

## Variational Treatment of Electronic and Mesonic Hydrogen Molecule Ions\*

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The Schrödinger equation for three Coulombic particles is formally reduced to an internal one. Solutions to this equation are sought via the variation principle without recourse to the Born-Oppenheimer expansion. Some calculations for electronic and mesonic isotopic hydrogen molecule ions demonstrate that even very simple trial functions give results comparable to those obtained from conventional Born-Oppenheimer treatments but with considerably less labor. Values for the total energies and internuclear distances for the ground and two lowest excited states are reported along with the separation of the centers of positive and negative charge which exists when the two nuclei have different masses.

### I. INTRODUCTION

AT the end of 1956, results of some liquid hydrogen bubble chamber experiments were reported<sup>1</sup> which seem to indicate that the process  $p+d \rightarrow \text{He}^3$  was catalyzed by  $\mu^-$  mesons by formation of a mesonic HD ion. The possible use of this process in controlled fusion reactions was discussed by Jackson<sup>2</sup> and more recently by Belyarev *et al.*<sup>3</sup> and Cohen *et al.*<sup>4</sup> The properties of the system  $(pud)^+$  are here of importance and a number of calculations and discussions of this ion and also of the molecule have appeared in the literature.<sup>5-9</sup> Most of these treatments use the Born-Oppenheimer approximation<sup>10</sup> including the necessary correction terms which are large because the ratio of the mesonic to the nucleonic mass is not small. It is, however, possible to avoid this approximation completely. Kolos *et al.*<sup>7</sup> did this by using a trial wave function which is a function of the relative coordinates of the three Coulombic particles and using the real masses of the particles in the Hamiltonian. The use of the relative coordinates will automatically take the motion of the center-of-mass of the system into account in a correct way. This method is therefore exact and, as in

all variational calculations the accuracy obtainable in practice depends only on the choice of the trial functions and the amount of numerical work which can be carried out. The method we have used is formally slightly different from the treatment of Kolos *et al.*,<sup>7</sup> but it is also exact and makes no use of the Born-Oppenheimer approximation. We have transformed the Hamiltonian in such a way that the operator representing the kinetic energy of the center-of-mass of the system is isolated. The remaining part, which is called the internal Hamiltonian, is then used in the Ritz variational procedure with trial functions of a form which closely resembles the physical picture one has of the  $\text{H}_2^+$  system. Our approach, when applied to  $\text{H}_2^+$ , is completely analogous to the He problem, the only difference being that the mass polarization operator, which has to be included as a small correction for a He atom with finite nuclear mass, is of great importance for  $\text{H}_2^+$ . In the coordinate system we use, the motion of the protons is referred to the electron as origin.

The existence of a bound state for a three Coulombic particle system requires that one particle has a charge of different sign from that of the other two. Even if one restricts oneself to particles all having charges of equal magnitude, as we will do, there are surprisingly many systems of physical interest such as  $\text{H}^-$ ,  $e^+e^-e^-$ ,  $(p\mu p)^+$ ,  $(pud)^+$ ,  $(d\mu d)^+$ ,  $\text{H}_2^+$ ,  $\text{HD}^+$ ,  $\text{D}_2^+$ . Of special interest are  $(pud)^+$  and  $\text{HD}^+$  because there is no restrictive exchange symmetry condition for these systems and one expects that they will have properties different from the systems having two identical particles.

In Sec. II we derive the Hamiltonian and give values for the physical parameters used in the calculation. The symmetry properties are discussed briefly in Sec. III. In Sec. IV the choice of trial function and some details regarding the calculations are discussed. The numerical results are given in Sec. V.

### II. THE HAMILTONIAN

The nonrelativistic Hamiltonian for three particles having masses and charges  $M_i$  and  $Z_i e$  ( $i=1, 2, 3$ ) and interacting Coulombically is

$$H_0 = -\sum_{i=1}^3 \frac{\hbar^2}{2M_i} \Delta_{q_i} + \sum_{j>i=1}^3 \frac{Z_i Z_j e^2}{|\mathbf{q}_i - \mathbf{q}_j|}, \quad (1)$$

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<sup>1</sup> L. W. Alvarez *et al.*, Phys. Rev. **105**, 1127 (1957).

<sup>2</sup> J. D. Jackson, Phys. Rev. **106**, 330 (1957).

<sup>3</sup> V. B. Belyarev, S. S. Gershtein, B. N. Zakharev, and S. P. Lomnev, Soviet Phys.—JETP **37** (10), 1171 (1960).

<sup>4</sup> S. Cohen, D. L. Judd, and R. J. Riddell, Jr., Phys. Rev. **119**, 397 (1960).

<sup>5</sup> H. Marshall and Th. Schmidt, Z. Physik **150**, 293 (1958).

<sup>6</sup> L. Spruch and M. Kelly, Phys. Rev. **116**, 911 (1959).

<sup>7</sup> W. Kolos, C. C. J. Roothaan, and R. Sack, Revs. Modern Phys. **32**, 178 (1960).

