THE GROUND STATE OF THE HYDROGEN MOLECULE ON THE BASIS OF THE RELATIVISTIC QUANTUM MECHANICS WITH THE AID OF THE WANG WAVE FUNCTION II.

Method for evaluation of the two-centre integrals occuring in the calculation of the retarded magnetic orbit-orbit interaction term

by

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§ 1.

The method of applying BREIT's relativistic two-electron equation to the case of hydrogen molecule is given in [1], dealing with the determination of the relativistic correction energy term of kinetic energy, arising, among others, in course of computation. Others publications [2], [3] contain the evaluation of the first, non-retarded part of the magnetic orbit-orbit interaction term. The Hamiltonion of the magnetic orbit-orbit interaction term is the following:

$$H_2 = \frac{e^2}{2\,m^2\,c^2}\left[\frac{\bar{p}_1\,\bar{p}_2}{r_{12}} + \frac{\sum_{i,j=1}^{3} x_{i_{12}}\,x_{j_{12}}\,p_{i_1}\,p_{j_2}}{r_{12}^3}\right]. \tag{1}$$

(Here the electron's charge is denoted by e, m is its mass, c stands for the velocity of light, $r_{12} = |\bar{r}_1 - \bar{r}_2|$ means the distance between the two electrons in atomic units. Further, $\bar{p}_1 = \frac{\hbar}{i}\,\mathrm{grad}_1$ resp. $\bar{p}_2 = \frac{\hbar}{i}\,\mathrm{grad}_2$ is the quantum mechanical momentum operator for the first resp. the second electron, $x_{i_{12}}$ stands for the i-th component of vector $\bar{r}_{12}$, meaning the difference of the radius vectors of the two electrons, and finally, p_{i_1} resp. p_{i_2} is the i-th component of the momentum operator of the first resp. of the second electron.)

The present paper gives a method to determinate the two-centre integrals occuring in course of computation of the second, retarded part of operator (1).

The evaluation of the energy term arising from the retarded part of Hamilton H_2 may be performed by determining the expectation value of the operator and by substituting in this expression the suitable parameter values. The expectation value in atomic units [4] is given by the integral

$$\bar{H}'' = -\frac{1}{2\,c^2}\int \Psi^*\left(\sum_{i,j=1}^{3}\frac{x_{i_{12}}\,x_{j_{12}}\,p_{i_1}\,p_{j_2}}{r_{12}^3}\right)\Psi\,dV_1\,dV_2, \tag{2}$$

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in which Ψ is the approximate wave function of WANG [5]:

$$\Psi = \frac{\sqrt{\frac{\alpha^3}{\pi}}\left[e^{-\alpha(r_{a_1}+r_{b_2})} + e^{-\alpha(r_{a_2}+r_{b_1})}\right]}{\sqrt{2(1+S^2)}}. \tag{3}$$

Here r_{a_1} and r_{a_2} resp. r_{b_1} and r_{b_2} are the distances of electrons 1 and 2 from nucleus a resp. b (see Fig. 1), α stands for a variation parameter which has

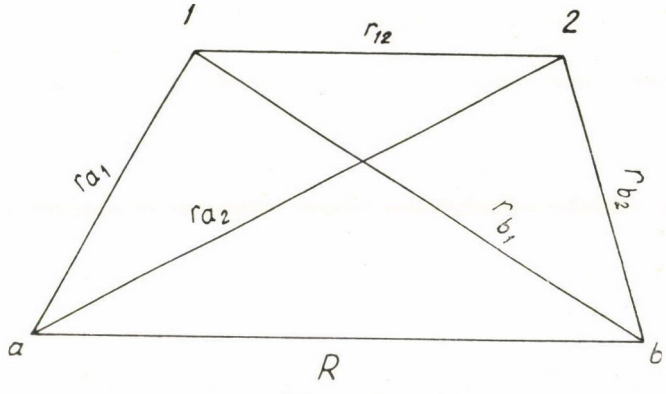

Figure 1.

given, according to WANG's non relativistic calculations, the minimal energy at the value $\alpha = 1{,}17$. Finally,

$$S^2 = \frac{\alpha^2}{\pi^2}\left|\int e^{-\alpha(r_{a_1}+r_{b_1})}\,dV_1\right|^2 = \frac{\alpha^2}{\pi^2}\left|\int e^{-\alpha(r_{a_2}+r_{b_2})}\,dV_2\right|^2 = e^{-2\alpha R}\left(1+\alpha R+\frac{\alpha^2 R^2}{3}\right)^2,$$

where R is the distance between the two nuclei [6].

