_i \leq 1$)], and

$$U[n_i] \equiv \frac{e^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n_i(\mathbf{r}) \cdot n_i(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}. \quad (3)$$

The number χ_i must reduce to 1 for any one-electron density. Equation (2) gives no correction to the exact $E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}]$. The energy-minimizing SIC orbitals $\psi_i(\mathbf{r})$ tend to be localized even when the canonical Kohn-Sham orbitals are not. The localized orbitals should be orthonormal, since the employed expressions for the density and kinetic energy of the orbitals assume that.

Perdew and Zunger²³ made the simple choice $\chi_i = 1$, as motivated by analogy with the Hartree-Fock theory, and found remarkable improvements over LSDA for atoms. In particular, they found that the energy-minimizing orbitals $\psi_i(\mathbf{r})$ (without off-diagonal Lagrange multipliers) had orbital energies that satisfied Eq. (1) and made LSDA SIC nearly M -electron self-interaction-free for atoms (in the sense of Sec. I). For atoms (Fig. 6 of Ref. 16), the SIC energy showed the correct (nearly) linear variation with electron number N between $M-1$ and M . Historically, the Perdew-Zunger (PZ)

SIC preceded and helped motivate the exact density functional theory for fractional particle number.¹⁵

Early SIC calculations for molecules included N₂ (Ref. 34) and Li₂.³⁵ Considerable time passed before the PZ SIC could be implemented for many molecules. In molecules, the off-diagonal Lagrange multipliers are unavoidable;^{34,35} moreover the method can be quite slow in comparison with implementation of the underlying E_{xc}^{DFA} . Eventually, it became clear²⁷⁻³¹ that the PZ SIC degrades the equilibrium properties of molecules, such as bond lengths, although it improves energy barriers.^{24,28}

Good equilibrium properties can be restored by scaling down³¹ the PZ SIC. In particular, the choice

$$\chi_i = \int d\mathbf{r} |\psi_i(\mathbf{r})|^2 \cdot \left(\frac{\tau_\sigma^W}{\tau_\sigma} \right)^k \leq 1 \quad (4)$$

is exact for all one-electron densities and has other advantages.³¹ In Eq. (4),

$$\tau_\sigma(\mathbf{r}) = \sum_{i(\sigma)} f_i |\nabla \psi_i|^2 \quad (5)$$

is the exact positive kinetic energy density for orbitals of spin σ , and

$$\tau_\sigma^W(\mathbf{r}) = |\nabla n_\sigma|^2 / 8n_\sigma \leq \tau_\sigma(\mathbf{r}) \quad (6)$$

is the von Weizsäcker model thereof. In Eq. (4), σ is the spin of orbital $\psi_i(\mathbf{r})$, and $k \geq 0$ is a scaling exponent, typically 1 or 2. $k=0$ recovers the PZ SIC ($\chi_i=1$). For densities with more than one electron of each spin, $k \rightarrow \infty$ recovers the uncorrected E_{xc}^{DFA} ($\chi_i=0$).

Consider the Kohn-Sham description of few-electron ground-state densities. If we have only one or fewer electrons, then $\tau_\sigma^W/\tau_\sigma=1$ and Eq. (4) gives $\chi_i=1$, the PZ SIC result. Thus scaled-down SIC is one-electron self-interaction-free. If we have only two or fewer electrons (i.e., one or fewer of each spin), then again³⁶ $\tau_\sigma^W/\tau_\sigma=1$ and Eq. (4) gives $\chi_i=1$, the PZ SIC result. Thus scaled-down SIC is also nearly two-electron self-interaction-free. For two or fewer electrons, all considered SIC's combine *exact* exchange (purely a self-interaction correction in this case) with self-interaction-corrected correlation. But, for $M > 2$, $\tau_\sigma^W/\tau_\sigma < 1$ in at least one spin channel, and there is no reason to expect that scaled-down SIC will be nearly M -electron self-interaction-free.

