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THE ELECTRON CHARGE - DENSITY DISTRIBUTION AND A PROTON INTERSITE SEPARATION IN HYDROGEN - BONDED FERROELECTRICS;
Part two (VARIOUS MATRIX ELEMENTS)

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ABSTRACT. A number of fairly accurate approximations which lead to various matrix elements are outlined with a full mathematical background. Integrations involve three types of a computational work, as follows.

(1) An electrostatic interaction between a bare proton (i.e. the undressed proton) with the system of 8 electrons which belong to a given oxygen atom.

(2) An electrostatic interaction between the nucleus of the oxygen atom and the electron attached to the proton.

(3) Finally, an electrostatic interaction among the electron attached to the proton and those 8 electrons which belong to the above mentioned oxygen atom.

Just how good are (or perhaps how reasonable are) the employed approximations is a question answered at the end of the present research paper, with the conclusion that developed methods fully justify the classical approach here employed. It should be emphasized that a strict quantum - mechanical approach (where one should have taken all exchange intergals into account) would infinitely complicate the theoretical background. Empirical evidence, given at the end of *Part one* seems to agree fairly well with numerical evaluations of the present research paper.

I. INTRODUCTION

There are three principal contributions as coming to the proton electrostatic potential energy, in a hydrogen - bonded system, to be treated by classical approximations.

First, there is an electrostatic interaction between a given bare proton (i.e. the proton without any electrons) ant the oxygen atom. This includes 8 bound electrons. Hence, it includes a purely proton - nucleus interaction, plus an interaction of the proton with the $(1s)^2$ electrons, plus another interaction of the proton with the $(2s)^2$ electrons, plus yet another interaction of the proton with the $(2p)^4$ electrons, two of them with the magnetic quantum number $m = 0$, another two electrons with $m \pm 1$. The relevant matrix elements are considered in Section II and Section III.

There is another electrostatic interaction coming from the nucleus of a given oxygen atom and the electron that is attached to the proton in a hydrogen - bonded system. This approach is rather starightforward quantum - mechanically and needs no further introduction, see Section IV.

Finally, the electron - electron interaction is one of the most difficult problems for handling within the present approach. In particular, it is a case with the electron associated with the proton which interacts with one of the electrons bound to the oxygen atom above mentioned. A similar problem is treated in a number of references, with a variable success, Heitler and London (1927), Hylleraas (1928), Sugiura (1927), and others. Our present method is based on the concept of a *contraction parameter*, exposed in Section V and Section VI.

Kašanin's excellent elementary textbook on higher mathematics (1949) was a great help in doing a specific numerical work in the last stage of the theoretical model.

Just how and why we could use the present set of approximations is related to the order of magnitude for various direct or exchange integrals. A qualitative discussion as to how and why this business might be justified is outlined in Section VII.

II. INTERACTION $V(O_1, P)$ AND DEFINITE INTEGRALS $I_{100}(R), I_{200}$

By definition from an earlier work, according to *Part one* of the present research paper, we can express the matrix element of an oxygen - bare proton interaction as follows,

$$V(O_1, P) = \Big[\frac{Z}{R} - 2 \cdot I_{100}(R) -$$

$$2 \cdot I_{200}(R) - 2 \cdot I_{210}(R) - 2 \cdot I_{21,m}(R)\Big] |e| \cdot q, \tag{2.1}$$

where m takes on two values: $-1, or +1$. Here the definite integrals designate contributions coming from the shells $(1s)^2, (2s)^2, (2p, m = 0)^2, (2p, m)^2$, respectively. The latter contribution is identical for $m = -1$ and $m = 1$, so we can take into account either one. Notice that a notation $O_1 P ... O_2$ is identical with the notation $AP...B$ in *Part one* of the present research paper. We shall employ the radial wave functions for the atom with $Z = 8$, according to *Part one*, while the spherical harmonics are taken as follows,

$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}, \quad Y_{10}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cdot cos\theta,$$

$$Y_{1,m}(\theta, \phi) = -m\sqrt{\frac{3}{8\pi}} \cdot sin\theta \cdot exp(mi\phi). \tag{2.2}$$

where here m takes on $-1, or +1$. Clearly those spherical harmonics are normalized according to the equation,

$$\int_0^{\pi} \int_0^{2\pi} Y^*_{\ell m}(\theta, \phi) Y_{\ell' m'}(\theta, \phi) sin\theta d\theta d\phi = \delta_{\ell\ell'} \delta_{mm'}. \tag{2.3}$$

