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Approximate exchange energy as a functional of the electron density. Light atoms[a]

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We derive an expression for the exchange energy integral in terms of the density for the case of light atoms containing s and p electrons. We start from an approximate functional form of the density matrix for an electron cloud in the presence of an attractive nucleus. An important restriction to consider is the Pauli principle. A correction factor is included to account for the multipole expansion in an average way. The results we obtain, both for closed and open shells, are within a few percent of the exact exchange integral.

I. INTRODUCTION

An approximate expression for the exchange integral for electron systems was proposed by Dirac,[1] and since then it has been extensively used, particularly in the X_α model.[2] The exchange integral stems from a typically quantum effect, namely the antisymmetrization of the N-electron wave function, hence, it does not have such a direct electrostatic interpretation as the Coulomb energy. The exchange energy is defined in terms of the density matrix, rather than the density. For the ground state however, it has been shown[3] that the total energy (including the electronic correlation) can be, in principle, expressed as a functional of the local density.

Dirac's approximation was originally introduced as a correction to the Thomas–Fermi model. It is an exact expression for the case of a homogeneous electron gas. The electron orbitals are taken as plane waves in the Fermi sea. For the case of a large number of electrons N, where statistical approximations are suitable, it is very good. For smaller N, however, it becomes poorer. On the other hand, it is in this case that the exchange energy is a sizeable fraction of the total energy, so a better approximation is called for.

The density for atoms in their ground state $\rho(r)$ varies smoothly, but is far from being constant. It is a monotonically decreasing function of r, and its logarithm has an almost constant slope piecewise.[4] This has led us to an approximation for the exchange potential[5] different from the one based on the homogeneous electron gas. A remarkable feature of this potential is that it has a correct asymptotic behavior, in contrast to the electron gas[6,7] and the X_α model.[2] This follows essentially from (a) considering an attractive nucleus, which immediately yields a Coulomb-type tail at large distances, and (b) incorporating the Pauli principle in the approximate functional form of the density matrix, which implies a correct normalization of the Fermi hole.

The computation of the exchange energy is more demanding than its corresponding potential. The main reason being that both idempotency of the density matrix and normalization of the total density are required to obtain a correct value of the integral. While this is automatically fulfilled in the homogeneous electron gas model, it is not a trivial matter for the case of more realistic inhomogeneous electron models. Making use of the multipole expansion for the electronic repulsion, we have been able to derive an expression which accounts for these two restrictions in an exact way, for the largest portion of the integral. The remainder is then evaluated with the aid of the approximate functional form used for the potential.[5] We deal first with the case of closed shells, and for open shell atoms we calculate the average exchange integral[8] with a slight modification, as explained in Sec. III.

Section II derives the approximate form of the exchange energy as a functional of the density, separating the large monopole contribution. In Sec. III we present numerical results for atoms with s and p electrons. Finally in Sec. IV we draw some general conclusions.

II. FUNCTIONAL FORM OF THE EXCHANGE ENERGY

We shall work with the spinless density matrix $\gamma(r_1, r_2)$ normalized to $\frac{1}{2}N$ throughout this paper. The extension to the local spin density formalism is straightforward. The starting point is the separation of the monopole term in the multipole expansion of the interelectronic repulsion:

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{4\pi}{2k+1} \frac{r_<^k}{r_>^{k+1}} Y_{km}^*(\Omega_1) Y_{km}(\Omega_2) , \qquad (2.1)$$

where, as usual, $r_<(r_>)$ denotes the smaller (greater) of r_1 and r_2 and Y_{km} are the spherical harmonics. Hence the exchange energy can be written also as a summation over k:

$$-E_x \equiv \int \frac{|\gamma(r_1, r_2)|^2}{r_{12}} dr_1 dr_2 = \sum_{k=0}^{\infty} I_k \qquad (2.2)$$

in atomic units. The integrals I_k are given by:

$$I_k = \sum_m \frac{4\pi}{2k+1} \int |\gamma(\mathbf{r}_1, \mathbf{r}_2)|^2 \frac{r_<^k}{r_>^{k+1}} Y_{km}^*(\Omega_1) Y_{km}(\Omega_2) d\mathbf{r}_1 d\mathbf{r}_2$$

$$(2.3)$$

The largest contribution to (2.2) is the first term, which is explicitly given by:

$$I_0 = \int d\mathbf{r}_1 \int d\Omega_2 \left(\frac{1}{r_1} \int_0^{r_1} |\gamma(\mathbf{r}_1, \mathbf{r}_2)|^2 r_2^2 dr_2 \right.$$

$$\left. + \int_{r_1}^{\infty} |\gamma(\mathbf{r}_1, \mathbf{r}_2)|^2 r_2 dr_2 \right) .$$

$$(2.4)$$

Completing the first integral form 0 to ∞, this can be rewritten as:

$$I_0 = \int d\mathbf{r}_1 \left(\frac{1}{r_1} \int |\gamma|^2 dr_2 + \int d\Omega_2 \int_{r_1}^{\infty} |\gamma|^2 \left(\frac{1}{r_2} - \frac{1}{r_1} \right) r_2^2 dr_2 \right) .$$

$$(2.5)$$

The integral over dr_2 can be performed exactly for the first term, in the case where γ is a Fock–Dirac density matrix. Again, this is the largest of the two terms in (2.5), as shall be shown in Sec. III. The second term is negative since $r_2 > r_1$ in the integral. Using the idempotency condition:

$$\int \gamma(\mathbf{r}_1, \mathbf{r}_2) \gamma(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_2 = \gamma(\mathbf{r}_1, \mathbf{r}_3) \qquad (2.6)$$

for the case $\mathbf{r}_1 = \mathbf{r}_3$, we obtain the first term in (2.5) directly as a functional of the density $\rho(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$. Hence a crude estimate of the exchange energy can be already written as:

$$I_0^{(1)} = \int \frac{\rho(\mathbf{r})}{r} d\mathbf{r} \quad (\text{a.u.}) \qquad (2.7)$$

with

$$\int \rho(\mathbf{r}) d\mathbf{r} = \frac{N}{2} . \qquad (2.8)$$

Before considering the second term in Eq. (2.5) let us pause for a moment to analyze (2.7). Since $\rho(\mathbf{r})$ gives the charge distribution of electrons in the atom, Eq. (2.7) can be interpreted as a minus first moment. In fact, it is equal in value to the nuclear (repulsion) integral for a unit charge $(Z = -1)$. Furthermore, comparing Eq. (2.7) with the Coulomb energy, with Eq. (2.8) in mind,

$$E_c = 2 \int \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \qquad (2.9)$$

gives a result for $I_0^{(1)}$ of the order of N times smaller, as it should, since we expect $I_0^{(1)}$ to be the main contribution to the atomic exchange energy. Secondly, since the contribution for $k \neq 0$ in Eq. (2.2) is negative, as well as the second term in Eq. (2.5), there is a partial cancellation between the two of them. For small N, where the former term $(k \neq 0)$ has a small magnitude (zero if only s electrons are present), $I_0^{(1)}$ overestimates the value of the exchange energy. For larger N, the trend will be reversed.

Let us now focus our attention on the second term in Eq. (2.5). A very good approximation obtains by using the approximate functional form[5]:

$$\gamma(\mathbf{r}_1, \mathbf{r}_2) \simeq A \exp[-\eta(r_1 + r_2)] . \qquad (2.10)$$

TABLE I. Exchange energy for closed shell atoms with s electrons.

Atom	E_x (a.u.)			
	present[a]	exact	Dirac[c]	$-E_{tot}$ (SCF)[b]
He	1.0694	1.0258	0.8841	2.86167
Be	2.6790	2.6664	2.3126	14.57237

[a] Equations (2.12) and (2.13) in the text.
[b] The density is calculated using the double ζ basis of Ref. 10.
[c] Equation (2.14) in the text. The last column is the total SCF energy with the same double ζ basis (Ref. 10).

For slowly varying $\eta(\mathbf{r})$ and evaluating A from the idempotency condition, Eq. (2.6), we obtain:

$$\int d\Omega_2 \int_{r_1}^{\infty} |\gamma|^2 \left(\frac{1}{r_2} - \frac{1}{r_1} \right) r_2^2 dr_2 \simeq - \frac{\rho(r_1)}{r_1} (1 + \eta \cdot r_1) e^{-2\eta r_1}$$

$$(2.11)$$

Hence

$$I_0[\rho(\mathbf{r}), \eta(\mathbf{r})] \simeq \int \frac{\rho}{r} [1 - (1 + \eta r) e^{-2\eta r}] d\mathbf{r} \qquad (2.12)$$

where η is a function of $\mathbf{r}$, obtained from the density as:

$$\eta(\mathbf{r}) = - \frac{1}{2} \frac{1}{\rho(\mathbf{r})} [\nabla \rho(\mathbf{r}) \cdot \nabla \rho(\mathbf{r})]^{1/2} . \qquad (2.13)$$

Hence the gradient of the density appears in a natural way in view of the particular form of the inhomogeneity of the electron density of atomic systems (cf. Ref. 9).