The argument of the preceding paragraph can also be applied to the local hybrid functional of Jaramillo *et al.*³⁷ or at least to its exchange part, leading to the conclusion that it is also one- and nearly two- but perhaps not nearly many-electron self-interaction-free.

IV. BINDING ENERGY CURVES FOR H₂⁺, B₂⁺, He₂⁺, LiH⁺, AND Ne₂⁺

Figure 1 shows the PBE GGA binding energy curve for B₂⁺, which shows serious shape errors, as well as the HF and the almost-exact CCSD(T) curves. B₂⁺ has almost a one-electron bond, as shown by the close agreement of the HF and CCSD(T) curves. Figure 1 of Ref. 13 also shows the LSDA, PBE GGA, and TPSS meta-GGA binding energy

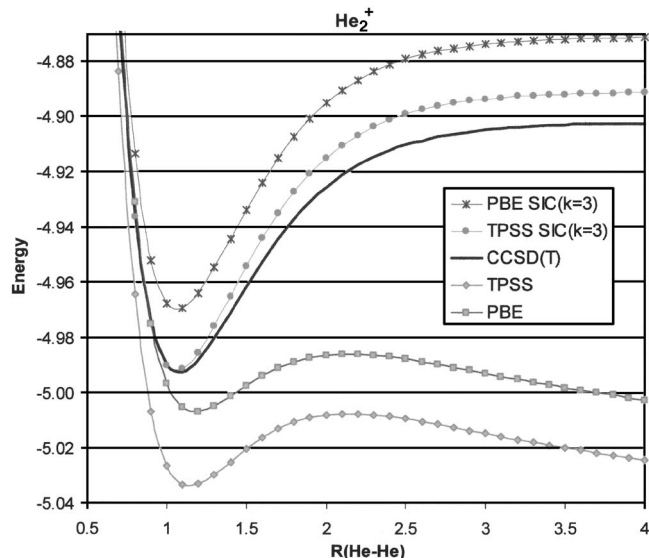


FIG. 3. Symmetric He₂⁺ ground-state energy curves (hartree) calculated with TPSS, PBE, and scaled-down SIC ($k=3$) using the 6-311G(d,p) basis set. We note that Perdew-Zunger ($k=0$) and scaled-down ($k > 0$) SIC curves do not change much from PBE to TPSS. For reference we also show the almost-exact CCSD(T)/cc-pVQZ binding energy curve. The interatomic distances are in Å. The SIC-PBE and SIC-TPSS asymmetric dissociation energy limits, -4.889 and -4.901 hartree, respectively, are lower than the symmetric dissociation limit by 0.0178 and 0.0099 hartree (11.2 and 6.2 kcal/mol) for any value of k . The exact nonrelativistic dissociation limit ($R \rightarrow \infty$) has the energy of -4.904 hartree. The experimental equilibrium bond length R_e is 1.081 Å (Ref. 38). Note that total energies are plotted here. The various dissociation energies are compared in Table I.

curves for a one-electron bond H₂⁺, which all show similar and serious shape errors, as well as the exact curve. The first problem for X₂⁺ (which we shall call the “compound midpoint error”) is that those approximate functionals place the symmetric dissociation limit $X^{+0.5} \cdots X^{+0.5}$ much lower in energy than the asymmetric one $X^{+1} \cdots X^0$, with which it should be degenerate; only the latter is accurately described. The second problem is that those approximate functionals make the energy at large R vary as $^{-|C| + e^2/4R}$, reflecting a Coulomb repulsion between the half-charged symmetric fragments that should be but is not canceled by long-range exchange. Since H₂⁺ is a one-electron molecule, and since all our self-interaction-corrected functionals (original Perdew-Zunger or scaled down) are one-electron self-interaction-free, all of them yield the exact curve for H₂⁺.

