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Exchange energies and density functionals for systems of fermions of arbitrary spin

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The Hartree-Fock exchange energy expression, the Dirac exchange functional, and other exchange functionals of the electron density are extended to fermions of arbitrary spin quantum number s. The explicit s dependence of the exchange energy provides illuminating insights into the meaning of exchange interactions, spin-scaling relations, and the self-interaction error. In particular, the spin-scaling relation for exchange functionals proves to be a special case of conversion between spin-unpolarized forms of the same functional appropriate for $s = 0$ and for $s > 0$. A rigorous definition of the many-particle self-interaction error suitable for one-orbital systems is formulated and interpreted as a set of exact constraints for exchange density-functional approximations.

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I. INTRODUCTION

The concept of exchange energy is a distinctive feature of the Hartree-Fock self-consistent field method [1] and the Kohn-Sham density-functional scheme [2]. In the Hartree-Fock method, the expectation value of the electron-electron repulsion operator $\hat{W}$ with a single Slater determinant of spin orbitals is a sum of two terms: the Coulomb energy and the exchange energy. The former is interpreted as the classical part of the electron-electron interaction energy, the latter as a nonclassical part. Each of these two terms is invariant under unitary transformations of the orbitals. In the Kohn-Sham formalism, the expectation value of $\hat{W}$ with a Slater determinant of Kohn-Sham spin orbitals is a sum of the Coulomb energy and the so-called exact exchange [3].

The Hartree-Fock and Kohn-Sham methods were originally devised for systems of electrons but have since been extended to multicomponent systems in which electrons, atomic nuclei, and other Coulombically interacting particles (such as positrons) are described in terms of orbitals [4–16]. Since particles other than electrons can have any spin quantum number s, the question of s dependence of the Hartree-Fock and density-functional energy expressions becomes relevant. This article shows that by investigating the Coulomb and exchange energy formulas for fermions of arbitrary spin quantum number s, one obtains stimulating insights into the meaning of exchange energy, the self-interaction error, spin-scaling relations, and other fundamental concepts of molecular quantum mechanics.

II. DERIVATION

A. Preliminaries

We begin with a straightforward derivation of the particle-particle interaction energy formula for a system of N unit-charge spin-s fermions described with a Slater determinant of spin orbitals. A spin orbital is a one-particle wave function of the form $\psi(\mathbf{x}) = \phi(\mathbf{r})\sigma(\omega)$, where $\mathbf{x} = (\mathbf{r}, \omega)$ denotes collectively the spatial and spin coordinates of the particle, $\phi(\mathbf{r})$ is a spatial orbital, and σ is a spin-state function. A Slater determinant is an antisymmetrized product of the spin orbitals,

$$\Phi = \frac{1}{(N!)^{1/2}} \sum_{k=1}^{N!} (-1)^{p_k} \hat{P}_k \{\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\cdots\psi_N(\mathbf{x}_N)\}, \quad (1)$$

where $\hat{P}_k$ is the operator generating the kth permutation of the N particles and p_k is the number of associated transpositions. We assume here that all spatial orbitals and hence all spin orbitals are orthonormal.

The total number of spin states of a spin-s fermion is

$$M = 2s + 1. \quad (2)$$

These M states will be denoted by Greek letters $\alpha, \beta, \gamma, \ldots$ and indexed by $\sigma = 1, 2, \ldots, M$, respectively. For example, when $s = 1/2$ (electrons), there are only two spin states: α ($\sigma = 1$, spin up) and β ($\sigma = 2$, spin down).