By definition,

$$I_{100}(R) = \int \frac{|\psi_{100}(r, \theta, \phi)|^2}{\sqrt{R^2 + r^2 - 2Rrcos\theta}} d\tau,$$

$$d\tau = r^2 dr sin\theta d\theta d\phi. \tag{2.4}$$

The integration over ϕ runs from 0 to 2π, to be performed at once leading to the factor 2π, while the integration over θ from 0 to π is performed in Section IV, by yielding two different cases: (a) (if $r < R$) and (b) (if $r > R$). Therefore we have to evaluate the integral

$$I_{100}(R) = 2\Big(\frac{8}{a_0}\Big)^3 \Big[2 \int_0^R \frac{exp(-16\rho) r^2 dr}{R} +$$

$$2\int_R^\infty \frac{exp(-16\rho)r^2dr}{\rho a_0}\Big],\quad \rho=\frac{r}{a_0}. \tag{2.5}$$

The first term in (2.5) comes from (a), whereas the second one comes from (b). In square brackets we add and subtract the following expression,

$$\int_R^\infty \frac{exp(-16\rho)r^2dr}{R},$$

so that one can write,

$$I_{100}(R)=\frac{1}{R}+4(\frac{8}{a_0})^3\int_R^\infty\Big(\frac{1}{\rho a_0}-\frac{1}{R}\Big)\cdot exp(-16\rho)r^2dr, \tag{2.6}$$

which can be transformed to

$$I_{100}(R)=\frac{1}{R}-\Delta I_{100}(R), \tag{2.7a}$$

$$\Delta I_{100}(R)=4*8^3\int_{R/a_0}^\infty\Big(\frac{1}{R}-\frac{1}{\rho a_0}\Big)\cdot exp(-16\rho)\rho^2d\rho\quad >\quad 0. \tag{2.7b}$$

In what follows we shall frequently make use of the integrals, without specifying an integration constant,

$$\int exp(-\lambda x)dx=-\frac{1}{\lambda}exp(-\lambda x),$$

$$\int xexp(-\lambda x)dx=-\Big(\frac{1}{\lambda^2}+\frac{1}{\lambda}x\Big)exp(-\lambda x),$$

$$\int x^2exp(-\lambda x)dx=-\Big(\frac{2}{\lambda^3}+\frac{2}{\lambda^2}x+\frac{1}{\lambda}x^2\Big)exp(-\lambda x)$$

$$\int x^3exp(-\lambda x)dx=-\Big(\frac{6}{\lambda^4}+\frac{6}{\lambda^3}x+\frac{3}{\lambda^2}x^2+\frac{1}{\lambda}x^3\Big)exp(-\lambda x),$$

$$\int x^4exp(-\lambda x)dx=-\Big(\frac{24}{\lambda^5}+\frac{24}{\lambda^4}x+\frac{12}{\lambda^3}x^2+\frac{4}{\lambda^2}x^3+\frac{1}{\lambda}x^4\Big)exp(-\lambda x). \tag{2.8}$$

Using a similar method we can transform the next integral as follows,

$$I_{200}(R)=\frac{1}{4}*8^3\int_0^\infty\Big((1-4\rho)^2exp(-8\rho)\rho^2\cdot\int_{-1}^1\frac{dx}{\sqrt{R^2+r^2-2Rrx}}\Big)d\rho, \tag{2.9}$$

which can be written as a sum of two integrals,

$$I_{200}(R) = \frac{1}{2} * 8^3 \Big[\int_0^{R/a_0} \frac{(1-4\rho)^2 exp(-8\rho)\rho^2}{R} d\rho +$$

$$\int_{R/a_0}^{\infty} \frac{(1-4\rho)^2 exp(-8\rho)\rho^2}{\rho a_0} d\rho \Big]. \tag{2.10}$$

Again, as in the previous case, we add and subtract the integral

$$\int_{R/a_0}^{\infty} \frac{(1-4\rho)^2 exp(-8\rho)\rho^2}{R} d\rho$$

to obtain

$$I_{200}(R) = \frac{1}{R} - \Delta I_{200}(R), \tag{2.11a}$$

$$\Delta I_{200}(R) = \frac{1}{2} * 8^3 \int_{R/a_0}^{\infty} \Big(\frac{1}{R} - \frac{1}{\rho a_0}\Big)(1-4\rho)^2 exp(-8\rho)\rho^2 d\rho \quad > \quad 0. \tag{2.11b}$$

III. INTEGRALS $K(R,r)$, $L(R,r)$, $I_{210}(R)$, AND AN OXYGEN - BARE PROTON INTERACTION IN TERMS OF A DEFINITE INTEGRAL $F(\xi)$

