Binding Energy of the Positronium Molecule*

R. R. Sharma

Department of Physics, Purdue University, Lafayette, Indiana

(Received 22 January 1968)

A suitable variational wave function has been used to obtain the binding energy of the positronium molecule, a stable complex consisting of two electrons and two positrons. We find the binding energy of the complex to be 0.948 eV. This shows that the previous calculations estimated the binding energy of the complex an order of magnitude too low.

I. INTRODUCTION

RECENTLY an accurate knowledge of the binding energy of the positronium molecule, a complex consisting of two electrons and two positrons, has become quite important. This is due to the experiments by Haynes[1] which prove the existence of a similar complex, namely, excitonic molecule in Si where the positive holes play a role of positrons. The history of such complexes goes back to 1946 when a theoretical analysis of Wheeler[2] did not establish the stable bound state for positronium molecule. Later on, Hylleraas and Ore[3] showed that the entity positronium molecule should be stable against dissociation.

No experimental evidence for the positronium molecule has yet been reported. However, as mentioned earlier, a similar complex, excitonic molecule has been observed experimentally by Haynes. According to his experiments the binding energy W_{x_2} of the excitonic molecule in Si was found to be ≤ 2 meV.[4] The binding energy[5] W_x of the exciton in the same host lattice is 8 meV. The ratio of W_x to W_{x_2} is therefore about 4. On the other hand the best available calculations of Ore[6] give the binding energy W_{Ps_2} of the positronium molecule as 0.135 eV. Also, the binding energy[2] W_{Ps} of the positronium (a complex consisting of an electron and a positron) is 6.8 eV. From these values the energy ratio W_{Ps}/W_{Ps_2} equals to nearly 50. It should be noticed that the energy ratio in this case is an order of magnitude higher than the ratio W_x/W_{x_2} in the previous case. Assuming the interaction between the particles to be Coulombic, one can see that the ratio (W_x/W_{x_2}) [or (W_{Ps}/W_{Ps_2})] is a function of the ratio of the mass of the electron to that the hole (or positron) and independent of the dielectric constant of the medium. The ratio of the mass of the electron to that of the hole in Si is nearly one (about 0.8) while the corresponding ratio is exactly one in the case of the positronium and positronium

molecule. Therefore we expect that the value of (W_{Ps}/W_{Ps_2}) should be close to the experimental value of (W_x/W_{x_2}). This leads one to believe that the estimate by Ore of the binding energy of the positronium molecule is very low. We have demonstrated that the binding energy of the positronium molecule is 0.948 eV which is about seven times higher than the value obtained by Ore.

In our calculations a five-parameter variational wave function has been used. The energy matrix elements were calculated by a method given by James and Coolidge.[7] In Sec. II we explain our procedure for estimating the binding energy of our system, namely the positronium molecule. The final Sec. III is devoted to the discussion.

II. PROCEDURE

The positronium molecule is regarded as a complex consisting of four particles, two electrons, and two positrons each of mass m_0, interacting with one another through a Coulomb potential. The Hamiltonian for the system is

$$\mathcal{H} = -(\hbar^2/2m_0)(\nabla_{+1}^2 + \nabla_{+2}^2 + \nabla_{-1}^2 + \nabla_{-2}^2) + V_0, \quad (1)$$

where V_0 is the potential of interaction given by

$$V_0 = e^2(1/r_{+1+2} + 1/r_{-1-2} - 1/r_{+1-1} \\ - 1/r_{+2-2} - 1/r_{+1-2} - 1/r_{+2-1}). \quad (2)$$

In Eq. (1) the first four terms are the kinetic energies of two positrons and two electrons with respect to a fixed origin O of a coordinate system. The positrons are designated by $+1$ and $+2$ and the electrons by -1 and -2. r_{+1+2} is the distance between the positrons $+1$ and $+2$. Other distances have a similar meaning.

Let the unit of length be $\hbar^2/(m_0 e^2)$ and the unit of energy be $m_0 e^4/\hbar^2$. In these units the Hamiltonian becomes

$$\mathcal{H} = -\tfrac{1}{2}(\nabla_{+1}^2 + \nabla_{+2}^2 + \nabla_{-1}^2 + \nabla_{-2}^2) + V_0, \quad (3)$$

where

$$V_0 = 1/r_{+1+2} + 1/r_{-1-2} - 1/r_{+1-1} \\ - 1/r_{+2-2} - 1/r_{+1-2} - 1/r_{+2-1}. \quad (4)$$

Now, we transform the Hamiltonian and eliminate the kinetic energy of the center of mass since it does not

* Supported by Advanced Research Projects Agency.
[1] J. R. Haynes, Phys. Rev. Letters **17**, 860 (1966).
[2] J. A. Wheeler, Ann. N. Y. Acad. Sci. **48**, 221 (1946).
[3] E. A. Hylleraas and A. Ore, Phys. Rev. **71**, 493 (1947).
[4] R. R. Sharma (to be published); see also Bull. Am. Phys. Soc. No. 1, **13**, 91 (1968). This theoretical analysis, which is similar to the one presented here, gives an energy equal to 0.70 MeV for the lowest bound state of the excitonic molecule in Si.
[5] J. R. Haynes, M. Lax, and W. F. Flood, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Academic Press Inc., New York, 1961), p. 423.
[6] A. Ore, Phys. Rev. **71**, 913 (1947).
[7] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

contribute to the binding energy of the system. For this purpose, we take a new set of coordinates defined by

$$\mathbf{R}_{c.m.} = \tfrac{1}{4}(\mathbf{r}_{+1}+\mathbf{r}_{+2}+\mathbf{r}_{-1}+\mathbf{r}_{-2}),$$

$$\mathbf{R} = \mathbf{r}_{+1}-\mathbf{r}_{+2},$$

$$\mathbf{R}_1 = \mathbf{r}_{-1}-\tfrac{1}{2}(\mathbf{r}_{+1}+r_{+2}), \quad (5)$$

$$\mathbf{R}_2 = \mathbf{r}_{-2}-\tfrac{1}{2}(\mathbf{r}_{+1}+\mathbf{r}_{+2}),$$

where $\mathbf{r}_{+1}$ and $\mathbf{r}_{+2}$ are the position vectors of the positrons $+1$ and $+2$ with respect to the origin O. Other vectors carry a similar meaning; $\mathbf{R}_{c.m.}$ in Eq. (5) denotes the center of mass of the system; $\mathbf{R}$ is the distance between the positrons; and $\mathbf{R}_1$ and $\mathbf{R}_2$ are the position vectors of the electrons -1 and -2 measured from the midpoint of the line joining the positrons.