Figure 3 of the present article shows symmetric energy curves for the three-electron molecule He₂⁺. The PBE GGA and TPSS meta-GGA show shape errors in comparison with CCSD(T) that are similar to their errors for H₂⁺. Similar shape errors for He₂⁺ are made by LSDA (Fig. 4). At infinite separation, the LSDA, PBE, and TPSS symmetric energy curves are below the asymmetric ones by about 97, 94, and 93 kcal/mol, respectively. This corresponds to a strongly upward-curved $E(N)-E(2)$ for He between $N=1$ and 2 (as expected for semilocal approximations; see Fig. 2). These errors are very substantially removed by the original or scaled-down self-interaction correction.

Figure 4 shows that the SIC total energy of He₂⁺ at large bond lengths is the same for any scaling exponent k , including the unscaled $k=0$. This follows because each dissociation

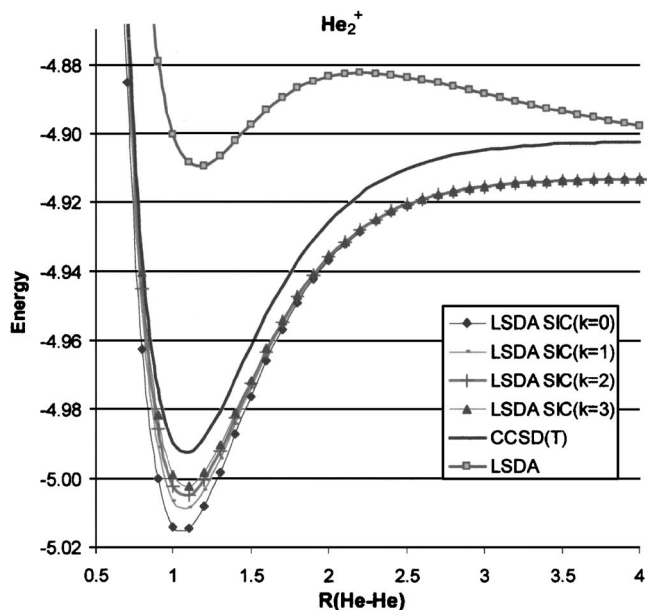


FIG. 4. He_2^+ symmetric ground-state energy curves (hartree) calculated with Perdew-Zunger SIC ($k=0$) and scaled-down SIC ($k=1,2,3$) LSDA using the 6-311G(d,p) basis set. For reference we also show LSDA/6-311G(d,p) and the almost-exact CCSD(T)/cc-pVQZ potential energy curve. The interatomic distances are in Å. The exact nonrelativistic dissociation limit ($R \rightarrow \infty$) has the energy of -4.904 hartree. The experimental equilibrium bond length R_e is 1.081 Å (Ref. 38). Note that total energies are plotted here. The various dissociation energies are compared in Table I.

fragment $\text{He}^{+0.5}$ has 1.5 (i.e., less than 2) electrons, and because our self-interaction-corrected functionals for all k reduce to that for $k=0$ in any ground state with 2 or fewer electrons (Sec. III). These functionals are nearly two-electron self-interaction-free, like the Perdew-Zunger $k=0$ functional, so they provide a greatly improved description of the dissociation limit.

The self-interaction corrections make the symmetric dissociation limit $\text{He}^{+0.5} \cdots \text{He}^{+0.5}$ nearly degenerate with the asymmetric one $\text{He}^{+1} \cdots \text{He}^0$, although a small spurious difference remains. The LSDA SIC, PBE SIC, and TPSS SIC (all k) asymmetric energies are lower by 2.4, 11.2, and 6.2 kcal/mol, respectively (see Fig. 3). This means that the energy of $\text{He}^{+0.5}$ calculated with these methods is above the straight line connecting $E(\text{He}^+)$ and $E(\text{He})$. The LSDA SIC is most nearly linear. The corresponding HF energy difference is 14.6 kcal/mol, showing that HF is less linear here than SIC.