<sup>8</sup> S. Cohen, D. L. Judd, and R. J. Riddell, Jr., Phys. Rev. **119**, 384 (1960); see also Phys. Rev. Letters **110**, 1471 (1958).

<sup>9</sup> S. Cohen, J. R. Hiskes, and R. J. Riddell, Jr., Phys. Rev. **119**, 1025 (1960).

<sup>10</sup> Briefly, the Schrödinger equation is solved for fixed nuclei and the "electronic energy" is thereafter used as a potential energy in the nuclear Schrödinger equation. See, e.g., M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1956), p. 116 and appendices VII and VIII.

where  $\mathbf{q}_j$  is the vector locating particle  $j$  in a space-fixed coordinate system. The Hamiltonian is inconvenient in this form because it contains implicitly a part due to the kinetic energy of translation while it is only the internal energy that is responsible for the physically interesting features. One way to circumvent this difficulty is to make use of the commutation of  $H_0$  with the total linear momentum and to require the wave function to be an eigenfunction of the total momentum with eigenvalue zero:

$$\mathbf{P}_{\text{total}}\Phi=0. \quad (2)$$

An equivalent procedure which will be employed here is to introduce new independent variables which permit separation of the Hamiltonian into a translational part and a purely internal part. The new variables are chosen to be the coordinates of the center of mass,

$$\mathbf{R}=(M_1+M_2+M_3)^{-1}\sum_{i=1}^3M_i\mathbf{q}_i, \quad (3)$$

and the coordinates of two of the particles relative to the third,

$$\mathbf{r}_1=\mathbf{q}_1-\mathbf{q}_3, \quad (4)$$

$$\mathbf{r}_2=\mathbf{q}_2-\mathbf{q}_3. \quad (5)$$

Particle number three is the one with charge of odd sign. Substitution of this transformation into (1) leads to the separated form

$$H_0=H_T+H, \quad (6)$$

where  $H_T$  is the kinetic energy due to translation,

$$H_T=-\frac{1}{2}\hbar^2(M_1+M_2+M_3)^{-1}\Delta_R, \quad (7)$$

and  $H$  is the internal energy,

$$H=-\frac{\hbar^2}{2}\left(\frac{1}{M_1}+\frac{1}{M_3}\right)\Delta_{r_1}-\frac{\hbar^2}{2}\left(\frac{1}{M_2}+\frac{1}{M_3}\right)\Delta_{r_2}-\frac{\hbar^2}{M_3}\nabla_{r_1}\cdot\nabla_{r_2}+V. \quad (8)$$

The cross derivative term, called the "mass polarization," is a consequence of the nonorthogonality of the new coordinates. It could be avoided by using an orthogonal transformation to effect the separation<sup>11</sup> but only at the expense of complication of the potential energy expressions and loss of a simple physical picture of the variables.

The internal Hamiltonian is put in reduced form by definition of a reduced mass,  $\mu$ ,

$$\frac{1}{\mu}=\frac{1}{2M_1}+\frac{1}{2M_2}+\frac{1}{M_3}, \quad (9)$$

and use of the units  $\mu e^4/\hbar^2$  for energy and  $\hbar^2/\mu e^2$  for length. It is useful to define two additional parameters: an asymmetry parameter,  $f$ , for the particles 1 and 2,

$$f=(M_2-M_1)/(M_2+M_1), \quad (10)$$

and an "atomic character" parameter,  $b$ ,

$$b=1-\mu/M_3. \quad (11)$$

The Hamiltonian may then be written

$$H=T_0+b f T_1+(b-1)T_2+V, \quad (12)$$

where

$$T_0=-\frac{1}{2}(\Delta_{r_1}+\Delta_{r_2}), \quad (13)$$

$$T_1=-\frac{1}{2}(\Delta_{r_2}-\Delta_{r_1}), \quad (14)$$

$$T_2=\nabla_{r_1}\cdot\nabla_{r_2}, \quad (15)$$

$$V=\frac{Z_1Z_2}{|\mathbf{r}_1-\mathbf{r}_2|}+\frac{Z_2Z_3}{r_2}+\frac{Z_1Z_3}{r_1}. \quad (16)$$

The entire operator  $H$  is to be treated according to the Rayleigh-Ritz variation technique for the solution of the Schrödinger equation,  $H\Psi=E\Psi$ , so that the Born-Oppenheimer or similar approximations are not necessary. For all systems we have considered  $|Z_j|=1$ , so the Hamiltonians in their reduced form will only differ in the values of  $b$  and  $f$ . Some of the values of these parameters are displayed in Table I.