Substituting into the expression (2) of the expectation value the wave function (3) and the components of the momentum operator expressed also in atomic units, then after having performed the multiplications, we get

$$\overline{H}_2'' = \frac{\alpha^6/2\,\pi^2\,c^2 \int \left\{\left[e^{-\alpha(r_{a_1}+r_{b_2})} + e^{-\alpha(r_{a_2}+r_{b_1})}\right]\frac{1}{r_{12}^3}\left[x_{12}^2\frac{\partial^2}{\partial x_1\,\partial x_2} + \right.\right.}{2(1+S^2)}$$

$$+ y_{12}^2\frac{\partial^2}{\partial y_1\,\partial y_2} + z_{12}^2\frac{\partial^2}{\partial z_1\,\partial z_2} + x_{12}\,y_{12}\left(\frac{\partial^2}{\partial x_1\,\partial y_2} + \frac{\partial^2}{\partial y_1\,\partial x_2}\right) + \tag{4}$$

$$+ x_{12}\,z_{12}\left(\frac{\partial^2}{\partial x_1\,\partial z_2} + \frac{\partial^2}{\partial z_1\,\partial x_2}\right) +$$

$$\left.\left. + y_{12}\,z_{12}\left(\frac{\partial^2}{\partial y_1\,\partial z_2} + \frac{\partial^2}{\partial z_1\,\partial y_2}\right)\right]\left[e^{-\alpha(r_{a_1}+r_{b_2})} + e^{-\alpha(r_{a_2}+r_{b_1})}\right]\right\} dV_1\,dV_2$$

$$2(1+S^2)$$

Taking into account the symmetry of the wave function with respect to the exchange of the two electrons and considering the axial symmetry of the hydrogen molecule, relations similar to equations (16) of [2, 3] between the integrals arising from (4) can be obtained.

Using these relations and performing the differentiations in rectangular coordinate system, after a simple but little lengthy calculation, one get for (4) the expression

$$(5) \qquad \overline{H}_2'' = \frac{\alpha^8}{2\pi^2 c^2} \frac{2\left(I_0^{\mathrm{I}} + I_0^{\mathrm{II}} + I_1^{\mathrm{I}} + I_1^{\mathrm{II}} + I_2^{\mathrm{I}} + I_2^{\mathrm{II}} + \frac{1}{2}\left(I_3^{\mathrm{I}} + I_3^{\mathrm{II}}\right)\right)}{1 + S^2},$$

where

$$(6a) \qquad I_0^{\mathrm{I}} = \int f(r_{a_1}, r_{b_2})\, x_{12}^2\, x_1\, x_2\, dV_1\, dV_2,$$

$$(6b) \qquad I_0^{\mathrm{II}} = \int f(r_{a_2}, r_{b_1})\, x_{12}^2\, x_1\, x_2\, dV_1\, dV_2,$$

$$(6c) \qquad I_1^{\mathrm{I}} = \int f(r_{a_1}, r_{b_2})\, x_{12}\, y_{12}\, x_1\, y_2\, dV_1\, dV_2,$$

$$(6d) \qquad I_1^{\mathrm{II}} = \int f(r_{a_2}, r_{b_1})\, x_{12}\, y_{12}\, x_1\, y_2\, dV_1\, dV_2,$$

$$(6e) \qquad I_2^{\mathrm{I}} = \int f(r_{a_1}, r_{b_2})\, x_{12}\, z_{12}\left[x_1\left(z_2 - \frac{R}{2}\right) + x_2\left(z_1 + \frac{R}{2}\right)\right] dV_1\, dV_2,$$

$$(6f) \qquad I_2^{\mathrm{II}} = \int f(r_{a_2}, r_{b1})\, x_{12}\, z_{12}\left[x_1\left(z_2 + \frac{R}{2}\right) + x_2\left(z_1 - \frac{R}{2}\right)\right] dV_1\, dV_2,$$

$$(6g) \qquad I_3^{\mathrm{I}} = \int f(r_{a_1}, r_{b_1})\, z_{12}^2\left(z_1 + \frac{R}{2}\right)\left(z_2 - \frac{R}{2}\right) dV_1\, dV_2,$$

$$(6h) \qquad I_3^{\mathrm{II}} = \int f(r_{a_2}, r_{b_1})\, z_{12}^2\left(z_1 - \frac{R}{2}\right)\left(z_2 + \frac{R}{2}\right) dV_1\, dV_2;$$

and where

$$(7a) \qquad f(r_{a_1}, r_{b_2}) = \frac{e^{-2\alpha(r_{a_1} + r_{b_2})}}{r_{12}^3 \cdot r_{a_1} \cdot r_{b_2}}$$

$$(7b) \qquad f(r_{a_2}, r_{b_1}) = \frac{e^{-\alpha(r_{a_1} + r_{a_2} + r_{b_2} + r_{b_1})}}{r_{12}^3 \cdot r_{a_2} \cdot r_{b_1}}.$$

As we see I^{I} is the Coulomb term of the expectation value $\overline{H}_2''$, while I^{II} is the exchange term.

Remark: in case of benzene a rough estimation has been carried out in [7] for the spin-orbit interaction term, for an integral similar to (6) containing $1/r_{12}^3$, but the analytical evaluation of such integrals — as far as we know — has not yet been performed.

§ 2.

The two-centre integrals (6a)—(6h) are not expressed in an explicit form. Therefore in this paper we give a method for approximate evaluation of such integrals. As a first step, we deal with integral (6a), the further ones may be calculated in a similar way.