Dissociation energies would normally be calculated as $E(\text{He}) + E(\text{He}^+) - E(\text{He}_2^+ \text{ equilibrium})$. Table I shows that the dissociation energies calculated in this way are high for uncorrected LSDA, PBE GGA, and TPSS meta-GGA, but rather realistic in comparison with the CCSD(T) standard after any version of self-interaction correction. Table I also shows how the SIC dissociation energies depend upon the scaling exponent k for each common functional (see also Fig. 4). The LSD SIC ($k=0$) value is significantly too large, as it is for the less problematic molecules studied in Ref. 31. The experimental data are taken from Ref. 38.

LiH^+ is another three-electron molecular cation, but an asymmetric one that dissociates to integer-charge fragments

TABLE I. Dissociation energy (kcal/mol) of He_2^+ calculated from $E(\text{He}) + E(\text{He}^+) - E(\text{He}_2^+, R_e)$ using various methods. The semilocal density functional approximations have been combined with Perdew-Zunger ($k=0$) and scaled-down ($k>0$) SIC.

Method	LSDA ^a	PBE ^a	TPSS ^a	CCSD(T) ^b
No SIC	85.6	77.9	80.4	56.8
SIC($k=0$)	62.3	52.2	57.5	
SIC($k=1$)	58.4	51.8	57.6	
SIC($k=2$)	56.1	51.6	57.7	
SIC($k=3$)	54.4	51.5	57.7	

^aCalculated with 6-311G(d,p) basis set.

^bCalculated with cc-pVQZ basis set. The experimental dissociation energy D_e is 57.0 kcal/mol (Ref. 38).

($\text{Li}^{+1} \cdots \text{H}^0$) even without self-interaction correction (Fig. 3 of Ref. 13). The exact dissociation limit (-7.780 hartree) (Refs. 39 and 40) is well approximated by the TPSS SIC ($k=0$ or 1) result (-7.781 compared to -7.786 hartree of the uncorrected TPSS). Figure 5 of the present article shows that self-interaction correction has little effect on the binding energy curve. The total energy is exactly independent of the scaling exponent k at large bond lengths (as it must be, since each dissociation fragment has two or fewer electrons), but there is little effect of k even at the equilibrium bond length, except in the LSDA SIC curves, where again $k=0$ exaggerates the atomization energy.

Ne_2^+ , like He_2^+ , is regarded as a “two-center, three-electron bond.” In He_2^+ , the molecular orbital configuration is $(\sigma_g 1s)^2 (\sigma_u^* 1s)^1$, while in Ne_2^+ , it is $\dots (\sigma_g 2p)^2 (\pi_u 2p)^4 (\pi_g^* 2p)^4 (\sigma_u^* 2p)^1$. The binding in Ne_2^+ presumably comes

