

**THE ELECTRON CHARGE - DENSITY DISTRIBUTION
AND A PROTON INTERSITE SEPARATION IN
HYDROGEN-BONDED FERROELECTRICS;
Part one (TRIAL FUNCTIONS)**

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ABSTRACT. A method to compute fairly accurately the potential energy $V(R)$ for a proton (by treating the proton P and the attached electron e as separate entities) is developed assuming the action of Coulomb forces between the proton, on one side, and the cations A , and B , on another side. Here R designates a distance separating A from P . Having started from a central-field approximation, where the electron trial wave functions are expressed in terms of a contraction parameter η to measure a departure of the radial factor of those functions from its hydrogen-like shape ($0 < \eta < 1$) due to an electrostatic interaction among the electrons themselves, we reduced a quantum-mechanical eigenvalue problem of the proton motion to a series expansion of an effective single-particle potential in the vicinity of its minimum, in the form of a three-dimensional harmonic oscillator,

$$V_{eff}(R) = k(R - R_{min})^2 - V_0.$$

Here V_0 , k , and R_{min} are certain parameters which are a result of the above introduced approximations when the cation A is identified with an oxygen atom. A similar series expansion also holds for an effective single-hydrogen potential in the vicinity of its minimum, with different values of V_0 , k , and R_0 . In general, for two given values of the contraction parameter, e.g. η_1 and η_2 , where the former value is larger as compared to the latter, the two potential minima E_1 and E_2 will take place at two different proton separation distances R_1 and R_2 , respectively, in such a way that $|E_1| > |E_2|$ and $R_1 < R_2$. Furthermore, a theory is developed to describe the simultaneous and independent action if both the cation A and the cation B are identified with the neutral oxygen atoms. We are able to present various series expansions, in a vicinity of the middle point from A to B , some of them being characterized by a single minimum, the others by two minima, depending on a particular value of η . We demonstrated that such a situation takes place at a critical value,

$$R_{cr} = R_{min} + b_{cr}.$$

By definition, there is a single-minimum (double-minimum) series expansion in a close vicinity of the point $R = R_{cr}$ if the following condition is fulfilled: $R < R_{cr}$ ($R > R_{cr}$), respectively.

I. INTRODUCTION

In order to deal with various interactions arising among the hydrogen atom (proton P + electron e) and an oxygen cluster (nucleus A + 8 electrons, $i = 1, 2, \dots, 8$) we had to introduce an effective electron - nucleus interaction of a Coulomb type through the concept of a "contraction" parameter, Section II and the appendix A. Effective interactions at the level of a proton are considered in Section II, Section III, and the appendix B (oxygen A - proton P). However, the interaction between the hydrogen atom (hereafter also called a dressed proton), thus including the electron as associated with the proton (also called a bare proton), and the oxygen cluster requires a special treatment, Section V (oxygen - hydrogen). By collecting all those interactions, from A on one side and B from another side, we were able to study the potential functions in relation to the empirical separation distance, R_{12} , Section VI (oxygen A - proton P - oxygen B). Here we discover the possibility of a transition from a state with a single-minimum potential well, for certain values of the mentioned separation distance, to a state with a double - minimum potential well. Empirical evidence is included so far as it is directly implied by the present mathematical method, Section VII.

II. A CENTRAL - FIELD APPROXIMATION AND A CONTRACTION PARAMETER η

First we estimate a contraction parameter η assuming that 8 electrons as bound by an oxygen nucleus are distributed quantum-mechanically among the most probable regions. We expose two different methods to evaluate η , one due to Condon and Shortley (1951), and the other due to a Thomas - Fermi equation.

In a central-field approximation we start with a single-electron solution of the appropriate quantum-mechanical equation as if this electron were the only subject to the action of a Coulomb field and then we include all the mutual interactions as acting among the electrons themselves by introducing a free parameter η . A single - particle electrostatic energy is then given by

$$V(r_i) = -Z \frac{e^2}{r_i} + \sum_{j=1}^Z \frac{e^2}{r_{ij}}, \quad (2.1)$$

with Z being in general the charge of the nucleus. Also we include in our analysis the interactions among the electrons themselves if we replace $V(r_i)$ by an effective single-particle potential,

$$V_{eff}(r_i) = -\eta Z \frac{e^2}{r_i}, \quad (2.2)$$

where η designates some contraction parameter, whose value lies in the interval $\in [0, 1]$. A theoretical justification for introducing this parameter is outlined in the appendix A.

First method to evaluate η . According to the result of Condon and Shortley (1951), achieved in a quantum theory of various atomic spectra, we can write

$$\eta = \frac{Z - N + 1}{Z}, \quad (2.3)$$

where N is the number of electrons within a given atomic shell. By a "shell" we shall understand a configuration filled with equivalent electrons, i. e. those which have the same principal n and orbital ℓ quantum numbers. Similarly, by a "subshell" we shall understand an electron pair whose z components of the spins are oriented antiparallel one with respect to the other. Hence η is changed from one shell to another. Taking $N = 4$ to meet the outer subshells one arrives at the value $\eta \approx 0.6$. If we include some of the inner subshells then N might be larger and therefore η might even be smaller.

Second method to evaluate η . A Thomas - Fermi equation, for this particular atomic cluster, leads to the quantity η as a function of a general coordinate r ,

$$V_{eff}(r) = -\frac{\eta Z e^2}{r}, \quad (2.4a)$$

$$\eta = f(4.303 \cdot r), \quad (2.4b)$$

where r is expressed in [\AA]. Depending on the subshells in question, one might apply two limiting values, $\eta \approx 0.7$ (1s-subshell) and $\eta \approx 0.4$ (2s-subshell, 2p-subshell).

It should be emphasized that the present method represents a combination of a Thomas - Fermi equation (mostly used in statistical physics), on one hand, and a Hartree - Fock method (mostly applied in relation to a perturbation theory) on the other hand, see Fock (1976, 1984). Although a Thomas - Fermi equation, as cited here in connection with equation (2.4b) according to the well-known textbook of Landau and Lifshitz (1977), implies the parameter η to be expressed as a function of r , the present approach nevertheless is based on a constant η regardless of electron subshells in question.

Using a Hartree - Fock approach we take the total wave function to be the product of individual wave functions as they are supposed to obey the Pauli exclusion principle. Some advantages of the present method in opposition to other methods (perturbation or similar expansions) are enumerated in Section III.