For fermionic particles that repel one another Coulombically, the average particle-particle interaction energy is the expectation value of the operator

$$\hat{W} = \sum_{i<j}^{N} \frac{1}{r_{ij}}, \quad (3)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The expectation value of $\hat{W}$ with the wave function Φ is given in terms of spin orbitals by the same formula for any s, namely [17],

$$W = \langle\Phi|\hat{W}|\Phi\rangle = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}([ii|jj] - [ij|ji]), \quad (4)$$

where we use the standard notation for two-particle integrals in terms of spin orbitals,

$$[ij|kl] = \iint \psi_i^*(\mathbf{x}_1)\psi_j(\mathbf{x}_1)r_{12}^{-1}\psi_k^*(\mathbf{x}_2)\psi_l(\mathbf{x}_2)\,d\mathbf{x}_1 d\mathbf{x}_2. \quad (5)$$

The dependence of W on s is not evident from Eq. (4) but emerges in transition to spatial orbitals.

B. Spin-unrestricted Slater determinants

Within the spin-unrestricted formalism, particles in different spin states σ occupy distinct spatial orbitals $\phi_{i\sigma}(\mathbf{r})$. We label the spin states by $\sigma = 1, 2, \ldots, M$ as explained below Eq. (2) and denote the total number of σ-state particles by N_σ. Substitution of a spin-unrestricted Slater determinant Φ into Eq. (4) gives

$$W = \frac{1}{2}\sum_{\sigma=1}^{M}\sum_{\sigma'=1}^{M}\sum_{i=1}^{N_\sigma}\sum_{j=1}^{N_{\sigma'}} J_{ij}^{\sigma\sigma'} - \frac{1}{2}\sum_{\sigma=1}^{M}\sum_{i=1}^{N_\sigma}\sum_{j=1}^{N_\sigma} K_{ij}^{\sigma\sigma}, \tag{6}$$

where

$$J_{ij}^{\sigma\sigma'} = \iint \phi_{i\sigma}^*(\mathbf{r}_1)\phi_{i\sigma}(\mathbf{r}_1)r_{12}^{-1}\phi_{j\sigma'}^*(\mathbf{r}_2)\phi_{j\sigma'}(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2 \tag{7}$$

are Coulomb integrals and

$$K_{ij}^{\sigma\sigma} = \iint \phi_{i\sigma}^*(\mathbf{r}_1)\phi_{j\sigma}(\mathbf{r}_1)r_{12}^{-1}\phi_{j\sigma}^*(\mathbf{r}_2)\phi_{i\sigma}(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2 \tag{8}$$

are exchange integrals. There are no exchange integrals with $\sigma \neq \sigma'$. Equation (6) generalizes the well-known two-electron energy formula of the spin-unrestricted Hartree-Fock (UHF) theory [17] to unit-charge fermions of arbitrary spin.

The first and the second terms in Eq. (6) are the electrostatic (Coulomb) and exchange energies, respectively. To see this, write the average particle-particle interaction energy as

$$W = \iint \frac{\Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)}{r_{12}}\,d\mathbf{r}_1 d\mathbf{r}_2, \tag{9}$$

where $\Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)$ is the diagonal part of the spin-free second-order reduced density matrix (2-RDM) derived from Φ. The 2-RDM itself has the same form for any s, namely,

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') = \frac{1}{2}\begin{vmatrix} \gamma(\mathbf{x}_1; \mathbf{x}_1') & \gamma(\mathbf{x}_1; \mathbf{x}_2') \\ \gamma(\mathbf{x}_2; \mathbf{x}_1') & \gamma(\mathbf{x}_2; \mathbf{x}_2') \end{vmatrix}, \tag{10}$$

where

$$\gamma(\mathbf{x}; \mathbf{x}') = \sum_{i=1}^{N} \psi_i(\mathbf{x})\psi_i^*(\mathbf{x}') \tag{11}$$

is the corresponding one-particle RDM (1-RDM). Integration of Eq. (10) over spin variables leads to

