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# Nonadiabatic variational calculations for the ground state of the positronium molecule

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For a four-particle system consisting of two electrons and two positrons, the nonadiabatic wave function is constructed with the use of an expansion in terms of explicitly correlated Gaussian-type basis functions and a Cartesian-coordinate laboratory frame. Motions of all particles are correlated at the same time in the wave function. The energy of the center-of-mass motion is effectively eliminated from the total nonrelativistic energy of the system by defining the variational principle based on the internal Hamiltonian. The ground-state energy is computed for different lengths of Gaussian expansions and values are compared with previous literature results. Our best estimation of the binding energy of the positronium molecule is 0.435 eV.

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## I. INTRODUCTION

The possibility of the formation of bound states between electrons and positrons was first theoretically predicted by Wheeler [1]. The earlier quantum-mechanical study performed by Hylleraas and Ore [2–4] confirmed the dynamical stability of such systems. Since this pioneering work, a large number of studies has been done on systems with positrons (for example, Refs. [5–7]), including the first experimental observation of the positronium negative ion $\mathrm{Ps}^-(e^+e^-e^-)$ [8]. Quantum-mechanical description of systems containing electrons and positrons represents a rather difficult task. Any correct theoretical approach to such systems requires an equivalent treatment of all particles since the masses of the electrons and positrons are the same, and the usual Born-Oppenheimer or adiabatic approximations cannot be applied. The internal energies of the $\mathrm{Ps}^-$ ion [9,10] and the PsH system [11], including series of resonance states [12], were determined variationally using wave functions explicitly dependent on the interparticular distances. Relatively less attention has been devoted to the $\mathrm{Ps}_2$ system, known as the positronium molecule, bipositronium or quadronium. The calculated value of the binding energy [i.e., $2E(\mathrm{Ps})-E(\mathrm{Ps}_2)$ for the positronium molecule varies from 0.116 eV (lowest) [2] to 0.948 eV (highest) [20]. There could be several reasons for such discrepancy. A more detailed analysis will be presented in the next section.

Theoretical calculations on $\mathrm{Ps}_2$ are important since the experimental results for this system are not yet available [13]. In the present study nonadiabatic calculations for the ground state of the positronium molecule are presented. The nonadiabatic method based upon an effective elimination of the center-of-mass motion [14,15] it utilized in this study. The variational wave function is constructed with the use of explicitly correlated Gaussian functions [16–19].

## II. POSITRONIUM MOLECULE

In this section we would like to briefly review previous theoretical investigations concerning the positronium molecule. The bound state for this system has been investigated theoretically in a number of studies; however, as mentioned before, the resulting values for the total energy have not been consistent. The first theoretical calculations were performed by Hylleraas and Ore [2] to find the binding energy of 0.116 eV, and reexamined later by Ore [3] to obtain the energy of 0.135 eV. The calculations were performed without an explicit separation of the center-of-mass motion. They assumed that "the motion of the center-of-mass of the cluster is irrelevant. . .". The first description of the internal state of the positronium molecule with explicit separation of the center-of-mass motion has been presented by Sharma [20]. He used the transformation $(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)\rightarrow(\mathbf{R}_{\mathrm{c.m.}},\mathbf{R},\mathbf{R}_1,\mathbf{R}_2)$, where 1 and 2 denote the electrons, and $A$ and $B$ denote the positrons, defined as

$$\mathbf{R}_{\mathrm{c.m.}}=\tfrac{1}{4}(\mathbf{r}_1+\mathbf{r}_2+\mathbf{r}_A+\mathbf{r}_B)\ , \tag{2.1}$$

and internal coordinates

$$\mathbf{R}=\mathbf{r}_A-\mathbf{r}_B\ , \tag{2.2}$$

$$\mathbf{R}_1=\mathbf{r}_1-\tfrac{1}{2}(\mathbf{r}_A+\mathbf{r}_B)\ , \tag{2.3}$$

$$\mathbf{R}_2=\mathbf{r}_2-\tfrac{1}{2}(\mathbf{r}_A+\mathbf{r}_B) \tag{2.4}$$

to separate the center-of-mass motion from the internal motion, and obtained the binding energy of 0.948 eV. This binding energy has been questioned by other authors [21] in that it could possibly contain some errors. In Table I we show results of some of the relevant calculations on the ground state of $\mathrm{Ps}_2$.