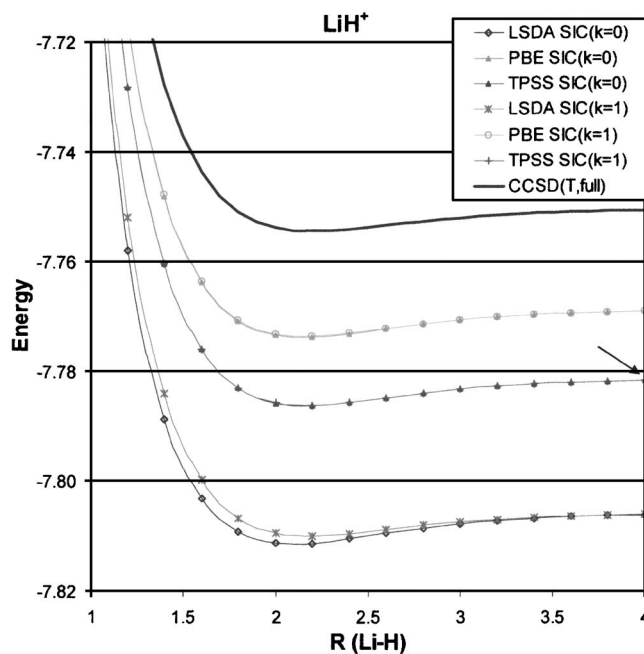


FIG. 5. LiH^+ ground-state energy curves (hartree) calculated with Perdew-Zunger SIC ($k=0$) and scaled-down SIC ($k=1$) applied to TPSS, PBE, and LSDA using the 6-311G(d,p) basis set. The interatomic distances are in Å. The exact nonrelativistic dissociation limit ($\text{Li}^+ \cdots \text{H}$ with $R \rightarrow \infty$) has the energy of -7.780 hartree (Refs. 39 and 40) (shown by an arrow). [The CCSD(T)/6-311G(d,p) total energy misses 67% of the correlation energy of the $\text{Li}^+ 1s$ core due to basis set limitation, but this does not affect the shape of the curve].

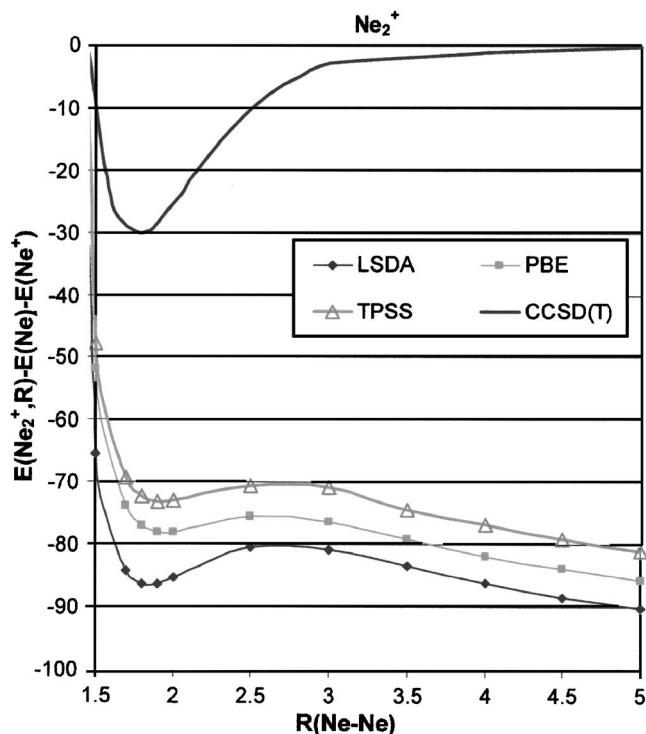


FIG. 6. Ne_2^+ ground-state $E(\text{Ne}_2^+, R) - E(\text{Ne}) - E(\text{Ne}^+)$ symmetric dissociation curves (kcal/mol) calculated with TPSS, PBE, LSDA, and CCSD(T) using the 6-311G(*d*) basis set. The interatomic distances are in Å. The experimental dissociation energy D_e is 32.2 ± 1.0 kcal/mol, and the equilibrium bond length R_e is 1.765 Å (Ref. 41).

from the three valence σ orbitals, as in He_2^+ . However, the symmetric dissociation product $\text{Ne}^{+0.5}$ has more than two electrons.

Figure 6 compares an accurate CCSD(T) symmetric dissociation curve for Ne_2^+ to those of the LSDA, PBE GGA, and TPSS meta-GGA approximations. These approximations make shape errors as in He_2^+ . Note that the energies on the Ne_2^+ figures (Figs. 6 and 7) are zeroed out at the sum of the energies of the integer-charge dissociation fragments (Ne^+ and Ne^0), unlike the preceding Figs. 3–5 for He_2^+ and LiH^+ . At large distances, the shape error grows to a compound midpoint error of about 90–100 kcal/mol depending on the functional, corresponding to strongly upward-curved $E(N) - E(10)$ for Ne with $9 < N < 10$. The experimental data are taken from Ref. 41.

