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Derivation and reinterpretation of the Fermi–Amaldi functional

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ABSTRACT

The Fermi–Amaldi correction to the electrostatic self-repulsion of the particle density is usually regarded as a semi-classical exchange functional that happens to be exact only for one- and closed-shell two-electron systems. We show that this functional can be derived quantum-mechanically and is exact for any number of fermions or bosons of arbitrary spin as long as the particles occupy the same spatial orbital. The Fermi–Amaldi functional is also size-consistent for such systems, provided that the factor N in its expression is understood as an orbital occupation number rather than the total number of particles. These properties of the Fermi–Amaldi functional are ultimately related to the fact that it is a special case of the self-exchange energy formula. Implications of our findings are discussed.

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A key objective of density-functional theory (DFT) is to devise accurate, broadly applicable approximations to the generally unknown total energy functional of the electron density. Explicit density functionals that are exact for a particular class of many-particle systems are especially prized as starting points and guides for developing practical density-functional approximations.[1–7]

The electrostatic self-repulsion (Coulomb) energy of the particle density $\rho(\mathbf{r})$,

$$E_J[\rho] = \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}', \tag{1}$$

is the simplest approximation to the electron–electron interaction energy, W. The model $W = E_J[\rho]$ is notably employed in the Thomas–Fermi theory[8–10] and is known to have poor accuracy for real atoms and molecules. For one-electron systems in particular, the exact W is zero, whereas $E_J[\rho]$ gives a spurious non-zero value known as the one-electron self-interaction error. The difference between $E_J[\rho]$ and the exact W grows with electron number N, more so if N is fractional.[11,12] Within the Kohn-Sham DFT,[13] the self-interaction error and all other shortcomings of $E_J[\rho]$ are supposed to be corrected by the exchange-correlation functional.[14]

Fermi and Amaldi[15] recognized the self-interaction problem with $E_J[\rho]$ early on and proposed a simple scaling correction that is usually justified as follows.[10,16,17] In a system of N indistinguishable electrons, electron i can be associated with an average one-electron density $\rho_i(\mathbf{r}) = \rho(\mathbf{r})/N$. Under this assumption, each electron experiences the Coulomb potential of the remaining $N-1$ electrons, given by

$$\tilde{v}(\mathbf{r}) = \sum_{i=1}^{N-1}\int \frac{\rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' = \frac{N-1}{N}\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \tag{2}$$

The total electron–electron interaction energy is then

$$W^{\mathrm{FA}}[\rho] = \frac{1}{2}\sum_{i=1}^{N}\int \rho_i(\mathbf{r})\tilde{v}(\mathbf{r})d\mathbf{r} = \frac{N-1}{N}E_J[\rho], \tag{3}$$

which one can write more suggestively as

$$W^{\mathrm{FA}}[\rho] = E_J[\rho] - \frac{1}{N}E_J[\rho]. \tag{4}$$

The second term on the right-hand side of Eq. (4) is the Fermi–Amaldi correction to $E_J[\rho]$.

Under uniform coordinate scaling of the density,[18] the Fermi–Amaldi correction behaves like the exchange energy of the Kohn–Sham DFT and, therefore, may be treated as an approximate exchange functional

$$E_X^{\mathrm{FA}}[\rho] = -\frac{1}{N}E_J[\rho] = -NE_J[\rho/N]. \tag{5}$$

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One may also regard the term $-E_J[\rho]/N$ as approximating the exchange-correlation energy.[19] The spin-polarized version of Eq. (5) can be obtained either by retracing the original argument for spin-polarized systems[20] or by applying the spin-scaling relation[21] to Eq. (5) with N treated as a density functional.

The following facts about the Fermi–Amaldi correction are well known.[19]

(1) $E_X^{\mathrm{FA}}[\rho]$ gives the Hartree–Fock (HF) exchange energy for one- and closed-shell two-electron systems.
(2) Energies, densities, and other properties obtained using Eq. (4) are generally poor relative to both experimental and HF values.
(3) The Kohn–Sham potential derived from $E_X^{\mathrm{FA}}[\rho]$ decays asymptotically as $-1/r$, which is the correct behavior of exact exchange-correlation potentials for Coulombic systems.[22]
(4) The Fermi–Amaldi correction is not size-consistent: in the limit of infinite separation between two systems A and B, $E_X^{\mathrm{FA}}[\rho_A + \rho_B] \neq E_X^{\mathrm{FA}}[\rho_A] + E_X^{\mathrm{FA}}[\rho_B]$.

