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Approximate Calculation of the Correlation Energy for the Closed Shells

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A formula is derived for the approximate calculation of the correlation energy, starting from knowledge of the one-electron and two-electron density matrices, calculated by the Hartree-Fock method.

The results that we have obtained in test calculations seem to be accurate enough (average error 2.5 %, highest error 8 %)

Key word: Correlation energy for closed shells

The scope of this research is the approximate determination of the correlation energy, starting from knowledge of the one-electron and two-electron density matrices, previously calculated by other methods, for example, using the H.F. equations. The method which we are proposing, extends the formula initially discovered by Wigner [1] and subsequently elaborated by various authors [2].

We maintain that this line of research is significant in as far as absolute *ab initio* calculations of the correlation energy are extremely laborious.

Let us consider, for simplicity, a closed shell and let $\Psi_{\text{H.F.}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$ be the one-determinant H.F. function where $\boldsymbol{x}_i$ indicates all the spatial and spin coordinates of the electron i. Let us write the correlated function of the system in the form:

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \Psi_{\text{H.F.}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) \prod_{i>j} (1 - \varphi(\boldsymbol{r}_i, \boldsymbol{r}_j)) \tag{1}$$

where $\boldsymbol{r}_i$ indicates all the spatial coordinates of the electron i. The function $\varphi(\boldsymbol{r}_i, \boldsymbol{r}_j)$ is thus defined:

$$\varphi(\boldsymbol{r}_i, \boldsymbol{r}_j) = \exp(-\beta^2 r^2)\left(1 - \Phi(\boldsymbol{R})\left(1 + \frac{r}{2}\right)\right) \tag{2}$$

where $r = |\boldsymbol{r}_i - \boldsymbol{r}_j|$; $\boldsymbol{R} = \frac{1}{2}(\boldsymbol{r}_i + \boldsymbol{r}_j)$.

Let us note that with this definition of the function $\varphi(\boldsymbol{r}_i, \boldsymbol{r}_j)$, (1) fulfils all the conditions of the cusp for $\boldsymbol{r}_i \to \boldsymbol{r}_j$ as demonstrated by Bingel [3]. It is clear from (1) and (2) that when the electrons are far apart the function is reduced to that of H.F., on the other hand, when a pair of electrons collide, the function becomes:

$$\Psi = \Psi_{\text{H.F.}} \Phi\left(\frac{\boldsymbol{r}_i + \boldsymbol{r}_j}{2}\right).$$

The region in which the function $\varphi(\mathbf{r}_i, \mathbf{r}_j)$ is appreciably different from zero depends on the value of β. The volume of this region may be taken to be:

$$V = 4\pi \int_0^\infty \exp(-\beta^2 r^2) r^2 \, dr = \frac{\pi^{3/2}}{\beta^3}. \tag{3}$$

In order to determine a reasonable value for β, let us assume that the volume given in (3) is proportional to the volume of exclusion in Wigner's formula [1]. Then one finds:

$$\frac{\pi^{3/2}}{\beta^3} = k\varrho^{-1}\,; \qquad \beta = k^{-1/3}\pi^{1/2}\varrho^{1/3} = q\varrho^{1/3}, \tag{4}$$

where ϱ indicates the electronic density and k the average number of the electrons in V.

Let us consider the two-electron density matrix without spin [4]:

$$\begin{aligned} P_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = N(N-1) \int & \Psi_{\text{H.F.}}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N) \prod_{i>j} (1 - \varphi(\mathbf{r}_i, \mathbf{r}_j)) \\ & \cdot (1 - \varphi(\mathbf{r}'_i, \mathbf{r}'_j)) \Psi_{\text{H.F.}}(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_3, \ldots, \mathbf{x}_N) \, d\mathbf{r}_3 \ldots d\mathbf{r}_N \, ds_1 \ldots ds_N \end{aligned} \tag{5}$$