It is easier to handle the integral (6a) if elliptical coordinates are used. As it is well known [8], x_i, y_i, z_i can be expressed in a suitable elliptical coordinate system, in the following way:

$$x_i = \frac{R}{2}\sqrt{(1-\nu_i^2)(\mu_i^2-1)}\cdot\cos\varphi_i$$

$$y_i = \frac{R}{2}\sqrt{(1-\nu_i^2)(\mu_i^2-1)}\cdot\sin\varphi_i \tag{8}$$

$$z_i = \frac{R}{2}\mu_i\nu_i\,,$$

where

$$\mu_i = \frac{r_{a_i}+r_{b_i}}{R}\,, \qquad \nu_i = \frac{r_{a_i}-r_{b_i}}{R}\,.$$

The function $f(r_{a_1}, r_{b_2})$ occuring in the integrand takes now the form

$$f(r_{a_1}, r_{b_2}) = \frac{e^{-\alpha R(\mu_1+\mu_2+\nu_1-\nu_2)}}{r_{12}^3(\mu_1+\nu_1)(\mu_2-\nu_2)\frac{R^2}{4}}\,. \tag{9}$$

$\frac{1}{r_{12}^3}$ occuring in function (9) can be developped into an infinite series. To this end let us substitute $1/r_{12}$ by the following series due to F. NEUMANN [9]:

$$\frac{1}{r_{12}} = \frac{2}{R}\sum_{n=0}^{\infty}\sum_{j=0}^{n} D_n^j P_n^j\begin{pmatrix}\mu_1\\ \mu_2\end{pmatrix} Q_n^j\begin{pmatrix}\mu_2\\ \mu_1\end{pmatrix} P_n^j(\nu_1)\,P_n^j(\nu_2)\cos j(\varphi_2-\varphi_1)\,. \tag{10}$$

Here $P_n^j(\nu_i)$ means the spherical harmonic of first kind, $Q_n^j(\mu_i)$ the spherical harmonic of second kind [10a],

$$D_n^j = \varepsilon_j(-1)^j(2n+1)\left[\frac{(n-j)!}{(n+j)!}\right]^2, \qquad (\varepsilon_0 = 1;\ \varepsilon_j = 2,\ j \geqq 1)\,;$$

and $P_n^j\begin{pmatrix}\mu_1\\ \mu_2\end{pmatrix}$ resp. $Q_n^j\begin{pmatrix}\mu_2\\ \mu_1\end{pmatrix}$ stand for the equalities

$$P_n^j\begin{pmatrix}\mu_1\\ \mu_2\end{pmatrix} = \begin{cases} P_n^j(\mu_1) & \text{if } \mu_1 \leqq \mu_2 \\ P_n^j(\mu_2) & \text{if } \mu_1 \geqq \mu_2 \end{cases}$$

$$Q_n^j\begin{pmatrix}\mu_2\\ \mu_1\end{pmatrix} = \begin{cases} Q_n^j(\mu_2) & \text{if } \mu_1 \leqq \mu_2 \\ Q_n^j(\mu_1) & \text{if } \mu_1 \geqq \mu_2\,. \end{cases}$$

We tacitly suppose that the series (10) may be integrated term by term, as this is always done in quantum chemical calculations (see e. g. [10b]).

The series of $1/r_{12}$ may be also expressed in the following form, making use of the cosine theorem [9]:

$$\frac{1}{r_{12}} = \frac{2}{R} \cdot \frac{1}{\sqrt{\begin{array}{l} -2 + (\mu_1^2 + \mu_2^2 + \nu_1^2 + \nu_2^2) - 2(\mu_1^2 \nu_1^2 + \mu_2^2 \nu_2^2) - \\ -2\mu_1\mu_2\nu_1\nu_2 - 2\sqrt{(\mu_1^2-1)(\mu_2^2-1)(1-\nu_1^2)(1-\nu_2^2)} \cdot \cos(\varphi_2-\varphi_1) \end{array}}} . \tag{11}$$

Again by the above used assumption[1] we derivate the series (10) term by term with respect to φ_1 resp. φ_2 and comparing the resulting expression with the one we get by derivating (11) with respect to φ_1 resp. φ_2 we arrive to

$$\frac{1}{r_{12}^3} = \frac{8}{R^3}[(\mu_1^2-1)(\mu_2^2-1)(1-\nu_1^2)]^{\frac{1}{2}} \sum_{n=0}^{\infty} \sum_{j=0}^{n} D_n^j P_n^j \begin{pmatrix} \mu_1 \\ \mu_2 \end{pmatrix} Q_n^j \begin{pmatrix} \mu_2 \\ \mu_1 \end{pmatrix} P_n^j(\nu_1) P_n^j(\nu_2) \times$$

$$\times j \frac{\sin j(\varphi_2 - \varphi_1)}{\sin(\varphi_2 - \varphi_1)} . \tag{12}$$