Due to its low accuracy for many-electron atoms and molecules, the Fermi–Amaldi exchange functional is not used for energy calculations on its own. Instead, it serves as an ingredient of other density-functional approximations[23–27] or as a source of "guide potentials" in Kohn–Sham inversion[28–30] and optimized effective potential techniques.[31–33]

We will now show that the Fermi–Amaldi correction can be derived without any semi-classical assumptions. The derivation will reveal that, with a proper reinterpretation of the factor N, the Fermi–Amaldi functional is size-consistent and exact for an entire class of many-particle systems. A number of other insights will result.

Consider a system of N identical particles, either fermions or bosons, each with a spin quantum number s ($s = 0, 1/2, 1, 3/2, \ldots$). The total number of spin states of each particle is $2s + 1$, referred to as spin multiplicity. In self-consistent field theories, particles are described by spin-orbitals, that is, one-particle wavefunctions of the form $\psi(\mathbf{x}) = \phi(\mathbf{r})\sigma(\omega)$, where $\phi(\mathbf{r})$ is a spatial orbital, $\sigma(\omega)$ is a one-particle spin function, and $\mathbf{x} = (\mathbf{r}, \omega)$ is a collective coordinate of the particle.

If all N particles occupy the same spatial orbital, say $\phi_1(\mathbf{r})$, then the normalized molecular orbital wavefunction of the system can be written as

$$\Phi = \phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2)\cdots\phi_1(\mathbf{r}_N)\Theta(\omega_1, \omega_2, \ldots, \omega_N), \tag{6}$$

where Θ is an N-particle spin function normalized to unity. The function Φ should be either symmetric (for bosons) or antisymmetric (for fermions) with respect to particle interchange. The symmetry of Φ is determined solely by Θ. The restriction to one spatial orbital implies that $N \leq 2s + 1$ if the particles are fermions. For bosons, N is unlimited.

Let us evaluate the expectation value of the particle–particle Coulomb repulsion operator

$$\hat{W} = \sum_{i<j}^{N} \frac{1}{r_{ij}}, \tag{7}$$

with the wavefunction of Eq. (6). Since $\hat{W}$ is spin-independent, the factor Θ is irrelevant. It does not even have to be a spin eigenfunction. Each term $1/r_{ij}$ contributes equally, and the number of such terms is the number of all possible pairs of particles. Therefore,

$$W = \langle\Phi|\hat{W}|\Phi\rangle = \frac{N(N-1)}{2} J_{11}, \tag{8}$$

where

$$J_{11} = \iint \frac{|\phi_1(\mathbf{r}_1)|^2 |\phi_1(\mathbf{r}_2)|^2}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \tag{9}$$

is the Coulomb integral. The total particle density derived from Φ is

$$\rho(\mathbf{r}) = N|\phi_1(\mathbf{r})|^2, \tag{10}$$

so the total Coulomb energy is just

$$E_J[\rho] = \frac{N^2}{2} J_{11}. \tag{11}$$

Combining Eqs. (8) and (11), we arrive at Eq. (4).

Thus, the Fermi–Amaldi correction of Eq. (5) is the exact exchange functional for any N-particle system described with a product of N spin-orbitals that have one common spatial part. The nature of the particles (fermions or bosons) and the behavior of the total wavefunction under particle interchange are irrelevant.

Exchange interactions within one spatial orbital are known as self-exchange.[11,34] The logic leading to Eq. (11) shows that, at least in one-orbital systems, the self-exchange has nothing to do with the indistinguishability of particles or their spins but depends only on $E_J[\rho]$ and N. This occurs because the Coulomb repulsion operator is spin-independent.

The above derivation of Eq. (5) suggests that there exists an intimate connection between the Fermi–Amaldi functional and the self-exchange energy. To elucidate this relationship in its full extent, we consider expectation values of $\hat{W}$ for three different types of many-particle wavefunctions, namely, Hartree products, Slater determinants, and permanents.