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \frac{1}{2}\sum_{\sigma=1}^{M} |\rho_{\sigma\sigma}(\mathbf{r}_1; \mathbf{r}_2)|^2, \tag{12}$$

where

$$\rho_{\sigma\sigma}(\mathbf{r}; \mathbf{r}') = \sum_{i=1}^{N_\sigma} \phi_{i\sigma}^*(\mathbf{r})\phi_{i\sigma}(\mathbf{r}') \tag{13}$$

is the spatial part of the σ-spin 1-RDM. The diagonal part of this 1-RDM is the σ-spin particle density,

$$\rho_\sigma(\mathbf{r}) \equiv \rho_{\sigma\sigma}(\mathbf{r}; \mathbf{r}), \tag{14}$$

and the total density is then given by

$$\rho(\mathbf{r}) = \sum_{\sigma=1}^{M} \rho_\sigma(\mathbf{r}). \tag{15}$$

Substitution of Eq. (12) into Eq. (9) yields

$$W = E_J + E_X, \tag{16}$$

where

$$E_J = \frac{1}{2}\iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}\,d\mathbf{r}_1 d\mathbf{r}_2 \tag{17}$$

is the Coulomb energy and

$$E_X = -\frac{1}{2}\sum_{\sigma=1}^{M}\iint \frac{|\rho_{\sigma\sigma}(\mathbf{r}_1; \mathbf{r}_2)|^2}{r_{12}}\,d\mathbf{r}_1 d\mathbf{r}_2 \tag{18}$$

is the exchange energy. Finally, using Eqs. (13)–(15) in Eqs. (17) and (18), we obtain

$$E_J = \frac{1}{2}\sum_{\sigma=1}^{M}\sum_{\sigma'=1}^{M}\sum_{i=1}^{N_\sigma}\sum_{j=1}^{N_{\sigma'}} J_{ij}^{\sigma\sigma'} \tag{19}$$

and

$$E_X = -\frac{1}{2}\sum_{\sigma=1}^{M}\sum_{i=1}^{N_\sigma}\sum_{j=1}^{N_\sigma} K_{ij}^{\sigma\sigma}, \tag{20}$$

in agreement with Eq. (6). Equations (19) and (20) generalize the standard UHF formulas for the electronic Coulomb and exchange energies to systems of Coulombically interacting unit-charge fermions of arbitrary spin.

C. Spin-restricted closed-shell Slater determinants

Within the spin-restricted formalism, orbitals $\phi_{i\sigma}(\mathbf{r})$ for different σ states are no longer treated as distinct but are conflated into one spatial orbital $\phi_i(\mathbf{r})$. We assume here that each $\phi_i(\mathbf{r})$ is filled to its maximum capacity M, so the total number of occupied spatial orbitals is N/M. For such closed-shell wave functions, Eq. (6) reduces to

$$W = \frac{M}{2}\sum_{i=1}^{N/M}\sum_{j=1}^{N/M}(MJ_{ij} - K_{ij}), \tag{21}$$

where

$$J_{ij} = \iint \phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_1)r_{12}^{-1}\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2 \tag{22}$$

and

$$K_{ij} = \iint \phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)r_{12}^{-1}\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2. \tag{23}$$

Accordingly, Eqs. (19) and (20) reduce to

$$E_J = \frac{M^2}{2}\sum_{i=1}^{N/M}\sum_{j=1}^{N/M} J_{ij} \tag{24}$$

and

$$E_X = -\frac{M}{2}\sum_{i=1}^{N/M}\sum_{j=1}^{N/M} K_{ij}, \tag{25}$$

respectively. For spin-restricted closed-shell Slater determinants, all σ-state 1-RDMs are equal, so

$$\rho_{\sigma\sigma}(\mathbf{r};\mathbf{r}') = \frac{\rho(\mathbf{r};\mathbf{r}')}{M}. \tag{26}$$

Inserting Eq. (26) into Eq. (18) and using the fact that the summation over σ gives a factor of M in the numerator, we obtain the expression for the exchange energy

$$E_X = -\frac{1}{2M}\iint \frac{|\rho(\mathbf{r}_1;\mathbf{r}_2)|^2}{r_{12}}\, d\mathbf{r}_1 d\mathbf{r}_2. \tag{27}$$

Equations (21), (24), (25), and (27) generalize the electron-electron interaction energy formulas of the spin-restricted closed-shell Hartree-Fock (RHF) and Kohn-Sham methods to fermions of arbitrary spin. Equivalent results stated in the language of Green's function theory may be found in Ref. [18]. These formulas are amenable to illuminating physical interpretations, which we now proceed to discuss.

