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Nonadiabatic variational calculations on dipositronium using explicitly correlated Gaussian basis functions

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Nonadiabatic variational calculations are described for dispositronium (e^+,e^+,e^-,e^-) using explicitly correlated Gaussian basis functions with angular momentum zero. An improved rigorous upper bound for the A_1 ground-state energy for dipositronium is achieved (-0.5159767 a.u.) leading to a corresponding bound for the binding energy, $\Delta\varepsilon_0 > 0.435$ eV, which is greater than previous estimates by 0.024 eV. This improved energy is obtained by exploiting the full permutational symmetry of the Hamiltonian including charge-reversal symmetry which was ignored in recent calculations. The first excited A_1 state, and the lowest B_1 and A_2 states of dipositronium are found to be unbound while the B_2 and E states appear to be metastable. For comparison, by the same method, the ^2S ground-state energy of the lithium atom is found to be -7.4767161 a.u., which lies 0.001343 a.u. above the accepted true energy. Expectation values for individual terms of the Hamiltonian along with moments of interparticle distances $\langle r^{\pm 1}\rangle$, $\langle r^{\pm 2}\rangle$, and $\langle \delta(r_{ij})\rangle$ are also reported.

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I. INTRODUCTION

Dipositronium [1], Ps_2, the molecule formed by two positronium atoms, has been the subject of several theoretical investigations [2,3]. Direct experimental observation of this short-lived species has not yet been reported. The present theoretical study of dipositronium achieves an improved estimate of its binding energy.

To date, Ps_2 has not been directly observed. Dipositronium might be produced when a high flux beam of slow positrons is focused on a metal surface where they pick up conduction electrons to form positronium atoms, which then dimerize and are desorbed from the surface: $2Ps \rightarrow Ps_2$. Mills [4] has estimated the yield ratio Ps_2:Ps in such an experiment. He finds Ps_2:Ps$=0.01$ using the dipositronium binding energy $\Delta\varepsilon_0 = 0.20$ eV. Under the same assumptions, but using our improved binding energy $\Delta\varepsilon_0 = 0.435$ eV, we find the much more favorable yield ratio Ps_2:Ps$=98$. Ps_2 has also been proposed to explain the anomalous positron peaks observed from superheavy nuclear collisions [5].

Ps_2 differs from conventional molecular electronic systems in several ways which affect the computational approach. All four particles have the same mass, which makes the Born-Oppenheimer and adiabatic approximations inappropriate. In addition to symmetry under exchange of indistinguishable particles, there is also symmetry under charge reversal in Ps_2. All interparticle correlations, whether between two electrons, two positrons, or between an electron and a positron, are expected to be equally important. Thus we use a fully nonadiabatic method, the complete dipositronium symmetry group, treat positrons and electrons on the same footing, and include all interparticle correlations.

Although the earliest Ps_2 calculations take account of its full symmetry [6,7], several recent calculations omit the charge-reversal symmetry of dipositrium. As a result, wave functions have mixed symmetry and estimated binding energies are too small. In one variational calculation [2], the only dipositronium symmetry included was electron exchange, while positron exchange and charge reversal were ignored. A recent Green's-function Monte Carlo (GFMC) calculation [3], treated bound complexes of two electrons and two holes with continuously variable mass ratio, $\sigma = m_\varepsilon / m_h$. Although the GFMC method will converge to the exact ground state by iterating from the initial trial function Ψ_T, the convergence is accelerated if Ψ_T already possesses the irreducible symmetry of the ground state. In the case just cited [3], the correct electron exchange and positron exchange symmetries were included in Ψ_T, but charge-reversal symmetry was ignored.

This paper is organized as follows. A center-of-mass transformation is applied to the Hamiltonian for four-particles interacting by Coulomb potentials. Correlated Gaussian basis functions are described. The symmetry group of dipositronium is specified as it acts on center-of-mass coordinates. The method of computation is briefly described including steps for symmetry adaptation of basis functions, matrix element evaluation, secular equation for linear variation, and optimization of nonlinear variational parameters. Results (energy and various expectation values) for the ground state and several low-lying excited states are presented and discussed. A complete description of our method together with computer listings and additional results can be found in D. B. Kinghorn's M.S. thesis [8]

II. THE HAMILTONIAN

Our treatment of dispositronium follows a general method applicable to any system of four particles with masses $\{M_1, M_2, M_3, M_4\}$ and charges $\{Q_1, Q_2, Q_3, Q_4\}$ interacting by Coulomb potentials and with relativistic effects ignored. Let

$$R_i = \begin{bmatrix} X_i \\ Y_i \\ Z_i \end{bmatrix} \tag{1}$$

denote the three-vector of Cartesian coordinates of the ith particle and let

$$P_i = \begin{bmatrix} P_{X_i} \\ P_{Y_i} \\ P_{Z_i} \end{bmatrix} \tag{2}$$

denote the conjugate momenta. Then the nonrelativistic Hamiltonian for this system is

$$\hat{H} = \hat{T} + \hat{V} \ , \tag{3}$$

with $\hat{T}$ and $\hat{V}$ given by

$$\hat{T} = \frac{\hat{P}_1^2}{2M_1} + \frac{\hat{P}_2^2}{2M_2} + \frac{\hat{P}_3^2}{2M_3} + \frac{\hat{P}_4^2}{2M_4} \ , \tag{4}$$

$$\hat{V} = \frac{Q_1Q_2}{R_{12}} + \frac{Q_1Q_3}{R_{13}} + \frac{Q_1Q_4}{R_{14}} + \frac{Q_2Q_3}{R_{23}} + \frac{Q_2Q_4}{R_{24}} + \frac{Q_3Q_4}{R_{34}} \ , \tag{5}$$

where $R_{ij} = |R_i - R_j|$ is the distance between particles i and j. Atomic units are used throughout so that $\hbar = e = m_e = a_0 = 1$ and energy is in hartree, $E_H = 27.2107$ eV.