Figure 7 shows what happens to the symmetric dissociation curve of Ne_2^+ when we apply self-interaction corrections. The Perdew-Zunger ($k=0$) corrections greatly improve the shape and the atomization energy, and LSDA SIC ($k=0$) nearly reproduces the degeneracy between $\text{Ne}^{+0.5} \cdots \text{Ne}^{+0.5}$ and $\text{Ne}^{+1} \cdots \text{Ne}^0$ (with less than 4 kcal/mol difference). But even a minor scaling down ($k=1$) destroys the good SIC ($k=0$) shapes [making $2E(\text{Ne}^{+0.5}) - E(\text{Ne}) - E(\text{Ne}^+)$ about equal to -40 kcal/mol, corresponding to an upward-curved $E(N) - E(10)$]. That is because the dissociation fragment $\text{Ne}^{+0.5}$ has more than two electrons, and the scaled-down SIC is not M -electron self-interaction-free for $M > 2$. The HF/6-311+G(3*df*) model has the opposite compound midpoint error [$2E(\text{Ne}^{+0.5}) - E(\text{Ne}) - E(\text{Ne}^+) = +36$ kcal/mol, corresponding to a downward-curved $E(N) - E(10)$].

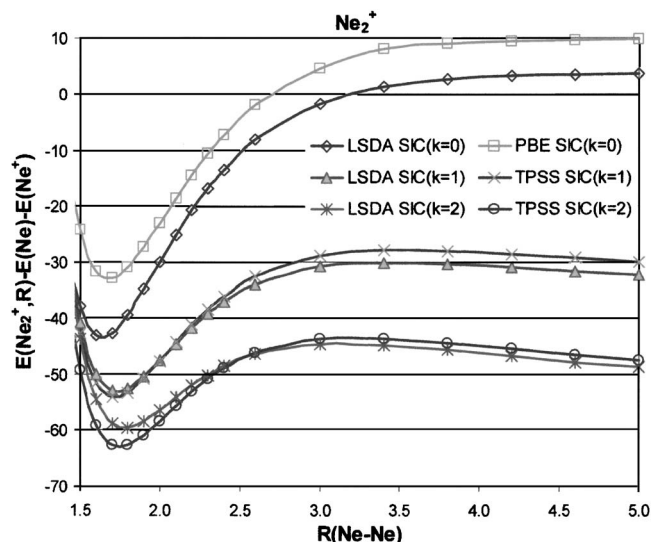


FIG. 7. Ne_2^+ ground-state $E(\text{Ne}_2^+, R) - E(\text{Ne}) - E(\text{Ne}^+)$ symmetric dissociation curves (kcal/mol) calculated with Perdew-Zunger SIC ($k=0$) and scaled-down SIC ($k=1$ and 2) applied to TPSS, PBE, and LSDA using the 6-311+G(3*df*) basis set. We note that Perdew-Zunger ($k=0$) and scaled-down ($k > 0$) SIC curves do not change much from PBE to TPSS. Using a smaller 6-311G(*d*) basis set introduces a small 1–2 kcal/mol upward shift in the curves around the equilibrium distance. The interatomic distances are in Å. The experimental dissociation energy D_e is 32.2 ± 1.0 kcal/mol, and the equilibrium bond length R_e is 1.765 Å (Ref. 41).

V. EXCHANGE-CORRELATION HOLE SUM RULES AND M -ELECTRON SELF-INTERACTION FREEDOM

The original unscaled Perdew-Zunger SIC sets $\chi_i = 1$ in Eq. (2), so it shares with Hartree-Fock theory the self-Coulomb correction $-\sum_i U[n_i]$, and this choice is special.