There are two more integrals to be evaluated,

$$K(R,r) = \int_{-1}^{1} \frac{x^2 dx}{\sqrt{R^2 + r^2 - 2Rrx}}, \tag{3.1}$$

$$L(R,r) = \int_{-1}^{1} \frac{(1-x^2) dx}{\sqrt{R^2 + r^2 - 2Rrx}}. \tag{3.2}$$

Start from the integral, where an integration constant is not specified,

$$\int \frac{x^2 dx}{\sqrt{R^2 + r^2 - 2Rrx}} = (a + bx + cx^2)\sqrt{R^2 + r^2 - 2Rrx}. \tag{3.3}$$

$$a = -\frac{2(R^2 + r^2)^2}{15(Rr)^3}; \tag{3.4a}$$

$$b = -\frac{2(R^2 + r^2)}{15(Rr)^2}; \tag{3.4b}$$

$$c = -\frac{1}{5Rr}. \tag{3.4c}$$

So we can distinguish two cases: (a) $(0 < r < R)$ and (b) $(R < r < \infty)$. By inserting the expressions for the coefficients a, b, c from equations (3.4a,b,c) we obtain,

$$K(R, r, [a]) = 2\frac{5R^2 + 2r^2}{15R^3}, \tag{3.5a}$$

$$K(R, r, [b]) = 2\frac{5r^2 + 2R^2}{15r^3}. \tag{3.5b}$$

$$K(R, r, [a]) + L(R, r, [a]) = \frac{2}{R}, \tag{3.6a}$$

$$K(R, r, [b]) + L(R, r, [b]) = \frac{2}{r}. \tag{3.6b}$$

Using a similar method we arrive at,

$$L(R, r, [a]) = \frac{20R^2 - 4r^2}{15R^3}, \tag{3.7a}$$

$$L(R, r, [b]) = \frac{20r^2 - 4R^2}{15r^3}. \tag{3.7b}$$

Therefore the next integral to be evaluated is given by

$$I_{210}(R) = \frac{1}{16} * 8^3 \Big[\int_0^{R/a_0} K(R, r, [a]) \cdot exp(-8\rho)\rho^2 d\rho +$$

$$\int_{R/a_0}^{\infty} K(R, r, [b]) \cdot exp(-8\rho)\rho^2 d\rho \Big]. \tag{3.8}$$

A similar definition holds for the next cited integral, independent of m, where $m = -1, or + 1$,

$$I_{21,m}(R) = \frac{1}{32} * 8^3 \Big[\int_0^{R/a_0} L(R, r, [a]) \cdot exp(-8\rho)\rho^2 d\rho +$$

$$\int_{R/a_0}^{\infty} L(R, r, [b]) \cdot exp(-8\rho)\rho^2 d\rho \Big]. \tag{3.9}$$

By using equations (3.6a,b) and (3.7a,b) we arrive at

$$\frac{3}{2}K(R,r,[a]) + \frac{3}{4}L(R,r,[a]) = \frac{2}{R} + \frac{r^2}{5R^3}, \tag{3.10a}$$

$$\frac{3}{2}K(R,r,[b]) + \frac{3}{4}L(R,r,[b]) = \frac{2}{r} + \frac{R^2}{5r^3}. \tag{3.10b}$$

For practical reasons it was easier to divide the evaluation of the interaction $V(O_1, P)$ into two parts,

$$V(O_1,P) = V_I(O_1,P) + V_{II}(O_1,P), \tag{3.11}$$

$$V_I(O_1,P) = \Big[\frac{4}{R} - 2I_{100}(R) - 2I_{200}(R)\Big]|e| \cdot q, \tag{3.12}$$

$$V_{II}(O_1,P) = \Big[\frac{4}{R} - 2I_{210}(R) - 2I_{21,m}(R)\Big]|e| \cdot q. \tag{3.13}$$

Having employed a huge number of transformations we were able to collect terms with the same exponent, $V_I(O_1, P)$ on one side, while $V_{II}(O_1, P)$ on the other side, in terms of a dimensionless quantity ξ,

$$V(O_1,P) = \frac{1}{a_0}F(\xi)|e| \cdot q, \quad \xi = \frac{R}{a_0}, \tag{3.14a}$$

$$F(\xi) = (16 + \frac{2}{\xi})exp(-16\xi) +$$

$$\Big[\frac{12}{\xi} + 52 + 128\xi + 256\xi^2 + \frac{3}{16\xi^3} + \frac{3}{2\xi^2}\Big] \cdot exp(-8\xi) - \frac{3}{16\xi^3}. \tag{3.14b}$$

IV. AN OXYGEN NUCLEUS O_1 - ELECTRON e INTERACTION AND A DEFINITE INTEGRAL $G_{(0)}(\xi)$

To evaluate the matrix elements as coming from the oxygen atom (nucleus + 8 electrons) with the electron as attached to the proton, as depicted in Figure 1(a), *Part one*, we must distinguish two types of contributions: those with a subscript (0) to be associated with the ground-state contribution as coming from the nucleus O_1 - electron e interaction and those with a subscript (1) to be associated with another contribution as coming from the mutual electron i - electron e interactions.