III. DISCUSSION

A. Classical limit

The Bohr-Planck correspondence principle [19] postulates that the quantum description of a system in terms of a quantum number n should reproduce the classical description in the double limit in which $n \to \infty$ and $h \to 0$, where h is the Planck constant, subject to the constraint that the product nh remain fixed. Since W does not depend on h, only the spin quantum number s is relevant for the purpose of analyzing the classical limit of W.

Observe that, in the $s \to \infty$ limit, Eqs. (21), (24), and (25) imply

$$\lim_{s\to\infty} \frac{E_J}{W} = 1, \quad \lim_{s\to\infty} \frac{E_X}{W} = 0. \tag{28}$$

This means that, for a closed-shell spin-restricted Slater determinant, E_X vanishes asymptotically in the classical limit, whereas the particle-particle interaction energy W approaches E_J. The result $W = E_J$ is classical. Thus, exchange interactions in closed-shell fermionic systems fall within the scope of the correspondence principle with respect to the spin quantum number.

B. Relationship to the Fermi-Amaldi correction

If there is only one spatial orbital occupied by $N \leqslant M$ fermions in permissible spin states, Eq. (6) reduces to

$$W = \frac{N(N-1)}{2} J_{11} = E_J - \frac{1}{N} E_J. \tag{29}$$

The quantity $-E_J[\rho]/N$ is known as the Fermi-Amaldi correction [20–22]. Equation (29) means that the Fermi-Amaldi correction is the exact exchange functional for any system of $N \leqslant M$ fermions, provided that the particles occupy the same spatial orbitals. One can show [23] that Eq. (29) is also exact for any number of identical Coulombically repelling bosons occupying the same spatial orbital, regardless of their spin quantum number.

C. Zero-spin fermions

Although the physical values of s for fermions are $1/2, 3/2, \ldots$, fermions with integer s values may also be considered. Imagine, for instance, fermions with $s = 0$. The maximum occupancy of each spatial orbital in this case is $M = 1$, so the difference between the spin-restricted and spin-unrestricted formalisms disappears. Any Slater determinant for zero-spin particles can be formally treated as spin restricted. Then Eq. (21) applies and gives

$$W = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}(J_{ij} - K_{ij}). \tag{30}$$

Alternatively, Eq. (30) can be obtained by setting $M = 1$ in the spin-unrestricted Eq. (6) and dropping the now redundant σ superscripts.

Apart from spin labels, Eq. (30) is the correct formula for a fully spin-polarized Slater determinant [17], that is, a Slater determinant in which all orbitals are singly occupied by particles in identical spin states. A fully spin-polarized Slater determinant for fermions with $s > 0$ is therefore interchangeable with a Slater determinant involving the same spatial orbitals for zero-spin fermions.

D. Dirac exchange functional for arbitrary *s* values

Consideration of fermions of arbitrary spin remains fruitful in the context of the Kohn-Sham density-functional theory. To demonstrate this, we will derive the s-dependent form of the Dirac exchange functional, also known as the local density approximation (LDA).

The LDA exchange functional of the spin-unpolarized electron density is given by

$$E_X[\rho] = -C_X \int \rho^{4/3}(\mathbf{r})\, d\mathbf{r}, \tag{31}$$

where

$$C_X = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}. \tag{32}$$

To generalize Eq. (31) to unit-charge fermions of arbitrary spin s, we retrace the standard derivation of the LDA [18] and observe how the factor M propagates.