For dipositronium [Ps_2 or $2(e^+,e^-)$], the masses and charges are given by

$$\{M_1,M_2,M_3,M_4\} = \{1,1,1,1\} \ ,$$

$$\{Q_1,Q_2,Q_3,Q_4\} = \{+1,+1,-1,-1\} \ .$$

The related hole-electron system has the same charges and masses $\{1/\sigma,1/\sigma,1,1\}$.

Center of mass

The center-of-mass separation is effected by the following transformation from real particle (upper case) to fictitious pseudoparticle (lower case) coordinates:

$$\begin{aligned} r_0 &= \frac{M_1}{m_0}R_1 + \frac{M_2}{m_0}R_2 + \frac{M_3}{m_0}R_3 + \frac{M_4}{m_0}R_4 \ , \\ r_1 &= -R_1 + R_2 \ , \\ r_2 &= -R_1 + R_3 \ , \\ r_3 &= -R_1 + R_4 \ , \end{aligned} \tag{6}$$

and momenta

$$\begin{aligned} p_0 &= P_1 + P_2 + P_3 + P_4 \ , \\ p_1 &= -\frac{M_2}{m_0}P_1 - \left[\frac{M_2}{m_0} - 1\right]P_2 - \frac{M_2}{m_0}P_3 - \frac{M_2}{m_0}P_4 \ , \\ p_2 &= -\frac{M_3}{m_0}P_1 - \frac{M_3}{m_0}P_2 - \left[-\frac{M_3}{m_0} - 1\right]P_3 - \frac{M_3}{m_0}P_4 \ , \\ p_3 &= -\frac{M_4}{m_0}P_1 - \frac{M_4}{m_0}P_2 - \frac{M_4}{m_0}P_3 - \left[\frac{M_4}{m_0} - 1\right]P_4 \ , \end{aligned} \tag{7}$$

so that transformed coordinates r and momenta p obey the canonical commutation rule $[p_i,r_j] = -i\delta_{i,j}$. In matrix form $r = TR$ and $p = (T^t)^{-1}P$, where

$$R = \begin{bmatrix} R_1 \\ R_2 \\ R_3 \\ R_4 \end{bmatrix} , \quad r = \begin{bmatrix} r_0 \\ r_1 \\ r_2 \\ r_3 \end{bmatrix} , \tag{8}$$

$$P = \begin{bmatrix} P_1 \\ P_2 \\ P_3 \\ P_4 \end{bmatrix} , \quad p = \begin{bmatrix} p_0 \\ p_1 \\ p_2 \\ p_3 \end{bmatrix} , \tag{9}$$

with the three-vector r_i representing the ith pseudoparticle's coordinates,

$$r_i = \begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix} , \tag{10}$$

and the three-vector p_i representing the ith pseudoparticle's conjugate momenta,

$$p_i = \begin{bmatrix} p_{x_i} \\ p_{y_i} \\ p_{z_i} \end{bmatrix} . \tag{11}$$

Now, since each of R_i, r_i, P_i and p_i is a three-vector, the transformation T: $R \rightarrow r$ is given by

$$T = \begin{bmatrix} \frac{M_1}{m_0} & \frac{M_2}{m_0} & \frac{M_3}{m_0} & \frac{M_4}{m_0} \\ -1 & 1 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ -1 & 0 & 0 & 1 \end{bmatrix} \otimes 1_3 \ , \tag{12}$$

where 1_3 is the 3×3 identity matrix. T is essentially a transformation on particle coordinate which treats the three components x, y, and z equivalently, as expressed in the tensor product, a form which appears repeatedly.

Using this transformation, the total Hamiltonian becomes $H_{\text{tot}} = H_{\text{c.m.}} + H_{\text{int}}$, where

$$H_{\text{c.m.}} = \frac{p_0^2}{2m_0} \tag{13}$$

and

$$H_{\mathrm{int}}=\frac{p_1^2}{2m_1}+\frac{p_2^2}{2m_2}+\frac{p_3^2}{2m_3}+\frac{p_1\cdot p_2}{M_1}+\frac{p_1\cdot p_3}{M_1}+\frac{p_2\cdot p_3}{M_1}+\frac{q_0q_1}{r_1}+\frac{q_0q_2}{r_2}+\frac{q_0q_3}{r_3}+\frac{q_1q_2}{r_{12}}+\frac{q_1q_3}{r_{13}}+\frac{q_2q_3}{r_{23}}\ , \tag{14}$$

where the masses and charges of the pseudoparticles become

$$m_0=M_1+M_2+M_3+M_4\ ,\quad m_1=\frac{M_1M_2}{M_1+M_2}\ ,\quad m_2=\frac{M_1M_3}{M_1+M_3}\ ,\quad m_3=\frac{M_1M_4}{M_1+M_4}\ , \tag{15}$$

and

$$q_0=Q_1\ ,\quad q_1=Q_2\ ,\quad q_2=Q_3\ ,\quad q_3=Q_4\ . \tag{16}$$

The subscript on H_{int} will be dropped for simplicity in the following.

The center-of-mass Hamiltonian (13) represents translational kinetic energy of a fictitious particle with mass m_0. Its continuum of energy eigenstates are ignored in the following. Interest lies in the discrete eigenstates of the internal Hamiltonian.

The internal Hamiltonian (14) represents the energy of three interacting fictitious particles with Cartesian coordinates $\{r_1,r_2,r_3\}$, masses $\{m_1,m_2,m_3\}$, and charges $\{q_1,q_2,q_3\}$. It includes the kinetic energy, mass polarization, and the Coulomb potentials for these particles interacting with one another and with a charge q_0 fixed at the origin.

For dipositronium, pseudoparticle masses and charges are $\{\frac{1}{2},\frac{1}{2},\frac{1}{2}\}$ and $\{+1,-1,-1\}$. Our objective is a variational calculation for eigenstates of dipositronium, for which we use a set of basis functions which simplify the computation of matrix elements over H_{int}.