### III. SYMMETRY PROPERTIES

$H_0$  has the usual invariance under all translations and rotations. The translational symmetry is already accounted for by removal of that degree of freedom from the problem. The rotational symmetry is less trivially disposed of since not all the angular momentum resides in the variable  $\mathbf{R}$ . It is possible, however, to separate the total angular momentum,  $\mathbf{J}_0$ , into a part due to the motion of the center of mass and a part due to the relative motion of the system about the center of mass. To demonstrate this we consider a nonsingular transformation  $D$  defining new variables  $\varrho_j$  from the old ones  $\mathbf{q}_k$ :

$$\varrho_j=\sum_k D_{jk}\mathbf{q}_k, \quad (17)$$

such that  $\varrho_0=\mathbf{R}$  and  $\varrho_1, \dots, \varrho_{N-1}$  are the vectors locating  $(N-1)$  of the particles relative to the center-of-mass. The corresponding transformation on the gradients is the inverse of  $D$ ,

$$\nabla_{\varrho_j}=\sum_k \nabla_{q_k}(D^{-1})_{kj}. \quad (18)$$

Thus  $\mathbf{J}_0$  is unchanged in form by the transformation

$$\mathbf{J}_0=-i\hbar\sum_j\mathbf{q}_j\times\nabla_{q_j}=-i\hbar\sum_k\varrho_k\times\nabla_{\varrho_k}, \quad (19)$$

but the first term,  $-i\hbar\mathbf{R}\times\nabla_R$ , is clearly the angular momentum of the center of mass in the space-fixed

<sup>11</sup> J. O. Hirschfelder and J. S. Dahler, Proc. Natl. Acad. Sci. U. S. 42, 363 (1956).

TABLE I. Values of parameters<sup>a</sup> in the Hamiltonian (12).

System	$b$	$f$	$\mu/m_e = \text{energy}$ in atomic units	Length in units of $a_H$
$H^-(M_3 = \infty)$	1	0	1	1
$H^-$	0.9994 5567	0	0.9994 5567	1.0005 4462
$(\mu\mu d)^-$	0.9467 <sub>0</sub>	0	195.58 <sub>8</sub>	0.0051 128
$(\mu\mu p)^-$	0.8988 <sub>6</sub>	0	185.70 <sub>6</sub>	0.0053 849
$(e^-e^-e^+)^-$	0.5	0	0.5	2
$(p\mu p)^+$	0.1011 <sub>4</sub>	0	185.70 <sub>6</sub>	0.0053 849
$(p\mu d)^{+b}$	0.07784 <sub>1</sub>	-0.33299	190.51 <sub>8</sub>	0.0052 488
$(d\mu d)^+$	0.05330 <sub>2</sub>	0	195.58 <sub>8</sub>	0.0051 128
$H_2^+$	0.0005 4433	0	0.9994 5567	1.0005 4462
$HD^{+b}$	0.0004 0841	-0.33299	0.9995 9159	1.0004 0857
$D_2^+$	0.0002 7245	0	0.9997 2755	1.0002 7252
$H_2^+(M_1=M_2=\infty)$	0	0	1	1

<sup>a</sup> Based on the following values taken from the *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957).  $m_p/m_e = 1836.13$ ,  $m_\mu/m_e = 206.6$ ,  $m_p/m_a = 0.500 384_9$ , 1 atomic unit (a.u.)  $= m_e e^2 \hbar^{-2} = 219 474.6_2 \text{ cm}^{-1} = 27.2097 \text{ ev}$ ,  $1a_H = \hbar^2 e^{-2} m_e^{-1} = 0.529 172 \text{ \AA}$ .

<sup>b</sup> Particle No. 1 is D.

coordinate system and the remainder,

$$\mathbf{J} = -i\hbar \sum_{j=1}^{N-1} \mathbf{e}_j \times \nabla_{\rho_j}, \quad (20)$$

must be the angular momentum relative to the center of mass.  $\mathbf{J}$  is unchanged by a new nonsingular transformation on the internal coordinates and it commutes both with  $H$  and  $H_T$ . Thus, the rotation symmetry can also be reduced to a purely internal problem and can be accounted for by choosing internal trial functions to be eigenfunctions of  $J^2$  and  $J_z$ .

$H$  is further unchanged by an inversion through the center-of-mass, and wave functions must be either symmetric or antisymmetric with respect to this operation. If two of the particles are identical, they have exchange symmetry of a type dictated by whether they are bosons or fermions. Since our Hamiltonian is spin-free and no more than two particles are involved, the wave function may be written as a product of a space part and a spin part regardless of the values of the spins involved. Because of this, only spatial symmetry need be considered, with the understanding that the spin function symmetry will give the correct exchange behavior for the product. Even if there are no identical particles in the system, the exchange symmetry may hold approximately because all the terms in  $H$  are symmetric except for the antisymmetric  $T_1$ , which may cause only slight mixing of the two symmetry types.

We will denote the symmetry of the functions used  $J_{\pm}^{a(s)}$  where  $J = S, P, D \dots$  as usual, and the subscript and superscript refer, respectively, to inversion symmetry and exchange symmetry of the space function.

To decide among the various choices for trial function symmetry, it is helpful to look at the known symmetry properties of the ground-state functions for the limiting cases. In He-like ions this is described by the spectroscopic term symbol  $^1S$ , which is equivalent to  $S_+^s$ . For the  $H_2^+$  molecule, one can take the results from treat-

ments based on the adiabatic Born-Oppenheimer approximation. The symmetry of the ground electronic state is described as  $\Sigma_g^+$ , the vibrational states are totally symmetric, and the symmetry of the rotational states is given by  $(-1)^J$  for both inversion and exchange. Hence, the ground rotational state in each of the vibrational states for the ground electronic state has the same symmetry,  $S_+^s$ .