In terms of the new coordinate system defined by Eq. (5), the Hamiltonian (3) is transformed into

$$\mathcal{3C} = -\tfrac{1}{8}\nabla_{c.m.}{}^2 - \nabla_R{}^2 - \tfrac{3}{4}\nabla_1{}^2 - \tfrac{3}{4}\nabla_2{}^2 - \tfrac{1}{2}\nabla_1\cdot\nabla_2 + V_0, \quad (6)$$

with

$$\nabla_{c.m.} = \frac{\partial}{\partial\mathbf{R}_{c.m.}}, \quad \nabla_R = \frac{\partial}{\partial\mathbf{R}}, \quad \nabla_1 = \frac{\partial}{\partial\mathbf{R}_1}, \quad \nabla_2 = \frac{\partial}{\partial\mathbf{R}_2}.$$

The first term in Eq. (6) is the kinetic energy of the center of mass of the system. Since this term does not con-

tribute to the binding energy of the system, we drop it and write

$$\mathcal{3C} = -\nabla_R{}^2 - \tfrac{3}{4}\nabla_1{}^2 - \tfrac{3}{4}\nabla_2{}^2 - \tfrac{1}{2}\nabla_1\cdot\nabla_2 + V_0. \quad (7)$$

We are now interested in getting the lowest eigenvalue of the Hamiltonian (7). To this end, we take a variational wave function Ψ of the form

$$\Psi = f(\mathbf{R})g(\lambda_1,\mu_1,\lambda_2,\mu_2,\rho_{12}), \quad (8)$$

where λ_1, μ_1, etc., are the elliptical coordinates, defined by

$$R\lambda_1 = r_{+1-1}+r_{+2-1}, \quad R\lambda_2 = r_{+1-2}+r_{+2-2},$$

$$R\mu_1 = r_{+1-1}-r_{+2-1}, \quad R\mu_2 = r_{+1-2}-r_{+2-2}, \quad (9)$$

$$R\rho_{12} = 2r_{-1-2}.$$

In eliptical coordinates the operator $\nabla_1{}^2$ has the form[8]

$$\nabla_1{}^2 = \frac{4}{R^2(\lambda_1{}^2-\mu_1{}^2)}\left\{\frac{\partial}{\partial\lambda_1}\left[(\lambda_1{}^2-1)\frac{\partial}{\partial\lambda_1}\right]\right.$$
$$\left.+\frac{\partial}{\partial\mu_1}\left[(1-\mu_1{}^2)\frac{\partial}{\partial\mu_1}\right]+\frac{\lambda_1{}^2-\mu_1{}^2}{(\lambda_1{}^2-1)(1-\mu_1{}^2)}\frac{\partial^2}{\partial\varphi_1{}^2}\right\}, \quad (10)$$

where φ_1 is the azimuthal angle for electron 1. One can obtain $\nabla_2{}^2$ from Eq. (10) on replacing 1 by 2. As regards the operator $\nabla_1\cdot\nabla_2$ we write

$$\nabla_1\cdot\nabla_2 = \frac{4}{R^2}\left[\frac{1}{(\lambda_1{}^2-\mu_1{}^2)(\lambda_2{}^2-\mu_2{}^2)}\left\{(\mu_1\mu_2(\lambda_1{}^2-1)(\lambda_2{}^2-1)+\lambda_1\lambda_2 M\cos(\varphi_1-\varphi_2))\frac{\partial}{\partial\lambda_1}\frac{\partial}{\partial\lambda_2}\right.\right.$$

$$+(\lambda_1\lambda_2(1-\mu_1{}^2)(1-\mu_2{}^2)+\mu_1\mu_2 M\cos(\varphi_1-\varphi_2))\frac{\partial}{\partial\mu_1}\frac{\partial}{\partial\mu_2}+(\mu_1\lambda_2(\lambda_1{}^2-1)(1-\mu_2{}^2)-\lambda_1\mu_2 M\cos(\varphi_1-\varphi_2))\frac{\partial}{\partial\lambda_1}\frac{\partial}{\partial\mu_2}$$

$$\left.+(\lambda_1\mu_2(1-\mu_1{}^2)(\lambda_2{}^2-1)-\lambda_2\mu_1 M\cos(\varphi_1-\varphi_2))\frac{\partial}{\partial\lambda_2}\frac{\partial}{\partial\mu_1}\right\}+\frac{M\sin(\varphi_1-\varphi_2)}{(\lambda_1{}^2-\mu_1{}^2)(\lambda_2{}^2-1)(1-\mu_2{}^2)}\left\{\lambda_1\frac{\partial}{\partial\lambda_1}\frac{\partial}{\partial\varphi_2}-\mu_1\frac{\partial}{\partial\mu_1}\frac{\partial}{\partial\varphi_2}\right\}$$

$$+\frac{M\sin(\varphi_1-\varphi_2)}{(\lambda_2{}^2-\mu_2{}^2)(\lambda_1{}^2-1)(1-\mu_1{}^2)}\left\{\mu_2\frac{\partial}{\partial\varphi_1}\frac{\partial}{\partial\mu_2}-\lambda_2\frac{\partial}{\partial\lambda_2}\frac{\partial}{\partial\varphi_1}\right\}+\{\cos(\varphi_1-\varphi_2)/M\}\frac{\partial}{\partial\varphi_1}\frac{\partial}{\partial\varphi_2}\right], \quad (11)$$

where

$$M^2 = (\lambda_1{}^2-1)(\lambda_2{}^2-1)(1-\mu_1{}^2)(1-\mu_2{}^2)$$

and φ_2 is the azimuthal angle for electron 2.