(5) can be written:

$$\begin{aligned} P_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = {} & P_{2\text{H.F.}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) (1 - \varphi(\mathbf{r}_1, \mathbf{r}_2) - \varphi(\mathbf{r}'_1, \mathbf{r}'_2) + \varphi(\mathbf{r}_1, \mathbf{r}_2)\varphi(\mathbf{r}'_1, \mathbf{r}'_2)) \\ & \prod_{\substack{i>j\geqq 1 \\ i\neq 2}} (1 - \varphi(\bar{\mathbf{r}}_i, \bar{\mathbf{r}}_j) - \varphi(\bar{\mathbf{r}}_i, \bar{\mathbf{r}}'_j) + \varphi(\bar{\mathbf{r}}_i, \bar{\mathbf{r}}_j)\, \varphi(\bar{\mathbf{r}}_i, \bar{\mathbf{r}}'_j)) \end{aligned}$$

where $\bar{\mathbf{r}}_i, \bar{\mathbf{r}}_j$ are suitable values of $\mathbf{r}_i, \mathbf{r}_j$, obtained applying the mean value theorem. From (2) we have that $\varphi(\bar{\mathbf{r}}_i, \bar{\mathbf{r}}_j) \ll 1$ because of the exponential factor. And so approximately:

$$\begin{aligned} P_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = {} & P_{2\text{H.F.}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) \\ & \cdot (1 - \varphi(\mathbf{r}_1, \mathbf{r}_2) - \varphi(\mathbf{r}'_1, \mathbf{r}'_2) + \varphi(\mathbf{r}_1, \mathbf{r}_2)\varphi(\mathbf{r}'_1, \mathbf{r}'_2)). \end{aligned} \tag{6}$$

From the fact that: $(N-1)P_1(\mathbf{r}_1; \mathbf{r}'_1) = \int P_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2) \, d\mathbf{r}_2$ and from the reasonable assumption:

$$P_1(\mathbf{r}_1, \mathbf{r}'_1) = P_{1\text{H.F.}}(\mathbf{r}_1, \mathbf{r}'_1) \tag{7}$$

one deduces:

$$\int P_{2\text{H.F.}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2) (\varphi(\mathbf{r}_1, \mathbf{r}_2)\varphi(\mathbf{r}'_1, \mathbf{r}_2) - \varphi(\mathbf{r}_1, \mathbf{r}_2) - \varphi(\mathbf{r}'_1, \mathbf{r}_2)) \, d\mathbf{r}_2 = 0 \tag{8}$$

$$E = E_{\text{H.F.}} + \frac{1}{2} \int P_{2\text{H.F.}}(\mathbf{r}_1, \mathbf{r}_2) (\varphi^2(\mathbf{r}_1, \mathbf{r}_2) - 2\varphi(\mathbf{r}_1, \mathbf{r}_2)) \frac{1}{r} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \tag{9}$$

(9) permits the calculation of the correlation energy, starting from knowledge of the $P_{2\text{H.F.}}(\mathbf{r}_1, \mathbf{r}_2)$ calculated at the points: $\mathbf{r}_1 = \mathbf{r}'_1$ and $\mathbf{r}_2 = \mathbf{r}'_2$. From (2) and (7),

with $\boldsymbol{r}_1=\boldsymbol{r}'_1$, we have:

$$\int \Phi^2(\boldsymbol{R}) P_{2\text{H.F.}}(\boldsymbol{r}_1,\boldsymbol{r}_2)\exp(-2\beta^2 r^2)\left(1+\frac{r}{2}\right)^2 d\boldsymbol{r}_2+2\int \Phi(\boldsymbol{R}) P_{2\text{H.F.}}(\boldsymbol{r}_1,\boldsymbol{r}_2)$$
$$\cdot\exp(-\beta^2 r^2)(1-\exp(-\beta^2 r^2))\left(1+\frac{r}{2}\right) d\boldsymbol{r}_2-\int\exp(-\beta^2 r^2)(2-\exp(-\beta^2 r^2))$$
$$\cdot P_{2\text{H.F.}}(\boldsymbol{r}_1,\boldsymbol{r}_2)\, d\boldsymbol{r}_2=0\,. \tag{10}$$