The obvious choice for calculation of ground-state properties would seem to be functions all of the type  $S_+^s$  when exchange symmetry is present, with some terms of the type  $S_-^s$  when the system is unsymmetric. This choice, when applied to  $H_2^+$ -like systems, will have the feature that the higher roots of the secular equation will be upper bounds for the excited vibrational levels.

#### IV. CHOICE OF TRIAL WAVE FUNCTIONS AND CALCULATION OF MATRIX ELEMENTS

This investigation was intended more to serve as a preliminary test of the practicality of doing calculations on simple molecular systems without using the Born-Oppenheimer approximation than to give extremely accurate results for the whole series of three Coulombic particle systems. Hence, it was desirable to use functions which were very simple but chosen in such a way that relatively few of them could give good descriptions of the molecular ions, electronic and mesonic. It is possible to choose such functions on physical grounds.

To reduce the labor in calculation of matrix elements, the functions were expressed in terms of the Hylleraas coordinates,<sup>12</sup>

$$\begin{aligned} s &= |\mathbf{r}_1| + |\mathbf{r}_2|, \\ t &= |\mathbf{r}_1| - |\mathbf{r}_2|, \\ u &= |\mathbf{r}_1 - \mathbf{r}_2|. \end{aligned} \quad (21)$$

Three angular coordinates are needed in addition to

<sup>12</sup> E. A. Hylleraas, *Z. Physik* **54**, 347 (1929). See also E. A. Hylleraas, *Norske Videnskaps-Akad. Oslo, Skrifter, Mat.-naturv. Kl. No. 6* (1932).

these for complete specification of the configuration, but  $S^s$  functions are independent of them and they may be omitted from the beginning.

The general function in the expansion was then taken of the form

$$\varphi_{kl} = u^k t^l \exp[-\frac{1}{2}s - \frac{1}{2}\gamma^{-2}(u-u_0)^2], \quad (22)$$

with the usual kind of scale parameter,  $\eta$ .<sup>13</sup>

The  $\exp[-\frac{1}{2}\gamma^{-2}(u-u_0)^2]$  dependence was used in order to describe the vibration of the two nuclei. This would be the correct ground-state eigenfunction, in fact, if the coordinate  $(u-u_0)$  really corresponded to a harmonic vibration. The higher  $u^k$  terms associated with excited vibrational states contribute, roughly speaking, anharmonicity corrections. Values of the nonlinear parameters  $\gamma$  and  $u_0$  were estimated from the experimental equilibrium distance and force constant for the electronic molecules. They were determined by approximate trial-and-error minimization of the energy obtained with a two-term function ( $\varphi_{00} + \varphi_{02}$ ) for the mesonic systems.

The  $t^l \exp(-\frac{1}{2}s)$  expansion was chosen because of the excellent result for the electronic energy of  $H_2^+$  obtained by James<sup>14</sup> using a two-term function of the type  $(1 + ct^2 u^{-2}) \exp(-ksu^{-1})$ . The difference between his variables  $t/u$ ,  $s/u$  and our  $t$  and  $s$  is somewhat offset by the effect of the Gaussian  $\exp[-\frac{1}{2}\gamma^{-2}(u-u_0)^2]$  in keeping  $u$  effectively near a constant value.

Powers of  $s$  were not included in the expansion in this pilot calculation, though it would be almost trivially simple to do so. They would certainly permit a lowering of the energy. In terms of the Born-Oppenheimer approximation, this lowering will be a result of a more accurate treatment of the electronic energy as a function of the internuclear distance. In more elaborate treatments this  $s$  dependence should not be omitted, but it was not expected to be particularly instructive at the present.

One disadvantage of the set (22) is that it is non-orthogonal and the question of approximate linear dependence arises. Unfortunately, this set develops a near singularity in the overlap matrix at a rather early stage. The ratio of the greatest and least eigenvalues of the overlap matrix has been used<sup>15</sup> as an indication of the severity of its near singularity. When the nonlinear parameters have the values used for the electronic systems, the ratio is  $4.56 \times 10^5$  with six functions, and  $6.41 \times 10^7$  for eight functions. The corresponding values for the functions used for the mesonic systems are  $1.02 \times 10^4$  and  $3.65 \times 10^5$ , respectively. This indicates that expansions of more than six terms are somewhat

unreliable for the former set. The latter could probably be extended to a few more terms, but not to really long expansions. One may get some understanding of this complication by looking at the analytical form of the set (22). When approaching the molecular limit, that is  $b \rightarrow 1$ , the nuclei become localized around a fixed internuclear distance,  $u_0$ . This implies that  $\gamma \rightarrow 0$  and the Gaussian gets very peaked, tending to a  $\delta$  function. The wavefunction is then essentially different from zero only for  $u$  values close to  $u_0$ . In this small range the different powers of  $u$  will be approximately linear dependent and as a consequence the overlap matrix will be almost singular. This limitation is one that is almost certain to turn up in sets chosen, as these are on the basis of their simplicity and physical appropriateness.