III. CORRELATED GAUSSIAN BASIS FUNCTIONS

Correlated Gaussian basis functions consist of exponential quadratic forms in the Cartesian coordinates of the system particles. In 1960, Boys [9] and Singer [10] proposed these basis functions for variational calculations on many-electron systems. Interest has continued in these basis functions [11–22].

The variational wave functions used in this work are constructed from correlated Gaussian functions centered at the origin. Their functional form is

$$\begin{aligned}f_k(r_1,r_2,r_3)=\exp[-(&r_1A_{11}^kr_1+2r_1A_{12}^kr_2\\&+2r_1A_{13}^kr_3+r_2A_{22}^kr_2\\&+2r_2A_{23}^kr_3+r_3A_{33}^kr_3)]\ ,\end{aligned} \tag{17}$$

which can be written in matrix form as

$$f_k(r_1,r_2,r_3)=\exp\left[-(r_1,r_2,r_3)\begin{bmatrix}A_{11}^k & A_{12}^k & A_{13}^k\\ A_{12}^k & A_{22}^k & A_{23}^k\\ A_{13}^k & A_{23}^k & A_{33}^k\end{bmatrix}\begin{bmatrix}r_1\\ r_2\\ r_3\end{bmatrix}\right]\ , \tag{18}$$

or more simply as

$$f_k(\mathfrak{r})=\exp[-(\mathfrak{r},A^k\mathfrak{r})]\ , \tag{19}$$

where $\mathfrak{r}$ is the vector

$$\mathfrak{r}=\begin{bmatrix}r_1\\ r_2\\ r_3\end{bmatrix}\ . \tag{20}$$

A^k is a 9×9 "exponent matrix" factored into three by three blocks A_{ij}^k describing correlation between particles i and j (or between coordinates x, y, and z of particle i if $i=j$). The quadratic form $(\mathfrak{r},A^k\mathfrak{r})$ and thus A_k must be positive definite in order for the norm $\langle f_k|f_k\rangle$ to exist. The elements of A_k are assumed to be scalar 3×3 matrices:

$$A_{ij}^k=a_{ij}^k\otimes 1_3\ . \tag{21}$$

That is, x, y, and z components are treated equally. This allows us to write A^k as

$$A^k=\mathcal{A}^k\otimes 1_3\ , \tag{22}$$

where

$$\mathcal{A}^k=\begin{bmatrix}a_{11}^k & a_{12}^k & a_{13}^k\\ a_{12}^k & a_{22}^k & a_{23}^k\\ a_{13}^k & a_{23}^k & a_{33}^k\end{bmatrix}\ . \tag{23}$$

By restricting the exponent matrices to block diagonal form, the basis functions become rotationally invariant and therefore they are angular momentum eigenfunctions with $J=0$. Our basis is also unchanged by inversion of all coordinates through the origin and therefore represents gerade states only. It remains to adapt the basis functions to permutational symmetry states.

IV. PERMUTATIONAL SYMMETRY

Permutational or exchange symmetry is present when particle coordinates and momenta can be interchanged without changing the Hamiltonian, that is, when two or more particles are indistinguishable (have the same mass and charge), or sometimes if pairs of particles carry the same mass and opposite charges, as happens in dipositronium. Elementary permutations of real particles induce transformations on pseudoparticles, as we now describe. Induced transformations are also sometimes elementary permutations of the pseudoparticles as happens for the lithium atom. In general, induced transformations are simple, although not elementary, permutations. We exhibit the induced transformations for the dipositronium example:

$$\text{Let}\left\{\begin{array}{l} R \text{ be the set of real particle position vectors,}\\ r \text{ be the set of pseudoparticle positions}\\ \quad\text{after center-of-mass transformation,}\\ \mathrm{T} \text{ be the transformation from } R\to r \text{ Eq.(12) ,}\\ \mathcal{P} \text{ be an element of the permutation}\\ \quad\text{group on real particles expressed}\\ \quad\text{in } 4\times 4 \text{ matrix form .}\end{array}\right. \tag{24}$$

Then, the permutation of real particles induces the following transformation on center-of-mass and internal coordinates:

$$T\mathcal{P}T^{-1}r=r' \ . \tag{25}$$

Further, since $\mathcal{P}$ interchanges particles with the same mass and thus leaves r_0 unchanged, it follows that $T\mathcal{P}T^{-1}$ is a direct sum of the 1×1 identity on r_0 and a 3×3 induced symmetry transformation on internal coordinates:

$$T\mathcal{P}T^{-1}=1_1\oplus\mathcal{T}_{\mathcal{P}} \ . \tag{26}$$

The entire effect of $\mathcal{P}$ is expressed by $\mathcal{T}_{\mathcal{P}}$ on $\mathfrak{r}$, recalling that $\mathfrak{r}$ is the vector with components r_1, r_2, and r_3. In this way, $\mathcal{P}$ on real particles induces $\mathcal{T}_{\mathcal{P}}$ on pseudoparticles.

Since the transformations $\mathcal{T}_{\mathcal{P}}$ multiply isomorphically with $\mathcal{P}$, we refer to them as "permutations," although in matrix form they may not be permutation matrices and they may not merely permute pseudoparticle coordinates. In the special case of atoms and when real particle 1 is the nucleus, then the transformations $\mathcal{T}_{\mathcal{P}}$ become elementary permutations on pseudoparticles. We next derive the form of $\mathcal{T}_{\mathcal{P}}$ for dipositronium.

A. Dipositronium symmetry

For dipositronium, we require the following real particle permutations: E, the identity; (12), interchange positrons; (34), interchange electrons; (12)(34), interchange positrons and interchange electrons; (13)(24) and (14)(23), charge reversals of class one; (1324) and (1423), charge reversals of class two.