Putting (9) and (12) into integral (6a), we obtain the following

$$I_{01}^{\mathrm{I}} = \frac{R^5}{32} \int_1^{\infty} \int_{-1}^{1} \int_0^{2\pi} (\mu_1 - \nu_1)(\mu_2 + \nu_2)(1 - \nu_2^2)(\mu_2^2 - 1) e^{-\alpha R(\mu_1+\mu_2+\nu_1-\nu_2)} \times$$

$$\times \sum_{n=0}^{\infty} \sum_{j=0}^{n} D_n^j P_n^j \begin{pmatrix} \mu_1 \\ \mu_2 \end{pmatrix} Q_n^j \begin{pmatrix} \mu_2 \\ \mu_1 \end{pmatrix} P_n^j(\nu_1) P_n^j(\nu_2) j \frac{\sin j(\varphi_2 - \varphi_1)}{\sin(\varphi_2 - \varphi_1)} \cos\varphi_1 \cdot \cos^3\varphi_2 \, d\tau , \tag{13}$$

$$I_{02}^{\mathrm{I}} = \frac{R^5}{32} \int_1^{\infty} \int_{-1}^{1} \int_0^{2\pi} (\mu_1 - \nu_1)(\mu_2 + \nu_2)(1 - \nu_1^2)(\mu_1^2 - 1) e^{-\alpha R(\mu_1+\mu_2+\nu_1-\nu_2)} \times$$

$$\times \sum_{n=0}^{\infty} \sum_{j=0}^{n} D_n^j P_n^j \begin{pmatrix} \mu_1 \\ \mu_2 \end{pmatrix} Q_n^j \begin{pmatrix} \mu_2 \\ \mu_1 \end{pmatrix} P_n^j(\nu_1) P_n^j(\nu_2) j \frac{\sin j(\varphi_2 - \varphi_1)}{\sin(\varphi_2 - \varphi_1)} \cdot \cos^3\varphi_1 \cdot \cos\varphi_2 \, d\tau , \tag{14}$$

$$I_{03}^{\mathrm{I}} = \frac{R^5}{32} \int_1^{\infty} \int_{-1}^{1} \int_0^{2\pi} (\mu_1 - \nu_1)(\mu_2 + \nu_2) \times$$

$$\times \sqrt{(1 - \nu_1^2)(1 - \nu_2^2)(\mu_1^2 - 1)(\mu_2^2 - 1)} \cdot e^{-\alpha R(\mu_1+\mu_2+\nu_1-\nu_2)} \times \tag{15}$$

$$\times \sum_{n=0}^{\infty} \sum_{j=0}^{n} D_n^j P_n^j \begin{pmatrix} \mu_1 \\ \mu_2 \end{pmatrix} Q_n^j \begin{pmatrix} \mu_2 \\ \mu_1 \end{pmatrix} P_n^j(\nu_1) P_n^j(\nu_2) j \frac{\sin j(\varphi_2 - \varphi_1)}{\sin(\varphi_2 - \varphi_1)} \cos^2\varphi_1 \cdot \cos^2\varphi_2 \, d\tau ;$$

where

$$I_{01}^{\mathrm{I}} + I_{02}^{\mathrm{I}} + I_{03}^{\mathrm{I}} = I_0^{\mathrm{I}} ; \; d\tau = d\mu_1 \, d\mu_2 \, d\nu_1 \, d\nu_2 \, d\varphi_1 \, d\varphi_2 .$$

[1] For a proof of this assumption we want to come back at another occasion.

It is easily seen, that the integrands of integrals (13)—(15) are the products of an infinite series and a function which is finite in the whole domain of integration. Again we suppose that the integrals (13)—(15) are integrable term by term and so we evaluate them. We wish to point out that our method does not contain a proof for the convergence of the series (12), it is to be hoped however that the numerical computations compared with the experimental results will justify its practibility.

By performing the integrations with respect to φ_1 and φ_2 in (13), (14) and (15) we obtain the following results:

(16)
$$\Omega_1 = \Omega_2 = 9\pi j\,[1-(-1)^j]\begin{cases}\left[1-\frac{1}{3}+\frac{1}{5}-+\ldots+\frac{(-1)^{r-1}}{j-1}\right] & \text{if } j=2r\\ \frac{\pi}{4} \quad \text{if } j=2r+1, & (r \text{ is an integer})\end{cases}$$

and for (15):

(17)
$$\Omega_3 = \frac{\Omega_2}{9}+8j(-1)^{j-1}\left[1-\frac{1}{3}+\frac{1}{5}-+\ldots+\frac{(-1)^{j-1}}{2j-1}\right].$$

Let us transform the product

$$P_n^j\begin{pmatrix}\mu_1\\ \mu_2\end{pmatrix} Q_n^j\begin{pmatrix}\mu_2\\ \mu_1\end{pmatrix} P_n^j(\nu_1)\,P_n^j(\nu_2)$$

occurring in (13) and (14) by the aid of the relation [11]:

$$P_n^j(\mu) = (1-\mu^2)^{\frac{j}{2}} P_n^{(j)}(\mu)\,,$$

$$Q_n^j(\mu) = (1-\mu^2)^{\frac{j}{2}} Q_n^{(j)}(\mu)\,.$$

Performing the productions in (13) and (14) and introducing the following notations

$$\Lambda_1 = \frac{R^5}{32}\sum_{n=0}^{\infty}\sum_{j=0}^{n} D_n^j\,\Omega_1$$

$$\Lambda_2 = \frac{R^5}{32}\sum_{n=0}^{\infty}\sum_{j=0}^{n} D_n^j\,\Omega_2\,,$$