The 1-RDM for a homogeneous gas of s-spin fermions confined in a cubic box of volume $V = L^3$ is

$$\rho(\mathbf{r}_1;\mathbf{r}_2) = \frac{M}{V}\sum_{\mathbf{n}}^{\text{occ.}} e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)}, \tag{33}$$

where $\mathbf{n} = (n_x, n_y, n_z)$ are state labels and

$$\mathbf{k} = \left(\frac{2\pi}{L}\right)^3 \mathbf{n} = \frac{8\pi^3}{V}\mathbf{n} \tag{34}$$

is the wave vector. A change of coordinates from $\mathbf{r}_1$ and $\mathbf{r}_2$ to $\mathbf{r} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ and $\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2$ transforms Eq. (33) into

$$\rho(\mathbf{r};\mathbf{u}) = \frac{M}{V}\sum_{\mathbf{n}}^{\text{occ.}} e^{i\mathbf{k}\cdot\mathbf{u}} \tag{35}$$

and the exact exchange formula of Eq. (18) into

$$E_X[\rho] = -\frac{1}{2M}\int d\mathbf{r}\int d\mathbf{u}\,\frac{|\rho(\mathbf{r};\mathbf{u})|^2}{u}. \tag{36}$$

Replacing the summation over **n** in Eq. (35) with integration over **k** in terms of spherical polar coordinates, we obtain

$$\begin{aligned}\rho(\mathbf{r};\mathbf{u}) &= \frac{M}{8\pi^3}\int_0^{k_F} dk\int_0^{2\pi} d\phi\int_0^{\pi} d\theta\, k^2\sin\theta e^{iku\cos\theta}\\ &= \frac{M}{2\pi^2}\,\frac{\sin(k_F u) - k_F u\cos(k_F u)}{u^3},\end{aligned} \tag{37}$$

where $k_F = |\mathbf{k}_F|$ specifies the highest occupied level. In the $u \to 0$ limit, Eq. (37) reduces to $\rho(\mathbf{r}) = (M/6\pi^2)k_F^3$, from which

$$k_F(\mathbf{r}) = \left[\frac{6\pi^2\rho(\mathbf{r})}{M}\right]^{1/3}. \tag{38}$$

Finally, substitution of Eq. (37) into Eq. (36) and integration over **u** give

$$E_X[\rho] = -\frac{M}{8\pi^3}\int k_F^4(\mathbf{r})\,d\mathbf{r} = -C_M\int \rho^{4/3}(\mathbf{r})\,d\mathbf{r}, \tag{39}$$

where

$$C_M = \frac{3}{4}\left(\frac{6}{M\pi}\right)^{1/3}. \tag{40}$$

For $M = 2$ (the fermions are electrons), Eq. (39) reduces to the conventional LDA of Eq. (31).

E. Generalized spin-scaling relation

Spin-scaling relations connect two forms of the same functional appropriate for one total and for multiple spin densities [3]. In particular, the spin-scaling relation applicable to exchange energy functionals of electron densities ($M = 2$) is [24]

$$E_X[\rho_\alpha, \rho_\beta] = \tfrac{1}{2}(E_X[2\rho_\alpha] + E_X[2\rho_\beta]). \tag{41}$$

Let us extend this relation to fermions of arbitrary spin by applying the argument of Ref. [24].

According to Eq. (18), the total exchange energy is a sum of separate σ-spin contributions,

$$E_X[\rho_\alpha, \rho_\beta, \ldots] = \sum_{\sigma=1}^{M} E_X[0, \ldots, \rho_\sigma, \ldots, 0]. \tag{42}$$

In a spin-unpolarized system of fermions, $\rho_\sigma = \rho/M$, so one should have

$$E_X[0, \ldots, \rho_\sigma, \ldots, 0] = \frac{1}{M}E_X[M\rho_\sigma]. \tag{43}$$

Combination of Eqs. (42) and (43) gives

$$E_X[\rho_\alpha, \rho_\beta, \ldots] = \frac{1}{M}\sum_{\sigma=1}^{M} E_X[M\rho_\sigma], \tag{44}$$

which generalizes Eq. (41) to arbitrary spin.

