Stability of the Negative Hydrogen Ion: Variational Approach with Electron Correlation

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Abstract: We present a study on the negative hydrogen ion, particularly following the works of Chandrasekhar [1, 2]. The conditions for the stability of this system are discussed as well as the methods used to achieve it. We also present the full analytical expression of the variational energy for a Chandrasekhar correlated wave function. Further, we stress the special structure concerning this ion in comparison with the other two-electron systems.

I. INTRODUCTION

The negative hydrogen ion (H^-) is an atomic system composed of two electrons bound to a proton. It belongs to the so-called helium isoelectronic sequence or two-electron systems, which we may denote as $(Z, -1, -1)$, where Z is the nuclear charge. At first sight it seems that the negative hydrogen could be described by the two-electron atoms formalism typically studied in introductory courses in atomic physics. However, perturbation and mean field approximations, such as the well-known Hartree-Fock method, fail completely when applied to H^- because the ground state (g.s.) energies obtained with these methods do not predict its stability. As it will be argued along the work this is due to the relevance of the interelectronic correlation in front of the Coulomb attraction with the nucleus.

The theoretical importance of the study of H^-, which only has a bound state and no excited states [3], is that it shapes the prototype of a three-body atomic system in the same way as the hydrogen atom is the prototype for two-body atomic systems. Therefore, one expects to benefit from the results in order to describe other non-trivial three-body systems with strong dependence in the interelectronic distance [4]. Historically, Bethe [5] and Hylleraas [6] were the first authors to discover the stability of H^- using the frame of the variational method with electron correlation against perturbation and mean field approximations. Since them, an extended study of this system has been done, like in the seminal works of Chandrasekhar [1, 2] and the accurate calculations of Frankowski and Pekeris [7], or Frolov [8], just to mention some.

The H^- ion was a necessity in astrophysics in order to explain the continuous absorption spectra of the Sun and other stellar atmospheres [1, 2, 9]. The concept of a hydrogen atom with a weakly bound second electron helped to describe the opacity of some stellar atmospheres with photon-absorption between $0.75 - 4$ eV [9]. Besides, it is remarkable that the H^- ion plays a central role in linear accelerators and in ion beams for nuclear fusion. Because of its extra electron, in comparison with neutral hydrogen, it is easier to accelerate to high energies [10].

The present work is organized as follows: in Sec. II we present the key concepts regarding stability and the use of the Rayleigh-Ritz method to guarantee it; in Sec. III different variational approaches are discussed using different trial wave functions; and in Sec. IV the shape of H^- is described.

II. STABILITY AND VARIATIONAL METHOD

To claim stability it is necessary to specify a method that ensures that a two-electron system $(Z, -1, -1)$ will not dissociate into a one-electron atom or ion $(Z, -1)$. In this case, hydrogen-like systems bring out the threshold of stability with a non-relativistic energy of the ground state $E_{th} = -Z^2/2$, assuming a nucleus of infinite mass. This expression is given in atomic units (a.u.) where $\hbar = e = m_e = 1$. Hence, the energies are proportional to the Hartree $E_h = e^4 m_e/\hbar^2 \simeq 27.2114$ eV and the distances to the Bohr radius $a_0 = \hbar^2/(e^2 m_e) \simeq 5.2918 \times 10^{-9}$ cm. The method used to compute the energies of the g.s. of these two-electron systems is described straightaway.

If H is the Hamiltonian describing the system and Ψ_n the set of orthonormal eigenfunctions, then the exact energies are the eigenvalues of the Hamiltonian, i.e. $E_n = \langle \Psi_n | H | \Psi_n \rangle$. Usually, the set of Ψ_n are unknown and the problem remains to seek an appropriate function ψ which differs from Ψ_n by an infinitesimal quantity $\delta\psi$, such that the energy $E[\psi]$ gives a value as close as possible to E_n. This condition can be obtained by imposing $E[\psi]$ to be stationary to first-order variations, i.e. $\delta E[\psi] = 0$. It can be shown [11] that if $\psi = \Psi_n + \delta\psi$ the difference between $E[\psi]$, under the stationary condition, and the exact energy E_n is second order in $\delta\psi$. Moreover, the functional $E[\psi]$ gives an upper bound to the exact ground state energy E_0, i.e. $E[\psi] \geq E_0$ [11].