From the above-listed results, the most reliable seems to be the calculations performed by Lee and co-workers [24] with the use of the Green's-function Monte Carlo

TABLE I. Calculations of binding energies of the positronium molecule $Ps_2$.

| Authors | Reference | Method | $\Delta E$ (eV) |
|---|---|---|---|
| Hylleraas and Ore | [2] | Variational | 0.116 |
| Ore | [3] | Variational[a] | 0.135 |
| Sharma | [20] | Variational[b] | 0.948 |
| Akimoto and Hanamura | [21] | Variational[c] | 0.187 |
| Huang | [22] | FPI[d] | 0.846 |
| Brinkman, Rice, and Bell | [23] | Variational | 0.197 |
| Lee, Vashista, and Kalia | [24] | GFMC[e] | 0.408±0.027 |
| Vinitsky and Vukajlovic | [25] | Variational[f] | 0.220 |
| Ho | [26] | Variational[g] | 0.411 |
| Vukajlovic and Vinitsky | [27] | Variational[f] | 0.221 |
| Kinghorn and Poshusta | [29] | Variational[h] | 0.435 |

[a] Linear combination of "atomic" and "ionic" functions.

[b] James-Collidge method.

[c] With elimination of the center-of-mass motion.

[d] Feyman's path integrals.

[e] Green's-function Monte Carlo.

[f] Adiabatic with coupled equations.

[g] With Hylleraas-type functions.

[h] With explicitly correlated Gaussian-type functions and elimination of the center-of-mass motion.

method. They obtained the binding energy of 0.408±0.027 eV, which was later confirmed by Ho [26], who found the binding energy of 0.411 eV in his variational calculation accomplished with a Hylleraas-type wave function. The above two historical calculations put the value of the binding energy of $Ps_2$ into proper perspective. To conclude this discussion, let us quote Drachman [28]:

"After the initial proof that the molecule ($Ps_2$) is actually bound (by at least 0.1 eV), a series of calculations of increased sophistication were performed. Unexpectedly, these did not lead to gradually increasing lower bonds of the dissociation energy as might have been expected. . .and it is hard to tell whether there are actual errors in some of the calculations or whether the apparently better results are due to better coordinate systems or trial functions."

In the next section we will present our calculations of the binding energy for the positronium molecule.

## III. METHODOLOGY

Let us consider the complete nonrelativistic Hamiltonian for the $Ps_2$ system,

$$H_{\text{tot}}=-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2+\nabla_A^2+\nabla_B^2)+\frac{1}{r_{12}}+\frac{1}{r_{AB}}-\frac{1}{r_{1A}}-\frac{1}{r_{1B}}-\frac{1}{r_{2A}}-\frac{1}{r_{2B}}, \tag{3.1}$$

where 1 and 2 denote the electrons and $A$ and $B$ the positrons, respectively. The four-particle nonadiabatic wave function utilized in this work has the following form:

$$\Psi_{\text{tot}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)=\sum_{k=1}^{M}C_k[P(A,B)P(1,2)\omega_k(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)]\times\Theta(A,B)\Theta(1,2), \tag{3.2}$$

with spatial function $\omega_k$ given as a one-center explicitly correlated Gaussian function,

$$\begin{aligned}\omega_k(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)&=\exp(-\alpha_1^k r_1^2-\alpha_2^k r_2^2-\alpha_A^k r_A^2-\alpha_B^k r_B^2-\beta_{12}^k r_{12}^2-\beta_{1A}^k r_{1A}^2-\beta_{1B}^k r_{1B}^2-\beta_{2A}^k r_{2A}^2-\beta_{2B}^k r_{2B}^2-\beta_{AB}^k r_{AB}^2)\\&=\exp[(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)(\mathbf{A}^k+\mathbf{B}^k)(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)^T],\end{aligned} \tag{3.3}$$

where $\mathbf{A}^k$ and $\mathbf{B}^k$ are defined as follows:

$$\mathbf{A}^k=\begin{bmatrix}\alpha_1^k & 0 & 0 & 0\\ 0 & \alpha_2^k & 0 & 0\\ 0 & 0 & \alpha_A^k & 0\\ 0 & 0 & 0 & \alpha_B^k\end{bmatrix}, \tag{3.3a}$$

$$\mathbf{B}^k=\begin{bmatrix}\beta_{12}^k+\beta_{1A}^k+\beta_{1B}^k & -\beta_{12}^k & -\beta_{1A}^k & -\beta_{1B}^k\\ -\beta_{12}^k & \beta_{12}^k+\beta_{2A}^k+\beta_{2B}^k & -\beta_{2A}^k & -\beta_{2B}^k\\ -\beta_{1A}^k & -\beta_{2A}^k & \beta_{1A}^k+\beta_{2A}^k+\beta_{AB}^k & -\beta_{AB}\\ -\beta_{1B}^k & -\beta_{2B}^k & -\beta_{AB}^k & \beta_{1B}^k+\beta_{2B}^k+\beta_{AB}^k\end{bmatrix}. \tag{3.3b}$$