A fully spin-polarized density of electrons ($M = 2$) can be viewed as an equal unpolarized density of zero-spin fermions ($M = 1$). From this it follows that the LDA exchange functional appropriate for a fully spin-polarized electron density is given by Eq. (39) with $M = 1$. The last result is traditionally obtained in a different way, by applying Eq. (41) to Eq. (31). Thus, the spin-scaling relations are manifestations of the s dependence of exchange functionals. Specifically, a spin-density exchange functional for spin-s particles is a sum of $2s + 1$ total-density forms of the same functional for spin-zero particles.

F. Exchange functionals for fermions of arbitrary spin

Density-functional approximations such as LDA, generalized gradient approximations (GGA) [25], and others [26] were originally developed for electrons ($s = 1/2$). The results of the preceding sections suggest that the exchange parts of those functionals also apply to Coulombically repelling unit-charge fermions of arbitrary spin s, after a simple modification of constant prefactors.

In particular, the LDA exchange functional for an arbitrary s is given by Eq. (39). Every GGA exchange for spin-s fermions must have the form

$$E_X[\rho] = -C_M\int \rho^{4/3}(\mathbf{r})F_X(\gamma)\,d\mathbf{r}, \tag{45}$$

where $F_X(\gamma)$ is an appropriate enhancement factor of the dimensionless reduced gradient

$$\gamma = \frac{|\nabla\rho|}{2k_F\rho} = \frac{|\nabla\rho|}{2(6\pi^2/M)^{1/3}\rho^{4/3}}, \tag{46}$$

where we used Eq. (38). The analytic form of $F_X(\gamma)$ is assumed to be the same for all s values. To adapt a hybrid exchange functional [27] to a given s, one would need to combine the M-dependent exact exchange functional given by Eq. (27) with an M-dependent GGA of Eq. (45). Modifications to account for non-unit charges of the interacting particles are also straightforward [14].

G. Many-particle self-interaction error

The dependence of W on particle spins also has implications for the notion of self-interaction error (SIE). It is a trivial fact that the exact particle-particle interaction energy for a single particle should be zero,

$$W = E_X[\rho] + E_J[\rho] = 0 \quad (N = 1). \tag{47}$$

As implied by Eq. (29), the exact exchange functional satisfies this condition. An approximate exchange functional $\tilde{E}_X[\rho]$ that violates Eq. (47) is said to have a one-particle SIE equal to

$$\Delta_1 = \tilde{E}_X[\rho] + E_J[\rho]. \tag{48}$$

The condition $\Delta_1 = 0$ has been generalized [28] to a fractional electron number as

$$\tilde{E}_X[q\rho] + E_J[q\rho] = 0 \quad (0 < q < 1), \tag{49}$$

where ρ is a one-particle density.

The SIE concept for $N \leqslant 1$ is therefore well understood [28–30]. By contrast, the many-electron SIE lacks a satisfactory definition [30–34]. One approach [29] to the

TABLE I. Coulomb energies and one- and two-electron SIEs of various exchange-only functionals. All quantities were evaluated using HF/UGBS2P densities and are in units of E_h.

		Δ_N			
System	$E_J[\rho]$	LDA	PBE	TPSS	LC-ωPBE
		$N = 1$			
H	0.3125	0.0445	0.0066	0.0000	−0.0002
He^+	0.6250	0.0889	0.0131	0.0000	0.0075
Li^{2+}	0.9375	0.1334	0.0197	0.0000	0.0152
Be^{3+}	1.2500	0.1778	0.0262	0.0000	0.0223
H_2^+[a]	0.3308	0.0426	0.0017	−0.0070	−0.0034
		$N = 2$			
H^-	0.8012	0.0517	−0.0024	−0.0058	−0.0086
He	2.0515	0.1417	0.0122	−0.0045	0.0002
Li^+	3.3034	0.2311	0.0258	−0.0041	0.0160
Be^{2+}	4.5541	0.3202	0.0392	−0.0039	0.0307
H_2[a]	1.1280	0.0737	0.0021	−0.0101	−0.0074