Next we have to solve the following equation for a radial factor of the wave function,

$$R_{n\ell}(r) = \frac{\chi(r)}{r}, \quad (2.5a)$$

$$\frac{d^2\chi}{dr^2} + \frac{2m_0E\chi}{\hbar^2} + \frac{2m_0\eta(r)Ze^2\chi}{\hbar^2r} - \frac{\ell(\ell+1)\chi}{r^2} = 0. \quad (2.5b)$$

Here m_0 is the electron mass, E is the energy of a bound state, \hbar is Planck's constant divided by 2π , see Novaković (1991). If we could solve equation (2.5b) with an arbitrary function $\eta(r)$ then we would have obtained the entire energy spectrum including the exact *state vectors* in a Hilbert space. (Alternatively we may call them the *basis elements* of the Hilbert space.) However it is the knowledge of the proton motion, separated from electron dynamics of a given oxygen cluster, which we require rather than the electron dynamics itself. Therefore we shall restrict our consideration to those electron wave functions which depend on various particular values of η .

For this reason we multiply equation (2.5b) with $a_{0,eff}$ and introduce a dimensionless length ρ and a dimensionless energy ϵ ,

$$\rho = \frac{r}{a_{0,eff}}, \quad \epsilon = \frac{E}{E_{a,eff}}. \quad (2.6)$$

A transformed equation for $\chi = \chi(\rho)$ is given by

$$\frac{d^2\chi}{d\rho^2} + 2\epsilon\chi + \frac{2Z\chi}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\chi = 0. \quad (2.7)$$

One should emphasize that the atomic length and the atomic energy have been rescaled according to the prescription,

$$a_{o,eff} = \frac{a_o}{\eta}, \quad E_{a,eff} = \eta^2 E_a, \quad a_0 = \frac{\hbar^2}{m_0 e^2}, \quad E_a = \frac{e^2}{a_0}. \quad (2.8)$$

III. ELECTRON TRIAL WAVE FUNCTIONS IN TERMS OF A CONTRACTION PARAMETER η

We can observe from equation (2.7) that the function $\chi(\rho)$ will satisfy the same type of equation as if the single-electron potential were given by $\eta Z e^2/r$. Hence, we can solve equation (2.7) for the radial factor of the wave function $R_{n\ell}(r)$ for any given energy level. Thus writing $a_{0,eff}$ instead of a_0 and multiplying each $R(r)$ with corresponding spherical harmonics we obtain a set of orthonormal basis state vectors in the Hilbert space,

$$\Phi_{n\ell m}(\rho, \theta, \phi) = R_{n\ell}(\rho) \cdot Y_{\ell m}(\theta, \phi). \quad (3.1)$$

Here m designates a magnetic quantum number.

It has to be emphasized that there will appear three important advantages while comparing the present method with an extensive use of the perturbation theory.

(a) All calculations with basis state vectors (3.1), although dependent on a particular contraction parameter η , will be exact and complete. For another value of η there will appear another set of the energy eigenvalues with the corresponding basis state vectors still exact and complete. Each particular eigenstate will be represented by a hydrogen-like wave function. Assuming an ideal separation of the proton coordinates from those as associated with the bound electrons within an oxygen cluster (adiabatic hypothesis) one is able to evaluate the proton potential energy in terms of the contraction parameter η .

(b) For the physical system composed of N electrons the total wave function will be a sum over various products, each running over one of the single-electron basis state vectors, antisymmetrized with respect to all the individual electron coordinates. We use a condensed form to construct the total wave function. Let us designate with $1, 2, \dots, i, \dots, N$ the set of all the electron coordinates necessary to specify the position of a given electron in ordinary space. Hence the total wave function may be written,

$$\Psi(1, 2, \dots, i, \dots, N) = \mathcal{A} \left[\phi([n_1], 1) \cdot \phi([n_2], 2) \cdot \dots \right. \\ \left. \phi([n_i], i) \cdot \dots \phi([n_N], N) \right], \quad (3.2a)$$

$$\mathcal{A} = \frac{1}{\sqrt{N!}} \sum_P \epsilon_P \cdot P(12\dots i\dots N). \quad (3.2b)$$

Here \mathcal{A} designates an antisymmetrization operator. Clearly, the products run over the sets of values of n , ℓ , and m , each set being designated for brevity as $[n_i]$, where

$i = 1, 2, \dots, N$. The sum in equation (3.2b) runs over all permutations P , with ϵ_P being the parity of a particular permutation. Here $\epsilon_P = \pm 1$ according to whether the permutation is even or odd, respectively. There are $N!$ various permutations, hence the total wave function in equation (3.2a) is normalized to 1. For a neutral atomic system N is equal to the electric charge of the nucleus, $N = Z$. If we apply the Pauli exclusion principle by letting the electrons fill the subshells successively, one after the other by starting from the ground state,

$$(1s)^2(2s)^2(2p)^4,$$

then, according to a Hartree - Fock approach, the antisymmetrization operator when applied to the wave functions in (3.2a,b) is equivalent to the successive filling of the lowest-order energy levels. Actually, the ordering of subshells and shells, according to the Pauli exclusion principle, when the subshells and shells are filled one after the other starting from the ground state upwards, is equivalent to the antisymmetrization operator. This particular advantage comes from the full orthogonality among the basis state vectors in equations (3.2a,b), separately over the radial factors which depend on n, ℓ and η , while separately over the spherical harmonics which depend on ℓ, m . The spin quantum number $s_z = 1/2$, or $-1/2$ is taken into account through the specific ordering of the above listed subshells. This approach is a reasonable approximation for single-particle operators, as there will appear various interactions of the kind: the proton P - electrons i , and the electron e - electrons i , where $i = 1, 2, \dots, 8$. Actually, by following the present method we take into account explicitly only the direct integrals, whereas the exchange integrals do not contribute, so far as the single-particle operators are in question. In physical terms, this is equivalent to saying that no exchange takes place either between the proton P and the electrons i , or the electron e and the electrons i , see Figure 1(a). This certainly is not absolutely correct, but represents a reasonable approach so far as the proton dynamics, within the framework of an adiabatic approximation, is in question.

We might describe the present approach as being semiclassical. On one hand it is a very good approximation so far as the proton does not exchange the coordinates with the electrons $i = 1, 2, \dots, 8$, as they are not identical particles in a quantum-mechanical sense. On the other hand, it is also a fair approximation so far as the electron e does not exchange its coordinates with those of the electrons i , where $i = 1, 2, \dots, 8$, because their energy states are so very much different mutually that there will appear an almost vanishingly small contribution coming from the overlap integrals. In other words, the treatment here undertaken is in a full agreement with classical electrostatics in a sense that an electron charge - density, although

expressed by a quantum-mechanical probability, is a subject of the laws of classical electrostatics.