Taking into account that the function $\exp(-\beta^2 r^2)$ decreases rapidly as $r\to\infty$, let us determine the function $\Phi(\boldsymbol{R})$ from the approximated relation that is derived from (10) by removing from under the sign the functions $\Phi(\boldsymbol{R})$ and $P_{2\text{H.F.}}(\boldsymbol{r}_1,\boldsymbol{r}_2)$ calculated at the point $\boldsymbol{r}_1=\boldsymbol{r}_2$. One finds:

$$\Phi^2(\boldsymbol{R})\int\exp(-2\beta^2 r^2)\left(1+\frac{r}{2}\right)^2 d\boldsymbol{r}+2\Phi(\boldsymbol{R})\int\exp(-\beta^2 r^2)(1-\exp(-\beta^2 r^2))$$
$$\cdot\left(1+\frac{r}{2}\right) d\boldsymbol{r}-\int\exp(-\beta^2 r^2)(2-\exp(-\beta^2 r^2))\, d\boldsymbol{r}=0 \tag{11}$$

from which:

$$\Phi^2(\boldsymbol{R})\left(\frac{3}{64}\sqrt{\frac{\pi}{8}}\frac{1}{\beta^2}+\frac{1}{8\beta}+\frac{1}{8}\sqrt{\frac{\pi}{2}}\right)+2\Phi(\boldsymbol{R})\left(\frac{3}{16\beta}-\frac{1}{8}\sqrt{\frac{\pi}{2}}+\frac{\sqrt{\pi}}{4}\right)$$
$$-\frac{\sqrt{\pi}}{2}+\frac{1}{8}\sqrt{\frac{\pi}{2}}=0 \tag{12}$$

the value of Φ in each point $\boldsymbol{R}$ depends only on value of β and thus on the electronic density at the point $\boldsymbol{R}$. It is easily deduced from (12) that:

$$\lim_{\beta\to 0}\Phi=1{,}715\beta\,;\qquad \lim_{\beta\to\infty}\Phi=1-\frac{1}{\sqrt{\pi}}\frac{1}{\beta}\,.$$

Thus, as β varies between 0 and ∞, Φ varies between 0 and 1. An excellent approximation of Φ is given by:

$$\Phi\simeq\frac{\sqrt{\pi}\beta}{1+\sqrt{\pi}\beta} \tag{13}$$

which differs from the exact solution (12) by less than 0.003. Putting $E_c=E-E_{\text{H.F.}}$ and giving Φ the value obtained from (12), one derives from (9):

$$E_c=-\frac{1}{2}\int P_{2\text{H.F.}}(\boldsymbol{r}_1,\boldsymbol{r}_2)\left(2\exp(-\beta^2 r^2)\left(1-\Phi(\boldsymbol{R})\left(1+\frac{r}{2}\right)\right)-\exp(-2\beta^2 r^2)\right.$$
$$\left.\cdot\left(1-\Phi(\boldsymbol{R})\left(1+\frac{r}{2}\right)\right)^2\right)\frac{d\boldsymbol{r}}{r}\,d\boldsymbol{R}$$
$$=-\frac{1}{2}\int P_{2\text{H.F.}}(\boldsymbol{R},\boldsymbol{R})\left(\int\frac{P_{2\text{H.F.}}(\boldsymbol{r}_1,\boldsymbol{r}_2)}{P_{2\text{H.F.}}(\boldsymbol{R},\boldsymbol{R})}\left(2\exp(-\beta^2 r^2)\left(1-\Phi(\boldsymbol{R})\left(1+\frac{r}{2}\right)\right)\right.\right.$$
$$\left.\left.-\exp(-2\beta^2 r^2)\left(1-\Phi(\boldsymbol{R})\left(1+\frac{r}{2}\right)\right)^2\right)\frac{d\boldsymbol{r}}{r}\right)d\boldsymbol{R}\,. \tag{14}$$

