Exchange energy functional from a Pauli correlation-factor model

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Abstract

The spherical average of the Hartree–Fock second-order density matrix is approximated through an ansatz similar to that proposed by McWeeny for the exact second-order density matrix. This leads to the definition of a Pauli correlation factor which produces the exchange hole. In this work, the Pauli correlation factor is modeled in order to obtain an exchange energy density functional. The factor satisfies the normalization condition of the second-order density matrix. Numerical results are presented for the atoms He–Ar.

Introduction

Many works have already been published dealing with the search for a good exchange energy functional, an important unknown part of the density functional theory [1]. In recent years, the generalized gradient approximations (GGAs) to the exchange energy functional, and to the correlation and exchange-correlation energy functionals, have reached relatively good accuracy in their numerical predictions [2–5]. The GGA is based on a partial resummation of the complete gradient expansion of the homogeneous electron gas functionals, including only first gradients of the density (for a critical discussion of GGAs, see Ref. 6). Despite the success of the GGA it is still interesting to search for other models more directly related to the second- or first-order density matrix and which do not use in any way the homogeneous electron density approximation. Atomic and molecular densities are certainly not homogeneous. In this vein, perhaps the most successful approach is that by Colle

and Salvetti [7] for the correlation energy, which in its density functional version [8] yields competitive numerical results. Other approaches more directly related to the present work are those of Lee and Parr [9] and Fuentealba [10] for the exchange-correlation energy, and Moscardó and San-Fabian [11] for the correlation energy. They are all based on modeling the spherical averaged second-order reduced density matrix. In this work the same route is followed to derive an exchange energy functional.

Theory

For an atomic or molecular system of N electrons ($N = N^\alpha + N^\beta$; N^α electrons of spin α and N^β electrons of spin β) the electronic density can be written in its spin components as

$$\rho(\vec{r}) = \rho^\alpha(\vec{r}) + \rho^\beta(\vec{r}) \tag{1}$$

and in a similar way, the second-order density matrix is written as

$$\rho_2(\vec{r}, \vec{r}') = \rho_2^{\alpha\alpha}(\vec{r}, \vec{r}') + \rho_2^{\alpha\beta}(\vec{r}, \vec{r}')$$
$$+ \rho_2^{\beta\alpha}(\vec{r}, \vec{r}') + \rho_2^{\beta\beta}(\vec{r}, \vec{r}') \tag{2}$$

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[1] Contribution No. 1.

The normalization conditions read

$$\int \rho^\sigma(\vec{r})\mathrm{d}\vec{r} = N^\sigma \qquad (3)$$

$$\iint \rho_2^{\sigma\sigma}(\vec{r},\vec{r}\,')\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' = \frac{N^\sigma(N^\sigma - 1)}{2} \qquad (4)$$

$$\iint \rho_2^{\sigma\sigma'}(\vec{r},\vec{r}\,')\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' = \frac{N^\sigma N^{\sigma'}}{2} \quad (\sigma \ne \sigma') \qquad (5)$$

where σ and σ' denote the possible spin components α or β.

By using Eq. (2) the electron–electron interaction energy can be written

$$E_{\text{e-e}} = \sum_{\sigma\sigma'} \iint \frac{\rho_2^{\sigma\sigma'}(\vec{r},\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' \qquad (6)$$

The wave function is antisymmetric so $\rho_2^{\sigma\sigma'}$ must have the property

$$\rho_2^{\sigma\sigma'}(\vec{r},\vec{r}\,') = \rho_2^{\sigma\sigma'}(\vec{r}\,',\vec{r}) \qquad (7)$$

and only its spherical average is needed to evaluate Eq. (6). This is an important conclusion because it reduces the problem from six to four variables.

Introducing the interparticle coordinates

$$\vec{r} = \tfrac{1}{2}(\vec{r} + \vec{r}\,') \qquad \vec{s} = \vec{r} - \vec{r}\,' \qquad (8)$$

the spherical average of ρ_2 is defined as

$$\rho_2(\vec{r},s) = \frac{1}{4\pi}\int \rho_2(\vec{r},\vec{r}\,')\mathrm{d}\Omega_s \qquad (9)$$

where the integral is over the angular variables of the vector $\vec{s}$.