These eight permutations form a group G_D, the permutation symmetry group of dipositronium.

The identity and interchange operations form a subgroup which commutes with the Hamiltonian of any system with masses $\{m_h,m_h,1,1\}$ and charges $\{+1,+1,-1,-1\}$. This subgroup is the symmetry group of all systems having $m_h\neq 1$, such as H_2. The charge-reversal symmetry operations, which enter only in the case $m_h=1$, the dipositronium case, arise fundamentally because the Hamiltonian commutes with these coordinate transformations. From another viewpoint, charge reversal may be considered as the remnant in the nonrelativistic theory of the charge-conjugation symmetry present in Dirac's relativistic electron theory.

B. Permutations on pseudoparticles

To find the exchange symmetry coordinate transformations on pseudoparticles induced by the real particle exchange permutations, we use Eq. (26). The results are as follows:

$$T\mathcal{P}_{(12)}T^{-1}=\begin{bmatrix}1&0&0&0\\0&-1&0&0\\0&-1&1&0\\0&-1&0&1\end{bmatrix} . \tag{27}$$

Therefore,

$$\mathcal{T}_{(12)}=\begin{bmatrix}-1&0&0\\-1&1&0\\-1&0&1\end{bmatrix} . \tag{28}$$

In the same way,

$$\mathcal{T}_{(1)}=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} , \tag{29}$$

$$\mathcal{T}_{(34)}=\begin{bmatrix}1&0&0\\0&0&1\\0&1&0\end{bmatrix} , \tag{30}$$

$$\mathcal{T}_{(14)(23)}=\begin{bmatrix}0&1&-1\\1&0&-1\\0&0&-1\end{bmatrix} , \tag{31}$$

$$\mathcal{T}_{(13)(24)}=\begin{bmatrix}0&-1&1\\0&-1&0\\1&-1&0\end{bmatrix} , \tag{32}$$

$$\mathcal{T}_{(1324)}=\begin{bmatrix}0&1&-1\\0&0&-1\\1&0&-1\end{bmatrix} , \tag{33}$$

$$\mathcal{T}_{(1423)}=\begin{bmatrix}0&-1&1\\1&-1&0\\0&-1&0\end{bmatrix} , \tag{34}$$

$$\mathcal{T}_{(12)(34)}=\begin{bmatrix}-1&0&0\\-1&0&1\\-1&1&0\end{bmatrix} . \tag{35}$$

These pseudoparticle operators are isomorphic to real particle permutations under the similarity transformation (26). Thus, we may use the permutation cycle notation to refer to both real and pseudoparticle "permutations."

C. Projection operators

Energy eigenstates of H_{int} transform irreducibility under the induced pseudoparticle symmetry group. Hence, we next develop the projectors for irreducible symmetry states of dipositronium.

The exchange symmetry group of the Hamiltonian for dipositronium G_D, consisting of the eight particle permutations defined above, is isomorphic to the point group D_{2d}, from which characters and irreducible representations may be taken. In this way, we obtain the following projection operators for irreducible symmetry under particle permutations:

$$e^{A_1}=\tfrac{1}{8}[E+(12)+(34)+(12)(34)+(1324)+(1423)+(13)(24)+(14)(23)]\ , \tag{36}$$

$$e^{A_2}=\tfrac{1}{8}[E-(12)-(34)+(12)(34)+(1324)+(1423)-(13)(24)-(14)(23)]\ , \tag{37}$$

$$e^{B_1}=\tfrac{1}{8}[E-(12)-(34)+(12)(34)-(1324)-(1423)+(13)(24)+(14)(23)]\ , \tag{38}$$

$$e^{B_2}=\tfrac{1}{8}[E+(12)+(34)+(12)(34)-(1324)-(1423)-(13)(24)-(14)(23)]\ , \tag{39}$$

$$e^E_{11}=\tfrac{1}{4}[E-(12)(34)+(13)(24)-(14)(23)]\ , \tag{40}$$

$$e^E_{12}=\tfrac{1}{4}[(12)-(34)-(1324)+(1423)]\ , \tag{41}$$

$$e^E_{21}=\tfrac{1}{4}[(12)-(34)+(1324)-(1423)]\ , \tag{42}$$

$$e^E_{22}=\tfrac{1}{4}[E-(12)(34)-(13)(24)+(14)(23)]\ . \tag{43}$$

These complete symmetry projectors have been used with results reported below. Some previous calculations have used partial symmetry projectors based on subgroups of G_D.

Subgroups of G_D belong to systems with less symmetry than dipositronium. Adaptation to irreducible symmetry of a subgroup corresponds to an induced representation of the full dipositronium symmetry group and leads to a mixed-symmetry state. As a first example, consider the subgroup $\{1,(34)\}$, whose antisymmetric projector on spin function $\alpha\beta$ generates the singlet coupled electron spin state which must be combined with the symmetric spin-free factor to satisfy the Pauli principle, and conversely for the triplet state. Projecting for spin-free states of a single pair of indistinguishable particles generates a state of mixed symmetry for dipositronium. Thus, the singlet and triplet electron projectors consist of the following mixtures of dipositronium symmetry states: singlet,

$$\tfrac{1}{2}[1+(34)]=e^{A_1}+e^{B_2}+\tfrac{1}{2}(e^E_{11}-e^E_{12}-e^E_{21}+e^E_{22})\ ; \tag{44}$$

and triplet,

$$\tfrac{1}{2}[1-(34)]=e^{A_2}+e^{B_1}+\tfrac{1}{2}(e^E_{11}+e^E_{12}+e^E_{21}+e^E_{22})\ . \tag{45}$$