All the matrix elements were computed using a desk calculator, with the aid of tables of the functions  $\Lambda$  to be defined below. The eigenvalues of  $Hc = E\Delta c$  were determined by two-dimensional Jacobi rotations using the electronic computer at the Quantum Chemistry Laboratory. The matrix elements were calculated with the scale factor  $\eta = 1$ . In the computer the matrices for the different operators in  $H$  are multiplied by the appropriate power of a chosen  $\eta$  and then the  $H$  matrix is formed. If the chosen  $\eta$  value gives  $\partial E / \partial \eta \approx 0$  for the state of interest, the calculations are stopped; otherwise a new  $\eta$  value is used and the process repeated. The other expectation values reported were computed using a desk calculator.

For simplicity each function of the type (22) was multiplied by a factor of  $(\frac{1}{2}\pi^{\frac{1}{2}}e^{-\delta}\gamma^{-1})^{\frac{1}{2}}$ , where  $\delta = -u_0 + \frac{1}{4}\gamma^2$ , since this caused a common factor to drop out of all the integrals. Each matrix element can then be expressed as a sum of integrals of the type:

$$\begin{aligned} & 2\gamma^{-1}\pi^{-\frac{1}{2}}e^{-\delta} \int_0^{\infty} u^Q \exp[-\gamma^{-2}(u-u_0)^2 - u] du \\ & = 2\pi^{-\frac{1}{2}}\gamma^Q \int_{-\kappa}^{\infty} (x+\kappa)^Q \exp(-x^2) dx = \Lambda(Q; \kappa; \gamma), \quad (23) \end{aligned}$$

with  $\kappa = u_0\gamma^{-1} - \frac{1}{2}\gamma$ .

The integrals  $\Lambda$  satisfy the recursion relationship

$$\kappa\Lambda(Q; \kappa; \gamma) = \gamma^{-1}\Lambda(Q+1; \kappa; \gamma) - \frac{1}{2}Q\gamma\Lambda(Q-1; \kappa; \gamma). \quad (24)$$

The values of  $\Lambda(0; \kappa; \gamma) = 1 + 2\pi^{-\frac{1}{2}} \int_0^{\kappa} \exp(-x^2) dx$  and  $\Lambda(1; \kappa; \gamma) = \gamma[\gamma\Lambda(0; \kappa; \gamma) + \pi^{-\frac{1}{2}} \exp(-\kappa^2)]$  were taken from the U. S. National Bureau of Standards table of the error function and its derivatives. The other  $\Lambda$  integrals were obtained on the electronic computer by use of the recursion relation. The maximum number of  $\Lambda$  integrals needed for the matrix elements is 7, and for most of them 2 or 3  $\Lambda$  integrals are sufficient. Each matrix element was calculated with 9 correct decimal figures.

<sup>13</sup> See, e.g., P. O. Löwdin, *J. Mol. Spectroscopy* **3**, 46 (1959).

<sup>14</sup> See L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, New York, 1935), p. 333.

<sup>15</sup> T. L. Bailey and J. L. Kinsey, preprint No. 45 from the Quantum Chemistry Group, Uppsala University, Uppsala, Sweden, July 1, 1960 (unpublished).

## V. RESULTS AND DISCUSSION

In this section the numerical results of the calculations are presented. Unless other units are specifically stated, all quantities are expressed in atomic units (a.u.) with the appropriate reduced mass put equal to 1. Experimental values are given for comparison when they are known. Otherwise, the best theoretical values available in the literature are quoted.

The different basic sets used, all having typical members of the form (22), will be identified by the following code:

- A. two functions:  $k=0$ ;  $l=0, 2$ .
- B. four functions:  $k=0, 1$ ;  $l=0, 2$ .
- C. six functions:  $k=0, 1, 2$ ;  $l=0, 2$ .
- D. eight functions:  $k=0, 1, 2, 3$ ;  $l=0, 2$ .
- E. four functions:  $k=0$ ;  $l=0, 1, 2, 3$ .
- F. eight functions:  $k=0, 1$ ;  $l=0, 1, 2, 3$ .
- G. twelve functions:  $k=0, 1, 2$ ;  $l=0, 1, 2, 3$ .

The sets E, F, and G are important only for the asymmetric system,  $\text{HD}^+$  and  $(p\mu d)^+$ , because the functions containing odd powers of  $l$  are connected to those containing even powers of  $l$  only by the term  $b/T_1$  in the Hamiltonian (12). The values of the nonlinear parameters used in the calculations are for the electronic systems  $\gamma=0.415$  and  $\kappa=u_0\gamma^{-1}-\frac{1}{2}\gamma=6.33$  and for the mesonic systems  $\gamma=1.7$  and  $\kappa=1.00$ . The energies were not fully minimized with respect to these parameters.

Results for the energies of the electronic systems are contained in Table II and those for the mesonic systems in Table III. Since the zero of potential energy was taken at infinite separation of all three particles, the energies computed are relative to that completely dissociated state. These energies are not the true binding energies because the three-body system dissociates at a lower energy into one free particle and a hydrogen atom-like two-particle system. The energy of this state is  $-\frac{1}{2}$  for the symmetric system. The asymmetric ones have two possibilities for this kind of dissociation, the one of lower energy being the one in which the free particle is the lighter of the two having like charge. The energy for this state is  $-1/[2(1+bf)]$ .