The spin functions representing the electron and positron singlet states are given as

$$\Theta(A,B)\Theta(1,2)=\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\beta(1)\alpha(2)] \times\frac{1}{\sqrt{2}}[\alpha(A)\beta(B)-\beta(A)\alpha(B)] \ . \qquad (3.4)$$

It was assumed that there is no spin coupling between the electrons and positrons. The spatial part of the variational nonadiabatic wave function Eq. (3.2) is symmetric with respect to exchanging electrons as well as positrons, which is achieved by the permutational operators $P(1,2)=(1,2)+(2,1)$ and $P(A,B)=(A,B)+(B,A)$. One could also consider the charge-reversal symmetry which corresponds to the simultaneous exchange of the two electrons against the two positrons [29]. We do not make an explicit use of this type of symmetry in this work. In function (3.3), motions of all particles are correlated through the squares of the interparticular distances present in the exponent. In a conventional nonadiabatic approach, the center-of-mass motion is explicitly separated from both the Hamiltonian and the wave function. In the present approach we remove the center-of-mass motion from the total Hamiltonian but not from the wave function. This leads to the following form of the variational functional:

$$J[\Psi_{\text{tot}}]=\frac{\langle\Psi_{\text{tot}}|H_{\text{tot}}-T_{\text{c.m.}}|\Psi_{\text{tot}}\rangle}{\langle\Psi_{\text{tot}}|\Psi_{\text{tot}}\rangle} =\frac{\langle\Psi_{\text{tot}}|H_{\text{int}}|\Psi_{\text{tot}}\rangle}{\langle\Psi_{\text{tot}}|\Psi_{\text{tot}}\rangle} \ , \qquad (3.5)$$

where

$$T_{\text{c.m.}}=\frac{1}{2M}\left[\sum_{i=1}^{N}\mathbf{p}_i\right]^2 . \qquad (3.6)$$

For the positronium molecule

$$T_{\text{c.m.}}=\tfrac{1}{8}(\mathbf{p}_1+\mathbf{p}_2+\mathbf{p}_A+\mathbf{p}_B)^2 =\tfrac{1}{8}\sum_{i=1,2,A,B}\ \sum_{j=1,2,A,B}\nabla_i\nabla_j \ , \qquad (3.7)$$

since $M=4$ (in a.u.).

The minimization of the above functional leads to lowering of the internal energy of the system because the functional Eq. (3.4) represents only the internal Hamiltonian. One can expect, after optimization, that the variational wave function should be a sum of products of the integral ground state and wave functions representing different states of the center-of-mass motion:

$$\Psi_{\text{tot}}=\Phi_{\text{int}}\sum_i a_i\phi^i_{\text{c.m.}} \ . \qquad (3.8)$$

However, since the internal Hamiltonian only acts on the internal wave function, the variational functional $J[\Psi_{\text{tot}}]$ becomes

$$\min\{J[\Psi_{\text{tot}}]\}=\min\left\{\frac{\langle\Phi_{\text{int}}|H_{\text{tot}}-T_{\text{c.m.}}|\Phi_{\text{int}}\rangle}{\langle\Phi_{\text{int}}|\Phi_{\text{int}}\rangle}\right\} , \qquad (3.9)$$

which according to variational principle is

$$\min\{J[\Psi_{\text{tot}}]\}\geq E_{\text{int}} \ . \qquad (3.10)$$

In Appendix A we present formulas for the integrals required to calculate the functional (3.5).

## IV. NUMERICAL RESULTS

Optimization of the functional Eq. (3.5) has been performed with the variational wave function expanded in terms of 16, 32, 64, 128, 210, and 300 explicitly correlated Gaussian functions. The numerical conjugate-gradient-optimization technique was employed. To indicate the extent of the optimization effort involved, it suffices to say, for example, for the wave function expanded into a series of 300 Gaussian functions one needs to optimize as many as 3000 exponential parameters. The results of the calculations are presented in Table II. For all the expansion lengths considered the optimizations were quite well converged, though with a large number of nonlinear parameters, one can never be sure whether a local or global minimum was reached or whether some more optimization would lead to further improvement of the results. Upon examining the convergence of the results with elongation of the expansion, one sees that the values of the binding energy are quite well converged. Our best result of 0.435 eV is identical with the recent result of Kinghorn and Poshusta [29]. The calculations of Kinghorn and Poshusta were also accomplished with the use of the correlated Gaussian functions but with an explicit elimination of the center-of-mass motion from both the Hamiltonian and from the wave function through a transformation to a center-of-mass coordinate system. Our best result for the total energy (−0.515 980 a.u.) is virtually identical to the best result of Kinghorn and Poshusta (−0.515 977 a.u.) and lower than the best literature value of Ho [26] (−0.515 105 a.u.). It should be mentioned that all the above results are rigorously variational.