A simple Hartree product of orthonormal spin-orbitals has the form

$$\Phi_H = \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\cdots\psi_N(\mathbf{x}_N). \tag{12}$$

The expectation value of $\hat{W}$ with this wavefunction is

$$\begin{aligned} W = \langle\Phi_H|\hat{W}|\Phi_H\rangle &= \sum_{i<j}^{N} [ii|jj] \\ &= \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} [ii|jj] - \frac{1}{2}\sum_{i=1}^{N} [ii|ii], \end{aligned} \tag{13}$$

where

$$[ij|kl] = \iint \psi_i^*(\mathbf{x}_1)\psi_j(\mathbf{x}_1) r_{12}^{-1} \psi_k^*(\mathbf{x}_2)\psi_l(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \tag{14}$$

is the standard quantum chemistry notation for two-particle repulsion integrals in terms of spin-orbitals.[35] Simple Hartree products of orthonormal orbitals are uncommon in modern quantum chemistry but can be conceptually and practically useful.[36]

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A Slater determinant is a fully antisymmetrized linear combination of Hartree products, as appropriate for fermions. It is given by

$$\Phi_F = \frac{1}{(N!)^{1/2}} \sum_{k=1}^{N!} (-1)^{p_k} \hat{P}_k \{\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\cdots\psi_N(\mathbf{x}_N)\}, \tag{15}$$

where $\hat{P}_k$ is the operator generating the kth permutation of the particles and p_k is the number of transpositions associated with that permutation. The expectation value of $\hat{W}$ with Φ_F is[35]

$$W = \langle \Phi_F | \hat{W} | \Phi_F \rangle = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} ([ii|jj] - [ij|ji]). \tag{16}$$

For bosons, the properly symmetrized linear combination of Hartree products is a permanent of spin-orbitals. A minor complication with permanents is that they may contain any particular spin-orbital more than once. Let the number of distinct occupied spin-orbitals be K ($1 \le K \le N$) and let m_i be the occupation number of the ith spin-orbital. Introducing K group functions defined by

$$g_i(m) = \psi_i(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\cdots\psi_i(\mathbf{x}_m), \tag{17}$$

we write the normalized permanent for $N = \sum_{i=1}^{K} m_i$ bosons as[37]

$$\Phi_B = \frac{\sum_{k=1}^{N!} \hat{P}_k \{g_1(m_1)g_2(m_2)\cdots g_K(m_K)\}}{(N!m_1!m_2!\cdots m_K!)^{1/2}}. \tag{18}$$

The factors $m_i!$ in the denominator account for the fact that permutations within each group $g_i(m)$ do not change the N-particle spin-orbital product. The expectation value of $\hat{W}$ with Φ_B is[37]

$$W = \langle \Phi_B | \hat{W} | \Phi_B \rangle = \frac{1}{2} \sum_{i=1}^{K} m_i(m_i - 1)[ii|ii] + \sum_{i<j}^{K} m_i m_j([ii|jj] + [ij|ji]). \tag{19}$$

To proceed further, we need to convert Eqs. (13), (16), and (19) to equivalent expressions in terms of spatial orbitals. We assume that each of the wavefunctions Φ_H, Φ_F, and Φ_B is constructed from K distinct spin-orbitals ($K = N$ for Φ_H and Φ_F, but $K \le N$ for Φ_B) given by

$$\psi_i(\mathbf{x}) = \phi_{i\sigma}(\mathbf{r})\sigma(\omega), \tag{20}$$

where $\phi_{i\sigma}(\mathbf{r})$ is the spatial part of $\psi_i(\mathbf{x})$. We will also need the occupation numbers of $\phi_{i\sigma}(\mathbf{r})$, which we denote by $n_{i\sigma}$. For fermions, all $n_{i\sigma} = 1$. For bosons, $n_{i\sigma} = m_i$.

According to Eqs. (13), (16), and (19), the wavefunctions Φ_H, Φ_F, and Φ_B constructed from a given set of K spin-orbitals generally produce different expectation values W. We will now see that all three values become equal if the orbitals $\phi_{i\sigma}(\mathbf{r})$ have zero differential overlap (ZDO) for like spins, that is,

$$\phi_{i\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r}) = 0 \quad \text{everywhere for } i \ne j. \tag{21}$$

The ZDO condition is less stringent than the requirement of infinite separation between $\phi_{i\sigma}(\mathbf{r})$ and $\phi_{j\sigma}(\mathbf{r})$, which will be invoked later to discuss the issue of size-consistency. Note also that Eq. (21) refers to molecular orbitals, not to atomic basis functions as in the ZDO approximation to the HF method.[38]