(c) Any interaction between the proton outside the oxygen cluster and the electrons within the oxygen cluster, by following the method of Condon and Shortley (1951), can be treated as a single-particle operator arising from the electron density - charge distributions according to the prescription just outlined. In this particular case the proton P - electron i (as attached to a given oxygen cluster) electrostatic potential energy

$$V(r[Pi]) = \frac{e^2}{r[Pi]} \quad (3.3)$$

can be treated without the use of any perturbation expansion as it would be necessary if the trial wave functions were not corrected for a mutual interaction arising among the electrons. It must be emphasized that the interaction (3.3) rescales according to equations (2.4a) and (2.8),

$$V_{eff}(r[Pi]) = \frac{\eta e^2}{a_0 \rho[Pi]}, \quad (3.4)$$

$$\rho[Pi] = \frac{r[Pi]}{a_{0,eff}}. \quad (3.5)$$

Concluding the present section, one can easily observe various rescalings after the use of the effective single-electron electrostatic potential energy (3.4). The atomic length rescales like a_0/η , the atomic energy rescales like $\eta^2 E_a$, whereas the potential involving the electrons of the oxygen cluster with other particles outside this cluster rescales like $\eta V(r[Pi])$, according to equations (3.3) and (3.4). Therefore one may say that energy terms in general will be decreased (hence a word "contraction" in the introduced definition), whereas the atomic lengths will be increased.

Having in mind all three items mentioned under (a) to (c) we assume that the present approach is established as a reasonable approximation so far as the distance R , separating A from P in Figure 1(a,b), is much larger compared to the outer electron subshells, i. e.

$$R = AP \gg \frac{a_0}{2}.$$

In practical terms we have to evaluate all definite integrals wherever they appear with the basis state vectors (3.1) and (3.2) and then replace the current variable according to the first of equations (2.8),

$$\frac{R}{a_0} \Rightarrow \frac{\eta R}{a_0}$$

where R designates a fixed distance. If numerical values of η were selected carefully then one should expect a reasonable approximation for the electrostatic potential energy of the bare proton in a Coulomb field as being generated by the oxygen cluster (nucleus plus its eight electrons). Actually we are interested in proton dynamics where the kinetic energy of the proton has a primary importance in view of the external electric field which is generated by a cation A , on one side, and a cation B , on the other side. This quantity will depend on R . We assume that the electron cloud e as bound to the proton P (hence a dressed proton) maintains a spherical charge distribution all the time. Therefore such a cloud, according to the laws of electrostatics, will not produce any electric field inside its own sphere. However, there will be a specific oxygen - hydrogen interaction, as a function of the same R , due to the spherical electron density - charge distribution.

In passing over to the next section we have to emphasize the importance of evaluating the contraction parameter from the first principles as accurate as possible. Unfortunately such a sophisticated approach is not available for the time being in any simple and reasonable manner. We can gain a fair amount of conviction at this point by following the arguments of the appendix A where this problem is considered in connection with the helium - atom problem.

IV. OXYGEN - PROTON INTERACTION IN TERMS OF A CONTRACTION PARAMETER η

Using a general vocabulary we shall say that a charge - density distribution of an electron cloud, as defined by Fock (1976, 1984), is a quantity given by

$$\text{Density} = -e \sum |\psi(\vec{r})|^2, \quad (4.1)$$

where the sum runs over all quantum numbers which are necessary to describe the many-electron system in a complete manner. Here \vec{r} designates the space coordinate, to be specified according to a particular model, but will actually depend on the selected origin of the coordinate system. The present mathematical model consists of evaluating the exact potential energy at the position of the proton P , along an atomic chain AP , as being generated by one given nucleus and eight surrounding electrons. A similar definition holds for the atomic line PB .

In general

$$V(A, P) = \left[\frac{Z}{R} - \sum_{i=1}^{n_1} \int \frac{\rho(\vec{r}_i) d\tau_i}{r[P_i]} - \sum_{i=1}^{n_2} \int \frac{\rho(\vec{r}_i) d\tau_i}{r[P_i]} \dots \right] |e| \cdot q, \quad (4.2)$$

where $Z = n_1 + n_2 + \dots$ designates the total number of electrons, n_1 in the first subshell, n_2 in the second subshell, etc. These two sums indicated in equation (4.2) run from 1 to n_1 and n_2 , respectively. A density of the electron charge taken at the point \vec{r}_i , of the i th electron, depicted in Figure 1(a) is given by

$$\rho(\vec{r}_i) = |\psi_{n\ell m}(r_i, \theta_i, \phi_i)|^2. \quad (4.3)$$

In general q is the proton charge to be taken identical with e (the electron charge being $-e$). In addition, $d\tau_i$ is a volume element defined by

$$d\tau_i = r_i^2 dr_i \sin\theta_i d\theta_i d\phi_i. \quad (4.4)$$

Finally, $r[Pi]$ is a distance separating the i th electron from the proton P , in Figure 1(a),

$$r[Pi] = \sqrt{R^2 + r_i^2 - 2Rr_i \cos\theta_i}, \quad (4.5)$$

where the Az axis is parallel to the $AP\dots B$ direction. Each electron wave function is a product of two factors, one being a function of the dimensionless coordinate, with the same notation as in the appendix B,

$$\rho = \frac{r_i}{a_0}.$$

It should be noticed that we employ the same Greek letter for a charge density and the dimensionless coordinate. Another factor contains spherical harmonics for various values of the orbital and magnetic quantum numbers.