Having in mind Figure 1(a), *Part one*, we can write

$$V(O_1,P) = V_{(0)}(O_1,e) + V_{(1)}(O_1,e), \qquad (4.1a)$$

$$V_{(0)}(O_1,e) = -Ze^2 \int \frac{|\psi(r,\theta,\phi)|^2}{r([O_1(e)])} d\tau, \qquad (4.1b)$$

$$\psi(r,\theta,\phi) = \frac{2}{a_0^{3/2}} exp(-\rho) \cdot Y_{00}(\theta,\phi), \qquad (4.1c)$$

$$V_{(1)}(O_1,e) = e^2 \sum_{i=1}^{8} \int \Big(\int \frac{|\chi(r_i,\theta_i,\phi_i)|^2}{r[ie]} d\tau_i \Big) \cdot$$

$$|\psi(r,\theta,\phi)|^2 d\tau. \qquad (4.1d)$$

In the above equations we used the notations as defined in *Part one* of this research paper. So all the coordinates with i refer to the oxygen nucleus O_1 while those coordinates without i refer to the proton P.

Therefore the oxygen nucleus O_1 - electron e interaction depends on the definite integral as follows,

$$V_{(0)}(O_1,e) = \frac{e^2}{a_0} G_{(0)}(\xi), \qquad (4.2a)$$

$$G_{(0)}(\xi) = -8 * \Big[\frac{1}{\pi} \int_0^{2\pi} \int_{-1}^{1} \int_0^{\infty} \frac{exp(-2\rho)\rho^2}{\sqrt{\xi^2 + \rho^2 + 2\xi\rho x}} d\rho dx d\phi \Big]. \qquad (4.2b)$$

The indicated integrations are rather straightforward. Having integrated over ϕ from 0 to 2π and over x from -1 to 1 and having used the result of various integrations listed in equations (2.8) we obtain,

$$G_{(0)}(\xi) = -16 \Big[\frac{2}{\xi} \int_0^{\xi} exp(-2\rho)\rho^2 d\rho + 2 \int_{\xi}^{\infty} exp(-2\rho)\rho d\rho \Big] =$$

$$\Big(\frac{8}{\xi} + 8 \Big) \cdot exp(-2\xi) - \frac{8}{\xi}. \qquad (4.3)$$

This furnishes the calculation of the first contribution to the matrix element as coming from an oxygen O_1 - electron e interaction. It merely includes the oxygen nucleus - electron interaction.

V. ELECTRON i - ELECTRON e INTERACTIONS AND A DEFINITE INTEGRAL $G_{(1)}(\xi)$

To perform the integrations leading to the latter definite integral, introduced in equation (4.1d), we shall expose two different approaches, one physical, another mathematical.

Physical approach to the electron i - electron e interaction. This problem has been already solved in *Part one*, based on the following physical picture of what is going on if one takes account of the two independent integrations, one localized around the oxygen nucleus O_1, while another around the proton P, according to Figure 1(a), *Part one.* The basic idea consists of dealing with those two integrations separately and independently one from another. In this approach we first integrate over the coordinates of the eight electrons which belong to the nucleus O_1, as if the z axis of the coordinate system were oriented along the $O_1 - e$ direction. Next we integrate over the coordinates of the electron, which is attached to the proton P, whose z axis is oriented along the hydrogen bond, i. e. along the $O_1 - P$ direction, as exposed in details in *Part one*, Figure 1(b).

Mathematical approach to an electron i - electron e interaction. This problem we shall outline in a general case of interest. Let the two centres of force be designated with A and P, with various coordinates, according to Figure 1(b), *Part one*,

$$Example(1), \quad r_1 = r[Ai], \quad r_2 = r[AP] = R, \quad r_{12} = r[Pi]; \qquad (5.1/1)$$

$$Example(2), \quad r_1 = r[Ai], \quad r_2 = r[Ae], \quad r_{12} = r[ie]. \qquad (5.1/2)$$

In general, the relevant matrix element will depend on the basis elements in a Hilbert space. Using an obvious notation to designate various quantum numbers which specify those basis elements, we can expand the relevant matrix element in terms of the Legendre polynomials, using a method similar to that in *Part one*, the appendix A, including the textbook of Whittaker and Watson (1952). Therefore we can write,

$$< n_1 n_2 \ell_1 \ell_2 m_1 m_2 | \frac{1}{r[12]} | n_1' n_2' \ell_1' \ell_2' m_1' m_2' >= \sum_{\ell=0}^{\infty} \frac{r_<^{\ell}}{r_>^{\ell+1}} \cdot P_\ell(cos\omega), \qquad (5.2a)$$

$$cos\omega = cos\theta_1 cos\theta_2 + sin\theta_1 sin\theta_2 \cdot cos(\phi_1 - \phi_2). \qquad (5.2b)$$