we get

$$I_{01}^{I} = \sum_{k=0}^{15} I_{01}^{1,k}$$

and

$$I_{02}^{I} = \sum_{k=0}^{15} I_{01}^{1,k}$$

where

$$
\begin{aligned}
I_{01}^{1,0} &= \quad A_1 H_n^j(1, \alpha R\,;\, 3, \alpha R)\, G_n^j(0\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{01}^{1,1} &= -A_1 H_n^j(1, \alpha R\,;\, 1, \alpha R)\, G_n^j(0\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{01}^{1,2} &= -A_1 H_n^j(1, \alpha R\,;\, 3, \alpha R)\, G_n^j(0\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{01}^{1,3} &= -A_1 H_n^j(1, \alpha R\,;\, 1, \alpha R)\, G_n^j(0\,;\, \alpha R)\, G_n^j(2\,;\, -\alpha R)\\
I_{01}^{1,4} &= \quad A_1 H_n^j(1, \alpha R\,;\, 2, \alpha R)\, G_n^j(0\,;\, \alpha R)\, G_n^j(1\,;\, -\alpha R)\\
I_{01}^{1,5} &= -A_1 H_n^j(1, \alpha R\,;\, 0, \alpha R)\, G_n^j(0\,;\, \alpha R)\, G_n^j(1\,;\, -\alpha R)\\
I_{01}^{1,6} &= \quad A_1 H_n^j(1, \alpha R\,;\, 2, \alpha R)\, G_n^j(0\,;\, \alpha R)\, G_n^j(3\,;\, -\alpha R)\\
I_{01}^{1,7} &= -A_1 H_n^j(1, \alpha R\,;\, 0, \alpha R)\, G_n^j(0\,;\, \alpha R)\, G_n^j(3\,;\, -\alpha R)\\
I_{01}^{1,8} &= -A_1 H_n^j(0, \alpha R\,;\, 3, \alpha R)\, G_n^j(1\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{01}^{1,9} &= \quad A_1 H_n^j(0, \alpha R\,;\, 1, \alpha R)\, G_n^j(1\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{01}^{1,10} &= \quad A_1 H_n^j(0, \alpha R\,;\, 3, \alpha R)\, G_n^j(1\,;\, \alpha R)\, G_n^j(3\,;\, -\alpha R)\\
I_{01}^{1,11} &= \quad A_1 H_n^j(0, \alpha R\,;\, 1, \alpha R)\, G_n^j(1\,;\, \alpha R)\, G_n^j(3\,;\, -\alpha R)\\
I_{01}^{1,12} &= -A_1 H_n^j(0, \alpha R\,;\, 2, \alpha R)\, H_n^j(1\,;\, \alpha R)\, G_n^j(1\,;\, -\alpha R)\\
I_{01}^{1,13} &= \quad A_1 H_n^j(0, \alpha R\,;\, 0, \alpha R)\, G_n^j(1\,;\, \alpha R)\, G_n^j(1\,;\, -\alpha R)\\
I_{01}^{1,14} &= \quad A_1 H_n^j(0, \alpha R\,;\, 2, \alpha R)\, G_n^j(1\,;\, \alpha R)\, G_n^j(3\,;\, -\alpha R)\\
I_{01}^{1,15} &= \quad A_1 H_n^j(0, \alpha R\,;\, 0, \alpha R)\, G_n^j(1\,;\, \alpha R)\, G_n^j(3\,;\, -\alpha R) \qquad (18)\\
I_{02}^{1,0} &= \quad A_2 H_n^j(3, \alpha R\,;\, 1, \alpha R)\, G_n^j(0\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{02}^{1,1} &= -A_2 H_n^j(1, \alpha R\,;\, 1, \alpha R)\, G_n^j(0\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{02}^{1,2} &= -A_2 H_n^j(3, \alpha R\,;\, 1, \alpha R)\, G_n^j(2\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{02}^{1,3} &= \quad A_2 H_n^j(1, \alpha R\,;\, 1, \alpha R)\, G_n^j(2\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{02}^{1,4} &= \quad A_2 H_n^j(3, \alpha R\,;\, 0, \alpha R)\, G_n^j(0\,;\, \alpha R)\, G_n^j(1\,;\, -\alpha R)\\
I_{02}^{1,5} &= -A_2 H_n^j(1, \alpha R\,;\, 0, \alpha R)\, G_n^j(0\,;\, \alpha R)\, G_n^j(1\,;\, -\alpha R)\\
I_{02}^{1,6} &= -A_2 H_n^j(3, \alpha R\,;\, 0, \alpha R)\, G_n^j(2\,;\, \alpha R)\, G_n^j(1\,;\, -\alpha R)\\
I_{02}^{1,7} &= \quad A_2 H_n^j(1, \alpha R\,;\, 0, \alpha R)\, G_n^j(2\,;\, \alpha R)\, G_n^j(1\,;\, -\alpha R)\\
I_{02}^{1,8} &= -A_2 H_n^j(2, \alpha R\,;\, 1, \alpha R)\, G_n^j(1\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{02}^{1,9} &= \quad A_2 H_n^j(0, \alpha R\,;\, 1, \alpha R)\, G_n^j(1\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{02}^{1,10} &= \quad A_2 H_n^j(2, \alpha R\,;\, 1, \alpha R)\, G_n^j(3\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{02}^{1,11} &= -A_2 H_n^j(0, \alpha R\,;\, 1, \alpha R)\, G_n^j(3\,;\, \alpha R)\, G_n^j(0\,;\, -\alpha R)\\
I_{02}^{1,12} &= -A_2 H_n^j(2, \alpha R\,;\, 0, \alpha R)\, G_n^j(1\,;\, \alpha R)\, G_n^j(1\,;\, -\alpha R)\\
I_{02}^{1,13} &= \quad A_2 H_n^j(0, \alpha R\,;\, 0, \alpha R)\, G_n^j(1\,;\, \alpha R)\, G_n^j(1\,;\, -\alpha R)\\
I_{02}^{1,14} &= \quad A_2 H_n^j(2, \alpha R\,;\, 0, \alpha R)\, G_n^j(2\,;\, \alpha R)\, G_n^j(1\,;\, -\alpha R)\\
I_{02}^{1,15} &= -A_2 H_n^j(0, \alpha R\,;\, 0, \alpha R)\, G_n(3\,;\, \alpha R)\, G_n^j(1\,;\, -\alpha R)
\end{aligned}
$$