For a fixed set of K spin-orbitals, Φ_H, Φ_F, and Φ_B produce the same total particle density,

$$\rho(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^{K} n_{i\sigma} |\phi_{i\sigma}(\mathbf{r})|^2, \tag{22}$$

and hence the same Coulomb self-repulsion energy,

$$E_J[\rho] = \frac{1}{2} \sum_{\sigma} \sum_{\tau} \sum_{i=1}^{K} \sum_{j=1}^{K} n_{i\sigma} n_{j\tau} J_{ij}^{\sigma\tau}, \tag{23}$$

where τ is an alternative spin index and

$$J_{ij}^{\sigma\tau} = \iint \frac{|\phi_{i\sigma}(\mathbf{r}_1)|^2 |\phi_{j\tau}(\mathbf{r}_2)|^2}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2. \tag{24}$$

Equations (22)–(24) hold for any set of orthonormal spin-orbitals, not only for ZDO orbitals.

Now consider Eqs. (13), (16), and (19) for systems described with ZDO orbitals. All integrals $[ii|ii]$ and $[ii|jj]$ appearing in these expressions survive the spin integration to give $J_{ii}^{\sigma\sigma}$ and $J_{ij}^{\sigma\tau}$, respectively. The integrals $[ij|ji]$ survive only if the ZDO spin-orbitals $\psi_i(\mathbf{x})$ and $\psi_j(\mathbf{x})$ are identical (the result is $J_{ii}^{\sigma\sigma}$). Using these rules, we obtain the same final result in all three cases,

$$W = E_J[\rho] + E_X^{\text{self}}[\rho], \tag{25}$$

where $E_J[\rho]$ is given by Eq. (23) and

$$E_X^{\text{self}}[\rho] = -\frac{1}{2} \sum_{\sigma} \sum_{i=1}^{K} n_{i\sigma} J_{ii}^{\sigma\sigma} \tag{26}$$

is the total self-exchange energy. In fact, Eq. (25) holds not just for Φ_H, Φ_F, and Φ_B, but for any normalized linear combination of permuted products $\hat{P}_k\Phi_H$ of ZDO orbitals.

Introducing particle densities associated with individual orbitals,

$$\rho_{i\sigma}(\mathbf{r}) = n_{i\sigma} |\phi_{i\sigma}(\mathbf{r})|^2, \tag{27}$$

and using the fact that

$$E_J[\rho_{i\sigma}] = \frac{n_{i\sigma}^2}{2} J_{ii}^{\sigma\sigma}, \tag{28}$$

we rewrite the self-exchange energy of Eq. (26) as an orbital-dependent density functional[11]

$$E_X^{\text{self}}[\rho] = -\sum_{\sigma} \sum_{i=1}^{K} \frac{E_J[\rho_{i\sigma}]}{n_{i\sigma}}. \tag{29}$$

For ZDO orbitals, this functional is identical with the full exact exchange but, unlike the latter, is not invariant under any unitary transformation of $\{\phi_{i\sigma}\}$ that breaks the ZDO condition.[39] Quantities whose definitions are tied to a particular set of orbitals are not uncommon. The average local ionization energy[40–42] is another example.[43]

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So far, we have used the spin-unrestricted formalism. To obtain the spin-restricted version of Eq. (29), we assume that all $\phi_{i\sigma}(\mathbf{r})$ with a given i are identical and equal to $\phi_i(\mathbf{r})$. The occupation number of $\phi_i(\mathbf{r})$ is

$$n_i = \sum_\sigma n_{i\sigma}, \tag{30}$$

and the associated orbital density is

$$\rho_i(\mathbf{r}) = n_i|\phi_i(\mathbf{r})|^2. \tag{31}$$

Repeating the arguments following Eq. (26) for this special case, we obtain

$$E_X^{\text{self}}[\rho] = -\sum_{i=1}^{K} \frac{E_J[\rho_i]}{n_i}. \tag{32}$$

Equations (29) and (32) can be further simplified if all distinct spatial orbitals are equally occupied and infinitely separated from one another. Examples of such systems include all one-electron atoms and ions, all closed-shell two-electron systems in the spin-restricted Hartree–Fock (RHF) formalism, infinitely stretched H_2 in the spin-unrestricted Hartree–Fock (UHF) formalism, systems consisting of any number of infinitely separated ground-state He atoms, infinitely stretched $HeLi^+$, etc. Counterexamples are Li and Be atoms and He atom clusters at finite inter nuclear separation R.