Here ω designates an angle closed by the vectors

$$\vec{r_1} = (r_i, \theta_i, \phi_i); \quad \vec{r_2} = (r', \theta', \phi')$$

whereas

$$r_<, \quad r_>$$

stand for the smaller or larger among the two introduced vectors. By repeating the arguments as exposed in *Part one*, the appendix A, we conclude that there are two different types of definite integrals, each time with the only contribution coming from the term $\ell = 0$, depending on which of the two separation distances is smaller or larger. Calling those two types (a) and (b) we can specify,

$$(a) \quad if \quad r_i < r', \quad (b) \quad if \quad r_i > r'.$$

In the case (a) we can perform the integration over the coordinates r_i first, from zero to $r_i = r'$ and then over the coordinates r'. Actually this operation is identical to *Second stage, Part one* in the previous approach. The important point here is to remember that the triangle AeP has been fixed during the outlined integration. This is equivalent to saying that the integration runs over a set of concentric spheres from the origin up to a maximum sphere with the radius $r_i = r'$. In the case (b), however, we can still perform the integration over r_i, but from $r_i = r'$ to $r_i = \infty$, while keeping the triangle AeP still fixed. This operation is identical to *Second stage, Part two* in the physical approach. This is equivalent to saying that the integration runs over a set of concentric spheres from a minimum sphere with the radius $r_i = r'$ up to infinity.

By doing so we obtain in either case,

$$r_i = \sqrt{r'^2 + r[ie]^2 - 2r'r[ie]cos\theta'},$$

$$r' = \sqrt{R^2 + r^2 + 2Rrcos\theta}. \tag{5.3}$$

Therefore we can write,

$$V_{(1)}(O_1, e) = \frac{e^2}{a_0} G_{(1)}(\xi), \tag{5.4a}$$

$$G_{(1)}(\xi) = \int M_{(1)}(\rho_1) |\psi(r, \theta, \phi)|^2 d\tau, \tag{5.4b}$$

$$\rho_1 = \sqrt{\xi^2 + \rho^2 + 2\xi\rho cos\theta}, \tag{5.4c}$$

$$d\tau = \rho^2 d\rho sin\theta d\theta d\phi, \quad \xi = \frac{R}{a_0}, \quad \rho = \frac{r[Pe]}{a_0}, \quad r[Pe] = r. \tag{5.4d}$$

The quantity $M_{(1)}(\rho_1)$ is readily obtained as a result of the previous calculation of the definite integral $F(\xi)$ if one takes on the operations: change the sign in $F(\xi)$ and then subtract the term $8/\xi$. Hence,

$$M_{(1)}(\rho_1) = \frac{8}{\rho_1} - F(\rho_1) = \frac{8}{\rho_1}$$

$$-(16 + \frac{2}{\rho_1}) exp(-16\rho_1)$$

$$-\Big[\frac{12}{\rho_1} + 52 + 128\rho_1 + 256\rho_1^2 + \frac{3}{16\rho_1^3} + \frac{3}{2\rho_1^2}\Big]\cdot$$

$$exp(-8\rho_1) + \frac{3}{16\rho_1^3}. \tag{5.5}$$

Integrations over θ from 0 to π can be performed at once, leading to a threefold sum over the quantity $M_{(1)}(\xi)$. Without specifying an integration constant we arrive at,

$$G_{(1)}(\xi) = 2\sum_{i=1}^{3}\int \frac{\rho}{\xi} exp(-2\rho) M_{(1)i}\cdot d\rho, \tag{5.6a}$$

$$M_{(1)1} = -\int (16y + 2) exp(-16y) dy =$$

$$(\frac{3}{16} + y)\cdot exp(-16y), \tag{5.6b}$$

$$M_{(1)2} = -\int \left(12 + 52y + 128y^2 + 256y^3\right) exp(-8y) dy$$

$$-\int\Big(\frac{3}{16y^2} + \frac{3}{2y}\Big) exp(-8y) dy =$$

$$\Big(\frac{51}{16} + \frac{27}{2}y + 28y^2 + 32y^3\Big)\cdot exp(-8y)$$

$$+\frac{3}{16y}\cdot exp(-8y), \tag{5.6c}$$

$$M_{(1)3} = \int\Big(\frac{8}{y} + \frac{3}{16y^3}\Big) y dy = 8y - \frac{3}{16y}, \quad y = \rho_1. \tag{5.6d}$$