[a] $R_{HH} = 2.0a_0$.

many-particle SIE is to define this quantity as

$$\mathrm{SIE} = \sum_{\sigma}\sum_{i=1}^{N_\sigma}(\tilde{E}_X[\rho_{i\sigma}] + E_J[\rho_{i\sigma}]), \tag{50}$$

where $\rho_{i\sigma} = |\phi_{i\sigma}|^2$ and $\phi_{i\sigma}$ are the orthonormal occupied orbitals. Since the right-hand side of Eq. (50) is not invariant under unitary transformations of the orbitals, it has been argued [35] that the proper choice of orbitals is the one which minimizes the total SIE-corrected energy. Other proposed definitions of the N-electron SIE involve many-electron wave functions [31], orbital-dependent quantities [32], density matrices [36], and plots of the total energy as a function of the fractional electron number [33].

In view of Eq. (29), we point out that, for N-particle systems in which all particles occupy one spatial orbital, the many-particle SIE of exchange functionals can be defined as

$$\Delta_N = \tilde{E}_X[\rho] + \frac{1}{N}E_J[\rho], \tag{51}$$

where ρ is a one-orbital density. For systems to which it applies, Eq. (51) is equivalent to Eq. (50) but has the conceptual advantage over the latter by being fashioned after the unambiguous Eq. (48). The exact exchange functional appropriate for spin-s particles would give $\Delta_N = 0$ for every admissible N ($N \leqslant M$ for fermions, any N for bosons).

Table I shows that the constraints $\Delta_1 = 0$ and $\Delta_2 = 0$ are generally violated by approximate exchange functionals of the electron density. The calculations were carried out with the Gaussian program [37] using the augmented universal Gaussian basis set (UGBS2P). The LDA has the greatest Δ_1 and Δ_2. The Perdew-Burke-Ernzerhof (PBE) GGA [25] and the Tao-Perdew-Staroverov-Scuseria (TPSS) meta-GGA [38] have smaller Δ_1 and Δ_2 by an order of magnitude. The range-separated hybrid LC-ωPBE is not radically better than PBE according to the Δ_N metric, even through the LC-ωPBE total energy varies almost linearly as a function of the fractional electron number [39].

The TPSS case is particularly instructive. The exchange part of this functional was designed to be exact for one-orbital two-electron exponential densities [38]. By Eq. (41), this implies that the TPSS exchange is also exact for one-electron exponential densities. As a consequence, the TPSS exchange gives $\Delta_1 = 0$ for the exponential densities of one-electron atomic ions and $\Delta_2 \approx 0$ for the approximately exponential densities of two-electron atomic cations. For densities that are not even approximately exponential (as in H_2^+ and H_2), the Δ_N errors of TPSS are greater.

IV. CONCLUSION

The idea to analyze the explicit s dependence of exact and approximate exchange energies is fruitful and leads to useful insights. In particular, the spin-scaling relation for exchange functionals emerges as a link between analytic expressions of a given $E_X[\rho]$ for $s > 0$ and that for $s = 0$. This means that any exchange functional developed for electrons can be readily adapted to fermions of any spin by a simple change of M-dependent prefactors. This conclusion is practically relevant to multicomponent density-functional theory [40–42] and to the theory of finite systems with uniform particle densities [43].

The explicit s dependence of exchange functionals may also serve as a framework for developing approximate functionals of the total electron density as opposed to spin-density functionals [44,45]. Our results imply that it might be meaningful to treat the factor M in Eqs. (39) and (45) as an $\mathbf{r}$-dependent function whose value depends on how much $\rho(\mathbf{r})$ is spin polarized.

Last but not least, the s dependence of the exact exchange functional motivates a rigorous definition of the many-particle SIE by Eq. (51) for systems where all particles occupy the same spatial orbital. This definition is practically useful because it furnishes informative tests for approximate exchange-energy functionals.

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