We consider a model with the following electron configuration,

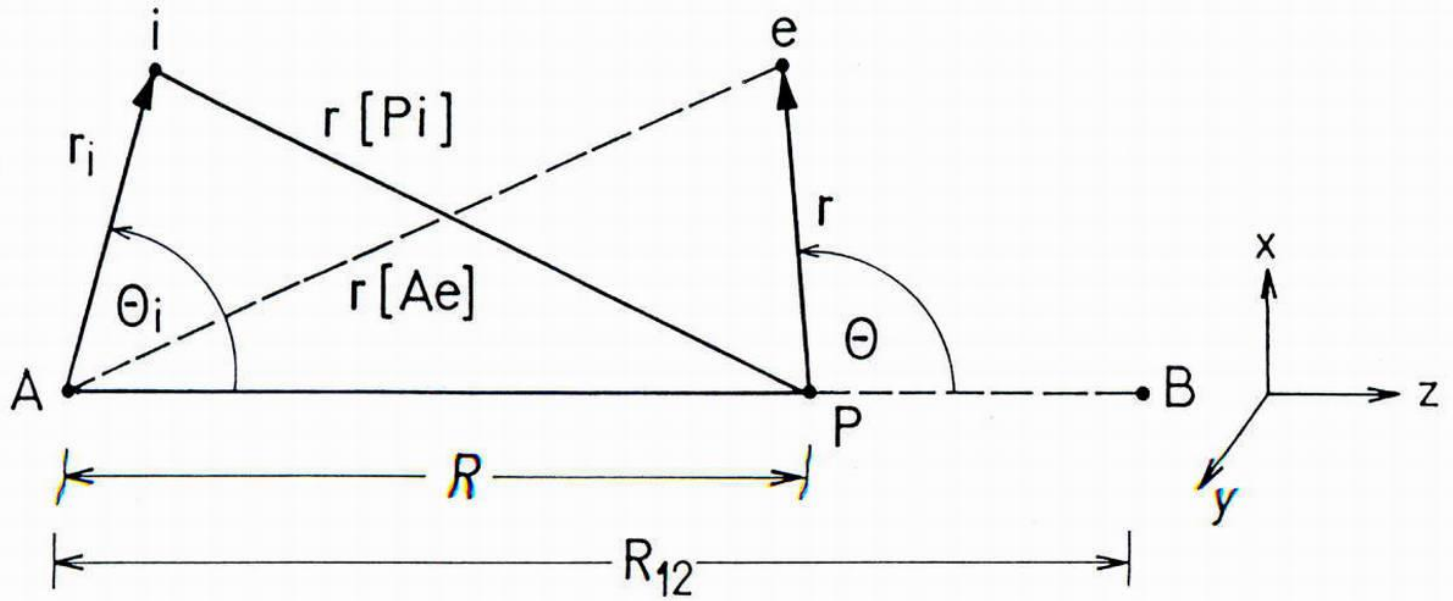
$$(1s)^2(2s)^2(2p)^4.$$

The integration over ϕ_i from 0 to 2π leads to a factor 2π , while the integration over θ_i from 0 to π requires a special attention. All definite integrals can be reduced to one of the following two expressions. If r_i runs from 0 to R , then

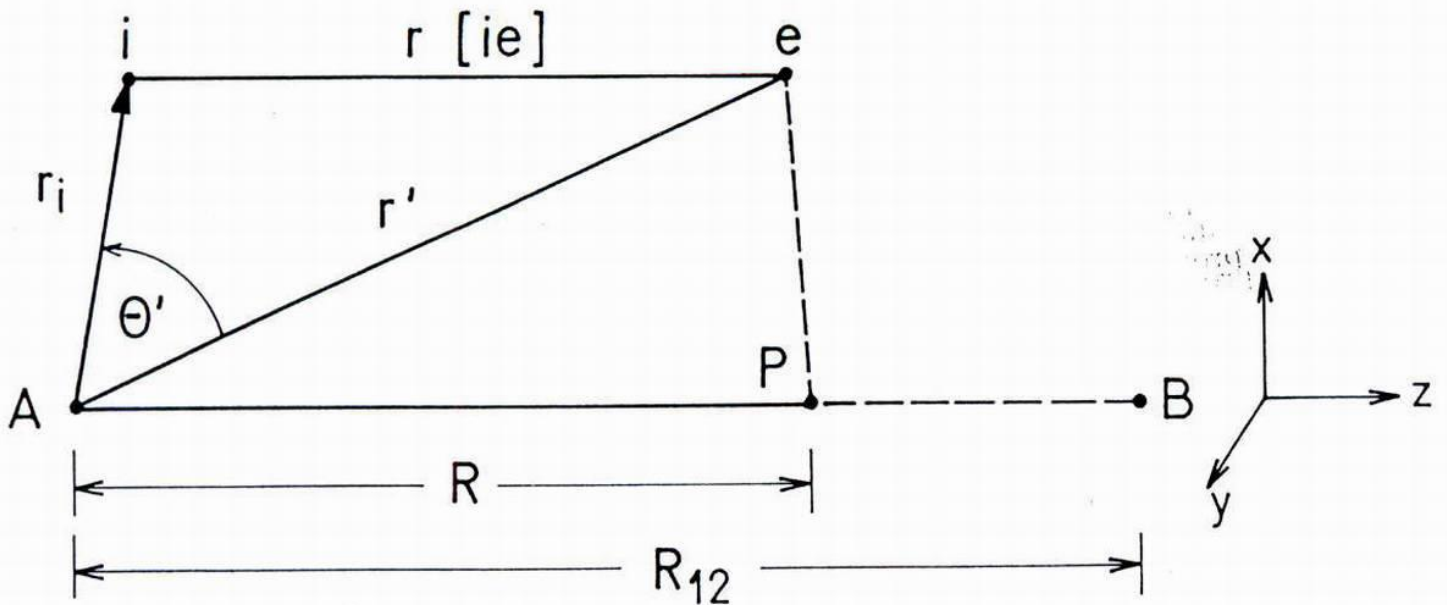
$$\int \frac{\sin\theta_i d\theta_i}{\sqrt{R^2 + r_i^2 - 2Rr_i \cos\theta_i}} = \frac{(R + r_i) - (R - r_i)}{Rr_i} = \frac{2}{R}. \quad (4.6a)$$

If however r_i runs from R to infinity then the above integral runs over to

$$\frac{(r_i + R) - (r_i - R)}{Rr_i} = \frac{2}{r_i}. \quad (4.6b)$$



a)



b)

Figure 1. (a) Relative coordinates of the oxygen nucleus, introduced as a cation A, one of its electrons i and the proton P; (b) The cation A, one of its electrons i , the proton P and its electron e . R is a distance separating the nucleus A from P, R_{12} is a distance separating the nucleus of the cation A from the nucleus of the cation B.

A similar method, in connection with the many-body problem, was considered by Sokolov, Ternov, and Zhukovskii (1984). Therefore, the electrostatic potential energy of the proton due to the oxygen cluster, in terms of a dimensionless coordinate $\xi = R/a_0$, is given by

$$V(A, P) = \frac{e^2}{a_0} F(\xi), \quad (4.7)$$

where, after a straightforward calculation, one arrives at

$$F(\xi) = \left(16 + \frac{2}{\xi}\right) \exp(-16\xi) + \left[\frac{12}{\xi} + 52 + 128\xi + 256\xi^2 + \frac{3}{16\xi^3} + \frac{3}{2\xi^2}\right] \exp(-8\xi) - \frac{3}{16\xi^3}. \quad (4.8)$$

This result holds for a single-electron potential $V(r_i)$ if there were no mutual interactions among the electrons. If however one includes those interactions then equations (4.7) and (4.8) will be transformed as follows. According to Section II, an effective single - electron potential $V_{eff}(r_i)$ will generate a similar expression, where one has to replace the dimensionless coordinate ξ with $\eta \cdot \xi$ and simultaneously replace e^2/a_0 with $\eta \cdot e^2/a_0$, η being a contraction parameter. Therefore,

$$V_{eff}(A, P) = \eta \cdot \frac{e^2}{a_0} F(\eta\xi). \quad (4.9)$$

In general terms, two various curves representing the quantity $V_{eff}(A, P)$ in equation (4.9), one for η_1 another for η_2 , with $\eta_1 > \eta_2$, are depicted in Figure 2. It may be observed that $|E_1| > |E_2|$, while at the same time the positions of the minima obey an opposite relationship, namely, $R_1 < R_2$.