Following the arguments of Sec. 2 C of Ref. 23, the scaled-down SIC exchange-correlation hole density around an electron at \mathbf{r} satisfies the sum rule,

$$\int d\mathbf{r}' \rho_{\text{xc}}^{\text{SIC}}(\mathbf{r}, \mathbf{r}') = -1 + \sum_i \chi_i (1 - f_i) f_i |\psi_i(\mathbf{r})|^2 / n(\mathbf{r}), \quad (7)$$

which reduces to -1 for all $f_i = 0$ or 1 but to a value between -1 and 0 for a system of fractional electron number. The choice $\chi_i = 1$ (original unscaled PZ SIC) makes the SIC sum rule identical to that for the Hartree-Fock theory [Eq. (48) of Ref. 23] and very similar to that of the exact density functional theory, compare Eqs. (84) and (101) of Ref. 16 [or see Eq. (37) of Ref. 42]. The common semilocal density functionals have hole densities (e.g., Ref. 43) that integrate to -1 . The exchange-correlation energy,

$$E_{\text{xc}} = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \cdot n(\mathbf{r}) \frac{\rho_{\text{xc}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (8)$$

is sensitive⁴⁴ to the sum rule on ρ_{xc} (and, to a lesser extent, to the detailed shape of ρ_{xc}). As the right-hand side of Eq. (7) becomes less negative, the right-hand side of Eq. (8) tends to do the same. That is what makes it possible for the PZ SIC approximation to be nearly M -electron self-interaction-free for all M . Any scaling down of this term loses this desirable property, restoring part of the M -electron self-interaction error of the semilocal functionals. From this perspective, the

unitarily invariant SIC that we proposed in Ref. 32 is also suspect. [Invariance of the energy and density under unitary transformation of the occupied orbitals of each spin is a feature of the Hartree-Fock (or Kohn-Sham) theory when the noninteracting wave function is a single Slater determinant. For fractional occupation numbers f_i , however, one must use the energy-minimizing localized orbitals to evaluate these properties and Eq. (7).]

We can see something more in Eq. (7). Suppose that only one orbital is fractionally occupied: $f=N-M+1$. Then $f(1-f)=(N-M+1)(M-N)$ is a downward-curving parabola, vanishing at $N=M$ and $M-1$, that (with the right positive coefficient) can additively correct the upward-curving parabola of the semilocal approximation for $E(N)$ pictured in Fig. 2. A similar argument⁴⁵ explains the close connection between SIC and a simplified LDA+U method; see also Ref. 46.

Hartree-Fock theory has been extended²³ to open systems by using normalized orbitals localized on each open system and fractional occupation numbers f_i in the range of $0 \leq f_i \leq 1$. Figure 8 of Ref. 47 and Fig. 2 of the present article for $4 < N < 5$ suggest that Hartree-Fock energies vary somewhat linearly between adjacent integer electron numbers. In fact, the Hartree-Fock total energy as a function of electron number N between the integers $M-1$ and M is not linear and can even curve downward,^{25,26,47} unlike the strong upward curving of the semilocal energy in Fig. 2. For one example, see $5 < N < 6$ in Fig. 2. For another example, Fig. 1 and Table V of Ref. 26 show that, in the Hartree-Fock theory, the energy of $\text{Ne}^{+0.5} \cdots \text{Ne}^{+0.5}$ is 35 kcal/mol above that of $\text{Ne}^{+1} \cdots \text{Ne}^{+0}$. This means that, within the Hartree-Fock theory, symmetry breaking^{25,26} can produce a proper dissociation limit for the binding energy of charged symmetric radicals. Because Hartree-Fock theory is more favorable to integer electron number, it can also avoid the spurious fractional-charge dissociations of asymmetric neutral molecules found from semilocal approximations, as shown in Fig. 4 of Ref. 19. The Hartree-Fock exchange hole satisfies²³ the sum rule of Eq. (7) with $\chi_i=1$, reminding us that M -electron self-interaction freedom for all M requires not only the $\chi_i=1$ sum rule but also a treatment of correlation (as pointed out, for example, in Refs. 25, 28, and 47).