An interesting question one is always curious about once a nonadiabatic wave function becomes available pertains to the structure of the system under consideration. The answer requires calculation of averaged interparticular distances. For the wave function expressed in terms of explicitly correlated Gaussian functions, the easiest to

TABLE II. Total binding energy calculated using different numbers of basis functions used in the expansion of the wave function. The total energy is expressed in atomic units and the binding energy in eV. (1 a.u.=27.211 396 1 eV.)

| Number of functions | Total energy | Binding energy[a] |
|---|---|---|
| 16 | −0.510 762 | 0.293 |
| 32 | −0.515 385 | 0.419 |
| 64 | −0.515 852 | 0.431 |
| 128 | −0.515 949 | 0.434 |
| 210 | −0.515 974 | 0.435 |
| 300 | −0.515 980 | 0.435 |

[a] Exact energy of the $e^+e^-$ system is equal to −0.25 a.u.

TABLE III. Averaged squares of the interparticle distances $\langle r_{ij}^2 \rangle$ calculated for different expansion lengths of the wave function. Results are in atomic units.

| Number of functions | $e^+e^+$ | $e^+e^-$ | $e^-e^-$ |
|---|---|---|---|
| 34 | 44.139 | 27.932 | 44.134 |
| 64 | 45.311 | 28.565 | 45.312 |
| 128 | 45.681 | 28.762 | 45.679 |
| 210 | 45.881 | 28.863 | 45.879 |
| 300 | 45.911 | 28.878 | 45.911 |

calculate are the averages of the squares of the distances. This can be accomplished with the procedure described in Appendix B. The results of the calculations for the $\mathrm{Ps}_2$ molecule are presented in Table III. Upon examining the results, one notices that the $e^-$-$e^-$ distance is virtually the same as $e^+$-$e^+$ distance. This is a reflection of the charge-reversal symmetry discussed above. The second observation is that the $e^+$-$e^-$ distance is significantly shorter than the $e^+$-$e^+$ and $e^-$-$e^-$ distances. This suggests that the $\mathrm{Ps}_2$ molecule is a complex of two Ps systems.

Finally, we should mention that although the lowest variational energy of the $\mathrm{Ps}_2$ system was achieved in the present study, there is a certain drawback to using Gaussian basis functions in expanding the wave function of a system with Coulombic interactions. The problem is related to smooth behavior of these functions at cusps leading to less perfect results than in the case of the Hylleraas-type functions fulfillment of the cusp condition. This problem will be investigated in our future studies.

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## APPENDIX A: INTEGRALS OVER GAUSSIAN FUNCTIONS

We would like to present here the explicit formulas for integrals required to determine the matrix elements of the Hamiltonian for the positronium molecule. These are particular cases of the formulas derived previously for integrals involving general explicitly correlated, multicenter Cartesian Gaussian functions [19].

The overlap integral can be obtained as

$$\begin{aligned} I_{\mathrm{ov}} &= \langle \omega_l(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B) | \omega_k(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B) \rangle \\ &= \pi^6 [\det(\mathbf{A}^{lk}+\mathbf{B}^{lk})]^{-3/2} , \end{aligned} \tag{A1}$$

where $\mathbf{A}^{lk} = \mathbf{A}^l + \mathbf{A}^k$ and $\mathbf{B}^{lk} = \mathbf{B}^l + \mathbf{B}^k$. The kinetic-energy integral has the following form:

$$\begin{aligned} T_{lk} &= \langle \omega_l(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B) | -\tfrac{1}{2} \sum_{i=1,2,A,B} \nabla_i^2 | \omega_k(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B) \rangle \\ &= \tfrac{1}{2} \sum_{i=1,2,A,B} I_{ii}^{lk} , \end{aligned} \tag{A2}$$

while the kinetic energy for the center-of-mass motion reads

$$T_{\mathrm{c.m.}lk} = \tfrac{1}{8} \sum_{i=1,2,A,B} \sum_{j=1,2,A,B} I_{ij}^{lk} . \tag{A3}$$