Each curve has a series expansion in the vicinity of its minimum, with a shape of a three-dimensional harmonic oscillator,

$$V_{eff}(R) = k(R - R_{min})^2 - V_0. \quad (4.10)$$

These expansions are characterized by

- (a) Example $\eta = 0.5$, $V_0 = 0.93[eV]$, $k = 5.52[eV \cdot \text{\AA}^{-2}]$, $R_{min} = 1.26[\text{\AA}]$.
- (b) Example $\eta = 0.6$, $V_0 = 1.12[eV]$, $k = 9.54[eV \cdot \text{\AA}^{-2}]$, $R_{min} = 1.05[\text{\AA}]$.
- (c) Example $\eta = 0.7$, $V_0 = 1.31[eV]$, $k = 15.16[eV \cdot \text{\AA}^{-2}]$, $R_{min} = 0.90[\text{\AA}]$.
- (d) Example $\eta = 1$, $V_0 = 1.87[eV]$, $k = 44.19[eV \cdot \text{\AA}^{-2}]$, $R_{min} = 0.63[\text{\AA}]$.

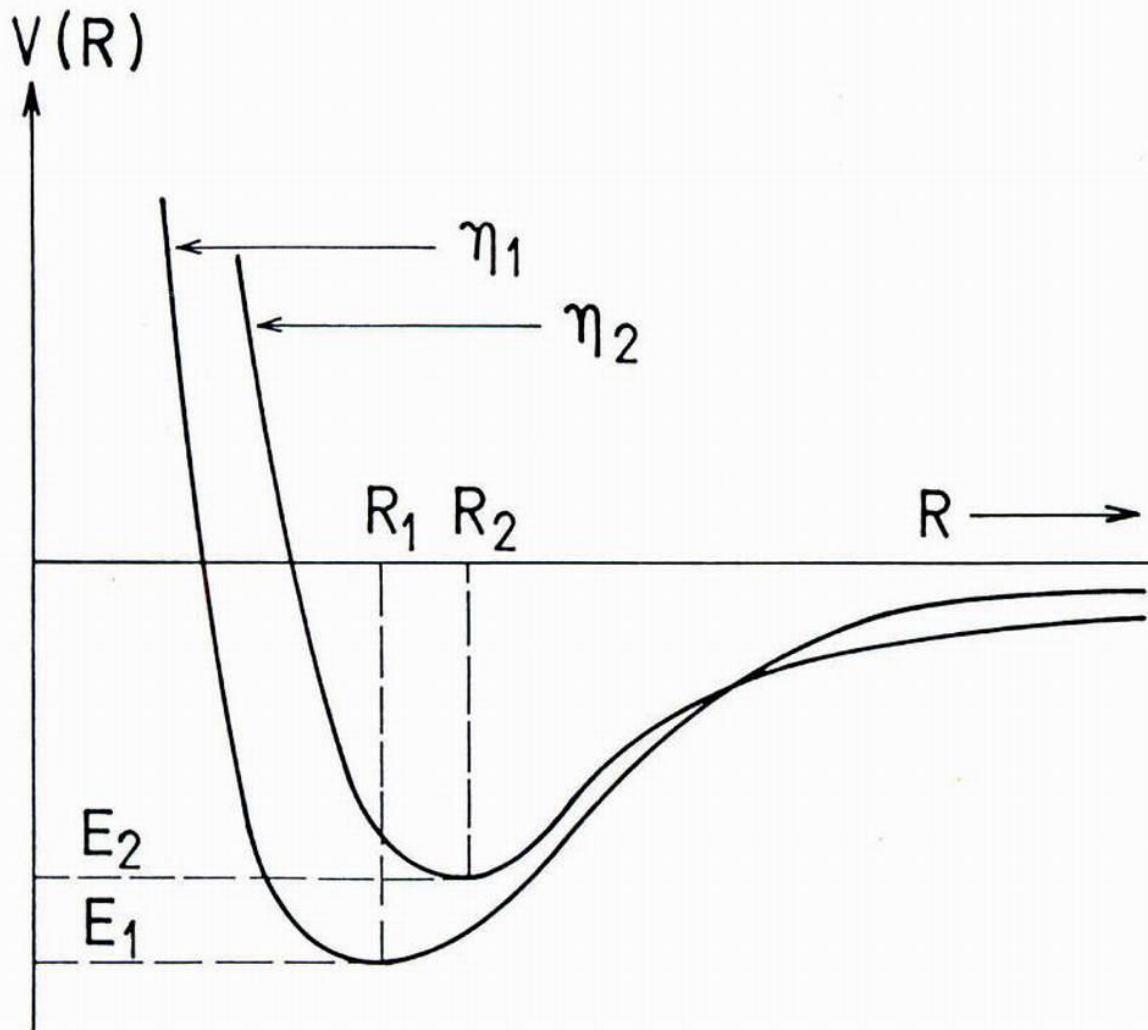


Figure 2. Potential energy of a proton $V(R)$ as generated by the oxygen cluster (nucleus +8 electrons) plotted qualitatively as a function of the $A - P$ separation distance R , for two different values of the contraction parameter η , where $\eta_1 > \eta_2$. Notice also that $|E_1| > |E_2|$, while $R_1 < R_2$.

V. OXYGEN A - ELECTRON e AND
 OXYGEN A - HYDROGEN $P + e$ INTERACTIONS
 AND A DIPOLE MOMENT OF THE O-H SYSTEM

The oxygen A - electron e interaction can be written,

$$V(A, e) = V_{(0)}(A, e) + V_{(1)}(A, e), \quad (5.1a)$$

$$V_{(0)}(A, e) = -8e^2 \int \frac{|\psi(r, \theta, \phi)|^2}{r[Ae]} d\tau, \quad (5.1b)$$

$$V_{(1)}(A, e) = e^2 \sum_{i=1}^8 \int \left(\int \frac{|\chi(r_i, \theta_i, \phi_i)|^2}{r[ie]} d\tau_i \right) \cdot |\psi(r, \theta, \phi)|^2 d\tau, \quad (5.1c)$$

$$\psi(r, \theta, \phi) = \frac{2}{a_0^{3/2}} \cdot \exp\left(-\frac{r}{a_0}\right) Y_{00}(\theta, \phi), \quad (5.2a)$$

$$\chi(r_i, \theta_i, \phi_i) = R_{nl}(r_i) \cdot Y_{lm}(\theta_i, \phi_i), \quad (5.2b)$$

$$\vec{r}_i \Rightarrow (r_i, \theta_i, \phi_i), \quad \vec{r} \Rightarrow (r, \theta, \phi). \quad (5.2c)$$

In equation (5.1a) the two terms designate respectively an electrostatic interaction energy $V_{(0)}$ arising from the oxygen nucleus and the electron e as attached to the proton P and a similar interaction energy $V_{(1)}$ arising from the eight electrons as attached to the oxygen cluster and the electron e , Figure 1(a) and Figure 1(b).