Making use of the relationship:

$$\int \frac{\exp(-\beta^2 r^2)}{r} F(\mathbf{r},\mathbf{R})\,d\mathbf{r} = 4\pi F(0,\mathbf{R}) \int_0^\infty \exp(-\beta^2 r^2) r\,dr + \frac{2\pi}{3} (\nabla_r^2 F(\mathbf{r},\mathbf{R}))_{r=0} \cdot \int_0^\infty \exp(-\beta^2 r^2) r^3\,dr\,.$$

ignoring terms of order >2 in the development of the $P_{2\text{H.F.}}\left(\mathbf{R}+\frac{\mathbf{r}}{2};\mathbf{R}-\frac{\mathbf{r}}{2}\right)$ and bearing in mind that $\beta = q\varrho^{1/3}$ and $P_{2\text{H.F.}}(\mathbf{R},\mathbf{R}) = \frac{1}{2}\varrho^2$, (14) now read with: $\left(K = \left(\frac{\nabla_r^2 P_{2\text{H.F.}}\left(\mathbf{R}-\frac{\mathbf{r}}{2};\mathbf{R}+\frac{\mathbf{r}}{2}\right)}{P_{2\text{H.F.}}\left(\mathbf{R}-\frac{\mathbf{r}}{2};\mathbf{R}+\frac{\mathbf{r}}{2}\right)}\right)_{r=0}\right)$:

$$\begin{aligned}
E_c = & -\pi \int \varrho^2(\mathbf{R}) \Bigg(2\int \exp(-\beta^2 r^2)\left(1-\Phi(\mathbf{R})\left(1+\frac{r}{2}\right)\right) r\,dr - \int \exp(-2\beta^2 r^2) \\
& \cdot \left(1-\Phi(\mathbf{R})\left(1+\frac{r}{2}\right)\right)^2 r\,dr + \frac{K}{3}\int \exp(-\beta^2 r^2)\left(1-\Phi(\mathbf{R})\left(1+\frac{r}{2}\right)\right) r^3\,dr \\
& - \frac{K}{6}\int \exp(-2\beta^2 r^2)\left(1-\Phi(\mathbf{R})\left(1+\frac{r}{2}\right)\right)^2 r^3\,dr\Bigg)\,d\mathbf{R} \\
= & -\pi \int \frac{\varrho^2(\mathbf{R})}{\beta^3}\Bigg(2\beta \int \exp(-t^2)\left(1-\Phi(\mathbf{R})\left(1+\frac{t}{2\beta}\right)\right) t\,dt - \frac{\beta}{2}\int \exp(-t^2) \\
& \cdot \left(1-\Phi(\mathbf{R})\left(1+\frac{t}{\beta\sqrt{8}}\right)\right)^2 t\,dt + \frac{K}{3\beta}\int \exp(-t^2)\left(1-\Phi(\mathbf{R})\left(1+\frac{t}{2\beta}\right)\right) t^3\,dt \\
& - \frac{K}{24\beta}\int \exp(-t^2)\left(1-\Phi(\mathbf{R})\left(1+\frac{t}{\beta\sqrt{8}}\right)\right)^2 t^3\,dt\Bigg)\,d\mathbf{R} \\
= & -\frac{\pi}{q^3}\int \varrho(\mathbf{R}) G(\beta,K)\,d\mathbf{R}\,.
\end{aligned} \tag{15}$$

Implementing (13), we obtain the following expression for the $G(\beta,K)$:

$$G(\beta,K) = \frac{0.121 - 0.0167W + 0.0458/\beta - 0.005W/\beta}{1 + 1.1284/\beta + 0.3183/\beta^2} \tag{16}$$

where $W = \frac{K}{\beta^2}$.