The above integrals are expressed in terms of the integral $I_{ij}^{lk}$ resulting from integration by parts of the integral involving the $\nabla_i \nabla_j$ operator:

$$\begin{aligned} I_{ij}^{lk} = \int \int \cdots \int [\nabla_i \omega_l(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)] \\ \times [\nabla_j \omega_k(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_A d\mathbf{r}_B . \end{aligned} \tag{A4}$$

As it was shown in our previous work, the integral $I_{ij}^{lk}$ can be expressed in terms of the generalized overlap integral as follows:

$$\begin{aligned} I_{ij}^{lk} = 4 \Bigg[ & \alpha_i^l \alpha_j^k J(\mathbf{r}_i,\mathbf{r}_i;1,1) + \alpha_i^l \sum_{s=1,2,A,B} b_{is}^k J(\mathbf{r}_i,\mathbf{r}_s;1,1) \\ & + \alpha_j^k \sum_{m=1,2,A,B} b_{jm}^l J(\mathbf{r}_i,\mathbf{r}_m;1,1) \\ & + \sum_{m=1,2,A,B} \sum_{s=1,2,A,B} b_{im}^l b_{js}^k J(\mathbf{r}_m,\mathbf{r}_s;1,1) \Bigg] , \end{aligned} \tag{A5}$$

where $b_{mn}^l$ denotes an element of the $\mathbf{B}^l$ matrix and the generalized overlap integral $J(\mathbf{r}_p,\mathbf{r}_q;n_1,n_2)$ is defined as

$$\begin{aligned} J(\mathbf{r}_p,\mathbf{r}_q;n_1,n_2) = \int \int \int \int \mathbf{r}_p^{n_1} \mathbf{r}_q^{n_2} \exp[-\mathbf{r}(\mathbf{A}^{lk}+\mathbf{B}^{lk})\mathbf{r}^T] \\ \times d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_A d\mathbf{r}_B . \end{aligned} \tag{A6}$$

It is more convenient to rewrite Eq. (A4) in the following form:

$$\begin{aligned} I_{ij}^{lk} = 4 \sum_{m=1,2,A,B} \sum_{s=1,2,A,B} (\alpha_m^l \delta_{mi} + b_{im}^l)(\alpha_s^k \delta_{sj} + b_{js}^k) \\ \times J(\mathbf{r}_m,\mathbf{r}_s;1,1) . \end{aligned} \tag{A7}$$

The integral with $n_1 = n_2 = 1$ can be calculated as a partial derivative of the overlap integral with respect to the $b_{pq}^{lk}$ element of the $\mathbf{B}^{lk}$ matrix,

$$J(\mathbf{r}_p,\mathbf{r}_q;1,1) = \frac{-1}{2-\delta_{pq}} \frac{\partial}{\partial b_{pq}^{lk}} \langle \omega_l | \omega_k \rangle , \tag{A8}$$

where $\delta_{sm}$ is the Kronecker delta. Using the expression for $J(\mathbf{r}_p,\mathbf{r}_q;1,1)$, integral $I_{ij}^{lk}$ becomes

$$\begin{aligned} I_{ij}^{lk} = -4 \sum_{m=1,2,A,B} \sum_{s=1,2,A,B} (\alpha_m^l \delta_{mi} + b_{im}^l)(\alpha_s^k \delta_{sj} + b_{js}^k) \\ \times \left[ \frac{1}{2-\delta_{ms}} \right] \frac{\partial}{\partial b_{ms}^{lk}} \langle \omega_l | \omega_k \rangle . \end{aligned} \tag{A9}$$

Further simplification can be made by introducing the expression for the first derivative of the overlap integral

$$I_{ij}^{lk}=6\frac{\langle \omega_l|\omega_k\rangle}{\det(\mathbf{A}^{lk}+\mathbf{B}^{lk})}W_{ij}\ , \tag{A10}$$

where

$$W_{ij}=\sum_{m=1,2,A,B}\ \sum_{s=1,2,A,B}(\alpha_m^l\delta_{mi}+b_{im}^l)(\alpha_s^k\delta_{sj}+b_{js}^k)\times\det(\mathbf{A}^{lk}+\mathbf{B}^{lk}|1_{ms})\ . \tag{A11}$$