The form (11) has been obtained starting from the Cartesian form of $\nabla_1\cdot\nabla_2$, namely,

$$\nabla_1\cdot\nabla_2 = \frac{\partial}{\partial x_1}\frac{\partial}{\partial x_2}+\frac{\partial}{\partial y_1}\frac{\partial}{\partial y_2}+\frac{\partial}{\partial z_1}\frac{\partial}{\partial z_2},$$

and replacing $\partial/\partial x_1$, etc., by

$$\frac{\partial}{\partial x_1} = \frac{\partial\lambda_1}{\partial x_1}\frac{\partial}{\partial\lambda_1}+\frac{\partial\mu_1}{\partial x_1}\frac{\partial}{\partial\mu_1}+\frac{\partial\varphi_1}{\partial x_1}\frac{\partial}{\partial\varphi_1}$$

and similar expressions. The partial derivatives $\partial\lambda_1/\partial x_1$,

etc., were obtained from the relations[8] connecting the Cartesian coordinates with elliptical coordinates.

If the wave function Ψ is normalized, the eigenvalue W of the system is given by

$$W = \langle\Psi|\mathcal{3C}|\Psi\rangle. \quad (12)$$

We immediately obtain

$$W = -\langle fg|\nabla_R{}^2|fg\rangle + \langle f|V(R)|f\rangle \quad (13)$$

with

$$V(R) = \langle g|H|g\rangle, \quad (14)$$

where

$$H = -\tfrac{3}{4}\nabla_1{}^2 - \tfrac{3}{4}\nabla_2{}^2 - \tfrac{1}{2}\nabla_1\cdot\nabla_2 + V_0. \quad (15)$$

[8] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1961), p. 367.

Following the treatment[7] for the hydrogen molecule we choose for g a variational wave function of the simple form

$$g = N^{-1/2} \sum_{mnjkp} C_{mnjkp} \Psi_{mnjkp},\qquad (16)$$

where

$$\Psi_{mnjkp} = (2\pi)^{-1} \exp[-\delta(\lambda_1+\lambda_2)]$$
$$\times (\lambda_1{}^m \lambda_2{}^n \mu_1{}^j \mu_2{}^k \rho^p + \lambda_1{}^n \lambda_2{}^m \mu_1{}^k \mu_2{}^j \rho^p).\quad (17)$$

The factor N is a normalization constant determined by

$$\langle g | g \rangle = 1 \qquad (18)$$

and δ and C_{mnjkp} are the variational parameters.

It can be shown that

$$V(R) = P/R^2 - Q/R,\qquad (19)$$

where

$$P = \frac{1}{N_0} \sum_{\substack{m_a n_a j_a k_a p_a;\ m_b n_b j_b k_b p_b}} C_{m_a n_a j_a k_a p_a} C_{m_b n_b j_b k_b p_b}$$
$$\times (u_{ab}{}^{(1)} + u_{ab}{}^{(2)} + u_{ab}{}^{(3)} + u_{ab}{}^{(4)}).\quad (20)$$

In Eq. (20),

$$u_{ab}{}^{(1)} = \tfrac{3}{2}P_1 + \tfrac{1}{2}[P_2 + 2P_3 + P_4 + 2(P_5 + P_6) + P_7],\quad (21)$$

where

$$P_1 = -\tfrac{1}{64}\{[(n_a-n_b)^2 - (k_a-k_b)^2 + (n_a+n_b) - (k_a+k_b) + (p_a-p_b)(n_a-n_b-k_a+k_b)]$$
$$\times \chi(00000) - 4\delta \chi(01000) - [(n_a-n_b)^2 - (n_a+n_b)]\chi(0-2000) + [(k_a-k_b)^2 - (k_a+k_b)]\chi(000-20)$$
$$+ [(p_a-p_b)^2 + (p_a+p_b) + (p_a-p_b)(n_a-n_b+k_a-k_b)][\chi(0200-2) - \chi(0002-2)] - (p_a-p_b)$$
$$\times (n_a-n_b-(k_a-k_b))[\chi(20000-2) + \chi(0020-2)] + 2(p_a-p_b)(n_a-n_b)\chi(1-111-2)$$
$$-2(p_a-p_b)(k_a-k_b)\chi(111-1-2)\},$$

$$P_2 = -\tfrac{1}{16}[m_b n_b\{z'(00000) + z(11110) - z(-11110) - z(1-1110) + z(-1-1110)\}$$
$$- n_b \delta \{z'(10000) + z(21110) - z(01110) - z(2-1110) + z(0-1110)\}$$
$$- m_b \delta \{z'(01000) + z(12110) - z(-12110) - z(10110) + z(-10110)\}$$
$$+ \delta^2 \{z'(11000) + z(22110) - z(02110) - z(20110) + z(00110)\}],$$

$$P_3 = -\tfrac{1}{16} j_b[n_b\{-z'(00000) + z(11-110) - z(11110) - z(1-1-110) + z(1-1110)\}$$
$$- \delta \{-z'(01000) + z(12-110) - z(12110) - z(10-110) + z(10110)\}],$$

$$P_4 = -\tfrac{1}{16} j_b k_b \{z'(00000) + z(11-1-10) - z(11-110) - z(111-10) + z(11110)\},$$

$$P_5 = -\tfrac{1}{16} p_b[n_b\{\chi(1111-2) - \chi(1-111-2) - \chi(0200-2) + \chi(0000-2) + z'(2000-2) - z'(0020-2)\}$$
$$- \delta \{\chi(1211-2) - \chi(1011-2) - \chi(0300-2) + \chi(0100-2) + z'(2100-2) - z'(0120-2)\}],$$

$$P_6 = -\tfrac{1}{16} k_b p_b[\chi(111-1-2) - \chi(1111-2) - \chi(0000-2) + \chi(0002-2) - z'(2000-2) + z'(0020-2)],$$

and

$$P_7 = -\tfrac{1}{16}(p_b+1)(p_b)[\chi(0002-2) - \chi(0200-2)].$$

Here the symbol $\chi(01000)$ stands for $\chi(m_a+m_b, n_a+n_b+1, j_a+j_b, k_a+k_b, p_a+p_b)$ which is defined by

$$\chi(m,n,j,k,p) = \frac{1}{4\pi^2} \int (\lambda_1{}^2 - \mu_1{}^2) \exp[-2\delta(\lambda_1+\lambda_2)]$$
$$\times \lambda_1{}^m \lambda_2{}^n \mu_1{}^j \mu_2{}^k \rho^p d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2.\quad (22)$$

In the same notation $z^\nu(11110)$ stands for $z^\nu(m_a+m_b+1, n_a+n_b+1, j_a+j_b+1, k_a+k_b+1, p_a+p_b)$, where

$$z^\nu(m,n,j,k,p) = \frac{1}{4\pi^2} \int \exp[-2\delta(\lambda_1+\lambda_2)]$$
$$\times \lambda_1{}^m \lambda_2{}^n \mu_1{}^j \mu_2{}^k \rho^p M^\nu \cos^\nu(\varphi_1 - \varphi_2)$$
$$\times d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2.\quad (23)$$

$z(mnjkp)$ is used for $z^0(mnjkp)$ for simplicity. Other quantities carry similar meanings.