A typical procedure to find out the best $E[\psi]$ is to assume a function depending on some *variational parameters*, i.e. $\psi[\alpha_1, \ldots, \alpha_N]$ usually called *trial wave function*, and to minimize $E[\psi]$ with respect to these parameters in order to get the best approximation to E_0. This approach is known as Rayleigh-Ritz variational method and

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VARIATIONAL ENERGIES				
	Z	$-E[Z_{\text{eff}}]$	$-E[a,b]$	$-E[a,b,c]$	$-E_{\text{nr}}$
H^-	1	0.472	0.51330	0.52592	0.52775
He	2	2.848	2.87566	2.90142	2.90372
Li^+	3	7.223	7.24875	7.27717	7.27991
Be^{2+}	4	13.598	13.62396	13.65255	13.65557
B^{3+}	5	21.973	21.99754	22.02776	22.03097
C^{4+}	6	32.348	32.37227	32.40290	32.40625
N^{5+}	7	44.723	44.74709	44.77799	44.78145
O^{6+}	8	59.098	59.12195	59.15306	59.15660

TABLE I: Ground state variational energies (in a.u.) of the first eight ions of the helium isoelectronic sequence. The energies correspond to the simple variational method (5), the two- and three-parameters Chandrasekhar wave functions using (8) and the best non-relativistic energy [7].

$\Psi[Z_{\text{eff}}]$		$\psi[a,b]$		$\psi'[a,b,c]$		
Z	Z_{eff}	a	b	a	b	c
1	0.68	1.03922	0.28322	1.07487	0.47745	0.31255
2	1.68	2.18317	1.18853	2.20842	1.43624	0.29271
3	2.68	3.29498	2.07091	3.29943	2.36182	0.27697
4	3.68	4.38973	2.98472	4.37442	3.29336	0.26880
5	4.68	5.47341	3.90126	5.43992	4.23120	0.26385
6	5.68	6.54910	4.82568	6.49888	5.17423	0.26054
7	6.68	7.61870	5.75614	7.55296	6.12144	0.25817
8	7.68	8.68348	6.69140	8.60320	7.07210	0.25639

TABLE II: Variational parameters that minimize the energies for the simple variational method and the two- and three-parameters of Chandrasekhar wave functions and the case with a frozen electron to $a = 1$.

can be summarized as

$$E[\alpha_k] = \min_{\alpha_k} \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0, \qquad (1)$$

where $E[\alpha_k]$ is the energy obtained with the trial wave function $\psi[\alpha_k]$ after minimizing it with respect the set of chosen variational parameters $\{\alpha_k\}$. Henceforth, the Rayleigh-Ritz variational method can be used to study stability. If one is able to propose a trial wave function depending on some variational parameters that describes the system and fulfills $E[\alpha_k] < E_{\text{th}} = -Z^2/2$, then stability is ensured. In the problem of the stability of the negative hydrogen it is enough to find out a certain ψ such that $E[\alpha_k]$ is lower than the energy of the neutral hydrogen atom -0.5 a.u.

III. GROUND STATE OF HELIUM ISOELECTRONIC SEQUENCE

The Hamiltonian of two-electron systems with a point-like, infinite mass nucleus in the electrostatic approximation can be written as

$$H = -\frac{\nabla_{\mathbf{r}_1}^2}{2} - \frac{\nabla_{\mathbf{r}_2}^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \qquad (2)$$

where r_1 and r_2 are the distances of each electron to the nucleus and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the separation between electrons. The first two terms in eq. (2) represent the kinetic energy of each electron, the following terms correspond to the Coulomb attraction between the electrons and the nucleus of charge Z, and to the Coulomb repulsion between the electrons.