Now, we restrict ourselves to modeling the spherical average part of the like-spin Hartree–Fock second-order density matrix, which is sufficient to evaluate the exchange energy. The matrix elements representing an electron pair of unlike spin do not contribute to the exchange energy. Hence they are not considered. For a spin-like electron pair, the ansatz

$$\rho_{2,\text{HF}}^{\sigma\sigma}(\vec{r},s) = \tfrac{1}{2}\Gamma^{\sigma\sigma}(\vec{r},s)[1 - F^\sigma(\vec{r},s)] \qquad (10)$$

is proposed, where

$$\Gamma^{\sigma\sigma'}(\vec{r},s) = \frac{1}{4\pi}\int \rho^\sigma(\vec{r} + \frac{\vec{s}}{2})\rho^{\sigma'}(\vec{r} - \frac{\vec{s}}{2})\mathrm{d}\Omega_s \qquad (11)$$

is the spherical average of the product $\rho^\sigma(\vec{r_1})$ $\rho^{\sigma'}(\vec{r_2})$.

The Pauli correlation factor $F^\alpha(\vec{r},s)$ is the generator of the exchange hole and responsible for the exchange energy.

Putting Eq. (10) into Eq. (6) and considering Eqs. (8), (9) and (11), the resulting equation for the electron–electron interaction energy is

$$E_{\text{e-e}} = 2\pi \sum_{\sigma,\sigma'} \left[\iint \Gamma^{\sigma\sigma'}(\vec{r},s)s\,\mathrm{d}s\,\mathrm{d}\vec{r} \right.$$
$$\left. - \iint \Gamma^{\sigma\sigma}(\vec{r},s)F^\sigma(\vec{r},s)s\,\mathrm{d}s\,\mathrm{d}\vec{r} \right] \qquad (12)$$

The first term on the right-hand side of Eq. (12) corresponds to the classical repulsion energy associated with $\rho(\vec{r})$, and the second is the exchange energy

$$E_{\text{x}} = -2\pi \sum_{\sigma} \iint \Gamma^{\sigma\sigma}(\vec{r},s)F^\sigma(\vec{r},s)s\,\mathrm{d}s\,\mathrm{d}\vec{r} \qquad (13)$$

Equation (13) is exact. However, it does not express the exchange energy as a functional of the density. To do this, it is necessary to model both terms under the integral signs. The first term can be expanded in a Taylor series around $s = 0$ [12] and, following Lee and Parr [9], summed over to yield a gaussian form

$$\Gamma^{\sigma\sigma}(\vec{r},s) = \rho^\sigma(\vec{r})^2 \mathrm{e}^{-s^2/\beta(\vec{r})} \qquad (14)$$

To a first approximation $\beta(\vec{r})$ is a function of $\vec{r}$ instead of a functional of ρ.

The principal contribution of this paper is to model the Pauli correlation factor $F(\vec{r},s)$ through the ansatz

$$F^\sigma(\vec{r},s) = \mathrm{e}^{-s^2/\gamma(\vec{r})}\left[1 - C^\sigma s^4 \rho^{4/3}\right] \qquad (15)$$

which is strongly motivated by a Taylor expansion similar to that of the first-order density matrix [12]. A similar expression has been used in a different context in Refs. 9 and 13. However, its validity can only be proved through numerical results. For a different ansatz, see Ref. 14. C^σ is a parameter to be determined. For the function $\gamma(\vec{r})$ and for $\beta(\vec{r})$

Table 1
Exchange energy (a.u.)

Atom	C^α	C^β	E_x^α	E_x^β	E_x	E_x (HF)	Deviation (%)
He	0.102	0.102	0.487	0.487	0.974	1.026	5
Li	0.357	0.082	0.812	0.786	1.598	1.781	10
Be	0.106	0.106	1.271	1.271	2.542	2.667	5
B	0.246	−0.041	1.880	1.732	3.612	3.744	4
C	0.315	−0.157	2.805	2.200	5.005	5.045	1
N	0.354	−0.250	4.061	2.673	6.734	6.596	2
O	0.268	−0.113	4.689	3.510	8.199	8.174	0.3
F	0.187	0.015	5.356	4.616	9.972	10.00	0.2
Ne	0.108	0.108	6.055	6.055	12.11	12.11	0
Na	0.212	0.100	6.662	6.977	13.64	14.02	3.0
Mg	0.109	0.109	8.014	8.014	16.02	15.99	0.2
Al	0.178	0.068	8.840	9.153	17.99	18.07	0.4
Si	0.231	0.041	9.886	10.23	20.12	20.28	0.8
P	0.269	0.020	11.17	11.28	22.45	22.64	0.8
Cl	0.155	0.065	13.92	13.89	27.81	27.51	1.0
Ar	0.109	0.109	15.29	15.29	30.58	30.19	1.0

in Eq. (14) a simple dimensional analysis suggests

$$\beta(\vec{r}) = k_1 \rho^{-2/3} \tag{16}$$

and

$$\gamma(\vec{r}) = k_2 \rho^{-2/3} \tag{17}$$

Substituting Eqs. (14) and (15) into Eq. (13) and expressing the exchange energy in terms of its spin contributions as $E_x = E_x^\alpha + E_x^\beta$, the equation obtained is

$$E_x^\sigma = (2\pi C^\sigma k_{12}^3 - \pi k_{12})$$
$$\times \int \frac{\rho^\alpha(\vec{r})^2}{\rho(\vec{r})^{2/3}} \, d\vec{r} \qquad (\sigma = \alpha, \beta) \tag{18}$$