In the last equation, $\det(\mathbf{A}^{lk}+\mathbf{B}^{lk}|1_{ms})$ denotes the result of the derivative $(\partial/\partial b_{ms}^{lk})\det(\mathbf{A}^{lk}+\mathbf{B}^{lk})$. It can be demonstrated that differentiation of the determinant $\det(\mathbf{A}^{lk}+\mathbf{B}^{lk})$ with respect to $b_{ms}^{lk}$ is equivalent to setting the $s$ column and $m$ row equal to zero, and replacing the element $(\mathbf{A}^{lk}+\mathbf{B}^{lk})_{ms}$ with 1. Using the expression for the integral $I_{ij}^{lk}$ allows us to express the kinetic-energy integral in the final form as

$$T_{lk}=3\frac{\langle \omega_l|\omega_k\rangle}{\det(\mathbf{A}^{lk}+\mathbf{B}^{lk})}\sum_{i=1,2,A,B}W_{ii} \tag{A12a}$$

and the integral of the center-of-mass motion as

$$T_{\text{c.m.}\,lk}=\frac{3}{4}\frac{\langle \omega_l|\omega_k\rangle}{\det(\mathbf{A}^{lk}+\mathbf{B}^{lk})}\sum_{i=1,2,A,B}\ \sum_{i=1,2,A,B}W_{ij}\ . \tag{A12b}$$

The Coulomb integral has the following form:

$$\langle \omega_l(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)|\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}|\omega_k(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_A,\mathbf{r}_B)\rangle=\int\int\int\int\exp[-\mathbf{r}(\mathbf{A}^{lk}+\mathbf{B}^{lk})\mathbf{r}^T]\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_Ad\mathbf{r}_B$$
$$=\pi^3[\det(\mathbf{A}^{lk}+\mathbf{B}^{lk};i,j)]^{-3/2}\frac{2\pi^{5/2}}{D(i,j)[D(i)+D(j)+2(\mathbf{B}^{(2)})_{ij}]^{1/2}}\ , \tag{A13}$$

where the determinant $\det(\mathbf{A}^{lk}+\mathbf{B}^{lk};i,j)$ does not contain columns and rows with indices $i$ and $j$, respectively, and the indexes $i$ and $j$ can be 1, 2, $A$, or $B$. The quantities $D(i)$, $D(j)$, $D(i,j)$, and $(\mathbf{B}^{(2)})_{ij}$ will be defined later in this section. The Coulomb integral results from a two-step integration. The first step, which we called "reduction," is the integration over coordinates of all particles except $i$ and $j$. The way of reduction is independent of the order of integration. The second step is the integration over coordinates of the $i$ and $j$ particles.

To demonstrate practical realization of the reduction scheme, let us consider the matrix element given by Eq. (A13). Let indices $p_1,p_2$ denote the particles not involved in the Coulombic interaction (i.e., if $i=2$ and $j=A$, then $p_1$ can be 1 and $p_2=B$, or $p_1=B$, $p_2=1$). Let us now reassign the particle labels so that $i=1$, $j=2$, $p_2=3$, $p_1=4$. It is required that the $\mathbf{A}^{lk}$ and $\mathbf{B}^{lk}$ matrices are rearranged accordingly. After integrating over $\mathbf{r}_{p_1}$ in Eq. (A13), one obtained the following result:

$$\pi^{3/2}(a_{p_1p_1}^{lk}+b_{p_1p_1}^{lk})^{-3/2}\int\int\int\exp[-(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_{p_2})(\mathbf{A}^{(1)}+\mathbf{B}^{(1)})(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_{p_2})^T]\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}d\mathbf{r}_id\mathbf{r}_jd\mathbf{r}_{p_2}\ , \tag{A14}$$

where $a_{p_1p_1}^{lk}$ denotes an element of the $\mathbf{A}^{lk}$ matrix and $\mathbf{A}^{(1)}$ is a 3×3 matrix that was obtained from $\mathbf{A}^{lk}$ by removing the $p_1$ row (the last row) and the $p_1$ column (the last column). $\mathbf{B}^{(1)}$ is also a 3×3 matrix that is obtained as

$$(\mathbf{B}^{(1)})_{mn}=(\mathbf{B}^{lk})_{mn}-\frac{1}{(\mathbf{A}^{lk})_{p_1p_1}+(\mathbf{B}^{lk})_{p_1p_1}}(\mathbf{B}^{lk})_{mp_1}(\mathbf{B}^{lk})_{np_1}\ , \tag{A15}$$

where $m,n\neq p_1$. The above expression is the result of the first reduction (i.e., integration over the coordinates of the $p_1$ electron). The integration of Eq. (A14) over the coordinates of the $p_2$ electron leads to the result