In the ground state of two-electron systems the spin wave function is a singlet, $\chi_{00}(\sigma_1, \sigma_2)$, which is antisymmetric. Therefore, the spatial contribution, $\Psi(\mathbf{r}_1, \mathbf{r}_2)$, is required to be symmetric, $\Psi(\mathbf{r}_2, \mathbf{r}_1) = \Psi(\mathbf{r}_1, \mathbf{r}_2)$, in order to have a globally antisymmetric wave function. Since (2)

is spin independent, the total wave function factorizes as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \sigma_1, \sigma_2) = \Psi(\mathbf{r}_1, \mathbf{r}_2)\chi_{00}(\sigma_1, \sigma_2). \qquad (3)$$

A. Simple variational method

The simplest attempt is to consider r_{12}^{-1} as a perturbation and solve (2) for two independent electrons. Thus, one can use $1s$ hydrogenic orbitals to describe each electron, i.e. $\varphi(\mathbf{r}) = u(r)Y_{00}(\theta, \phi)$, where $u(r) = 2Z^{3/2} \exp(-Zr)$ and $Y_{00}(\theta, \phi) = 1/\sqrt{4\pi}$. Additionally, if one assumes that both electrons feel the same effective nuclear charge, Z_{eff}, the resulting spatial normalized wave function reads

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = (Z_{\text{eff}}^3/\pi) \exp(-Z_{\text{eff}}(r_1 + r_2)). \qquad (4)$$

Then, one finds that $\langle \Psi | H | \Psi \rangle = Z_{\text{eff}}^2 - 2ZZ_{\text{eff}} + 5Z_{\text{eff}}/8$ [11], and the Rayleigh-Ritz variational method lead to a g.s. energy

$$E[Z_{\text{eff}}] = \min_{Z_{\text{eff}}} \langle \Psi | H | \Psi \rangle = -Z_{\text{eff}}^2, \qquad (5)$$

where $Z_{\text{eff}} = Z - 5/16$. The energies concerning this model and the effective nuclear charges are given in columns $E[Z_{\text{eff}}]$ of Table I and $\psi[Z_{\text{eff}}]$ of Table II. For $Z \geq 2$ the energies are rather good in comparison with the best non-relativistic calculations [7], column E_{nr} of Table I, taking into account the simplicity of the method. This is because for increasing values of Z Coulomb attraction with the nucleus becomes more important and the electron repulsion r_{12}^{-1} less important. On the contrary, the result of eq. (5) fails to predict H^- stability since in this case $E[Z_{\text{eff}}] = -0.4727 > -0.5$. This suggests that treating the electrons of the H^- system as if they were exactly equal is not valid and that a special treatment is needed.

B. Breaking single-particle orbital symmetry

As pointed out in the introduction Bethe [5] and Hylleraas [6] were the first authors to prove the stability of the negative hydrogen. But it was Chandrasekhar [1] who first introduced a clever wave function to describe the H^- system which leads to a beautiful physical picture. The key concept introduced by Chandrasekhar was to break the symmetry between the two electrons, which is a way to introduce implicitly the electron correlation. Hence, if one assigns different effective nuclear charges to the electron orbitals, the unnormalized trial radial wave function reads

$$\psi(r_1, r_2) = e^{-ar_1}e^{-br_2} + e^{-br_1}e^{-ar_2}, \qquad (6)$$

where a and b are variational parameters representing the effective nuclear charges of the electrons. Computing the matrix elements of the Hamiltonian (2) one gets

$$E[a,b] = \frac{\langle \psi|H|\psi \rangle}{\langle \psi|\psi \rangle} = \frac{T + V + U}{N}, \qquad (7)$$

where N is the norm, T the kinetic energy, and V and U are the nucleus-electron and the electron-electron Coulomb potential energies, respectively. The analytical expressions of these quantities are given by Eqs. (15), (16), (17) and (18) in the appendix, respectively, setting $c = 0$ in those expressions.