In Table I we present results for two closed shell systems, He and Be, where the expression (2.12) is directly applicable, since only I_0 contributes in the case of s electrons. The density ρ was calculated using the optimized double ζ orbitals, Slater-type orbitals (STO) from Clementi and Roetti.[10] Comparison with the exact evaluation of the exchange integral using the same set of orbitals, yields an error of 0.043 a.u. and 0.008 a.u. for He and Be, respectively. The value for the Dirac approximation (in a.u.):

$$-E_x^D[\rho(\mathbf{r})] = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int [2\rho(\mathbf{r})]^{4/3} d\mathbf{r} \qquad (2.14)$$

is also shown in Table I, as well the total self-consistent field (SCF), with the same basis set.

We should finally notice, en passant, that for the trivial case of the hydrogen atom, the expression (2.12) is exact. Hence it is cancelled by the self interaction of the Coulomb integral (2.9). In this case there is no spurious many-body contribution for the H atom.

III. RESULTS FOR s AND p ELECTRON ATOMS

Two corrections to Eq. (2.12) are considered in this section. The first one is the multipole correction, i.e., including higher values of k in the sum in Eq. (2.2). The second one appears only for open shell systems, where we want to compute a configuration average.

In case there are p electrons present, we want to estimate a correction I_2 in a simple fashion. The term $k = 1$ arises only from s-p interactions in this case, so we will disregard it. For $k = 2$, the angular integration

TABLE II. Average exchange energy for atoms from He to Ar.

Atom	$-I_0^{(1)}$ (a.u.)[a]	present[b]	$-E_x$ (a.u.) exact[c]	Dirac[d]	E_{tot} (SCF)[e] (Slater average)
He	1.6873	1.0694	1.0258	0.8841	2.86167
Li	2.7714	1.7586	1.7227	1.4612	7.43272
Be	4.2042	2.6790	2.6664	2.3126	14.57237
B	5.4374	3.5268	3.5760	3.0217	24.52792
C	6.8222	4.6245	4.6695	3.8735	37.65748
N	8.4498	6.0476	6.0174	4.9747	54.29135
O	10.3896	7.8320	7.6526	6.4303	74.76388
F	12.7312	10.0252	9.6640	8.3953	99.40132
Ne	15.5599	12.6787	12.1190	11.0409	128.53512
Na	17.6421	14.0308	13.9700	12.7150	161.85003
Mg	19.9618	15.7918	15.9989	14.6144	199.60700
Al	22.0911	17.5233	17.9632	16.3546	241.87306
Si	24.3030	19.4157	20.0496	18.1849	288.83128
P	26.6465	21.5128	22.2898	20.1753	340.64511
S	29.1569	23.8369	24.6944	22.3889	397.47589
Cl	31.8819	26.4044	27.3162	24.9200	459.47963
Ar	34.8638	29.2246	30.1879	27.8652	526.81513

[a]Equation (2.7) in the text with the average density Eq. (3.5).
[b]Equations (3.4) and (3.5) in the text.
[c]Equation (3.3) in the text, using the double ζ basis of Ref. 10.
[d]Equation (2.14) in the text, using the average density Eq. (3.5).
[e]The total SCF energy with the double ζ basis (Ref. 10), but using the Slater average over configurations (Ref. 8).

in Eq. (2.3) yields[8] a Gaunt coefficient $c^{(2)}$ (p, p) and only the p-p interactions contribute. We shall estimate it by taking a factor proportional to the number of p electrons present and taking into account the extra power of r due to the behavior at the origin:

$$\gamma_{pp}(\mathbf{r}_1, \mathbf{r}_2) \simeq \frac{N - N_s}{N} r_1 r_2 \gamma(\mathbf{r}_1, \mathbf{r}_2) \ , \qquad (3.1)$$

where N_s is the number of s electrons. An estimate of I_2 is hence given by:

$$I_2 \simeq \left(1 - \frac{N_s}{N}\right) c^{(2)}(p0; p0) I_0 \ , \qquad (3.2)$$

and this will be enough for our present purposes.