$$\pi^{3/2}(a_{p_1p_1}^{lk}+b_{p_1p_1}^{lk})^{-3/2}\pi^{3/2}(a_{p_2p_2}^{(1)}+b_{p_2p_2}^{(1)})^{-3/2}\int\int\exp[-(\mathbf{r}_i,\mathbf{r}_j)(\mathbf{A}^{(2)}+\mathbf{B}^{(2)})(\mathbf{r}_i,\mathbf{r}_j)^T]\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}d\mathbf{r}_i,d\mathbf{r}_j\ , \tag{A16}$$

where $\mathbf{A}^{(2)}$ is a 2×2 matrix that was obtained from $\mathbf{A}^{lk}$ by removing $p_1$ and $p_2$ rows (last two rows) and $p_1$ and $p_2$ columns (last two columns). Similarly, $\mathbf{B}^{(2)}$ is a 2×2 matrix generated as follows:

$$(\mathbf{B}^{(2)})_{mn}=(\mathbf{B}^{(1)})_{mn}-\frac{\det(\mathbf{A}^{lk}+\mathbf{B}^{lk};i,j,p_2)}{\det(\mathbf{A}^{lk}+\mathbf{B}^{lk};i,j)}(\mathbf{B}^{(1)})_{mp_2}(\mathbf{B}^{(1)})_{np_2}\ , \tag{A17}$$

where $m,n\neq p_1,p_2$. In the final step, the integration over the coordinates of $i$ and $j$ particles is performed, leading to the following result for the Coulomb integral:

$$\int\int\exp[-(\mathbf{r}_i,\mathbf{r}_j)(\mathbf{A}^{(2)}+\mathbf{B}^{(2)}(\mathbf{r}_i,\mathbf{r}_j)^T]\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}d\mathbf{r}_id\mathbf{r}_j=\frac{2\pi^{5/2}}{D(i,j)[D(i)+D(j)+2(\mathbf{B}^{(2)})_{ij}]^{1/2}}\ , \tag{A18}$$

where

$$D(i)=(\mathbf{A}^{(2)})_{ii}+(\mathbf{B}^{(2)})_{ii},\quad D(j)=(\mathbf{A}^{(2)})_{jj}+(\mathbf{B}^{(2)})_{jj}\ ,$$

and

$$D(i,j)=\begin{vmatrix} (\mathbf{A}^{(2)})_{ii}+(\mathbf{B}^{(2)})_{ii} & (\mathbf{B}^{(2)})_{ij} \\ (\mathbf{B}^{(2)})_{ij} & (\mathbf{A}^{(2)})_{jj}+(\mathbf{B}^{(2)})_{jj} \end{vmatrix} . \tag{A19}$$

## APPENDIX B: AVERAGES OF THE SQUARES OF INTERPARTICULAR DISTANCES

The $\langle r_{ij}^2 \rangle$ were calculated with the use of the standard expectation value formula

$$\begin{aligned} \langle r_{ij}^2 \rangle &= \langle \Psi_{\mathrm{tot}} | r_{ij}^2 | \Psi_{\mathrm{tot}} \rangle \\ &= \sum_{k=1}^{M} \sum_{l=1}^{M} C_l C_k \langle P(A,B)P(1,2)\omega_l | r_{ij}^2 | P(A,B)P(1,2)\omega_k \rangle . \end{aligned} \tag{B1}$$

The matrix element involving the square of the interparticular distance can be easily evaluated by differentiation of the overlap integral with respect to the sum of appropriate correlation exponents (the calculation for $\langle r_{12}^2 \rangle$ is shown):

$$\langle \omega_l | r_{12}^2 | \omega_k \rangle = \left[ -\frac{\partial}{\partial \beta_{12}^{lk}} \right] \langle \omega_l | \omega_k \rangle = \pi^{9/2} \left[ -\frac{\partial}{\partial \beta_{12}^{lk}} \right] [\det(\mathbf{A}^{lk}+\mathbf{B}^{lk})]^{-3/2} . \tag{B2}$$