The expression for $u_{ab}{}^{(2)}$ is obtained from $u_{ab}{}^{(1)}$ by making the substitutions $[m_a \leftrightarrow n_a, j_a \leftrightarrow k_a]$. Similarly $u_{ab}{}^{(3)}$ is obtained from $u_{ab}{}^{(1)}$ by making the transformations $[m_b \leftrightarrow n_b, j_b \leftrightarrow k_b]$ and $u_{ab}{}^{(4)}$ by $[m_a \leftrightarrow n_a, j_a \leftrightarrow k_a, m_b \leftrightarrow n_b, j_b \leftrightarrow k_b]$.

N_0 in Eq. (20) denotes the sum

$$N_0 = \sum_{\substack{m_a n_a j_a k_a p_a;\ m_b n_b j_b k_b p_b}} C_{m_a n_a j_a k_a p_a} C_{m_b n_b j_b k_b p_b}$$
$$\times \{S_{ab}{}^{(1)} + S_{ab}{}^{(2)} + S_{ab}{}^{(3)} + S_{ab}{}^{(4)}\},\quad (24)$$

where

$$S_{ab}{}^{(1)} = \tfrac{1}{64}[\chi(02000) - \chi(00020)].\quad (25)$$

The expressions for $S_{ab}{}^{(2)}$, $S_{ab}{}^{(3)}$, and $S_{ab}{}^{(4)}$ can be obtained by making the changes in $S_{ab}{}^{(1)}$ similar to those required for obtaining $u_{ab}{}^{(2)}$, $u_{ab}{}^{(3)}$, and $u_{ab}{}^{(4)}$ from $u_{ab}{}^{(1)}$.

The parameter Q in Eq. (19) designates

$$Q = \frac{1}{N_0} \sum_{\substack{m_a n_a j_a k_a p_a;\ m_b n_b j_b k_b p_b}} C_{m_a n_a j_a k_a p_a} C_{m_b n_b j_b k_b p_b}$$
$$\times \{v_{ab}{}^{(1)} + v_{ab}{}^{(2)} + v_{ab}{}^{(3)} + v_{ab}{}^{(4)}\},\quad (26)$$

where

$$v_{ab}^{(1)} = -\tfrac{1}{64}[\chi(02000) - \chi(00020) \\ + 2\chi(0200-1) - 2\chi(0002-1) - 8\chi(01000)]. \quad (27)$$

The quantities $v_{ab}^{(2)}$, $v_{ab}^{(3)}$, and $v_{ab}^{(4)}$ are obtained from $v_{ab}^{(1)}$ in a manner similar to that used for obtaining $u_{ab}^{(2)}$, $u_{ab}^{(3)}$, and $u_{ab}^{(4)}$ from $u_{ab}^{(1)}$.

The normalization constant N appearing in Eq. (16) and defined by Eq. (18) is related to N_0 by

$$N = N_0 R^6. \quad (28)$$

The variational function g in Eq. (16) is a function of R through the normalization constant N and therefore, in view of Eq. (28), is proportional to inverse cube of R. We choose $f(\mathbf{R}) = R^{-2}F(R)$, where $F(R)$ is the eigenfunction of the operator

$$-d^2/dR^2 + P/R^2 - Q/R \quad (29)$$

corresponding to its lowest eigenvalue. This completes the choice of the form of the wave function. The expectation value W of $\mathcal{K}$ is, then, given by[9]

$$W = -2Q^2 E_0 [1 + \{1 + 4P\}^{1/2}]^{-2}, \quad (30)$$

with

$$E_0 = m_0 e^4 / 2\hbar^2, \quad (31)$$

where we have restored the original cgs units. The binding energy W_{Ps_2} of the positronium molecule is the energy absorbed when the system dissociates into two positronium units, so that

$$W_{\mathrm{Ps}_2} = -W - 2W_{\mathrm{Ps}}, \quad (32)$$

where W_{Ps} is the binding energy of the positronium which is simply

$$W_{\mathrm{Ps}} = \tfrac{1}{2}E_0. \quad (33)$$

Substituting Eqs. (30) and (33) into Eq. (32), we have

$$W_{\mathrm{Ps}_2} = E_0[2Q^2\{1 + (1+4p)^{1/2}\}^{-2} - 1]. \quad (34)$$

In Eq. (34), P and Q are the functions of the variational parameters δ and C_{mnjkp}. In order to evaluate P and Q we need to calculate the integrals $\chi(mnjkp)$ and $z^{\nu}(mnjkp)$ defined by Eqs. (22) and (23), respectively. Evaluation of these integrals was accomplished by the method used by James and Coolidge.[7]

For our calculation we have selected five values of $mnjkp$ for the variational parameters C_{mnjkp}. These are (00000), (00020), (00110), (10000), and (00001). In actual calculation the coefficient C_{00000} was kept fixed equal to unity, while δ and other parameters C_{00020}, C_{00110}, C_{10000}, and C_{00001} were varied in order to maximize W_{Ps_2}. The maximum value of W_{Ps_2} so obtained is $0.06967E_0 = 0.948$ eV.

The numerical values of the variational parameters and the integrals $\chi(mnjkp)$, $z(mnjkp)$, and $z'(mnjkp)$ required for the calculation are listed in the Appendix.

[9] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958), p. 128.

These integrals are used to calculate $u_{ab}^{(1)}$, $v_{ab}^{(1)}$, $S_{ab}^{(1)}$, etc., and N_0, P, and Q which are also given in the Appendix.