In the limit of infinite mutual separation of all distinct occupied spatial orbitals, the system consists of noninteracting one-orbital fragments, so the total Coulomb energy becomes strictly additive over fragment densities. If, in addition, each fragment contains the same number of particles, say n, both Eqs. (29) and (32) reduce to the following explicit functional of the total density:

$$E_X^{\text{self}}[\rho] = -\frac{1}{n}E_J[\rho]. \tag{33}$$

This functional looks like the Fermi–Amaldi correction of Eq. (5) except that it contains n instead of N in the denominator. Unlike the original Fermi–Amaldi functional, however, Eq. (33) is manifestly size-consistent. For one-orbital systems, where $n = N$, Eq. (33) becomes identical with Eq. (5).

Thus, the Fermi–Amaldi correction is essentially a special case of the self-exchange energy formula. Since the self-exchange is the exact exchange for ZDO orbitals, Eq. (33) is also exact for any Hartree product, Slater determinant, or permanent in which all distinct spatial orbitals are infinitely separated and equally occupied. This is possible within both the RHF and UHF formalisms.

Table I confirms that the revised Fermi–Amaldi functional of Eq. (33) is exact for a Slater determinant involving infinitely separated spatial orbitals of equal occupation n. For electrons, $n = 2$ within the RHF formalism and $n = 1$ within the UHF formalism. The ratio E_J/E_X^{HF} is exactly n in all cases. We used the nearly saturated universal Gaussian basis set[44] (UGBS) here, but the same conclusions would have been reached using any basis set.

When applied to many-particle systems with non-ZDO orbitals such as found in atoms (Table II), Eqs. (29), (32), and (33) are only approximations to the exact exchange. The accuracy of Eqs. (29) and (32) is determined by how closely the distinct occupied orbitals satisfy the ZDO condition. Atomic orbitals overlap substantially,

TABLE I. Examples of Slater determinants (Φ_F) for which the revised Fermi–Amaldi correction of Eq. (33) is identical with the HF exchange functional. The energies (in units of E_h) were calculated using the HF/UGBS orbitals.

System[a]	Φ_F	N	n	E_J	E_X^{HF}
H	UHF	1	1	0.312 500	−0.312 500
H_2 $(R \to \infty)$	UHF	2	1	0.625 000	−0.625 000
H_2 $(R \to \infty)$	RHF	2	2	0.512 932	−0.256 466
He	RHF	2	2	2.051 538	−1.025 769
He_2 $(R \to \infty)$	RHF	4	2	4.103 076	−2.051 538
He_4 $(R_{ij} \to \infty)$	RHF	8	2	8.206 152	−4.103 076
$HeLi^+$ $(R \to \infty)$	RHF	4	2	5.354 911	−2.677 455

[a] R is the internuclear distance.

TABLE II. HF, LDA, and Fermi–Amaldi-type exchange energies (in units of E_h) for various atoms. The HF and LDA values are self-consistent and calculated using the DGDZVP basis set. The Fermi–Amaldi-type energies are evaluated using the HF/DGDZVP orbitals.

Atom	N	HF	LDA	Eq. (5)	Eq. (32)[a]
He	2	−1.0245	−0.8534	−1.0245	−1.0245
Be	4	−2.6379	−2.2799	−1.7766	−2.5863
Ne	10	−12.0603	−10.9414	−6.6099	−10.0575
Mg	12	−15.9332	−14.5314	−7.9754	−13.0864
Ar	18	−30.0902	−27.7605	−12.8533	−23.3047
Ca	20	−35.1146	−32.5100	−14.2346	−26.8845
Zn	30	−69.5781	−65.4080	−25.8884	−48.3889
Kr	36	−93.5924	−88.3718	−32.4969	−62.9519
Cd	48	−148.7203	−141.3078	−46.5337	−94.3478
Xe	54	−178.8458	−170.3750	−53.2975	−110.9894
Error[b]		0.0%	8.5%	51.2%	22.0%

[a] Self-exchange evaluated using canonical HF orbitals.
[b] Mean absolute percentage error with respect to the HF values.

which explains the large relative error of $E_X^{\text{self}}[\rho]$ in terms of canonical orbitals (22.0%). This result can be improved to 17.3% by using the Edmiston–Ruedenberg orbitals[39] that minimize the inter-orbital repulsion (not included in Table II). The 22.0% error of Eq. (32) is better than the 51.2% error of Eq. (5) but poorer than the 8.5% accuracy of the local density approximation (LDA). The revised Fermi–Amaldi functional of Eq. (33) gives dismal results for real atoms (>300% error, not included in Table II) because it is based on the drastic assumption that $J_{ij} = 0$ for $i \neq j$, which does not hold for atoms even approximately.