The quantities H_n^j and G_n^j in the above formulae are [12]:

$$H_n^j(m, \alpha; p, \beta) = \tag{19}$$

$$= \int_1^\infty\int Q_n^{(j)}\begin{pmatrix}\mu_1\\ \mu_2\end{pmatrix} P_n^{(j)}\begin{pmatrix}\mu_2\\ \mu_1\end{pmatrix} e^{-(\alpha\mu_1+\beta\mu_2)}\left[(\mu_1^2-1)(\mu_2^2-1)^{\frac{\nu}{2}}\right]\mu_1^m\,\mu_2^p\,d\mu_1\,d\mu_2$$

$$G_n^j(m;\alpha) = \int_{-1}^{+1} P_n^{(j)}(\nu)\,(1-\nu^2)^{\frac{j}{2}}\,e^{-\alpha\mu}\,\nu^m d\nu\,. \tag{20}$$

We shall determine in § 3 the auxiliary functions (19) and (20).

The form of integral I_{03}^{I} differs from those of I_{01}^{I} and I_{02}^{I}. A detailed computation shows that

$$I_{03}^{\mathrm{I}} = \frac{R^5}{16}\sum_{n=0}^{\infty}\sum_{j=0}^{n} D_n^j\,\Omega_3 \int_1^\infty\int_{-1}^{1} e^{-\alpha R(\mu_1+\mu_2+\nu_1-\nu_2)}\cdot(\mu_1-\nu_1)(\mu_2+\nu_2)\times \tag{21}$$

$$\times P_n^{(j)}\begin{pmatrix}\mu_1\\ \mu_2\end{pmatrix} Q_n^{(j)}\begin{pmatrix}\mu_2\\ \mu_1\end{pmatrix} P_n^{(j)}(\nu_1)\,P_n^{(j)}(\nu_2)\left[(1-\nu_1^2)(1-\nu_2^2)(\mu_1^2-1)(\mu_2^2-1)\right]^{\frac{j+1}{2}} d\mu_1 d\mu_2 d\nu_1 d\nu_2\,.$$

Let us now transform the integrand so that the upper indexes of functions P and Q should be twice the exponent of the expression in parenthesis. This transformation is necessary to express the integral (21) by using auxiliary functions (19) and (20).

We can perform the transformation on the basis of following relations[10]:

$$P_{n+1}^{(j+1)}(\mu) = (2n+1)\,P_n^{(j)}(\mu) + P_{n-1}^{(j+1)}(\mu)\,. \tag{22}$$

$$Q_{n+1}^{(j+1)}(\mu) = (2n+1)\,Q_n^{(j)}(\mu) + Q_{n-1}^{(j+1)}(\mu) \tag{23}$$

$$(n-j+2)\,P_{n+1}^{(j+1)}(\mu) = (2n+1)\,\mu\,P_n^{(j+1)} - (n+j+1)\,P_n^{(j+1)}(\mu)\,. \tag{24}$$

For brievity's sake we omit the lengthy calculations and give only its final result:

$$P_n^{(j)}(\mu)\cdot Q_n^{(j)}(\mu) = \frac{P_{n+1}^{(j+1)}(\mu)\cdot Q_{n+1}^{(j+1)}(\mu) - (2\gamma-1)\,P_{n-1}^{(j+1)}(\mu)\cdot Q_{n-1}^{(j+1)}(\mu)}{(2n+1)^2}\,,$$

$$P_n^{(j)}(\nu) = \frac{P_{n+1}^{(j+1)}(\nu) - P_{n-1}^{(j+1)}(\nu)}{2n+1}\,,$$

where

$$\gamma = \frac{(4n^2-1)\mu^2 - [4n(n+j)+(2n-1)]\mu + (n+j)(n+j+1)}{(n-j+1)(n-j+2)}\,.$$