III. DISCUSSION

We have obtained the binding energy of the positronium molecule which is about a factor of 7 higher than the value obtained by Ore. There are four main reasons why our value differs so much from the value calculated by Ore. First, the Hamiltonian of the system was not transformed properly in Ref. 6 in order to eliminate the kinetic energy of the center of mass. Second, the kinetic energies of the electrons were calculated by Ore relative to the midpoint of the line joining the positrons. The values so obtained for the kinetic energies of the electrons were then taken to be the kinetic energies of the positrons. This is objectionable since, according to the symmetry of the problem, these are strictly the values of the kinetic energies of the positrons relative to the midpoint of the line joining the electrons. Third, in view of the complexity of the problem, the form of the variational function employed by Ore is inferior to our wave function. Ore's wave function contains only four electron-positron distances while we have selected a general form of the wave function which explains the binding energy of the hydrogen molecule most accurately. Finally, the wave function used by Ore contains only two variational parameters against five variational parameters contained in our wave function.

ACKNOWLEDGMENTS

APPENDIX

The aim of this appendix is to list the numerical values of the integrals, the variational parameters, and other quantities involved in the computation of the binding energy. The maximum value of W_{Ps_2} equal to 0.948 eV has been obtained by varying the variational parameters δ and C_{mnjkp}. Corresponding to the maximum value of W_{Ps_2} the variational parameters which we obtain are $\delta = 2.20$ and $C_{00020} = 1.0$; $C_{00110} = -0.79730$; $C_{10000} = 0.036824$; $C_{00001} = -0.023818$; and $C_{00000} = 0.0033784$. For simplicity the parameters C_{mnjkp} have been presented in decreasing order of magnitude and reducing the largest one (C_{00020}) to unity. The calculation of the binding energy requires the integrals $z(mnjkp)$, $z'(mnjkp)$, and $\chi(mnjkp)$ for different values of $mnjkp$. These integrals are calculated following the method explained in Ref. 7. In Tables I, II, and III we give the values of $z(mnjkp)$, $z'(mnjkp)$, and $\chi(mnjkp)$, respectively, for $\delta = 2.20$. Those integrals which vanish because

TABLE I. The numerical values of $z(mnjkp)$ for $\delta = 2.20$.

m	n	j	k	p	$z(mnjkp)$	m	n	j	k	p	$z(mnjkp)$
0	0	2	2	0	0.34604×10^{-5}	0	0	3	1	1	-0.23295×10^{-5}
0	0	2	4	0	0.20762×10^{-5}	0	1	1	1	1	-0.48729×10^{-5}
0	0	4	2	0	0.20762×10^{-5}	0	2	1	1	1	-0.62163×10^{-5}
0	1	2	2	0	0.42468×10^{-5}	0	2	1	3	1	-0.36701×10^{-5}
0	2	2	2	0	0.53907×10^{-5}	0	2	2	2	1	0.76276×10^{-5}
0	2	2	4	0	0.32344×10^{-5}	0	2	3	1	1	-0.36702×10^{-5}
0	2	4	2	0	0.32344×10^{-5}	0	3	1	1	1	-0.82753×10^{-5}
0	3	2	2	0	0.71358×10^{-5}	1	0	1	1	1	-0.48729×10^{-5}
1	0	0	2	0	0.12740×10^{-4}	1	0	1	3	1	-0.28739×10^{-5}
1	0	0	4	0	0.76442×10^{-5}	1	0	2	2	1	0.57987×10^{-5}
1	0	2	2	0	0.42468×10^{-5}	1	0	3	1	1	-0.28739×10^{-5}
1	0	2	4	0	0.25481×10^{-5}	1	1	0	2	1	0.21426×10^{-5}
1	0	4	2	0	0.25481×10^{-5}	1	1	1	1	1	-0.60147×10^{-5}
1	1	0	0	0	0.46908×10^{-4}	1	1	1	3	1	-0.35503×10^{-5}
1	1	0	2	0	0.15636×10^{-4}	1	1	2	2	1	0.73082×10^{-5}
1	1	0	4	0	0.93816×10^{-5}	1	1	3	1	1	-0.35503×10^{-5}
1	1	2	0	0	0.15636×10^{-4}	1	2	1	1	1	-0.76858×10^{-5}
1	1	2	2	0	0.52120×10^{-5}	1	2	1	3	1	-0.45413×10^{-5}
1	1	2	4	0	0.31272×10^{-5}	1	2	2	2	1	0.95949×10^{-5}
1	1	4	0	0	0.93816×10^{-5}	1	2	3	1	1	-0.45413×10^{-5}
1	1	4	2	0	0.31272×10^{-5}	1	3	1	1	1	-0.10252×10^{-4}
1	2	0	2	0	0.19848×10^{-4}	2	0	1	1	1	-0.62163×10^{-5}
1	2	0	4	0	0.11909×10^{-4}	2	0	1	3	1	-0.36702×10^{-5}
1	2	2	2	0	0.66159×10^{-5}	2	0	2	2	1	0.76276×10^{-5}
1	2	2	4	0	0.39695×10^{-5}	2	0	3	1	1	-0.36702×10^{-5}
1	2	4	2	0	0.39695×10^{-5}	2	1	1	1	1	-0.76858×10^{-5}
1	3	2	2	0	0.87576×10^{-5}	2	2	1	1	1	-0.98408×10^{-5}
2	0	2	2	0	0.53907×10^{-5}	2	2	1	3	1	-0.58200×10^{-5}
2	0	2	4	0	0.32344×10^{-5}	2	2	2	2	1	0.12568×10^{-4}
2	0	4	2	0	0.32344×10^{-5}	2	2	3	1	1	-0.58200×10^{-5}
2	1	0	2	0	0.19848×10^{-4}	2	3	1	1	1	-0.13157×10^{-4}
2	1	2	2	0	0.66159×10^{-5}	3	0	1	1	1	-0.82753×10^{-5}
2	2	2	2	0	0.83980×10^{-5}	3	2	1	1	1	-0.13157×10^{-4}
2	2	2	4	0	0.50388×10^{-5}	0	0	1	1	2	-0.10424×10^{-4}
2	2	4	2	0	0.50388×10^{-5}	0	2	1	1	2	-0.17515×10^{-4}
2	3	2	2	0	0.11117×10^{-4}	1	0	1	1	2	-0.13232×10^{-4}
3	0	2	2	0	0.71358×10^{-5}	1	1	1	1	2	-0.16796×10^{-4}
3	2	2	2	0	0.11117×10^{-4}	1	2	1	1	2	-0.22233×10^{-4}
0	0	1	1	1	-0.39535×10^{-5}	2	0	1	1	2	-0.17515×10^{-4}
0	0	1	3	1	-0.23295×10^{-5}	2	2	1	1	2	-0.29431×10^{-4}
0	0	2	2	1	0.45935×10^{-5}						