We obtain the cases specified as (a) and (b),

$$G_{(1)}(\xi, case[a]) = \frac{2}{\xi}\int_0^{\xi} exp(-2\rho)\cdot$$

$$\Big[M_{(1)1} + M_{(1)2} + M_{(1)3}\Big](case[a])\rho d\rho, \tag{5.6e}$$

$$G_{(1)}(\xi, case[b]) = \frac{2}{\xi}\int_{\xi}^{\infty} exp(-2\rho)\cdot$$

$$\Big[M_{(1)1} + M_{(1)2} + M_{(1)3}\Big](case[b])\rho d\rho. \tag{5.6f}$$

VI. THE SUM OF $G_{(0)}(\xi) + G_{(1)}(\xi)$

Therefore the definite integrals $G_{(0)}$ and $G_{(1)}$ if collected will produce the following contributions in terms of a dimensionless coordinate ξ. In the former case the integrand is given by,

$$\Big[...\Big](case[a]) = \Big(\frac{3}{16} + \xi + \rho\Big)exp\big[-16(\xi+\rho)\big]$$

$$-\Big(\frac{3}{16} + \xi - \rho\Big)exp\big[-16(\xi-\rho)\big] + \Big[\frac{51}{16} + \frac{27}{2}(\xi+\rho)$$

$$+28(\xi+\rho)^2 + 32(\xi+\rho)^3\Big]exp\big[-8(\xi+\rho)\big]$$

$$-\Big[\frac{51}{16} + \frac{27}{2}(\xi-\rho) + 28(\xi-\rho)^2 + 32(\xi-\rho)^3\Big]\cdot$$

$$exp\big[-8(\xi-\rho)\big] + \frac{3}{16(\xi+\rho)}exp\big[-8(\xi+\rho)\big]$$

$$-\frac{3}{16(\xi-\rho)}exp\big[-8(\xi-\rho)\big] + 8(\xi+\rho) - \frac{3}{16(\xi+\rho)}$$

$$-8(\xi-\rho) + \frac{3}{16(\xi-\rho)}. \tag{6.1}$$

To obtain the integrand in the latter case we have to perform the following replacements,

$$\Big[...\Big](case[a]) \Rightarrow \Big[...\Big](case[b])$$

$$\xi+\rho \Rightarrow \rho+\xi, \quad \xi-\rho \Rightarrow \rho-\xi.$$

$$G_{(0)}(\xi) + G_{(1)}(\xi) = \frac{2}{\xi}exp(-16\xi)\frac{43+144\xi}{9*16*18^2}$$

$$+\frac{2}{\xi}\Big[\frac{3+16\xi}{16*14^2} - \frac{(3+16\xi)\xi}{16*14} + \frac{2}{14^3} - \frac{2\xi}{14^2}$$

$$
\begin{gathered}
+\frac{\xi^2}{14}-\frac{3-16\xi}{16*18^2}-\frac{(3-16\xi)\xi}{16*18}-\frac{2}{18^3} \\
-\frac{2\xi}{18^2}-\frac{\xi^2}{18}\Bigr]exp(-2\xi) \\
-\frac{2}{\xi}\Bigl(\frac{3+16\xi}{16*14^2}+\frac{2}{14^3}\Bigr)exp(-16\xi) \\
+\frac{2}{\xi}\Bigl[\frac{51}{16*10^2}+\frac{27}{10^3}+\frac{6*28}{10^4}+\frac{24*32}{10^5} \\
+\Bigl(\frac{27}{2*10^2}+\frac{4*28}{10^3}+\frac{18*32}{10^4}\Bigr)\xi \\
+\Bigl(\frac{28}{10^2}+\frac{6*32}{10^3}\Bigr)\xi^2+\frac{32\xi^3}{10^2}\Bigr]exp(-8\xi) \\
-\frac{2}{\xi}\Bigl[-\frac{51\xi}{16*6}+\frac{51-8*27\xi}{16*6^2} \\
+\frac{(51-8*27\xi)\xi}{16*6}+\frac{27-56\xi}{6^3}+\frac{(27-56\xi)\xi}{6^2} \\
+\frac{(27-56\xi)\xi^2}{12}+\frac{6(28-32\xi)}{6^4}+\frac{6(28-32\xi)\xi}{6^3} \\
+\frac{3(28-32\xi)\xi^2}{6^2}+\frac{(28-32\xi)\xi^3}{6}+\frac{24*32}{6^5} \\
+\frac{24*32\xi}{6^4}+\frac{12*32\xi^2}{6^3}+\frac{4*32\xi^3}{6^2}+\frac{32\xi^4}{6}\Bigr]exp(-8\xi) \\
+\frac{2}{\xi}\Bigl[-\Bigl(\frac{51}{16*6}+\frac{51}{16*10}\Bigr)\xi+\frac{(51-8*27\xi)}{16*6^2} \\
-\frac{51+8*27\xi}{16*10^2}+\frac{27-56\xi}{6^3}-\frac{27+56\xi}{10^3} \\
+\frac{6(28-32\xi)}{6^4}-\frac{6(28+32\xi)}{10^4}+\frac{24*32}{6^5} \\
-\frac{24*32}{10^5}\Bigr]exp(-2\xi)-\frac{1}{40\xi}exp(-8\xi)-\frac{3}{8\xi} \\
+\frac{2}{5\xi}exp(-2\xi)+N(\xi).
\end{gathered}
\tag{6.2}
$$