Substituting now the above expressions into integral (21) and making use of auxiliary functions (19) and (20) we have for

$$I_{03}^{1} = \sum_{i=0}^{2} I_{03}^{1,i}$$

where

$$I_{03}^{1,0} = \Bigg\{ \frac{\Lambda_3}{(2n+1)^2} H_{n+1}^{j+1}(1, \alpha R; 1, \alpha R) +$$

$$+ \frac{\Lambda_3}{(2n+1)^2}\left[1 + \frac{(n+j)(n+j+1)}{(n-j+1)(n-j+2)}\right] \cdot H_{n-1}^{j+1}(1, \alpha R; 1, \alpha R) -$$

$$- \frac{2\Lambda_3[4n(n+j)+(2n-1)]}{(2n+1)^2(n-j+1)(n-j+2)} H_{n-1}^{j+1}\begin{pmatrix} 2, \alpha R; 1, \alpha R \\ 1, \alpha R; 2, \alpha R \end{pmatrix} +$$

$$+ \frac{2\Lambda_3(4n^2-1)}{(2n+1)^2(n-j+1)(n-j+2)} H_{n-1}^{j+1}\begin{pmatrix} 3, \alpha R; 1, \alpha R \\ 1, \alpha R; 3, \alpha R \end{pmatrix}\Bigg\} \times$$

$$\times \frac{[G_{n+1}^{j+1}(0; R\alpha) - G_{n-1}^{j+1}(0; \alpha R)]\,[G_{n+1}^{j+1}(0; -\alpha R)\, G_{n-1}^{j+1}(0; -\alpha R)]}{(2n+1)^2};$$

and

$$\Lambda_3 = \frac{R^5}{16} \sum_{n=0}^{\infty} \sum_{j=0}^{n} D_n^j \Omega_3 .$$

$I_{03}^{1,1}$ and $I_{03}^{1,2}$ may be evaluated in a similar manner.

§ 3.

Now we calculate the auxiliary functions $H_l^M(m, \alpha; n, \beta)$ and $G_l^M(i; \alpha)$. As it is known (see [12])

$$G_l^M(i; \alpha) = (-1)^{i+l+M}\left[\frac{2(l+M)!}{(2l+1)(l-M)!}\right]^{\frac{1}{2}} \cdot B_i^{Ml}(\alpha),$$

$$H_l^M(m, \alpha; n, \beta) = (-1)^M \frac{(l+M)!}{(l-M)!} \Phi_{m,n}^{Ml}(\alpha, \beta).$$

The functions $B_i^{Ml}(\alpha)$ were calculated by RÜDENBERG [13]:

$$B_{i+1}^{Ml} = a_M(l)\, B_i^{M(l-1)} + a_M(l+1)\, B_i^{M(l+1)},$$

$$B_0^{Ml} = \frac{1}{\alpha^M}\left[\frac{(l+M)!}{(l-M)!}\right] B_0^{0l}.$$

Here

$$a_M(l) = a_0(l)\left[1 - \frac{M^2}{l^2}\right]^{\frac{1}{2}}, \quad a_0(l) = (4 - 1/l^2)^{-\frac{1}{2}},$$

and

$$B_l^{0l} = [2(2l+1)]^{\frac{1}{2}}\, b_i^l(\alpha),$$

where

$$b_0^l(\alpha) = \left(\frac{\pi}{2\alpha}\right)^{\frac{1}{2}} \cdot I_{l+\frac{1}{2}}(\alpha)$$

($I_\nu(\alpha)$ stands for the modified Bessel function), and

$$(2l+1)\, b_0^l(\alpha) = \alpha\,[b_0^{l-1}(\alpha) - b_0^{l+1}(\alpha)]\,.$$

Finally,

$$\begin{cases} b_n^0(\alpha) = \dfrac{1}{\alpha}\left(\operatorname{sh}\alpha - n b_{n-1}^0(\alpha)\right) & \text{if } n \text{ is even} \\ b_n^0(\alpha) = \dfrac{1}{\alpha}\left(\operatorname{ch}\alpha - n b_{n-1}^0(\alpha)\right) & \text{if } n \text{ is odd.} \end{cases}$$

Owing to [13] we evaluate the function $\Phi_{nm}^{Ml}(\alpha, \alpha)$ in four steps. At first, we determine the function $\Phi_{00}^{00}(\alpha, \alpha)$, then $\Phi_{nm}^{00}(\alpha, \alpha)$, later $\Phi_{nm}^{0l}(\alpha, \alpha)$ and finally $\Phi_{nm}^{Ml}(\alpha, \alpha)$. The steps in details are the following:

1) $$\Phi_{00}^{00}(\alpha\alpha) = \Phi(\alpha\alpha) = \frac{1}{\alpha^2} e^{-2\alpha}\,[2\,E(\alpha) - E(2\,\alpha)]$$

where

$$E(\alpha) = \frac{1}{2}\,[C + \ln 2\,\alpha - e^{2\alpha}\, Ei(-\,2\,\alpha)]\,,$$

(C = the Euler's constant).