TABLE II. The numerical values of $z'(mnjkp)$ for $\delta = 2.20$.

m	n	j	k	p	$z'(mnjkp)$	m	n	j	k	p	$z'(mnjkp)$
0	0	2	0	−1	0.28451×10^{-6}	3	1	0	0	−1	0.47703×10^{-5}
0	0	2	2	−1	0.84019×10^{-7}	0	0	0	0	1	-0.15043×10^{-5}
0	0	3	1	−1	0.76535×10^{-7}	0	0	0	2	1	-0.29328×10^{-6}
0	0	4	0	−1	0.12193×10^{-6}	0	0	1	1	1	-0.53701×10^{-7}
0	1	2	0	−1	0.37304×10^{-6}	0	0	2	0	1	-0.29328×10^{-6}
0	1	2	2	−1	0.10923×10^{-6}	0	1	0	0	1	-0.21559×10^{-5}
0	1	3	1	−1	0.98778×10^{-7}	0	1	0	2	1	-0.42104×10^{-6}
0	1	4	0	−1	0.15987×10^{-6}	0	1	2	0	1	-0.42104×10^{-6}
0	2	2	0	−1	0.50420×10^{-6}	0	1	1	1	1	-0.75135×10^{-7}
1	0	2	0	−1	0.37304×10^{-6}	0	2	0	0	1	-0.32332×10^{-5}
1	1	2	0	−1	0.49353×10^{-6}	1	0	0	0	1	-0.21559×10^{-5}
2	0	0	0	−1	0.25210×10^{-5}	1	1	0	2	1	-0.60624×10^{-6}
2	0	0	2	−1	0.50420×10^{-6}	1	1	0	0	1	-0.30993×10^{-5}
2	0	1	1	−1	0.30558×10^{-6}	1	1	1	1	1	-0.10587×10^{-6}
2	0	2	0	−1	0.50420×10^{-6}	1	1	2	0	1	-0.60624×10^{-6}
2	1	0	0	−1	0.33687×10^{-5}	1	2	0	0	1	-0.46639×10^{-5}
2	1	0	2	−1	0.67375×10^{-6}	2	1	0	0	1	-0.46639×10^{-5}
2	1	1	1	−1	0.40350×10^{-6}	0	0	0	0	2	-0.43074×10^{-5}
2	1	2	0	−1	0.67375×10^{-6}	0	1	0	0	2	-0.64466×10^{-5}
2	2	0	0	−1	0.46501×10^{-5}	1	1	0	0	2	-0.96482×10^{-5}
3	0	0	0	−1	0.35312×10^{-5}						

TABLE III. The numerical values of $\chi(mnjkp)$ for $\delta = 2.20$.

m	n	j	k	p	$\chi(mnjkp)$
0	0	0	0	−1	0.37922×10^{-4}
0	0	0	2	−1	0.12010×10^{-4}
0	0	0	4	−1	0.70436×10^{-5}
0	0	0	6	−1	0.49668×10^{-5}
0	0	1	1	−1	0.34906×10^{-5}
0	0	1	3	−1	0.19967×10^{-5}
0	0	1	5	−1	0.13874×10^{-5}
0	0	2	0	−1	0.95806×10^{-5}
0	0	2	2	−1	0.34927×10^{-5}
0	0	2	4	−1	0.21561×10^{-5}
0	0	3	1	−1	0.17834×10^{-5}
0	0	3	3	−1	0.10893×10^{-5}
0	0	4	2	−1	0.19232×10^{-5}
0	1	0	0	−1	0.45155×10^{-4}
0	1	0	2	−1	0.14330×10^{-4}
0	1	1	1	−1	0.41096×10^{-5}
0	1	1	3	−1	0.23549×10^{-5}
0	1	0	4	−1	0.84122×10^{-5}
0	1	2	0	−1	0.11432×10^{-4}
0	1	2	2	−1	0.41647×10^{-5}
0	2	0	0	−1	0.55192×10^{-4}
0	2	0	2	−1	0.17557×10^{-4}
0	2	0	4	−1	0.10318×10^{-4}
0	2	1	1	−1	0.49488×10^{-5}
0	2	1	3	−1	0.28415×10^{-5}
0	2	2	0	−1	0.14006×10^{-4}
0	2	2	2	−1	0.50971×10^{-5}
0	2	3	1	−1	0.25434×10^{-5}
0	2	4	0	−1	0.72748×10^{-5}
0	3	0	0	−1	0.69690×10^{-4}
0	3	0	2	−1	0.22232×10^{-4}
0	3	1	1	−1	0.61265×10^{-5}
0	3	2	0	−1	0.17734×10^{-4}
0	4	0	0	−1	0.91630×10^{-4}
1	0	0	0	−1	0.48259×10^{-4}
1	0	0	2	−1	0.15364×10^{-4}
1	0	0	4	−1	0.90330×10^{-5}
1	0	1	1	−1	0.43734×10^{-5}
1	0	1	3	−1	0.25131×10^{-5}
1	0	2	2	−1	0.45343×10^{-5}
1	0	3	1	−1	0.22637×10^{-5}
1	1	0	0	−1	0.57647×10^{-4}
1	1	0	2	−1	0.18385×10^{-4}
1	1	1	1	−1	0.51809×10^{-5}
1	1	1	3	−1	0.29818×10^{-5}
1	1	2	0	−1	0.14924×10^{-4}
1	1	2	2	−1	0.54269×10^{-5}
1	1	3	1	−1	0.26893×10^{-5}
1	2	0	0	−1	0.70725×10^{-4}
1	2	0	2	−1	0.22602×10^{-4}
1	2	1	1	−1	0.62847×10^{-5}
1	2	1	3	−1	0.36237×10^{-5}
1	2	2	0	−1	0.18355×10^{-4}
1	2	2	2	−1	0.66713×10^{-5}
1	2	3	1	−1	0.32729×10^{-5}
1	3	0	0	−1	0.89694×10^{-4}
1	3	1	1	−1	0.78483×10^{-5}
2	0	0	2	−1	0.20507×10^{-4}
2	0	1	1	−1	0.56773×10^{-5}
2	1	0	0	−1	0.76769×10^{-4}
2	1	1	1	−1	0.67726×10^{-5}