(Ho [2] used the electron singlet projector for dipositronium.) Alternately, adaptation to the positron singlet and triplet states is effected by

$$\tfrac{1}{2}[1+(12)]=e^{A_1}+e^{B_2}+\tfrac{1}{2}(e^E_{11}+e^E_{12}+e^E_{21}+e^E_{22}) \tag{46}$$

and

$$\tfrac{1}{2}[1-(12)]=e^{A_2}+e^{B_1}+\tfrac{1}{2}(e^E_{11}-e^E_{12}-e^E_{21}+e^E_{22})\ . \tag{47}$$

As a second example, consider the subgroup for exchange of electrons and exchange of positrons $\{1,(12),(34),(12)(34)\}$, which is the symmetry group of H_2 and also of the variable-mass excitonic hole-electron complex. It allows adaptation to both electron and positron symmetry states but ignores charge-reversal symmetry. The projection operators for this subgroup correspond to spin eigenstate projectors for the two electrons and the two positrons. These are as follows in the notation (electron multiplicity|positron multiplicity): (triplet|triplet),

$$\tfrac{1}{4}[1-(34)][1-(12)]=e^{A_2}+e^{B_1}\ ; \tag{48}$$

(triplet|singlet),

$$\tfrac{1}{4}[1-(34)][1+(12)]=\tfrac{1}{2}(e^E_{11}+e^E_{12}+e^E_{21}+e^E_{22})\ ; \tag{49}$$

(singlet|triplet),

$$\tfrac{1}{4}[1+(34)][1-(12)]=\tfrac{1}{2}(e^E_{11}-e^E_{12}-e^E_{21}+e^E_{22})\ ; \tag{50}$$

and (singlet|singlet),

$$\tfrac{1}{4}[1+(34)][1+(12)]=e^{A_1}+e^{B_2}\ . \tag{51}$$

The latter projector (singlet|singlet) was used by Lee, Vashista, and Kalia [3] for dipositronium.

D. Matrix elements between symmetry-adapted basis functions

For the energy calculations, we require matrix elements in the form [23]

$$\langle e^\alpha_{rs} f_k | e^\alpha_{rt} f_l\rangle \text{ (overlap type)} \tag{52}$$

and

$$\langle e^\alpha_{rs} f_k | H | e^\alpha_{rt} f_l\rangle \text{ (Hamiltonian type)}\ , \tag{53}$$

and for other expectation values, certain additional matrix elements

$$\langle e^\alpha_{rs} f_k | \mathcal{O} | e^\alpha_{rt} f_l\rangle\ , \tag{54}$$

where e^α_{rs} is a permutation symmetry projection operator, f_k and f_l are primitive basis functions, H is the Hamiltonian, and $\mathcal{O}$ is an arbitrary operator.

For overlap and Hamiltonian matrix elements, we exploit the commutation between permutations with both the identity and the Hamiltonian:

$$\langle e^\alpha_{rs} f_k | e^\alpha_{rt} f_l\rangle=\langle f_k | (e^\alpha_{rs})^\dagger e^\alpha_{rt} f_l\rangle=\langle f_k | e^\alpha_{st} f_l\rangle\ , \tag{55}$$

$$\langle e^\alpha_{rs} f_k | H | e^\alpha_{rt} f_l\rangle=\langle f_k | H | (e^\alpha_{rs})^\dagger e^\alpha_{rt} f_l\rangle=\langle f_k | H | e^\alpha_{st} f_l\rangle\ . \tag{56}$$

The benefit of this is that the double summation over permutations in bra and ket becomes a single summation in ket alone, effectively reducing the effort by a factor the order of the group. For example, the overlap matrix element between A_1 symmetry-adapted basis functions becomes

$$\langle e^{A_1} f_k | e^{A_1} f_l\rangle=\sum_{i=1}^{8}\langle f_k | \mathcal{P} f_l\rangle\ . \tag{57}$$

The result is that only the ket receives the permutation projection operator, as expected from orthogonality between bras and kets with different symmetry. For operators $\mathcal{O}$ which do not commute with permutations, such as r_{ij}^n, this simplification cannot be made.

The action of the permutation $\mathcal{P}$ on the basis function f_k is represented by $\mathcal{T}_{\mathcal{P}} f_k$ as follows:

$$\mathcal{T}_{\mathcal{P}} f_k = \exp[-(\mathbf{r}, B^k \mathbf{r})] \ , \tag{58}$$

where

$$B^k = \mathcal{T}_{\mathcal{P}}^t \mathcal{A}^k \mathcal{T}_{\mathcal{P}} \otimes \mathbf{1}_3 \ . \tag{59}$$

That is, particle permutations effect a congruence transformation of exponent matrices in basis functions. For example, using Eqs. (23), (28), and (58), the exchange of real particles 1 and 2 transforms $\mathcal{A}^k$ into

$$\begin{aligned} B_{(12)}^k &= \mathcal{T}_{(12)}^t \mathcal{A}^k \mathcal{T}_{(12)} \otimes \mathbf{1}_3 \\ &= \begin{bmatrix} a_{11}^k + 2a_{12}^k + 2a_{13}^k + a_{22}^k + 2a_{23}^k + a_{33}^k & -(a_{12}^k + a_{22}^k + a_{23}^k) & -(a_{13}^k + a_{23}^k + a_{33}^k) \\ -(a_{12}^k + a_{22}^k + a_{23}^k) & a_{22}^k & a_{23}^k \\ -(a_{13}^k + a_{23}^k + a_{33}^k) & a_{23}^k & a_{33}^k \end{bmatrix} \otimes \mathbf{1}_3 \ . \end{aligned} \tag{60}$$

V. COMPUTER METHODS

The computer code for our calculations consists of approximately 2500 lines of C source code. Program development was done on a NeXT workstation taking advantage of the symbolic mathematics packages MAPLE V [24] and MATHEMATICA [25] for function prototyping, formula validation and code generation. After debugging and testing, the final code was run using double precision on an IBM ES/3090-300J mainframe computer to obtain the results reported.