This formula suggest the approximation:

$$\begin{aligned}
\int \frac{P_{2\text{H.F.}}(\mathbf{r}_1,\mathbf{r}_2)}{P_{2\text{H.F.}}(\mathbf{R},\mathbf{R})}\Bigg(2\exp(-\beta^2 r^2)\left(1-\Phi(\mathbf{R})\left(1+\frac{r}{2}\right)\right) - \exp(-2\beta^2 r^2) \\
\cdot \left(1-\Phi(\mathbf{R})\left(1+\frac{r}{2}\right)\right)^2\Bigg)\frac{d\mathbf{r}}{r} = \frac{4\pi}{\varrho(\mathbf{R})} H(\beta,W)
\end{aligned} \tag{17}$$

Table 1. Comparison between the values obtained starting from the approximate function (18) and these obtained by the whole numerical integration of the same function starting from (17)

β	W	Approximation	Integral	Error
2.383	−2.109	0.00837	0.00868	−0.00031
2.108	−1.957	0.00843	0.00843	0
1.662	−1.985	0.00799	0.00791	+0.00008
1.481	−2.093	0.00768	0.00763	+0.00005
1.322	−2.251	0.00733	0.00733	0
1.183	−2.456	0.00691	0.00706	−0.00015
1.060	−2.711	0.00650	0.00675	−0.00025
0.692	−4.355	0.00491	0.00541	−0.0005
0.509	−6.546	0.00390	0.00430	−0.0004
0.376	−10.105	0.00313	0.00319	−0.00006

and taking into account (16), we look for a function $H(\beta, W)$ of the type:

$$H(\beta, W)=a\frac{1+bW\exp(-c/\beta)}{1+d/\beta}\,.$$

The exact value of (17) in the simple case of the atom He was calculated numerically at various distances from the nucleus and so was obtained:

$$H(\beta, W)=0.01565\frac{1+0.173\,W\exp(-0.58/\beta)}{1+\dfrac{0.8}{\beta}}\,. \tag{18}$$

The accuracy of this approximation is shown in the Table 1. Using (18) in (14) the formula finally becomes:

$$E_c=-0.04918\int\varrho(\boldsymbol{R})\frac{1+0.173\,W\exp(-0.58/\beta)}{1+\dfrac{0.8}{\beta}}\,d\boldsymbol{R} \tag{19}$$

with $\beta=2.29\,\varrho(\boldsymbol{R})^{1/3}$; $W=0.3814\,\varrho^{-8/3}\left(\nabla_r^2 P_{2\text{H.F.}}\left(\boldsymbol{R}-\frac{r}{2};\boldsymbol{R}+\frac{r}{2}\right)\right)_{r=0}$.

One can check the accuracy of this expression for the correlation energy using the Table 2.

With reference to the approximate expression for the correlation energy, we observe:

a) All the coefficients that appear in (19), were obtained starting from the data relative only to the atom He.

b) The time for the numerical calculation of the integral (19) (a few seconds) is extremely small, compared to the H.F. part of the calculation.

c) The errors, tabulated in Table 2, stay below 8 %, with a mean value of 2.5%.

Despite the fact that the derivation of (19) depends on several rough approximations, this formula nevertheless seems to calculate the correlation energy accurately enough to be applied to many chemical problems.

Table 2. Values of the correlation energy obtained from (19) and compared with those of other authors. The density matrices are calculated using the H.F. functions, which given the reported energy values

System	$E_{\mathrm{H.F.}}$	Correlation Energy (a.u.) This paper	Ref.	Error %
He	− 2.861678 [9]	−0.0416	−0.0420 [5]	1
Li^+	− 7.236413 [9]	−0.0438	−0.0435 [6]	0.7
Be^{++}	− 13.611256 [9]	−0.0441	−0.0443 [6]	0.4
Be	− 14.573014 [9]	−0.0926	−0.0940 [5]	1.5
B^+	− 24.237555 [9]	−0.106	−0.112 [6]	5
Ne	−128.54698 [9]	−0.374	−0.372 [5]	0.5
CH_4	− 40.20452 [10]	−0.289	−0.283 [7]	2
H_2O	− 76.0384 [11]	−0.336	−0.364 [8]	8
			−0.340 [12]	1

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