m	n	j	k	p	$\chi(mnjkp)$
2	2	0	0	−1	0.94580×10^{-4}
2	2	1	1	−1	0.82843×10^{-5}
0	0	0	0	0	0.38135×10^{-4}
0	0	0	2	0	0.12712×10^{-4}
0	0	0	4	0	0.76271×10^{-5}
0	0	0	6	0	0.54479×10^{-5}
0	0	2	0	0	0.99435×10^{-5}
0	0	2	2	0	0.33145×10^{-5}
0	0	2	4	0	0.19887×10^{-5}
0	0	4	2	0	0.17514×10^{-5}
0	1	0	0	0	0.46803×10^{-4}
0	1	0	2	0	0.15601×10^{-4}
0	1	0	4	0	0.93605×10^{-5}
0	1	2	0	0	0.12203×10^{-4}
0	1	2	2	0	0.40678×10^{-5}
0	1	4	0	0	0.64484×10^{-5}
0	2	0	0	0	0.59409×10^{-4}
0	2	0	2	0	0.19803×10^{-4}
0	2	0	4	0	0.11882×10^{-4}
0	2	2	0	0	0.15490×10^{-4}
0	2	2	2	0	0.51635×10^{-5}
0	2	4	0	0	0.81854×10^{-5}
0	3	0	0	0	0.78642×10^{-4}
0	3	0	2	0	0.26214×10^{-4}
0	3	2	0	0	0.20505×10^{-4}
0	4	0	0	0	0.10963×10^{-3}
1	0	0	0	0	0.51482×10^{-4}
1	0	0	2	0	0.17161×10^{-4}
1	0	0	4	0	0.10296×10^{-4}
1	0	2	2	0	0.45878×10^{-5}
1	1	0	0	0	0.63183×10^{-4}
1	1	0	2	0	0.21061×10^{-4}
1	1	2	0	0	0.16891×10^{-4}
1	2	0	0	0	0.80202×10^{-4}
1	2	0	2	0	0.26734×10^{-4}
1	2	2	0	0	0.21441×10^{-4}
1	3	0	0	0	0.10617×10^{-3}
2	0	0	2	0	0.24452×10^{-4}
2	1	0	0	0	0.90027×10^{-4}
2	2	0	0	0	0.11428×10^{-3}
0	0	0	0	1	0.50145×10^{-4}
0	0	0	2	1	0.17777×10^{-4}
0	0	0	4	1	0.10936×10^{-4}
0	0	1	1	1	-0.38868×10^{-5}
0	0	1	3	1	-0.22866×10^{-5}
0	0	2	2	1	0.48368×10^{-5}
0	1	0	0	1	0.63350×10^{-4}
0	1	0	2	1	0.22390×10^{-4}
0	1	1	1	1	-0.48119×10^{-5}
0	1	2	0	1	0.17759×10^{-4}
0	2	0	0	1	0.83401×10^{-4}
0	2	0	2	1	0.29370×10^{-4}
0	2	1	1	1	-0.61706×10^{-5}
0	2	2	0	1	0.23271×10^{-4}
0	3	0	0	1	0.11555×10^{-3}
1	0	0	2	1	0.25244×10^{-4}
1	1	0	0	1	0.90258×10^{-4}
1	2	0	0	1	0.11840×10^{-3}
0	0	0	2	2	0.29773×10^{-4}
0	1	0	0	2	0.10287×10^{-3}
0	2	0	0	2	0.14038×10^{-3}

of the following properties are not included in these tables. When j and k are not both even,

$$z(mnjko) = 0, \tag{A1}$$

$$\chi(mnjko) = 0, \tag{A2}$$

and for any set of values of $mnjk$,

$$z'(mnjko) = 0. \tag{A3}$$

The expressions (A1), (A2), and (A3) can easily be derived if one starts with the definition of these integrals, namely, Eqs. (22) and (23).

Making use of Tables I–III we calculate $u_{ab}^{(1)}$, $v_{ab}^{(1)}$, $S_{ab}^{(1)}$, etc. The values of $u_{ab}^{(1)}$, $u_{ab}^{(2)}$, $u_{ab}^{(3)}$, and $u_{ab}^{(4)}$ are compiled in Tables IV–VII while the values of $v_{ab}^{(1)}$, $v_{ab}^{(2)}$, $v_{ab}^{(3)}$, and $v_{ab}^{(4)}$ are tabulated in Tables VIII–XI. In Table XII we list the values of $S_{ab}^{(1)}$. The

TABLE IV. The values of $u_{ab}^{(1)} \times 10^5$ for $\delta = 2.20$.

a\ b	(00000)	(00020)	(00110)	(10000)	(00001)
(00000)	0.96530	0.32177	-0.016287	1.3030	1.1717
(00020)	0.32177	0.38374	0.016287	0.43438	0.45883
(00110)	-0.016287	-0.0097725	0.14605	-0.016973	-0.17069
(10000)	1.3031	0.43438	-0.024376	1.8568	1.7039
(00001)	1.1717	0.47875	-0.17069	1.6732	1.9757

TABLE V. The values of $u_{ab}^{(2)} \times 10^5$ for $\delta = 2.20$.

a\ b	(00000)	(00020)	(00110)	(10000)	(00001)
(00000)	0.96530	0.321767	-0.016287	1.3031	1.1717
(00020)	0.25170	0.083898	-0.0097725	0.34838	0.33840
(00110)	-0.016287	-0.0097725	0.14605	-0.016973	-0.17069
(10000)	1.0059	0.33531	-0.0095696	1.3580	1.2962
(00001)	1.1717	0.47875	-0.17069	1.6732	1.9757

TABLE VI. The values of $u_{ab}^{(3)} \times 10^5$ for $\delta = 2.20$.