The minimization with respect to a and b leads to the variational energies shown in column $E[a,b]$ of Table I. For H^- we obtained $E[a,b] = -0.51330$, which is more negative that the ionization threshold of -0.5, and thanks to the Rayleigh-Ritz principle we can ensure that this is our first prediction of the negative hydrogen stability. We also notice that the energies have improved with respect to the approximation of two electrons equally screened with Z_{eff}. Some important concepts can be found behind this result, like that binding is achieved as long as one of the electrons shields part of the nuclear charge to the other. The values of the variational parameters, $\psi[a,b]$ column of Table II, bring out this picture where a peripheral electron feels an effective nuclear charge of $b \simeq 0.28$ whereas the internal one feels $a \simeq 1.04$ as being slightly "pushed" towards the nucleus. As a matter of fact, if one considers the rough approximation of freezing one of the electrons to feel a unity charge, e.g. $a = 1$, stability is also achieved since $E[1,b] = -0.51259$ for $b = 0.27889$.

To minimize $E[a,b]$ of (7) we have use a downhill simplex method [12] in FORTRAN double precision. In order to give account of the numerical accuracy of our energies, we have used the virial theorem. If one considers a scaling such that $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_n) \to \lambda^{3n/2}\Psi(\lambda\mathbf{r}_1, \ldots, \lambda\mathbf{r}_n)$, where λ is a scaling factor that preserves the norm, the expectation value of the Hamiltonian remains stationary for $\lambda = 1$. Therefore, for (2) one obtains that the energy scales as $E(\lambda) = \lambda^2 T(\lambda = 1) + \lambda V_{tot}(\lambda = 1)$ with minimum value for $\lambda = 1$, i.e. $T = -V_{tot}/2$ [4, 13]. We
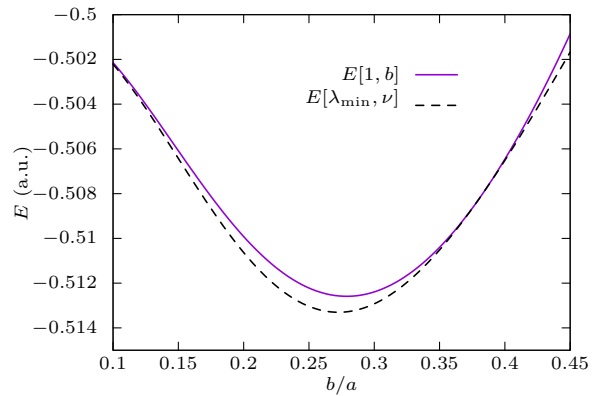

FIG. 1: Variational energies of Chandrasekhar wave function (6) setting $a = 1$ (hence, $b/a = b$) and using the virial theorem (where $b/a = (1 - \nu)/(1 + \nu)$).

obtained that our energies fulfill the virial theorem to the sixth, and sometimes to the eighth, decimal. As an example, for the negative hydrogen $T = 0.513302893$, $V_{tot}/2 = -0.513302889$ and $E[a,b] = -0.513302886$. Likewise, the values of the energies and the variational parameters were tested by changing the seeds (initial values) that the simplex subroutine requires to start the calculation.

The virial theorem can also be used to reduce by one the number of parameters to minimize. If we consider a scaling $a = \lambda(1 + \nu)$ and $b = \lambda(1 - \nu)$ one gets that the energy reaches its minimum when the scale factor is $\lambda_{min} = -V_{tot}(\lambda = 1)/2T(\lambda = 1)$ with a value

$$E(\lambda_{min}) = -\frac{V_{tot}^2(\lambda = 1)}{4NT(\lambda = 1)}, \qquad (8)$$

where the minimization must be done only for ν. We have also checked that the minimization of (8) with respect to ν indeed gives the same values of a, b and $E[a,b]$, particularly $\lambda_{min} \simeq 0.66$ and $\nu \simeq 0.57$ for H^-. Figure 1 shows the energy curves of the frozen-electron approximation, $E[1,b]$, and using the virial theorem (8) as a function of b/a. It is clear that the energy curve using the virial theorem provides a deeper minimum than the frozen-electron approximation.