Here the function $N(\xi)$ is defined by two different and yet independent integrations as follows,

$$\begin{aligned} N(\xi) = \frac{3}{8}exp(2\xi)\Big[ln5 + \int_0^{\xi}\frac{1}{\rho}\Big(exp(-10\rho)- \\ exp(-2\rho)\Big)d\rho\Big] \\ +\frac{3}{8}exp(-2\xi)\Big[ln5 - \int_0^{\xi}\frac{1}{\rho}\Big(exp(-6\rho)- \\ exp(2\rho)\Big)d\rho\Big] \end{aligned} \tag{6.3}$$

If $0 < \xi < 3$, then one can expand the above introduced function in terms of ξ , by following one of Kašanin's methods in an excellent textbooks on higher mathematics, see Kašanin (1949). To secure the accuracy better than 10^{-6} for each term appearing in the above expansion series we had to take a large number of terms depending on the required accuracy. Hence,

$$\begin{aligned} N(\xi) = \frac{3}{8}exp(2\xi)\Big[ln5 - \sum_{n=1}^{30}\frac{(-2\xi)^n}{n*n!} \\ +\sum_{n=1}^{100}\frac{(-10\xi)^n}{n*n!}\Big] + \frac{3}{8}exp(-2\xi)\cdot \\ \Big[ln5 + \sum_{n=1}^{30}\frac{(2\xi)^n}{n*n!} - \sum_{n=1}^{70}\frac{(-6\xi)^n}{n*n!}\Big]. \end{aligned} \tag{6.4a}$$

If, however, $2 < \xi < 6$ we developed another expansion series, with the same accuracy 10^{-6},

$$\begin{aligned} N(\xi) = \frac{3}{8}\Big[1 - exp(-4\xi)\Big]\cdot\Big[\frac{1}{2\xi} + \sum_{n=1}^{4}\frac{(-1)^n * n!}{(2\xi)^{n+1}}\Big] \\ -\frac{3}{8}exp(-8\xi)\Big[\frac{1}{10\xi} + \sum_{n=1}^{10}\frac{(-1)^n * n!}{(10\xi)^{n+1}}\Big] \\ +\frac{3}{8}exp(-2\xi)ln15 + \frac{3}{8}exp(-8\xi)\Big[\frac{1}{6\xi} + \sum_{n=1}^{10}\frac{(-1)^n * n!}{(6\xi)^{n+1}}\Big] \\ +\frac{3}{4}exp(-2\xi)\sum_{n=1}^{50}\frac{(2\xi)^{2n-1}}{(2n-1)(2n-1)!}. \end{aligned} \tag{6.4b}$$

It must be emphasized that those two expansion series, one given by equation (6.4a) another by (6.4b), are identical in the overlapping interval, i. e. if $2 < \xi < 3$, or at least they must be close one to another. Indeed, all computer results show , up to the accuracy of 10^{-6} already introduced for each term separately, that one can neglect a difference appearing between $N(\xi)$, equation (6.4a), and $N(\xi)$, equation (6.4b), in this particular interval.

VII. DISCUSSION AND CONCLUSIONS

The present study is a systematic approach to the problem of a mutual electrostatic interaction within a many - body physical system. It represents, on one hand, a specific historic approach from some early days of quantum theory up to the most recently developed highly sophisticated computational methods.

For a physical background the reader is recommended to look at the following references, Backer *et al* (1990), Blokhintsev (1976), Davis (1963), Dirac (1962), Edmonds (1960), Messiah (1961), Novaković (1991, 1997), Pauling and Wilson (1935), Reid and Öhrn (1963), Roman (1965), Schiff (1976), Shull and Lödin (1959). A rather sophisticated mathematical background may be found in: Dirac (1962), Mitrinović (1972), Roman (1965), Whittaker and Watson (1952).