The first contribution is readily written as

$$V_{(0)}(A, e) = \frac{e^2}{a_0} G_{(0)}(\xi), \quad (5.3a)$$

$$G_{(0)}(\xi) = \left(\frac{8}{\xi} + 8 \right) \exp(-2\xi) - \frac{8}{\xi}. \quad (5.3b)$$

The second term in equation (5.1a) can be evaluated by using two separate and yet independent computing stages.

First stage to compute oxygen A - electron e interaction. We fix the variables r, θ, ϕ in order to integrate over the variables r_i, θ_i, ϕ_i , i. e. over $d\tau_i$. As indicated this includes also the factor

$$\frac{1}{r[ie]}$$

in equation (5.1c) which is a part of the indicated integration. We then obtain a dimensionless function similar to $F(\xi)$ as given by equation (4.8). In this particular function we have to make the following replacements. The electron e in Figure 1 (lower view), being attached to the proton P , will play the part of the proton P with $-e$ replacing e . Hence, by replacing ξ whenever it appears with another variable ρ_1 defined by the equation,

$$\rho_1 = \frac{r[Ae]}{a_0}, \quad r[Ae] = r', \quad (5.4)$$

we will be able to perform the integration over $d\tau$. Therefore, equation (5.1c) goes over to

$$V_{(1)}(A, e) = \frac{e^2}{a_0} G_{(1)}(\xi), \quad (5.5a)$$

$$G_{(1)}(\xi) = \int M_{(1)}(\rho_1) |\psi(r, \theta, \phi)|^2 d\tau, \quad (5.5b)$$

$$\rho_1 = \frac{1}{a_0} \sqrt{R^2 + r^2 + 2Rrcos\theta}. \quad (5.5c)$$

It should be emphasized that $\psi(r, \theta, \phi)$ in equations (5.5a,b) is identical to that in equation (5.2a). During this integration we identify the Az axis with the $A - e$ direction in Figure 1(a,b). This completes the *First stage*.

Second stage to compute oxygen A - electron e interaction. Next we go over to compute the introduced quantity $M_{(1)}(\rho_1)$. Having done the replacements as prescribed in the *First stage*, by which the electron e must formally take the place of the proton P in Figure 1(b), and having subtracted a pure proton - nucleus interaction, we arrive at

$$M_{(1)}(\rho_1) = \frac{8}{\rho_1} - F(\rho_1), \quad (5.6)$$

where $F(\rho_1)$ is given by equation (4.8) with ρ_1 instead of ξ . Clearly, the replacement of $-e$ by e (since the electron has replaced the proton in the present operation) is visible in a total change of sign in equation (5.6). Hence the full meaning of the expression introduced in equation (5.6),

$$M_{(1)}(\rho_1) = \frac{8}{\rho_1} - \left(16 + \frac{2}{\rho_1}\right) \exp(-16\rho_1) - \left[\frac{12}{\rho_1} + 52 + 128\rho_1 + 256\rho_1^2 + \frac{3}{16\rho_1^3} + \frac{3}{2\rho_1^2}\right].$$

$$\exp(-8\rho_1) + \frac{3}{16\rho_1^3}. \quad (5.7a)$$

$$\rho_1 = \sqrt{\xi^2 + \rho^2 + 2\xi\rho\cos\theta}, \quad \rho = \frac{r[Pe]}{a_0}. \quad (5.7b)$$

The integration over $d\tau$, i. e. over ρ and θ in equation (5.5b), with the help of equations (5.7a,b) will not produce any confusion over using the same letter ρ as in Section IV and the appendix B. Notice that $r[Pe]$ in equation (5.7b) is identical with r in Figure 1(a). This completes the *Second stage*.

Putting together the interactions oxygen nucleus A - electron e and electrons ($i = 1, 2, \dots, 8$) - electron e we can write an oxygen - hydrogen (i.e. the dressed proton) interaction in the form,

$$V_{eff}(A, H) = \eta \cdot \frac{e^2}{a_0} \left[F(\eta\xi) + G_{(0)}(\eta\xi) + G_{(1)}(\eta\xi) \right], \quad (5.8)$$

where η is approximately the same contraction parameter as in Sections II to IV. A huge number of definite integrals on which $G_{(1)}(\xi)$ depends are given explicitly in *Part two* of the present manuscript. These various curves representing the quantity

$$V_{eff}(A, H)$$

in equation (5.8) are similar to the curves already depicted qualitatively in Figure 2.

Each curve has a series expansion in the vicinity of its minimum, similar to equation (4.10). These expansions are characterized by

- (a) Example $\eta = 0.5$, $V_0 = 3.34[eV]$, $k = 21.48[eV \cdot \text{\AA}^{-2}]$, $R_{min}(H) = 1.05[\text{\AA}]$.
- (b) Example $\eta = 0.6$, $V_0 = 4.01[eV]$, $k = 37.13[eV \cdot \text{\AA}^{-2}]$, $R_{min}(H) = 0.88[\text{\AA}]$.
- (c) Example $\eta = 0.7$, $V_0 = 4.67[eV]$, $k = 58.96[eV \cdot \text{\AA}^{-2}]$, $R_{min}(H) = 0.75[\text{\AA}]$.
- (d) Example $\eta = 1$, $V_0 = 6.68[eV]$, $k = 171.91[eV \cdot \text{\AA}^{-2}]$, $R_{min}(H) = 0.53[\text{\AA}]$.