C. Explicit introduction of the correlation

The results obtained in the previous section are rather satisfactory as a first approach. The model leads to both good values of the energies and a realistic physical description of the ion. But since the Hamiltonian (2) depends explicitly on the interelectronic distance r_{12}, it is not possible to approach the exact energy without introducing this variable explicitly into the trial wave function [4, 13]. Following the work of Chandrasekhar [1] we add a linear term in the electronic distance to (6). Thus, a more sophisticated correlated trial wave function is

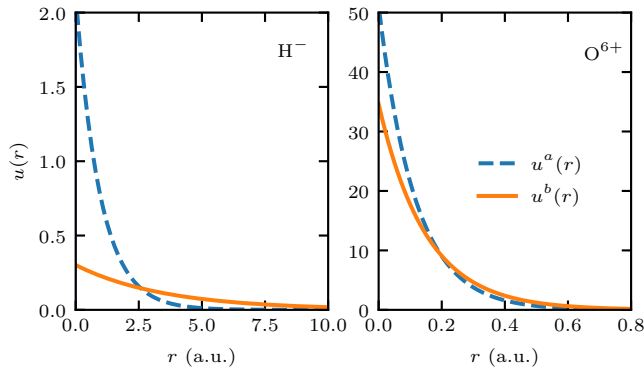$$\psi'(r_1, r_2, r_{12}) = \psi(r_1, r_2)(1 + cr_{12}), \qquad (9)$$

FIG. 2: Normalized radial orbitals (a.u.) of the inner (dashed line) and outer (continuous line) single-particle electron orbitals of the H^- and O^{6+}.

Z	$\langle r_i \rangle$	$\sqrt{\langle r_i^2 \rangle}$	$\frac{\sigma_{r_i}}{\langle r_i \rangle}\%$	$\langle r_{12} \rangle$	$\sqrt{\langle r_{12}^2 \rangle}$	$\frac{\sigma_{r_{12}}}{\langle r_{12} \rangle}\%$
1	3.1126	4.1230	86.9	5.0200	5.8308	59.0
2	0.9379	1.1126	63.8	1.3957	1.5735	52.0
3	0.5745	0.6731	61.0	0.8473	0.9520	51.2
4	0.4149	0.4839	60.0	0.6098	0.6843	50.9
5	0.3248	0.3779	59.5	0.4765	0.5345	50.8
6	0.2669	0.3101	59.1	0.3912	0.4386	50.7
7	0.2266	0.2630	58.9	0.3318	0.3719	50.7
8	0.1968	0.2283	58.7	0.2880	0.3228	50.6

TABLE III: Mean value, root-mean-square value and relative dispersion of the distance to the nucleus of each electron r_i and the interelectronic distance r_{12}, in a.u., using the wave function (6). Here, $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$.

where c is the new variational parameter. Hence, the new variational energy is

$$E[a,b,c] = \frac{\langle \psi'|H|\psi' \rangle}{\langle \psi'|\psi' \rangle} = \frac{T' + V' + U'}{N'}. \tag{10}$$

where N', T', V' and U' are the corresponding norm, kinetic energy and nucleus-electron and electron-electron Coulomb potential energies, respectively. The analytical expressions of this quantities, given by Eqs. (15)–(18) in the appendix, were calculated by the author. It is to remark that the calculations become much more complicated than when using (6). On the one hand, (9) introduces additional matrix elements to N', V' and U' in comparison with N, V and U using (6):

$$N' = \langle \psi|\psi \rangle + 2c\langle r_{12} \rangle + c^2\langle r_{12}^2 \rangle, \tag{11}$$

$$V' = -2Z\left[\langle r_i^{-1} \rangle + 2c\langle r_{12}r_i^{-1} \rangle + c^2\langle r_{12}^2 r_i^{-1} \rangle\right], \tag{12}$$

$$U' = \langle r_{12}^{-1} \rangle + 2c\langle \psi|\psi \rangle + c^2\langle r_{12} \rangle, \tag{13}$$