Energy calculations were carried out by first insuring that the exponent matrices $\mathcal{A}^k$ are positive definite. Then the integral formulas and symmetry projectors were used to construct the Hamiltonian and overlap matrices. The resulting secular equation was solved for eigenvalues and eigenvectors. These steps were repeated at each point as nonlinear variational parameters were varied. After optimization criteria were satisfied, various expectation values were computed.

The exponent matrices $\mathcal{A}^k$ are expressed in terms of their orthonormal eigenvectors and the logarithms of their eigenvalues. The logarithmic parameterization of the eigenvalues assures positive definiteness of the $\mathcal{A}^k$. Namely, $\mathcal{A}^k$ is given by

$$\mathcal{A}^k = U_k D_k U_k^t \ , \tag{61}$$

where U_k is the 3×3 rotation matrix with Eulerian angles ψ_k, ϕ_k, and θ_k [26] and D_k is a diagonal matrix with exponentials of α_k, β_k, and γ_k on the diagonal. This treatment of the exponent matrices $\mathcal{A}^k$ also opens the optimization domain to all real numbers, thus eliminating the need for direct optimization constraints. Initial values of the parameters were chosen in the ranges given below

$$\begin{aligned} -7 < \alpha_k, \beta_k, \gamma_k < 7 \ , \\ -\pi < \psi_k, \phi_k, \theta_k < \pi \ . \end{aligned} \tag{62}$$

Integral evaluation formulas [9,10,27] were coded explicitly for the four-particle case. Derivations and coding for these formulas can be found in [8]. The secular equation was solved by first performing a Cholesky decomposition [28] on the Hamiltonian and overlap matrices followed by tridiagonalization. The energy eigenvalues and eigenvectors were then obtained using a QL algorithm with implicit shifts [29,30] to assure accuracy in the smallest eigenvalues.

Optimization of nonlinear parameters is always a difficult task in variational calculations. Schemes such as tempering have been proposed to reduce the effort in optimization [31–33]. A simple iterative procedure was adopted here to build up partially optimized wave functions. Initially a set of $N = 10$ randomly selected basis functions $\{f_k, k = 1, \ldots, N\}$ was fully optimized for all 60 nonlinear variational parameters. In each subsequent iterative step a single randomly chosen new basis function f_{N+1} was added and the 12 parameters of $\{f_N, f_{N+1}\}$ were optimized. The basis size was incremented, $N = N + 1$, and another iteration was performed. Iterations were repeated until the desired basis size was reached. The individual optimization steps were carried out using Powell's method, as described in Ref. [34].

VI. RESULTS

The principal results of this work are presented in Tables I–V. We report expectation values for the individual terms of the Hamiltonian together with the scale factor $\eta = -V/(2T)$, scaled energy, the moments r, r^2, and $1/r^2$, and probability density of particle i at position j.

Results are reported to at most eight significant figures and seven decimal digits. Internal consistency was checked by computing $2\langle r_i \cdot r_j \rangle$ (not reported) and comparing with $\langle r_{ij}^2 \rangle - \langle r_i^2 \rangle - \langle r_j^2 \rangle$ values which are computed from different integral formulas. These values were equal in all 12 digits that were generated in the output. Energy calculations run on the NeXT workstation (52-bit precision [35]) and the IBM ES/3090-300J computer (56-bit precision [36]) with identical input produce expectation values that agree to eight decimal digits. Therefore,

TABLE I. Expectation values for the lithium atom ^{2}S ground state. Comparison with results of King using 602 Hylleraas-type functions. $\langle \mathcal{O}_i \rangle \equiv \langle \sum_{i=1}^{3} \mathcal{O}_i \rangle$ and $\langle \mathcal{O}_{ij} \rangle \equiv \langle \sum_{i<j} \mathcal{O}_{ij} \rangle$. All values in a.u. The notation 2.36. . .[−5] means 2.36. . .$\times 10^{-5}$.

Expectation value	Number of terms 50	100	300	King [37]
$\langle -\frac{1}{2}\nabla_i^2 \rangle$	7.463 9280	7.475 6831	7.474 5560	7.478 059
$\langle -\nabla_i \cdot \nabla_j \rangle$	2.367 8936[−5]	2.356 4312[−5]	2.359 9518[−5]	2.3605[−5]
$\left\langle \frac{1}{r_i} \right\rangle$	−17.134 819	−17.153 266	−17.148 610	−17.154 33
$\left\langle \frac{1}{r_{ij}} \right\rangle$	2.197 9117	2.202 1997	2.197 3148	2.198 211
$\langle r_i \rangle$	4.950 7241	4.928 0162	4.981 4168	4.989 538
$\langle r_{ij} \rangle$	8.589 2444	8.545 8302	8.651 8393	9.668 427
$\langle r_i^2 \rangle$	17.720 905	17.535 002	18.181 145	18.354 74
$\langle r_{ij}^2 \rangle$	35.576 966	35.211 563	36.501 956	36.848 09
$\langle \delta(r_i) \rangle$	12.395 708	13.236 602	13.255 136	13.841 82
η	1.000 6031	0.999 9768	1.000 1428	1.000 0007
Energy	−7.472 9577	−7.475 3599	−7.476 7161	−7.478 059

we report results to at most seven decimal digits and at most eight significant figures.

A. Lithium-atom results

We have applied our method to the ground state of the lithium atom to compare with benchmark calculations. In Table I expectation values are reported in the form $\langle \mathcal{O}_i \rangle = \langle \sum_{i=1}^{3} \mathcal{O}_i \rangle$ and $\langle \mathcal{O}_{ij} \rangle = \langle \sum_{i<j} \mathcal{O}_{ij} \rangle$ for direct comparison with the results of King [37] as computed from 602 Hylleraas-type basis functions. We take the convergence of our results toward those of King as evidence of the correctness of our procedure.