Even though the sets used were quite small, it is seen that the ground-state energies are fairly accurate, especially for the electronic systems. The excited vibrational states are somewhat less well described, but the energies are still remarkably close to the actual values. The vibrational frequencies, being small differences between large numbers are especially sensitive to errors in the location of the energy levels. For  $\text{H}_2^+$ , using the six-term wave function (C) giving the lowest ground-state energy, our calculations yield the values  $2456\text{ cm}^{-1}$  and  $3123\text{ cm}^{-1}$  for the first and second vibrational frequencies. The separation theorem<sup>16</sup> tells us that the roots to our secular equation are upper bounds to the exact eigenvalues, and using the three upper bounds we obtain for  $\text{H}_2^+$  the first and second vibrational frequencies  $2437\text{ cm}^{-1}$  and  $2834\text{ cm}^{-1}$ , respectively. The experimental<sup>17</sup> values are  $2173\text{ cm}^{-1}$  and  $2049\text{ cm}^{-1}$ .

TABLE II. Energies for the electronic systems. <sup>a</sup> Nonlinear parameters:  $\gamma=0.415$ ,  $\kappa=6.33$ , in atomic units.

System	Basis type	order	Scale factor	$-E_0$	$-E_1$	$-E_2$	
$\text{H}_2^+(\infty)$	A	2	1.352	0.599 517			
	B	4	1.3583	0.599 616	0.593 358		
	C	6	1.3583	0.600 803	0.594 745	0.584 057	
	"Exact"			0.602 64 <sup>b</sup>			
$\text{D}_2^+$	A	2	1.349	0.598 078			
	B	4	1.3523	0.598 136	0.589 041		
	C	6	1.3523	0.598 332	0.590 091	0.578 083	
$\text{HD}^+$	A	2	1.347	0.597 364			
	B	4	1.3499	0.597 410	0.586 886		
	C	6	1.3499	0.597 446	0.587 777	0.574 762	
	E	2×2	1.34656	0.597 364			
	F	2×4	1.3497	0.597 410	0.586 890		
	F	2×4	1.3223	0.597 204	0.587 130		
$\text{H}_2^+$	A	2	1.345	0.596 651			
	B	4	1.3475	0.596 688	0.584 743		
	C	6	1.3475	0.596 689	0.585 494	0.571 256	
	C	6	1.330	0.596 605	0.585 580	0.571 964	
	C	6	1.283	0.595 535	0.584 941	0.572 659	
	Cohen <i>et al.</i> <sup>c</sup>				0.597 249	0.587 266	0.577 863
	Experimental <sup>d</sup>				0.597 405	(0.587 499)	(0.578 158)

<sup>a</sup> Where more than one scale-factor is listed for any set, the eigenvalue for which the scale-factor is optimized is italicized.

<sup>b</sup> E. A. Hylleraas, *Z. Physik* **71**, 739 (1931).

<sup>c</sup> See reference 9.

<sup>d</sup> See reference 17. Kolos *et al.*<sup>7</sup> gives  $E_0 = -0.59715$  a.u.

<sup>16</sup> See e.g., P. O. Löwdin, *Advances in Chemical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. 2, p. 266.

<sup>17</sup> G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).

TABLE III. Energies for the mesonic systems.<sup>a</sup> Nonlinear parameters:  $\gamma=1.7$ ,  $\kappa=1.00$ , in atomic units.

System	type	Basis order	Scale factor	$-E_0$	$-E_1$	$-E_2$
$(d\mu d)^+$	A	2	1.307	0.555 696		
	B	4	1.312	0.555 836	0.460 817	
	C	6	1.312	0.556 531	0.480 883	0.332 921
	D	8	1.312	0.557 896	0.483 393	0.408 025
$(p\mu d)^+$	D	8	1.152	0.551 598	0.490 130	0.433 420
	A	2	1.291	0.548 681		
	B	4	1.295	0.548 755	0.435 420	
	C	6	1.2947	0.549 639	0.455 624	0.288 241
	D	8	1.295	0.551 167	0.462 312	0.356 501
	E	2×2	1.2907	0.549 770		
	F	2×4	1.294975	0.549 969	0.437 482	0.358 674
	F	2×4	1.0055	0.528 104	0.463 367	0.441 676
	F	2×4	0.8884	0.506 692	0.460 423	0.448 520
G	2×6	1.2947	0.550 889	0.458 047	0.391 283	
$(p\mu p)^+$	A	2	1.274	0.542 184		
	B	4	1.2785	0.542 290	0.412 916	
	C	6	1.28	0.544 272	0.432 985	0.274 324
	D	8	1.28	0.545 962	0.444 291	0.311 417

<sup>a</sup> Where more than one scale-factor is listed for any set, the eigenvalue for which the scale-factor is optimized is italicized.