Let us next consider the case of open shell atoms. The average energy (defined in Ref. 8) is a weighted mean over the possible configurations arising from the open shell. A glance at expressions (2.7) and (2.8) indicates that the appropriate modification for open shells is to compute the density and its norm $\bar{N}$ as a weighted mean. One aspect, however, requires additional thought. In both the Coulomb integral (2.9) and exchange energy (2.2) we have included the self interaction term (which obviously cancels out for the *exact* expressions). This implies that the mean over configurations must include this term. The usual average[8] is performed over all *different* pairs of electrons in the open shell for the Coulomb plus exchange energy. We instead, shall define a modified weighted average including the self interacting pair. In terms of the Slater integrals G^k, we have (in a.u.):

$$-\bar{E}_x = \frac{1}{2} \sum_{ij} \frac{N_i N_j}{2} [(2l_i + 1)(2l_j + 1)]^{-1/2}$$

$$\times \sum_k c^{(k)}(l_i 0; l_j 0) G_k(i, j) \qquad (3.3)$$

the summation over shells i, j unrestricted. Here N_i is the occupation number of shell i.

From the considerations above, the approximate exchange energy, both for open and closed shells, in case of s and p electrons, is given (in a.u.) by:

$$-E_x[\bar{\rho}(r)] = \left(1 + \frac{2}{5} \frac{\bar{N}_p}{\bar{N}}\right) \int \frac{\bar{\rho}}{r} [1 - (1 + \bar{\eta}r) e^{-2\bar{\eta}r}] dr \ , \qquad (3.4)$$

where we have already substituted the value $\frac{2}{5}$ of $c^{(2)}$ (p, p) (Ref. 8). The quantities in (3.4) are defined thus:

$$\bar{\rho}(r) = \frac{1}{2} \sum_i \frac{N_i^2}{4l_i + 2} R_{n_i l_i}^2(r) \ , \qquad (3.5a)$$

$$\bar{\eta}(r) = -\frac{1}{2\bar{\rho}} [\nabla \bar{\rho} \cdot \nabla \bar{\rho}]^{1/2} \ , \qquad (3.5b)$$

$$\bar{N} = \sum_i \frac{N_i^2}{4l_i + 2} \ , \qquad (3.5c)$$

with $\bar{\rho}$ normalized to $\frac{1}{2} \bar{N}$. Table II includes the value of the mean exchange energy computed with Eqs. (3.5), using double ζ basis.[10] Comparison is made with the exact mean exchange as defined in (3.3) and Dirac's expression Eq. (2.14) with $\bar{\rho}$, using the same basis set. We have also included the raw estimate $I_0^{(1)}$ from Eq. (2.7) using again $\bar{\rho}$. We note immediately that for heavier atoms, the estimate becomes better. The error in (3.4) is only a few percent of the exact value (3.3) and is obviously much smaller with respect to the total energy.

IV. CONCLUSIONS

The main result of this paper is given in Eqs. (3.5). The approximate exchange energy is very good for atoms with s and p electrons. We have limited ourselves to

this case, because it is precisely for few electron atoms that the homogeneous electron gas approximation fails. Hence Eqs. (3.5) should be preferred in these cases. The approximation should be very useful for core electrons in molecules. This is particularly suited for linear combination of atomic orbitals (LCAO) calculations, where atomic orbitals are used explicitly.

Unlike the electron gas model, the inversion problem of expressing the integrands in I_k, Eq. (2.3) in terms of the density (and its gradient) does not have a unique solution. This is an unfortunate situation, which we had already remarked in connection with the local exchange potential.[5] It is precisely for this reason that Eq. (2.7) is so useful in our case. Since it only relies on the idempotency of γ and its trace, it is independent of the particular form of the density matrix. Hence we can use expression (2.7) in two different ways: (a) as a guideline to find a more exact functional form, as we did in Eq. (2.11); (b) as a rough estimate of the exchange energy, particularly for larger N.

We can include in principle the contributions from d, $f, \ldots$ electrons in a fashion similar to the development in Sec. III for p electrons. In practice, however, the inaccuracies introduced with such an oversimplified treatment induces one to use simpler expressions like Eq. (2.7) or the statistical approximation for larger N values. Further developments are being pursued, however, in order to improve upon the accuracy, both for small and large number of electrons.

ACKNOWLEDGMENT

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