Clearly, here we find a possibility to discover a fundamental difference in the interpretation of $R(+)$ as compared to $R(H)$. While, on one hand, $R(+)$ is a genuine distance separating the bare proton from the oxygen nucleus (i. e. the quantity R) then, on the other hand, a similar quantity $R(H)$ can be considered as the most probable position of the hydrogen atom (hence a dressed proton). By

subtracting these two effective interactions one obtains the purely oxygen atom A - single electron e interaction. Hence,

$$V_{eff}(A, e) = V_{eff}(A, H) - V_{eff}(A, P). \quad (5.9)$$

The potential function in (5.9) does not show any minimum, but reveals an overlap in passing from one value of η to another. In particular, this overlap is in the interval $R \in [0.35, 0.55] [\text{\AA}]$. For this reason one might introduce a dipole moment $\vec{\mu}$ of the OH physical system connecting those two points through the relation,

$$\mu = q[R(+)] - R(-)], \quad (5.10)$$

where q is the charge of the proton, $R(-)$ is a position of the most probable negative charge - density concentration. It should be emphasized that this difference, according to example (c), equation (4.10), $\eta = 0.7$, $R_{min} = R(+)] = 0.90 [\text{\AA}]$, lies in the interval

$$[0.35, 0.55] [\text{\AA}]. \quad (5.11)$$

This interval may account for a large fraction of the OH dipole moment, see Section VII.

VI. PARTICLE MOTION ASSOCIATED WITH A DOUBLE - MINIMUM POTENTIAL WELL

By collecting the results of Section IV and Section V we can estimate the potential energy which is responsible for the motion of the bare light particles (protons, deuterons) as coming from both oxygen clusters. Therefore,

$$V_{eff}(A, P) + V_{eff}(P, B) =$$

$$\eta \cdot \frac{e^2}{a_0} \left[F(\eta\xi) + F(\eta(\xi_{12} - \xi)) \right], \quad (6.1a)$$

$$\xi_{12} = \frac{R_{12}}{a_0}. \quad (6.1b)$$

We considered how the effective potential function in equations (6.1a,b) behaves as if the contraction parameter η and the empirical separation distance R_{12} change simultaneously and independently one from the other.

(1) According to equation (4.10), if $\eta = 0.6$, $R_{min} = 1.05[\text{\AA}]$, then the potential function in equation (6.1a,b) would be represented by a single-minimum potential well, $V_{single}(R)$, up to a certain value of

$$R < R_{cr} = R_{min} + b_{cr},$$

but would be represented by a double-minimum potential well, $V_{double}(R)$, for

$$R > R_{cr} = R_{min} + b_{cr}$$

depending on η . One arrives at the following expansions, in [eV], while R in [\AA],

$$\begin{aligned} V_{single}(R) = & -1.827 + 0.256(R - 1.26)^2 + \\ & 26.476(R - 1.26)^4 + 54.244(R - 1.26)^6, \end{aligned} \quad (6.2a)$$

$$\begin{aligned} V_{double}(R) = & -1.798 - 0.037(R - 1.27)^2 + \\ & 24.380(R - 1.27)^4 + 50.563(R - 1.27)^6, \end{aligned} \quad (6.2b)$$

where the critical values are within the interval

$$R_{cr} \in [1.26, 1.27] \quad [\text{\AA}], \quad (6.2c)$$

$$2b_{cr} \in [0.42, 0.44] \quad [\text{\AA}]. \quad (6.2d)$$

(2) According to equation (4.10), if $\eta = 0.7$, $R_{min} = 0.90[\text{\AA}]$, then the potential function has two expansions similar to those in equations (6.2a,b,c,d). We find,

$$\begin{aligned} V_{single}(R) = & -2.131 + 0.406(R - 1.08)^2 + \\ & 57.225(R - 1.08)^4 + 159.581(R - 1.08)^6, \end{aligned} \quad (6.3a)$$

$$\begin{aligned} V_{double}(R) = & -2.092 - 0.132(R - 1.09)^2 + \\ & 51.974(R - 1.09)^4 + 147.014(R - 1.09)^6, \end{aligned} \quad (6.3b)$$

$$R_{cr} \in [1.08, 1.09] \quad [\text{\AA}], \quad (6.3c)$$

$$2b_{cr} \in [0.36, 0.38] \quad [\text{\AA}]. \quad (6.3d)$$

Empirically, there is a simple relationship connecting an equilibrium distance R_{12} , which separates the nucleus of A from the nucleus of B , with an escape

radius of the bare proton, R_{esc} , and the elementary length b , a property to be associated with the $O_1H...O_2$ physical system,

$$R_{12} = 2R_{esc} + 2b. \quad (6.4)$$

Here R_{esc} is associated with the first orbital motion of the bare proton in a three-dimensional harmonic oscillator, whereas b depends on external forces which act on the $O_1H...O_2$ physical system. We expect therefore that b is a result of a mutual interaction between this particular physical system and its environment. For the present model we can estimate this quantity on the basis of equations (6.2a,b,c,d) and (6.3a,b,c,d). The result is

$$2b = 0.78 - 0.6 \cdot \eta \quad [\text{\AA}], \quad (6.5)$$

which varies between 0.36 and 0.44 [\AA], provided that η varies between 0.6 and 0.7. Mass-dependent effects, although small, will take place, but they have been neglected in the present paper.

VII. EMPIRICAL EVIDENCE AND CONCLUSIONS

There are three crucial points where the present mathematical model can be tested and justified: a dissociation energy D , an equilibrium distance R_{eq} , and a dipole moment $\mu(OH)$. We shall compare our results with those in: Coggeshall (1950), Lippincot (1953 -1957), Reid (1959), Totsuji and Matsubara (1994).

The value of D , when reduced to a single diatomic molecule OH amounts to approximately 4.36 [eV]. The present model yields a spectrum of values for the potential minimum, depending on the contraction parameter η , ranging from 3.34 [eV] (for $\eta = 0.5$ which is close to the value, according to the approach of Condon and Shortley (1951), 4.67 [eV] (for $\eta = 0.7$, a value which follows from the application of a Thomas - Fermi equation), according to equation (5.8), examples (a) to (c). The radius of the lowest orbit of a proton around oxygen varies from 1.05 [\AA] (in the former case) to 0.75 [\AA] (in the latter case), according to equation (5.8), examples (a) to (c).

An empirical value for the dipole moment $\mu(OH)$ is quoted by Coggeshall (1950), $1.51 \cdot 10^{-18}$ electrostatic units. We have no exact algorithm how to calculate this important physical quantity. However, one can achieve a reasonably successful estimation of the order of magnitude involved in a distance separating the center of the positive charge, $R(+)$, from a similar center of the negative charge, $R(-)$. Indeed, by implying classical arguments one may associate the quantity $R(+)$ with the point of the actual position of the bare proton if charge distributions were

evaluated according to the principle of Fock (1976, 1984), Section II, whereas the quantity $R(-)$ would really correspond to a distorted picture as it would be obtained by the electron cloud surrounding the bare proton. Here, an attractive force on the electron by the oxygen nucleus is slightly more effective than the repulsive force on the proton by the same nucleus. Hence, there would appear a difference in the separation distance, the nucleus versus the bare proton as compared to the nucleus versus the electron. Using obvious notations, one can write,

$$R(+)-R(-)=R_{min}[V_{eff}(O_1,P)]-R_{min}[V_{eff}(O_1,e)]. \quad (7.1)$$

Therefore, the introduced difference, in all cases considered, equals anything from 0.35 up to 0.55 [\AA]. This may numerically account for a large fraction of the observed value of the dipole moment. In addition, this interval is close to the numerical Bohr radius of the outer subshells associated with the oxygen atom, namely a 2s-subshell and a 2p-subshell, whose effective radii may be estimated from,

$$a(2s)=a(2p)\approx\frac{4a_0}{\eta Z}=\in[0.38,0.44][\text{\AA}]. \quad (7.2)$$

With $Z=8$, $\eta\approx 0.6$ up to $\eta\approx 0.7$, equation (7.2) leads to the above mentioned interval.