The Fermi–Amaldi correction and self-exchange are often present in self-interaction correction schemes.[11,45–47] In particular, the Vosko–Wilk scheme[45] for an arbitrary exchange functional $E_X[\rho]$ may be written in the spin-unpolarized form as

$$E_X^{\text{VW}}[\rho] = E_X[\rho] - N(E_X[\rho/N] + E_J[\rho/N]). \tag{34}$$

The right-hand side of Eq. (34) contains the conventional Fermi–Amaldi correction, as pointed out by Engel and Dreizler.[48]

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The Perdew–Zunger scheme[11] applied to an arbitrary $E_X[\rho]$ in the spin-unpolarized form is

$$E_X^{\mathrm{PZ}}[\rho] = E_X[\rho] - \sum_{i=1}^{K}\left(E_X[\rho_i] + \frac{1}{2}E_J[\rho_i]\right), \tag{35}$$

where $K = N/2$ and $\rho_i(\mathbf{r}) = 2|\phi_i(\mathbf{r})|^2$. Here, the right-hand side contains the self-exchange functional of Eq. (32) for electrons $(n_i = 2)$.

The proposed theory of the Fermi–Amaldi correction also suggests that, at least for one-orbital densities, the many-particle self-interaction error can be defined unambiguously. As shown above, Eq. (5) is the exact exchange functional for any permissible number of particles (fermions or bosons) occupying one spatial orbital. This implies that the quantity

$$\Delta_N = E_X[\rho] + \frac{1}{N}E_J[\rho] \tag{36}$$

should vanish for any N-particle one-orbital density ($N \le 2s + 1$ for spin-s fermions). An approximate exchange functional $E_X[\rho]$ that violates the condition $\Delta_N = 0$ for a particular N can be said to have an N-particle self-interaction error of magnitude $|\Delta_N|$. Evaluation of Δ_N for standard exchange functionals of the electron density gives instructive results.[49]

In summary, we have shown that the Fermi–Amaldi correction of Eq. (5) is the exact exchange functional for any system of fermions or bosons described with a product of spin-orbitals that share the same spatial part. The symmetry of this product under particle interchange is irrelevant. The Fermi–Amaldi functional becomes size-consistent for such one-orbital systems if the denominator N is understood as an orbital occupation number rather than the total number of particles. Our derivation also reveals that the Fermi–Amaldi correction is in effect a special case of the orbital-dependent self-exchange energy formula. More precisely, the self-exchange energy functional of Eq. (29) reduces to the Fermi–Amaldi-type pure density functional of Eq. (33) for systems with equally occupied and infinitely separated orbitals.

The self-exchange is equivalent to the full exact exchange for systems where occupied same-spin orbitals have ZDO. This is why fully localized molecular orbitals are best suited for the Perdew–Zunger self-interaction correction scheme.[11,46] For real atoms and molecules, Eqs. (29) and (33) are not exact and their errors reflect the extent to which the orbitals used in the calculation violate the ZDO and infinite separation conditions, respectively.

The analytic form of the exact functionals of Eqs. (5) and (33) serves as a reminder that the exact universal density functional must depend explicitly on the particle number.[50,51] The fact that orbital occupation numbers naturally arise in rigorously derived density functionals such as $E_X^{\mathrm{FA}}[\rho]$ lends support to the broader use of orbital occupancies as ingredients of density-functional approximations.

This work also has implications for the Levy–Perdew–Sahni DFT,[52] an alternative to the Kohn–Sham scheme based on a Schrödinger-like differential equation for the square root of the electron density. The revised Fermi–Amaldi functional of Eq. (33) gives the exact exchange energy of the fictitious one-orbital reference system of the Levy–Perdew–Sahni scheme, and is to that theory what the HF-type exchange functional is to the Kohn–Sham DFT. In other words, Eq. (33) is the "exact exchange" of the Levy–Perdew–Sahni DFT. Such realizations revive the hopes of devising usefully accurate approximations to the Levy–Perdew–Sahni universal functional and thereby fulfilling the promise of orbital-free DFT.[53]

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Ivan P. Bosko: Conceptualization (equal); Methodology (equal); Software (lead); Writing – original draft (equal); Writing – review & editing (supporting). **Viktor N. Staroverov**: Conceptualization (equal); Funding acquisition (lead); Methodology (equal); Writing – original draft (equal); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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