where the mean values are referred to wave function (6). On the other hand, for the kinetic energy the term $\langle \psi'|\nabla_{\mathbf{r}_1}^2 + \nabla_{\mathbf{r}_2}^2|\psi' \rangle$ introduces twelve extra matrix elements with respect to T, involving derivatives of the wave function (6) and different powers of r_{12}. We do not provide the whole expression for the sake of brevity. Not in vain, the minimizations of these expressions improves the energies greatly. Looking at column $E[a,b,c]$ of Table I we notice that our energies have improved to the point that they approach significantly the best non-relativistic values, E_{nr} [7]. In fact, for H^- the deviation of our energy $E[a,b,c] = -0.52592$ with respect to $E_{nr} = 0.52775$ [7] is about 0.35 % whereas for the two parameters, $E[a,b]$, was 2.75 %. Using (9), the external electron feels an effective nuclear charge $b \simeq 0.48$, which is greater than the one obtained for (6). This means that now the peripheral electron is more bound, showing how correlation plays a central role in the stability of H^-. In turn, the internal electron is still slightly pushed toward the nucleus feeling an effective nuclear charge $a \simeq 1.08$, which is slightly greater than the one using (6).

As in Sec. III B, we have used the virial theorem to validate the accuracy of our energies. For example, for

the negative hydrogen $T' = 0.5259187369$, $V'_{tot}/2 = -0.5259187365$ and $E[a,b,c] = -0.5259187360$ and for most of the other systems the virial theorem is fulfilled to the sixth decimal. Also, the same test has been done for the variational parameters obtaining a clear convergence to the values given in Table II.

Another aspect regarding the stability of two-electron systems is the critical (minimum) charge required by the nucleus to keep binding. The problem is left to compute $E[a,b,c]$ and compare it with the threshold energy $-Z^2/2$, and vary Z until $E[a,b,c] = -Z_c^2/2$. Using the wave function (9) we obtained a critical charge $Z_c \simeq 0.9197$, quite close to the value $Z_c \simeq 0.9107$ obtained with more sophisticated calculations [4, 13].

In order to approach the exact g.s. energy, in the literature has been common to use Hylleraas-like trial wave functions [6], i.e.

$$\Psi = e^{-\alpha s}\sum c_{lmn}s^\ell t^m u^n, \tag{14}$$

where $s = r_1 + r_2$, $t = r_2 - r_1$ and $u = r_{12}$, and α, $c_{\ell nm}$ are variational parameters. The best non-relativistic energies, as the ones given in column E_{nr} of Table I, were computed with generalizations of (14) using expansions that included hundreds of variational coefficients [7, 8].

IV. CHARACTERIZATION OF THE H^- ION

To get a clearer idea of the internal structure of H^- we present some information that helps to "shape" it. For this purpose we rewrite wave function (6) in the form $u^a(r_1)u^b(r_2) + u^b(r_1)u^a(r_2)$, where $u^\alpha(r) = 2\alpha^{3/2}\exp(-\alpha r)$ are the normalized single-particle radial functions (orbitals).

Figure 2 shows the behaviour of the radial orbital of each electron, u^a and u^b, in the negative hydrogen ion and in the positive two-electron oxygen ion. In the case of O^{6+}, where $a \simeq 8.68$ and $b \simeq 6.69$ (see Table II), the radial orbitals of each electron behave in a similar fashion, falling off quickly when moving away from the

nucleus. This agrees with the strong Coulomb attraction that in O^{6+} binds both electrons close to the nucleus. On the other hand, the electrons in H^- behave completely different. While the radial orbital of the internal electron ($a \simeq 1.04$) also falls off quickly for large distances from the nucleus, the radial orbital of the external electron ($b \simeq 0.28$) decays much more slowly, indicating weak interaction with the nucleus. In fact, the expectation values of the distances, shown in Table III, give account of the predominance of the Coulomb attraction for high Z values and the importance of correlation for lower values. The mean size of the orbits of the electrons, $\langle r_1 \rangle = \langle r_2 \rangle$, is quite greater for the negative hydrogen, $\langle r_i \rangle \simeq 3.11$, in comparison with the results for the helium and the positive ions. For example, in O^{6+} we have $\langle r_i \rangle \simeq 0.20$. Same conclusions can be obtained studying $\sqrt{\langle r_i^2 \rangle}$. It is also remarkable that the average separation between electrons $\langle r_{12} \rangle$ in H^- is much greater than $\langle r_i \rangle$, whereas for O^{6+} both distances are quite close. The relative dispersion of r_i and r_{12} (Table III) also is much larger in H^- than in the other two-electron systems.