It is also important to emphasize that the present result for the quantity $R_{min}(+)$, which is identical to R_{min} , may be compared to a semiempirical analysis of Reid (1959) who quotes

$$R_e(OH)\approx 1.092[\text{\AA}]; \quad R_e(OD)\approx 1.082[\text{\AA}]. \quad (7.3)$$

In the present analysis we find a fair agreement between our figures and those of Reid (1959).

A similar method oriented to evaluate the shape of the potential function as associated with the motion of an electron in a mutual field as coming from three sources: a cation A , with a charge Z_A , a bare proton P , with a charge Z_P , and another cation B , with another charge Z_B , which satisfy the condition of an electric neutrality, $Z_A+Z_P+Z_B=1$, was developed by Totsuji and Matsubara (1994). However, this method of Totsuji and Matsubara does not take into account a specific charge - density concentration as coming from various electron shells and subshells.

APPENDIX A: PERTURBATION EXPANSIONS AND
A JUSTIFICATION FOR THE INTRODUCTION
OF A CONTRACTION PARAMETER η

Let us expose our method on a simple physical system like helium (nucleus + 2 electrons) with a total Hamiltonian in the form

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \frac{e^2}{r_{12}}, \quad (A1)$$

where the first two operators include the kinetic and potential energies of two electrons, while the third operator is just an electron - electron interaction. All perturbation expansions will involve the matrix elements of the type,

$$\langle n_1 n_2 \ell_1 \ell_2 m_1 m_2 | \frac{e^2}{r_{12}} | n'_1 n'_2 \ell'_1 \ell'_2 m'_1 m'_2 \rangle, \quad (A2)$$

where the introduced quantum numbers refer to the unperturbed stationary states of the two electrons in question. Here one can expand the electron - electron interaction in terms of Legendre polynomials as follows,

$$\frac{1}{r_{12}} = \sum_{\ell=0}^{\infty} \frac{r_{<}^{\ell}}{r_{>}^{\ell+1}} \cdot P_{\ell}(\cos\theta). \quad (A3)$$

In equation (A3) θ designates an angle closed by those two electrons, see Baker *et al* (1990), Davis (1963), Edmonds (1960), Schiff (1976), Whittaker and Watson (1952), all quoted in *Part two* of the present paper. The symbols \langle and \rangle are used to indicate respectively the smaller or larger among the position vectors,

$$r_1, \quad r_2.$$

The Legendre polynomial can be written as a product over similar polynomials which are associated with either one or another electron motion. Using an obvious notation we write

$$\cos\theta = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2), \quad (A4)$$

$$P_{\ell}(x) = P_{\ell}(x_1)P_{\ell}(x_2) + 2 \sum_{m=1}^{\ell} \frac{(\ell - m)!}{(\ell + m)!} \cdot P_{\ell}^m(x_1)P_{\ell}^m(x_2) \cdot \cos m(\phi_1 - \phi_2), \quad (A5)$$

$$x = \cos\theta, \quad x_1 = \cos\theta_1, \quad x_2 = \cos\theta_2. \quad (\text{A6})$$

Here $P_\ell^m(x)$ is an associated Legendre polynomial. By doing so we can write the relevant matrix element as a sum over various Legendre polynomials. A general conclusion is based on the orthogonality property of the corresponding eigenvectors. Furthermore one can introduce the expansion,

$$P_\ell(x) = \sum_{n=0}^{\ell} c_{\ell n} \cdot x^{\ell-2n}, \quad (\text{A7})$$

with certain expansion coefficients $c_{\ell n}$. We know that the zeroth-order coefficient is given by

$$c_{\ell 0} = \frac{(2\ell)!}{2^\ell \cdot (\ell!)^2}. \quad (\text{A8})$$

Using equations (A5) to (A8) we conclude that only the term with $\ell = 0$ contributes, whereas all the remaining terms give no contribution. Hence an electron - electron interaction in equation (A1) is reduced to the expression

$$\frac{e^2}{r_>}$$

in order to compete the original electron - nucleus interaction in such a way as if each term is replaced by

$$-\frac{e^2}{r_1} + \frac{e^2}{r_>} \Rightarrow -\frac{\eta \cdot e^2}{r_1}, \quad (\text{A9})$$

$$-\frac{e^2}{r_2} + \frac{e^2}{r_>} \Rightarrow -\frac{\eta \cdot e^2}{r_2}. \quad (\text{A10})$$

So we see that η will take a numerical value larger than 0 but still smaller than 1. This completes a justification for the introduction of a contraction parameter η mentioned in Section II, in connection with the best electron trial wave functions. It should be emphasized that the present exposition may also be extended to include a physical system like oxygen (nucleus + 8 electrons), with η still being between 0 and 1. For a special mathematical approach to the helium - atom problem one should follow the genuine expositions of Davis (1963) and Baker *et al* (1990), already cited in *Part two* of the present research paper.

APPENDIX B: HYDROGEN - LIKE RADIAL
WAVE FUNCTIONS IN TERMS OF η

Here we bring the radial wave functions for the three lowest-order stationary states (1s, 2s, 2p) which are frequently used in the present paper. These are,

$$R_{10}(\rho) = 2 \left[\frac{\eta Z}{a_0} \right]^{3/2} \cdot \exp(-\eta Z \rho), \quad (B1)$$

$$R_{20}(\rho) = \frac{1}{\sqrt{2}} \left[\frac{\eta Z}{a_0} \right]^{3/2} (1 - \eta Z \rho/2) \cdot \exp(-\eta Z \rho/2), \quad (B2)$$

$$R_{21}(\rho) = \frac{1}{2\sqrt{6}} \left[\frac{\eta Z}{a_0} \right]^{3/2} \eta Z \rho \cdot \exp(-\eta Z \rho/2), \quad (B3)$$

$$\rho = \frac{r[A_i]}{a_0} = \frac{r_i}{a_0}. \quad (B4)$$

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