2) $$\Phi_{nm}^{00} = \frac{m}{\alpha}\,\Phi_{(m-1)n}^{00} + \frac{n}{\alpha}\,\Phi_{m(n-1)}^{00} - \frac{mn}{\alpha^2}\,\Phi_{(m-1)(n-1)}^{00} + \frac{1}{\alpha^2}\,R_{mn}(\alpha, \alpha)\,,$$

where

$$R_{mn}(\alpha, \alpha) = G_m(\alpha)\, e^{-\alpha} + e^{-\alpha}\, G(\alpha) - G_{m+n}(2\,\alpha)$$

$$G_0(\alpha) = \frac{e^{-\alpha}}{2}\,[C + \ln 2\,\alpha - e^{2\alpha}\, Ei(-\,2\,\alpha)]$$

$$G_1(\alpha) = \frac{e^{-\alpha}}{2}\,[C + \ln 2\,\alpha + e^{2\alpha}\, Ei(-\,2\,\alpha)]$$

$$G_n(\alpha) = G_{n-2}(\alpha) - A_{n-2}(\alpha)$$

$$A_0(\alpha) = \frac{e^{-\alpha}}{\alpha}$$

$$\alpha\, A_n(\alpha) = n\, A_{n-1}(\alpha) + e^{-\alpha}\,.$$

3) $$\Phi_{mn}^{0l}(\alpha, \alpha) = \left(\frac{2\,l-1}{l}\right)^2 \varphi_{mn}^l\,;$$

$$\varphi_{mn}^l = \frac{b_{l-2}}{b_{l-1}}\,\varphi_{mn}^{l-2} + \psi_{mn}^{l-1}\,, \qquad (l \geqq 2)$$

and

$$b_0 = 1,\ b_l = 4 - \frac{1}{l^2} \quad (l \geqq 1)\,,$$

where

$$\psi^l_{mn} = \psi^{l-2}_{mn} + b_l \varphi^l_{(m+1)(n+1)} + b_{l-2} \varphi^{l-2}_{(m+1)(n+1)} - b_{l-1}(\varphi^{l-1}_{(m+2)n} + \varphi^{l-1}_{m(n+2)}); \quad (l \geqq 2).$$

For $l = 0,1$ we use the formula

$$\varphi^1_{mn} = \psi^0_{mn} = \varphi^0_{(m+1)(n+1)} - A_m(\alpha) \cdot A_n(\alpha) - A_{mn}(\alpha, \alpha),$$

where

$$A_{00}(\alpha, \alpha) = \frac{1}{2\alpha} A^2_0(\alpha),$$

$$A_{mn}(\alpha, \alpha) = \frac{1}{2\alpha} [m A_{(m-1)n} + n A_{m(n-1)} + A_m(\alpha) \cdot A_n(\alpha)],$$

and

$$\psi^1_{mn} = 3\varphi^1_{(m+1)(n+1)} + \varphi^1_{mn} - \varphi^0_{(m+1)(n+1)} - \varphi^0_{(m+2)n} - \varphi^0_{m(n+2)} + A_m(\alpha) \cdot A_{n+1}(\alpha) + A_{(m+1)}(\alpha) \cdot A_n(\alpha).$$

4) Finally, using the function Φ^{0l}_{mn}, we obtain the function Φ^{Ml}_{mn} with the aid of the following recurrence formula:

$$\Phi^{(M+1)l}_{mn}(\alpha,\alpha) = \Phi^{Ml}_{(m+1)(n+1)}(\alpha, \alpha) - \left(\frac{l+M}{2l+1}\right)\Phi^{M(l-1)}_{mn}(\alpha, \alpha) - \left(\frac{l+1-M}{2l+1}\right)\Phi^{M(l+1)}_{mn}(\alpha,\alpha).$$

Since the integrals occuring in our calculations are extremely involved, the numerical computations will be carried out by electronic computer. The numerical results of these calculations will be published elsewhere.

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ИЗУЧЕНИЕ ОСНОВНОГО СОСТОЯНИЯ МОЛЕКУЛЫ ВОДОРОДА НА ОСНОВАНИИ ОТНОСИТЕЛЬНОЙ КВАНТОВОЙ МЕХАНИКИ С ПОМОЩЬЮ ВОЛНОВОЙ ФУНКЦИИ WANG-A, II.

G. KARDOS и J. LADIK

Резюме

Работа содержит метод вычисления математического ожидания члена взаимного воздействия магнитной траектории — траектории, одного из членов коррекционной энергии, получаемых редукцией уравнения двух электронов относительной квантовой механики, уравнения BREIT-а.

В первой части показывается, что это математическое ожидание получается в виде выражения восьми двухцентровых интегралов. Эти интегралы имеют вид, выраженный в эллиптических координатах. Расстояние между двумя электронами выражается с помощью ряда Нейманна [9].

В знаменателе встречающихся интегралов фигурирует куб r_{12} — расстояния друг от друга. Выражая $\frac{1}{r_{12}}$, с одной стороны, с помощью теорема косинуса, с другой стороны, разложением в ряд Нейманна и дифференцируя оба выражения по φ_i (угол азимута одного из электронов), получаем ряд для $\frac{1}{r_{12}^3}$. Эти интегралы удалось получить как функции параметров α и R(α — вариационный параметр, R — расстояние между двумя ядрами), с помощью вспомогательных функций [12], которые могут быть вычисленны с помощью рекурсивных формул. Способ опирается на метод K. RÜDENBERG-а.

Численное определение фигурирующих в работе интегралов будет произведено позже. Полученные таким образом результаты будут опубликованны в другой работе.