Using the Hartree-Fock energy of $-7.432\,7269E_H$ [38] and the semiempirical estimate for the nonrelativistic ground-state energy $-7.478\,060\,326(10)E_H$ [39] or $-7.478\,0601E_H$ [40] we find that our 50-term wave function supplies 88.7% of the correlation energy, our 100-term wave function gives 94%, and our 300-term wave function gives 97%.

B. Dipositronium ground-state results

Our principal objective in this work is the ground-state energy for dipositronium. Table II lists this energy value along with the symmetry inequivalent expectation values computed with a wave function consisting of 300 correlated Gaussian functions adapted to the A_1 ground-state symmetry. Figure 1 shows the energy convergence rate.

The energy value $-0.515\,9767E_H$ is a new rigorous upper bound for the ground-state energy of dipositronium, giving a lower bound to the binding energy of $0.015\,9767E_H$ or 0.435 eV. The most often cited value for this binding energy is 0.411 eV, given by Ho [2], simi-

TABLE II. Dipositronium A_1 ground-state expectation values (in a.u.).

Expectation value	Using 300 terms
$\langle -\frac{1}{2}\nabla_1^2 \rangle = \langle -\frac{1}{2}\nabla_2^2 \rangle = \langle -\frac{1}{2}\nabla_3^2 \rangle$	0.258 0026
$\langle -\nabla_1 \cdot \nabla_2 \rangle = \langle -\nabla_1 \cdot \nabla_3 \rangle$	−0.130 7751
$\langle -\nabla_2 \cdot \nabla_3 \rangle$	0.003 5477
$\left\langle \frac{1}{r_1} \right\rangle = \left\langle \frac{1}{r_{23}} \right\rangle$	0.220 9106
$\left\langle \frac{1}{r_2} \right\rangle = \left\langle \frac{1}{r_3} \right\rangle = \left\langle \frac{1}{r_{12}} \right\rangle = \left\langle \frac{1}{r_{13}} \right\rangle$	−0.368 4508
η	0.999 9724
Energy	−0.515 9767
$\langle r_1 \rangle = \langle r_{23} \rangle$	6.025 2578
$\langle r_2 \rangle = \langle r_3 \rangle = \langle r_{12} \rangle = \langle r_{13} \rangle$	4.483 1482
$\langle r_1^2 \rangle = \langle r_{23}^2 \rangle$	46.171 736
$\langle r_2^2 \rangle = \langle r_3^2 \rangle = \langle r_{12}^2 \rangle = \langle r_{13}^2 \rangle$	29.010 841
$\left\langle \frac{1}{r_1^2} \right\rangle = \left\langle \frac{1}{r_{23}^2} \right\rangle$	0.073 5062
$\left\langle \frac{1}{r_2^2} \right\rangle = \left\langle \frac{1}{r_3^2} \right\rangle = \left\langle \frac{1}{r_{12}^2} \right\rangle = \left\langle \frac{1}{r_{13}^2} \right\rangle$	0.303 0608
$\langle \delta(r_1) \rangle = \langle \delta(r_{23}) \rangle$	0.000 6347
$\langle \delta(r_2) \rangle = \langle \delta(r_3) \rangle = \langle \delta(r_{12}) \rangle = \langle \delta(r_{13}) \rangle$	0.021 8511

TABLE III. Dipositronium $2A_1$ and B_1 excited-state expectation values (in a.u.). (The $2A_1$ state was run on the NeXT computer.)

Expection value	$2A_1$ symmetry 150 terms	B_1 symmetry 150 terms
$\langle -\frac{1}{2}\nabla_1^2\rangle=\langle -\frac{1}{2}\nabla_2^2\rangle=\langle -\frac{1}{2}\nabla_3^2\rangle$	0.249 4216	0.250 0140
$\langle -\nabla_1\cdot\nabla_2\rangle=\langle -\nabla_1\cdot\nabla_3\rangle$	−0.125 0288	−0.125 9492
$\langle -\nabla_2\cdot\nabla_3\rangle$	0.000 6360	−0.000 1156
$\left\langle \frac{1}{r_1}\right\rangle=\left\langle \frac{1}{r_{23}}\right\rangle$	0.014 8958	0.023 7912
$\left\langle \frac{1}{r_2}\right\rangle=\left\langle \frac{1}{r_3}\right\rangle=\left\langle \frac{1}{r_{12}}\right\rangle=\left\langle \frac{1}{r_{13}}\right\rangle$	−0.257 0402	−0.261 7633
η	1.000 6842	0.999 4144
Energy	−0.499 5262	−0.499 4428
$\langle r_1\rangle=\langle r_{23}\rangle$	84.155 931	50.077 940
$\langle r_2\rangle=\langle r_3\rangle=\langle r_{12}\rangle=\langle r_{13}\rangle$	43.581 289	26.539 738
$\langle r_1^2\rangle=\langle r_{23}^2\rangle$	8304.4934	2845.9485
$\langle r_2^2\rangle=\langle r_3^2\rangle=\langle r_{12}^2\rangle=\langle r_{13}^2\rangle$	4158.2685	1428.9827
$\left\langle \frac{1}{r_1^2}\right\rangle=\left\langle \frac{1}{r_{23}^2}\right\rangle$	0.000 3800	0.000 7351
$\left\langle \frac{1}{r_2^2}\right\rangle=\left\langle \frac{1}{r_3^2}\right\rangle=\left\langle \frac{1}{r_{12}^2}\right\rangle=\left\langle \frac{1}{r_{13}^2}\right\rangle$	0.249 1765	0.249 9425
$\langle \delta(r_1)\rangle=\langle \delta(r_{23})\rangle$	0.0	0.0
$\langle \delta(r_2)\rangle=\langle \delta(r_3)\rangle=\langle \delta(r_{12})\rangle=\langle \delta(r_{13})\rangle$	0.019 1130	0.019 3266

lar to the value (0.41 eV) given by Lee, Vashista, and Kalia [3].