V.   CONCLUSIONS

We conclude that the negative hydrogen ion is a special atomic system whose stability depends completely on the electron correlation. The implicit introduction of the correlation by splitting the electron orbitals in wave function (6) provides a large amount of correlation energy, binding the system and improving the energy values of the simple variational method. Furthermore, the explicit introduction of the correlation r_{12} improves the energy greatly in comparison with the best value [7].

It ought to be mentioned that the usage of the discussed trial wave functions is not a mere mathematical tool to achieve stability. It is necessary because mean field theories and other approximations do not take into account correlation, preventing the possibility of predicting stability for the negative hydrogen ion.

We also remark that the Chandrasekhar wave functions, although being simple and containing just two or three parameters, allow a physical description of H^- that is obscured in other multiparameter wave functions. The study of the radial orbitals of the electrons bring out a clear picture of the polarization of this ion in agreement with the hypothesis when studying the energy and its

variational parameters.

VI.   APPENDIX

The following expression were obtained by computing each matrix element of $\langle \psi' | H | \psi' \rangle$ integrating only for the spatial part, since the angular contribution is $(4\pi)^2$ for each term, which finally cancels out with the angular contribution of the norm.

$$N' = \frac{1}{8a^3b^3} + \frac{8}{(a+b)^6} + c^2 \left[\frac{3}{8} \frac{a^2+b^2}{a^5b^5} + \frac{192}{(a+b)^8} \right]$$
$$+ c \left[\frac{3a^4 + 9a^3b + 11a^2b^2 + 9ab^3 + 3b^4}{8a^4b^4(a+b)^3} + \frac{70}{(a+b)^7} \right] \tag{15}$$

$$T' = \frac{a^2+b^2}{16a^3b^3} + \frac{8ab}{(a+b)^6} + c \left[-5\frac{a^2 - 12ab + b^2}{(a+b)^7} \right.$$
$$\left. + \frac{3a^6 + 9a^5b + 10a^4b^2 + 6a^3b^3 + 10a^2b^4 + 9ab^5 + 3b^6}{16a^4b^4(a+b)^3} \right]$$
$$+ c^2 \left[\frac{3a^4 + 2a^2b^2 + 3b^4}{16a^5b^5} - 16\frac{a^2 - 10ab + b^2}{(a+b)^8} \right] \tag{16}$$

$$V' = -Z \left[\frac{a+b}{8a^3b^3} + \frac{8}{(a+b)^5} \right.$$
$$+ c \left(\frac{3a^4 + 8a^3b + 8a^2b^2 + 8ab^3 + 3b^4}{8a^4b^4(a+b)^2} + \frac{60}{(a+b)^6} \right)$$
$$\left. + c^2 \left(\frac{3}{16} \frac{2a^3 + a^2b + ab^2 + 2b^3}{a^5b^5} + \frac{144}{(a+b)^7} \right) \right] \tag{17}$$

$$U' = \frac{5}{2} \frac{1}{(a+b)^5} + \frac{a^2 + 3ab + b^2}{8a^2b^2(a+b)^3} + c \left[\frac{1}{4a^3b^3} + \frac{16}{(a+b)^6} \right]$$
$$+ c^2 \left[\frac{1}{16} \frac{3a^4 + 9a^3b + 11a^2b^2 + 9ab^3 + 3b^4}{a^4b^4(a+b)^3} + \frac{35}{(a+b)^7} \right] \tag{18}$$

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