a\ b	(00000)	(00020)	(00110)	(10000)	(00001)
(00000)	0.96530	0.25170	-0.016287	1.0059	1.1717
(00020)	0.32177	0.083898	0.016287	0.33531	0.45883
(00110)	-0.016287	0.016287	0.14506	-0.016973	-0.17069
(10000)	1.3031	0.34838	-0.024376	1.3580	1.7039
(00001)	1.1717	0.31848	-0.17069	1.3269	1.9757

TABLE VII. The values of $u_{ab}^{(4)} \times 10^5$ for $\delta = 2.20$.

a\ b	(00000)	(00020)	(00110)	(10000)	(00001)
(00000)	0.96530	0.25170	-0.016287	1.0059	1.1717
(00020)	0.25170	0.13300	-0.0097725	0.26229	0.33840
(00110)	-0.016287	0.016287	0.14605	-0.016973	-0.17069
(10000)	1.0059	0.26229	-0.0095696	1.1647	1.2962
(00001)	1.1717	0.31848	-0.17069	1.3269	1.9757

TABLE VIII. The values of $v_{ab}^{(1)} \times 10^5$ for $\delta = 2.20$.

a\ b	(00000)	(00020)	(00110)	(10000)	(00001)
(00000)	0.37712	0.14313	-0.0092253	0.51828	0.54341
(00020)	0.14313	0.090230	-0.0045440	0.19517	0.21303
(00110)	-0.0092253	-0.0045440	0.036696	-0.011786	-0.054080
(10000)	0.51828	0.19517	-0.011786	0.75351	0.78566
(00001)	0.54341	0.21303	-0.054080	0.78566	0.90795

TABLE IX. The values of $v_{ab}^{(2)} \times 10^5$ for $\delta = 2.20$.

a\ b	(00000)	(00020)	(00110)	(10000)	(00001)
(00000)	0.37712	0.14313	-0.0092253	0.51828	0.54341
(00020)	0.10066	0.036696	-0.0045440	0.14162	0.15513
(00110)	-0.0092253	-0.0045440	0.036696	-0.011786	-0.054080
(10000)	0.47111	0.17802	-0.011786	0.64670	0.69995
(00001)	0.54341	0.21303	-0.054080	0.78566	0.90795

TABLE X. The values of $v_{ab}^{(3)} \times 10^5$ for $\delta = 2.20$.

a\ b	(00000)	(00020)	(00110)	(10000)	(00001)
(00000)	0.37712	0.10066	-0.0092253	0.47111	0.54341
(00020)	0.143130	0.036696	-0.0045440	0.17802	0.21303
(00110)	-0.0092253	-0.0045440	0.036695	-0.011786	-0.054080
(10000)	0.51828	0.14162	-0.011786	0.64670	0.78566
(00001)	0.54341	0.15513	-0.054080	0.69995	0.90795

TABLE XI. The values of $v_{ab}^{(4)} \times 10^5$ for $\delta = 2.20$.

a\ b	(00000)	(00020)	(00110)	(10000)	(00001)
(00000)	0.37712	0.10066	-0.0092253	0.47111	0.54341
(00020)	0.10066	0.053828	-0.0045440	0.12554	0.15513
(00110)	-0.0092253	-0.0045440	0.036696	-0.011786	-0.05408
(10000)	0.47111	0.12554	-0.011786	0.61119	0.69995
(000001)	0.54341	0.15513	-0.05408	0.69995	0.90795

TABLE XII. The values of $S_{ab}^{(1)} \times 10^5$ for $\delta = 2.20$.

a\ b	(00000)	(00020)	(00110)	(10000)	(00001)
(00000)	0.072965	0.019025	0.	0.098501	0.10254
(00020)	0.019025	0.010053	0.	0.025683	0.028803
(00110)	0.	0.	0.0049606	0.	-0.0060688
(10000)	0.098501	0.025683	0.	0.14035	0.14556
(00001)	0.10254	0.028803	-0.0060688	0.14556	0.17282

values of $S_{ab}^{(2)}$ are the same as $S_{ab}^{(1)}$ with the exception that

$$S_{ab}^{(2)} = 0.0049606 \quad [\text{for } a \equiv (00020),\ b \equiv (00020)],$$
$$S_{ab}^{(2)} = 0.026333 \quad [\text{for } a \equiv (00020),\ b \equiv (10000); \quad (A4)$$

and also for

$$a \equiv (10000),\ b \equiv (00020)], \quad (A5)$$

and

$$S_{ab}^{(2)} = 0.13298 \quad [\text{for } a \equiv (10000),\ b \equiv (10000)]. \quad (A6)$$

The values of the elements $S_{ab}^{(3)}$ and $S_{ab}^{(4)}$ are the same as those of the elements $S_{ab}^{(2)}$ and $S_{ab}^{(1)}$, respectively. In other words,

$$S_{ab}^{(3)} = S_{ab}^{(2)} \quad (A7)$$

and

$$S_{ab}^{(4)} = S_{ab}^{(1)}. \quad (A8)$$

With the help of Tables IV–XII it can be seen that

$$u_{ab}^{(1)} + u_{ab}^{(2)} + u_{ab}^{(3)} + u_{ab}^{(4)}$$
$$= u_{ba}^{(1)} + u_{ba}^{(2)} + u_{ba}^{(3)} + u_{ba}^{(4)}, \quad (A9)$$

$$v_{ab}^{(1)} + v_{ab}^{(2)} + v_{ab}^{(3)} + v_{ab}^{(4)}$$
$$= v_{ba}^{(1)} + v_{ba}^{(2)} + v_{ba}^{(3)} + v_{ba}^{(4)}, \quad (A10)$$

$$S_{ab}^{(1)} = S_{ba}^{(1)} = S_{ab}^{(4)} = S_{ba}^{(4)}, \quad (A11)$$

$$S_{ab}^{(2)} = S_{ba}^{(2)} = S_{ab}^{(3)} = S_{ba}^{(3)}. \quad (A12)$$

Using the tabulated integrals and the variational parameters given above, we obtain $N_0 = 0.44601 \times 10^{-6}$, $P = 23.548$, and $Q = 7.8665$. These values of P and Q are finally used to compute W_{Ps_2} from Eq. (34).