By adding the second row to the first row and then the second column to the first column in the determinant in the last expression, one eliminates the correlation exponent $\beta_{12}^{lk}$ from all elements except the diagonal (2,2) element. By differentiating the resulting determinant with respect to $\beta_{12}^{lk}$, one obtained the final formula for $\langle \omega_l | r_{12}^2 | \omega_k \rangle$:

$$\langle \omega_l | r_{12}^2 | \omega_k \rangle = -\tfrac{3}{2}\pi^{-3} \langle \omega_l | \omega_k \rangle^{5/3} \begin{vmatrix} \alpha_1^{lk}+\alpha_2^{lk}+\beta_{1A}^{lk}+\beta_{1B}^{lk}+\beta_{2A}^{lk}+\beta_{2B}^{lk} & -\beta_{1A}^{lk}-\beta_{2A}^{lk} & -\beta_{1B}^{lk}-\beta_{2B}^{lk} \\ -\beta_{1A}^{lk}-\beta_{2A}^{lk} & \alpha_A^{lk}+\beta_{1A}^{lk}+\beta_{2A}^{lk}+\beta_{AB}^{lk} & -\beta_{AB}^{lk} \\ -\beta_{1B}^{lk}-\beta_{2B}^{lk} & -\beta_{AB}^{lk} & \alpha_B^{lk}+\beta_{1B}^{lk}+\beta_{2B}^{lk}+\beta_{AB}^{lk} \end{vmatrix} . \tag{B3}$$

[1] J. A. Wheeler, Ann. N.Y. Acad. Sci. **48**, 219 (1946).

[2] E. A. Haylleraas and A. Ore, Phys. Rev. **71**, 493 (1947).

[3] A. Ore, Phys. Rev. **71**, 913 (1947).

[4] A. Ore, Phys. Rev. **83**, 665 (1951).

[5] *Positronium and Muonium Chemistry,* edited by H. J. Ache, Advances in Chemistry Series Vol. 1975 (American Chemical Society, Washington, D.C., 1979).

[6] *Atomic Physics with Positrons,* edited by J. W. Humbertson and E. A. G. Armour (Plenum, New York, 1987).

[7] *Positronium and Positronium Chemistry,* edited by D. M. Schreder and Y. C. Jean, Studies in Physical and Theoretical Chemistry Vol. 57 (Elsevier, Amsterdam, 1988).

[8] A. P. Mills, Jr., Phys. Rev. Lett. **46**, 717 (1981).

[9] A. K. Bhatia and R. J. Drachman, Phys. Rev. **28**, 2523 (1983).

[10] A. M. Florov, Z. Phys. D **2**, 61 (1986).

[11] Y. K. Ho, Phys. Rev. A **34**, 609 (1986); C. F. Labeda and D. M. Schrader, Phys. Rev. **178**, 24 (1969).

[12] A. K. Bhatia and R. J. Drachman, Phys. Rev. A **42**, 5117 (1990); Y. K. Ho, Phys. Rep. **99**, 1 (1983).

[13] *Positron Scattering in Gases,* edited by J. W. Humbertson and M. R. C. McDowell (Plenum, New York, 1983).

[14] P. M. Kozlowski and L. Adamowicz, J. Chem. Phys. **95**, 6681 (1991).

[15] P. M. Kozlowski and L. Adamowicz, J. Chem. Phys. **97**, 5063 (1992).

[16] S. F. Boys, Proc. R. Soc. London Ser. A **258**, 402 (1960).

[17] K. Singer, Proc. R. Soc. London Ser. A **258**, 412 (1960).

[18] W. A. Lester, Jr. and M. Krauss, J. Chem. Phys. **41**, 1407 (1964); **42**, 2990 (1965).

[19] P. M. Kozlowski and L. Adamowicz, J. Comput. Chem. **13**, 602 (1992).

[20] R. R. Sharma, Phys. Rev. **171**, 36 (1968).

[21] O. Akimoto and E. Hanamura, Solid State Commun. **10**, 253 (1972).

[22] W.-T. Huang, Phys. Status Solidi **60**, 309 (1973).

[23] W. F. Brinkman, T. M. Rice, and B. Bell, Phys. Rev. B **8**, 1570 (1973).

[24] M. A. Lee, P. Vashishta, and R. K. Kalia, Phys. Rev. Lett. **51**, 2422 (1983).

[25] S. Vinitsky and F. R. Vukajlovic, Phys. Rev. B **31**, 6079 (1985).

[26] Y. K. Ho, Phys. Rev. A **33**, 3584 (1986).

[27] F. R. Vukajlovic and S. Vinitsky, Phys. Lett. A **118**, 185 (1986).

[28] R. J. Drachman, in *Atomic Physics with Positrons,* edited by J. W. Humbertson and E. A. G. Armour (Plenum, New York, 1987).

[29] D. B. Kinghorn, M. Sci. thesis, Washington State University, Pulman, 1992 (unpublished); D. B. Kinghorn and R. D. Poshusta, Phys. Rev. A **47**, 3671 (1993).