VI. CONCLUSIONS

A density functional for the exchange-correlation energy is nearly M -electron self-interaction-free if it yields a realistic, nearly linear variation of the total energy with electron number N between the integers $M-1$ and M . Our results show that a universally useful approximate functional must be nearly M -electron self-interaction-free for all M . Common approximations (LSDA, GGA, meta-GGA, and global hybrid) are not even one-electron self-interaction-free. The midpoint energy error for a compact open system X, $E(X;M-0.5)-[E(X;M)+E(X;M-1)]/2$, provides a useful but incomplete quantification of nonlinearity for $M-1 < N < M$.

The Perdew-Zunger self-interaction correction²³ (SIC) makes these common approximations exactly one- and (at

least for atoms) nearly M -electron self-interaction-free ($M > 1$). As shown here the latter property is not a consequence of the former. Separate work on the hyper-GGA (Ref. 21) shows that one-electron self-interaction-free approximations can easily fail to be even two-electron self-interaction-free.

In this work, we have tested our scaled-down³¹ Perdew-Zunger SIC, which is exactly one- and nearly two- but not many-electron self-interaction-free. This scaling can improve equilibrium properties and preserve good energy barriers.³¹

Self-interaction errors in binding energy curves are most severe when dissociation leaves a noninteger electron number on each dissociation fragment. In LiH^+ , where the dissociation fragments have integer electron numbers, the common functionals and the tested SIC's work reasonably. In H_2^+ , where dissociation leaves half an electron on each fragment, the common functionals fail badly but all one-electron self-interaction-free methods are exact. In He_2^+ , where dissociation leaves 1.5 electrons (or more generally between 1 and 2) on each fragment, all nearly two-electron self-interaction-free methods are accurate. But in Ne_2^+ , where dissociation leaves more than two electrons on each fragment, only the original, unscaled Perdew-Zunger SIC is qualitatively correct. We found similar functional performances in separate studies¹⁹ of the spurious fractional-charge dissociation of a molecule XY ($Y \neq X$).

Common semilocal density functionals are accurate for compact systems of integer electron number, such as atoms and molecules near equilibrium. But they fail for certain stretched bond situations, including stretched X_2^+ , because they make the total energy variation fall below a straight line for electron numbers N between integers M and $M-1$ in a fragment of the stretched system, so that the midpoint energy error for X is negative. That in turn is because they are based upon exchange-correlation hole densities that integrate to -1 , even in open systems of fluctuating electron number where the exact hole should integrate to a value between 0 and -1 . (Of course the hole density integrates to -1 over any system of fixed electron number, but a fragment does not have fixed electron number so part of the hole around an electron in one fragment is located on other fragments, as shown for stretched H_2^+ in Fig. 3 of Ref. 25.) The original and unscaled Perdew-Zunger SIC and the Hartree-Fock approximation are based upon holes with a more correct sum rule, so they produce energy variations that are either nearly linear or (in the case of Hartree-Fock theory) can lie above the straight line connection.

The Hartree-Fock or exact-exchange-only approximation is also one-but not many-electron self-interaction-free. Its midpoint energy error is small for one- and two-electron ground-state densities but can be large and positive for many-electron densities. When this error is positive, symmetry breaking can improve the description of stretched X_2^+ by minimizing the energy with integer electron numbers on the fragments (e.g., $\text{X}^{+1} \cdots \text{X}^0$).²⁵

It remains a problem to construct functionals that are accurate for compact systems both at and between integer particle numbers. The long-range-corrected hybrid functionals (e.g., Refs. 48 and 49) treat the long-range part of the Coulomb interaction in the Hartree-Fock theory. They are

not exactly one-electron self-interaction-free, but may or may not be nearly M -electron self-interaction-free for all M , and are reasonably accurate for the binding energy curves of H_2^+ ,⁴⁸ Ar_2^+ ,⁴⁹ etc. It remains to be seen if hyper-GGA's (Refs. 21, 50, and 51) are nearly M -electron self-interaction-free.

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