The total ground-state energy for  $H_2^+$  is 130 887  $\text{cm}^{-1}$  using our six-term function whereas the experimental<sup>17</sup> value is 131 044  $\text{cm}^{-1}$ . It is of interest to note that even the two-term function (A) gives very satisfactory results for the electronic systems.

Our ground-state energies for the mesonic systems are uniformly slightly inferior to those of Cohen *et al.*<sup>8</sup> and Kolos *et al.*,<sup>7</sup> an unsurprising fact in consideration of the much greater elaborateness of their calculations. Neither of these works gives an energy for any excited  $S^s$  states. For the  $(p\mu d)^+$  system we observe that the inclusion of the odd powers of  $t$  has considerably lowered the ground-state energy as can be seen by comparing the results for the two corresponding sets, A and E, B and F, C and G. In Table IV our results are compared with the results obtained by Cohen *et al.*<sup>4</sup> and Kolos *et al.*<sup>7</sup>

It is illuminating to consider the change in character of three Coulombic particle systems as  $b$  goes from 1 to 0, that is from the atomic to the molecular ion. Let us first consider the total energy  $E_0$  in reduced units for systems with two identical particles. For  $b=1$  we have  $E_0 = -0.52775$ ,<sup>18</sup>  $\partial E_0/\partial b = -0.03288$ ,<sup>18</sup> and

$\partial^2 E_0/\partial b^2 = -0.06$ ,<sup>19</sup> for  $b=0.5$ ,  $E_0 = -0.52399$ ,<sup>7</sup> and for  $b=0$ ,  $E_0 = -0.60264$  (reference a, Table II). Obviously there is a maximum  $E_0$  for some  $b$  value. We conjecture that this maximum will occur for  $b = \frac{2}{3}$ . This is suggested by the fact that  $b = \frac{2}{3}$  corresponds to the masses  $M_1 = M_2 = \frac{1}{2}M_3$ , and for these masses the center-of-mass is exactly halfway between the "nucleus" and the center of mass of the two identical particles. The  $b$  value might then be used as a criterion of atomic character ( $b > \frac{2}{3}$ ) and molecular character ( $b < \frac{2}{3}$ ). From this point of view the system  $(e^+e^+e^-)^+$  has molecular character, and one would expect that a trial function emphasizing this character should give good results. It is also interesting to consider the change in the correlated motion of the two identical particles as  $b$  goes from 1 to 0. For  $b=1$ , that is  $H^{-1}$  ( $M_3 = \infty$ ), the Coulomb repulsion between the electrons is responsible for the correlation, which may be split up in two terms, radial and angular. For  $H^{-1}$  the radial correlation is dominant and we do not find the electrons at an approximately constant distance apart. The mass

TABLE IV. Total energies in eV for mesonic molecular ions.<sup>a</sup>

System	Cohen <i>et al.</i> <sup>b</sup>	Present work	Kolos <i>et al.</i> <sup>c</sup>
$(p\mu p)^+$	2771	2759	2778
$(p\mu d)^+$	2878	{ 2856 <sup>d</sup>	...
		{ 2857 <sup>e</sup>	
$(d\mu d)^+$	2986	2969	2981

<sup>a</sup> The total energy of  $(p\mu)$  is 2526 eV and of  $(d\mu)$  2661 eV using the constants given in Table I.

<sup>b</sup> See reference 4.

<sup>c</sup> See reference 7.

<sup>d</sup> Using function G, which contains both odd and even powers of  $t$ .

<sup>e</sup> Using function D. The function C, which is identical to the symmetric part of G, gives 2849 eV.

<sup>18</sup> C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

TABLE V. Expectation values  $\langle u \rangle$  in atomic units for the ground state.

System \ Function	A	B	C	D
$H_2^+(\infty)$	2.02968	2.07455	2.01308	
$D_2^+$	2.03426	2.06278	2.04365	
$HD^+$	2.03729	2.06057	2.05359	
$H_2^+$	2.04032	2.05977	2.06053	
$(d\mu d)^+$	2.67159	2.69302	2.66129	2.65225
$(p\mu d)^+$	2.70534	2.73504	2.76850	2.79022
$(p\mu p)^+$	2.74259	2.77505	2.84614	2.89134

<sup>19</sup> A. Fröman, preprint No. 34 from the Quantum Chemistry Group, Uppsala University, Uppsala, Sweden, December 1, 1959 (unpublished).

TABLE VI. Values of  $\delta$  defined in Eq. (26) for the ground states.

System	H <sup>-</sup>	e <sup>+</sup> e <sup>+</sup> e <sup>-</sup>	(pμp) <sup>+</sup>	(pμd) <sup>+</sup>	(dμd) <sup>+</sup>	H <sub>2</sub> <sup>+</sup>	H <sub>2</sub> <sup>+</sup> (∞)
δ	274×10 <sup>-6</sup>	170×10 <sup>-6</sup>	127×10 <sup>-6</sup>	323×10 <sup>-6</sup>	773×10 <sup>-7</sup>	142×10 <sup>-21</sup>	0
Reference	18	19		This work			

polarization gives an angular correlation effect and, as  $b \rightarrow 0$ , this gets more important than the radial effect caused by the Coulomb repulsion: the two identical particles then tend to be on opposite sides of the "nucleus" which for H<sub>2</sub><sup>+</sup> is the electron, and the distance between them tends to a constant value. As  $b$  goes from 1 to 0 the correlation changes from essentially radial type due to the Coulomb repulsion, to angular type, caused by the combined effort of the mass polarization and the Coulomb repulsion.