Equation (18) is the working equation of this paper. It permits the exchange energy for electronic systems to be evaluated. Note that for closed shell atoms it transforms in a X_α approximation of the kind $K \int \rho^{4/3} d\vec{r}$, where the constant K depends on the number of electrons. There are three parameters $(C^\alpha, C^\beta$ and $k_{12})$ to deal with; k_{12} is a parameter formed by the quotient $k_1 k_2/(k_1 + k_2)$; thus, it is not necessary to determine $\beta(\vec{r})$ and $\gamma(\vec{r})$ independently. To evaluate C^α and C^β one can resort to the normalization condition of Eq. (4). Inserting into Eq. (4) the corresponding model of $\rho_{2,\text{HF}}^{\sigma\sigma}$, the

equation obtained is

$$N^\sigma = \left[(\pi k_{12})^{3/2} - \frac{15}{4} C^\sigma \pi^{3/2} k_{12}^{7/2} \right]$$
$$\times \int \frac{\rho^\sigma(\vec{r})^2}{\rho(\vec{r})} \, d\vec{r} \qquad (\sigma = \alpha, \beta) \tag{19}$$

which permits us to determine C^α and C^β, having only k_{12} as an adjustable parameter.

Results and discussion

All the calculations were done using as input the Hartree–Fock atomic wave functions given by Clementi and Roetti [15]. The parameter k_{12} was fitted to obtain the Hartree–Fock exchange energy of the Ne atom. The value of 0.5525 was obtained.

The calculated exchange energies for the atoms He–Ar are presented in Table 1, together with the values of the parameters C^α and C^β, which are determined through Eq. (19). The Hartree–Fock values for the exchange energy are also presented to compare with. Except for the lighter atoms, the deviations are almost always lower than 1%. This is a promising result in view of the method's being only a local approximation with only one adjustable parameter.

Table 2
Comparison of atomic exchange energies (a.u.)

Atom	LDA[a]	Becke[a]	This work	E_x (HF)
He	0.884	1.024	0.974	1.026
Li	1.538	1.774	1.598	1.781
Be	2.312	2.659	2.542	2.667
B	3.272	3.732	3.612	3.744
C	4.459	5.037	5.005	5.045
N	5.893	6.594	6.734	6.596
O	7.342	8.179	8.199	8.174
F	9.052	10.03	9.972	10.00
Ne	11.03	12.15	12.11	12.11
Na	12.79	14.05	13.64	14.02
Mg	14.61	16.02	16.02	15.99
Al	16.53	18.09	17.99	18.07
Si	18.59	20.29	20.12	20.28
P	20.79	22.64	22.45	22.64
Cl	25.35	27.51	27.81	27.51
Ar	27.86	30.18	30.58	30.19

[a] Ref. 4.

In Table 2 the results of this paper are compared with two other models for the exchange energy functional. The widely used local density approximation (LDA) given by

$$E_x^{LDA} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\int(\rho_\alpha^{4/3} + \rho_\beta^{4/3})\mathrm{d}\vec{r} \qquad (20)$$

comes from the homogeneous electron gas model. The gradient corrected approach of Becke [4]

$$E_x^B = E_x^{LDA}$$

$$-\beta\sum_\sigma\int\frac{(\nabla\rho_\sigma)^2}{\rho_\sigma^{4/3}}\left[1 + \gamma\frac{(\nabla\rho_\sigma)^2}{\rho_\sigma^{8/3}}\right]^{-4/5}\mathrm{d}\vec{r} \qquad (21)$$

is based on an exchange hole model.

Table 2 shows that Eqs. (18) and (19) of this paper give results considerably better than the LDA but not as good as the results using Becke's functional. This is reasonable because our approach takes account of the inhomogeneous atomic density near $s = 0$, so it is better than the LDA, but it does not include gradient corrections, so it is not a competitor of Becke's functional.

The approach followed in this paper is not only interesting because of its numerical predictions, which could be improved, for instance, by introducing gradient corrections, but also for its direct connection with the second-order density matrix. This permits us to think of better models using more information than the normalization condition. The sum rule could be good at improving the modeling of the Pauli correlation factor.

The approach followed in this paper can also be analyzed as the spin polarization extension of the local density approximation introduced by Lee and Parr [9] under the name "modified gaussian approximation". For the noble gas atoms the improvement in the results is clear.

Acknowledgment

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