On the other hand, the many - body problem above mentioned has a deep root in a specific application of the Pauli exclusion principle. To see this we must introduce some symmetric and antisymmetric combinations for a coupled physical system which contains two nonequivalent electrons. (Electrons are identical, but may occupy stationary states with different atomic systems; hence they might be nonequivalent).

Assume for the sake of simplicity that one electron is described by a wave function $\psi(1)$ in a given Hilbert space, while another nonequivalent electron is described by another wave function $\chi(2)$ in another Hilbert space. Hence, these wave functions are elements of two different Hilbert spaces.

Now we can construct the above mentioned combinations,

$$\phi_s(1,2), \quad \phi_a(1,2)$$

as elements in a composite Hilbert space. Each element in the mentioned composite Hilbert space will be reperesented by a direct product of the two above introduced wave functions. We may write,

$$\phi_s(1,2) = C\Big[\psi(1)\cdot\chi(2) + \psi(2)\cdot\chi(1)\Big], \tag{7.1a}$$

$$\phi_a(1,2) = D\Big[\psi(1)\cdot\chi(2) - \psi(2)\cdot\chi(1)\Big]. \tag{7.1b}$$

Here C and D are certain normalization factors to be determined by the condition,

$$\int\int \phi_s^* \phi_s d\tau_1 d\tau_2 = \int\int \phi_a^* \phi_a d\tau_1 d\tau_2 = 1, \tag{7.2}$$

where $d\tau_1$ and $d\tau_2$ designate some volume elements depending on the coordinate systems employed. Our next task is to compute the relevant matrix elements of the electron - electron interaction, e^2/r_{12}, with an obvious meaning of the used symbols.

We obtain for the energy of the relevant stationary state,

$$E_s = \int\int \phi_s^*(1,2) \frac{e^2}{r_{12}} \phi_s(1,2) d\tau_1 d\tau_2, \tag{7.3a}$$

$$E_a = \int\int \phi_a^*(1,2) \frac{e^2}{r_{12}} \phi_a(1,2) d\tau_1 d\tau_2. \tag{7.3b}$$

Using wave functions (7.1a,b) the matrix elements (7.3a,b) can be transformed as follows,

$$E_s = 2C^2 \Big(J + K \Big), \tag{7.4a}$$

$$E_a = 2D^2 \Big(J - K \Big). \tag{7.4b}$$

Here J is a direct integral, K is an exchange integral. Furthermore,

$$C = \frac{1}{\sqrt{2 + 2\Delta}}; \quad D = \frac{1}{\sqrt{2 - 2\Delta}}.$$

$$J = \int\int |\psi(1)|^2 \frac{e^2}{r_{12}} |\chi(2)|^2 d\tau_1 d\tau_2. \tag{7.5a}$$

$$\Delta = \int\int \big[\psi(1) \cdot \chi(2)\big]^* \big[\psi(2) \cdot \chi(1)\big] d\tau_1 d\tau_2, \tag{7.5b}$$

$$K = \int\int \big[\psi(1) \cdot \chi(2)\big]^* \frac{e^2}{r_{12}} \big[\psi(2) \cdot \chi(1)\big] d\tau_1 d\tau_2. \tag{7.5c}$$

Generally speaking the exchange integrals can be neglected altogether. Indeed, it is an empirical fact that the hydrogen bond has a length $2a_0 \approx 1.06\mathring{A}$, according to evidence presented in Section VII, *Part one*. Here a_0 is a classical radius of the first Bohr orbit in a hydrogen atom. What is more important, the classical radius of the oxygen atom is estimated to be in the range $(2/3)a_0$, which makes the separation distance proton - oxygen nucleus something like $(5/3)a_0$. This shows that a proton - oxygen nucleus separation distance is a quantity considerably smaller than the estimated hydrogen bond $(2a_0)$ above mentioned. Therefore, we can conclude, with a high degree of confidence, that there is a small overlapping among the two electron wave functions, one coming from the electron associated with the proton, another from that electron associated with a given oxygen atom. In mathematical terms,

$$C \approx D \approx \frac{1}{\sqrt{2}}; \quad \Delta \approx K \approx 0;$$
$$E_s \approx E_a \approx J. \tag{7.6}$$

Hence the conclusions as follows.

(i) An overlap among the electron wave functions is rather weak. Hence, all overlapping integrals appearing in equations (7.5b,c), i. e. quantities Δ, K, can be neglected in studying dynamical behaviour of the hydrogen bond.

(ii) Electrostatic interactions among the electrons, on one side, and between the proton and the electrons associated with the oxygen atom, on the other side, may be treated classically. In other words, the direct integrals like J in equation (7.5a) can be treated classically according to the rules of classical electrodynamics.

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