In Table V, the average internuclear distance,  $R_0 = \langle u \rangle$ , in the ground state are tabulated. Conversion of the values obtained with six functions (C) for the electronic systems into Angström units gives:

$$R_0[\text{H}_2^+(\infty)] = 1.0653; \quad R_0(\text{HD}^+) = 1.0871;$$

$$R_0(\text{D}_2^+) = 1.0817; \quad R_0(\text{H}_2^+) = 1.0910.$$

These values may be compared with the experimental  $R_e = 1.06_0$  A.<sup>17</sup> This number is the value of  $R$  for minimum potential energy for the nuclei and is in general not the same as  $R_0$ , the average internuclear distance. For H<sub>2</sub><sup>+</sup>(∞),  $R_e$  and  $R_0$  should be equal as they approximately are in our result. Owing to the anharmonicity  $R_0$  will generally be larger than  $R_e$  and our results show the expected trend. For the mesonic systems no experimental results are available. The eight-term function (D) gives

$$R_0[(d\mu d)^+] = 0.007\ 176\ \text{A};$$

$$R_0[(p\mu d)^+] = 0.007\ 750\ \text{A};$$

$$R_0[(p\mu p)^+] = 0.008\ 239\ \text{A}.$$

The internuclear distance for the mesonic systems is remarkably short and should be compared with the range of the nuclear forces which is of the order 10<sup>-5</sup> A.

For the same eight-term functions, average values of  $u^2$  were calculated for the mesonic systems in order to get some measure of the average vibrational amplitudes. Values obtained for the relative root-mean-square displacement  $x$ ,

$$x = \left[ \frac{\langle u^2 \rangle - \langle u \rangle^2}{\langle u \rangle^2} \right]^{\frac{1}{2}}, \quad (25)$$

TABLE VII. Charge separation,  $\rho_{\text{av}}$  in atomic units for ground states.

Function	HD <sup>+</sup>	(pμd) <sup>+</sup>
E	0.0004479	0.16281
F	0.0005373	0.18584

are

$$x_0[(d\mu d)^+] = 0.2985,$$

$$x_0[(p\mu d)^+] = 0.3056,$$

$$x_0[(p\mu p)^+] = 0.3155.$$

These large values were to be expected in view of the rather broad Gaussian function, i.e., small "force constants," required for those systems. Kolos *et al.*<sup>7</sup> obtained for the system e<sup>+</sup>e<sup>+</sup>e<sup>-</sup>,  $x_0 = 0.5254$  and for H<sub>2</sub><sup>+</sup>(∞)  $x_0$  is, of course, zero.

A further quantity of importance for the mesonic ions is the probability of the two nuclei being sufficiently close for the nuclear forces to act. For our model, with only a Coulomb potential, this is effectively the probability density for zero separation of the nuclei, i.e., the expectation value for  $\delta^{(3)}(\mathbf{r}_{12})$ . If our function is  $\psi = \sum_k c_k \varphi_k$ , where  $\varphi_0 \equiv \varphi_{00}$  is defined in (22) and all other terms contain powers of  $u$  or  $t$ , then

$$\delta \equiv \langle \delta^{(3)}(\mathbf{r}_{12}) \rangle = 4c_0^2 \eta^3 (\pi \gamma^2)^{-\frac{1}{2}} \exp(-\kappa^2). \quad (26)$$

The values computed with the largest basis we have used in the calculations are reported in Table VI.

For HD<sup>+</sup> and (pμd)<sup>+</sup> a "charge asymmetry" exists, i.e., a separation of the centers of positive and negative charge. The expression for this separation in terms of the Hylleraas coordinates is

$$\rho_{\text{av}} = \langle \rho \rangle = \frac{1}{2} \langle st/u \rangle, \quad (27)$$

which is easily derived from the fact that we have axial symmetry around the "electronic" axis so we need only the distance,  $\rho$ , between the projection of the "nucleus" on this axis and the midpoint between the "electrons." The values obtained are given in Table VII. The value for HD<sup>+</sup> is to be compared to the dipole moment of the neutral HD molecule which has been estimated by Blinder<sup>20</sup> to be  $\mu_{\text{HD}} = 8.89 \times 10^{-4}$  Debye unit. When the proper conversion factors are used we obtain for HD<sup>+</sup>  $\rho_{\text{av}} = 1.37 \times 10^{-4}$  Debye unit, which supports the qualitative idea that  $\rho_{\text{av}}(\text{HD}^+)$  should be about one half  $\mu_{\text{HD}}$ . For (pμd)<sup>+</sup> we obtain  $\rho_{\text{av}} = 2.48 \times 10^{-3}$  Debye unit.

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<sup>20</sup> S. M. Blinder, J. Chem. Phys. 32, 105 (1960).