Lee, Vashista, and Kalia used a Green's-function Monte Carlo method to compute ground-state energy values for a system of two holes and two electrons at various mass ratios, $\sigma=m_e/m_h$. The limiting energy at $\sigma=1$ was reported for the dipositronium ground-state energy. Their trial function Ψ_T has the symmetry of H_2, as projected by the (singlet|singlet) projector of Eq. (51). Now the dipositronium ground-state projector can be written in the form

$$e^{A_1}=\tfrac{1}{4}[1+(12)+(34)+(12)(34)](1+\mathrm{CR}) , \tag{63}$$

where CR denotes any charge-reversal permutation. Therefore, a basis adapted to (singlet|singlet) symmetry of H_2 is biased against dipositronium unless the basis contains both f_k and $\mathrm{CR}f_k$. If the charge-reversed basis function is absent, as in the trial function of Lee, Vashista, and Kalia then a mixed state with A_1+B_2 symmetry for dipositronium results, and the GFMC propagation labors to remove excited states of both B_1 and A_1 symmetries. Lee, Vashista, and Kalia report the ground-state energy of Ps_2 as $-0.515\pm0.002E_H$ (approximately), a range which includes our bound $-0.515\,9767E_H$. Convergence for this method would certainly be faster with a trial function adapted to the correct A_1 symmetry of the ground state.

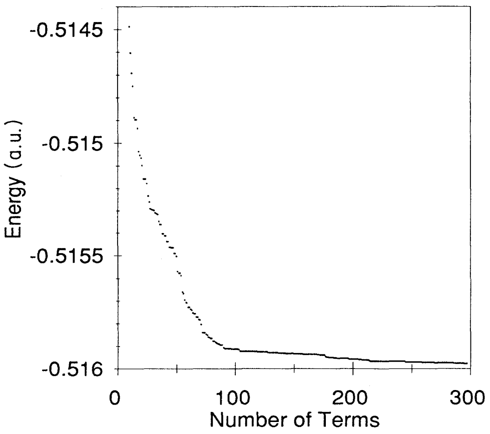

FIG. 1. Energy convergence with number of basis functions for the dipositronium A_1 ground state.

Ho [2] used a 400-term Hylleraas-type wave function to compute a dipositronium ground-state energy of $-0.515\,105E_H$. However, this wave function is merely

TABLE IV. Dipositronium A_2 and B_2 excited-state expectation values (in a.u.).

Expection value	A_2 symmetry 100 terms	B_2 symmetry 140 terms
$\langle -\frac{1}{2}\nabla_1^2\rangle=\langle -\frac{1}{2}\nabla_2^2\rangle=\langle -\frac{1}{2}\nabla_3^2\rangle$	0.156 2762	0.157 6422
$\langle -\nabla_1\cdot\nabla_2\rangle=\langle -\nabla_1\cdot\nabla_3\rangle$	−0.068 2579	−0.070 9823
$\langle -\nabla_2\cdot\nabla_3\rangle$	−0.019 7603	−0.015 6775
$\left\langle \frac{1}{r_1}\right\rangle=\left\langle \frac{1}{r_{23}}\right\rangle$	0.010 6933	0.115 7360
$\left\langle \frac{1}{r_2}\right\rangle=\left\langle \frac{1}{r_3}\right\rangle=\left\langle \frac{1}{r_{12}}\right\rangle=\left\langle \frac{1}{r_{13}}\right\rangle$	−0.161 5048	−0.215 3062
η	0.999 2447	0.998 7059
Energy	−0.312 0805	−0.314 4689
$\langle r_1\rangle=\langle r_{23}\rangle$	106.133 83	12.597 185
$\langle r_2\rangle=\langle r_3\rangle=\langle r_{12}\rangle=\langle r_{13}\rangle$	56.309 106	10.187 899
$\langle r_1^2\rangle=\langle r_{23}^2\rangle$	12 462.771	203.091 83
$\langle r_2^2\rangle=\langle r_3^2\rangle=\langle r_{12}^2\rangle=\langle r_{13}^2\rangle$	6263.0014	153.235 66
$\left\langle \frac{1}{r_1^2}\right\rangle=\left\langle \frac{1}{r_{23}^2}\right\rangle$	0.000 1356	0.023 2360
$\left\langle \frac{1}{r_2^2}\right\rangle=\left\langle \frac{1}{r_3^2}\right\rangle=\left\langle \frac{1}{r_{12}^2}\right\rangle=\left\langle \frac{1}{r_{13}^2}\right\rangle$	0.129 8737	0.150 8694
$\langle \delta(r_1)\rangle=\langle \delta(r_{23})\rangle$	0	0.000 1168
$\langle \delta(r_2)\rangle=\langle \delta(r_3)\rangle=\langle \delta(r_{12})\rangle=\langle \delta(r_{13})\rangle$	0.009 5760	0.010 7880

adapted to electron singlet symmetry with Eq. (44). This results in a mixed state of A_1+B_2+E symmetry for dipositronium. Again, symmetry adaptation to a subgroup symmetry without including charge-reversed basis functions introduces a bias against the true eigenstates of dipositronium. Other expectation values also suffer from incomplete symmetry adaptation. For example, in Table II, the values $\langle R_{12}\rangle=\langle r_1\rangle$ and $\langle R_{34}\rangle=\langle r_{23}\rangle$ are equal by charge-reversal symmetry but were found to be unequal by Ho.

In lieu of adiabatic molecular geometry concepts, the spatial distribution of Ps_2 is described by the moments of interparticle distances shown in Table II. The average separation of the two positrons or of the two electrons is $\langle R_{12}\rangle=\langle R_{34}\rangle=6.03$ bohrs. The average separation between an electron and a positron is smaller, $\langle R_{13}\rangle=\langle R_{14}\rangle=\cdots=4.48$ bohrs, as expected from Coulomb attraction versus repulsion. However, the widths of the distribution, as measured by rms uncertainties, $\Delta R_{12}=3.14$ bohrs and $\Delta R_{13}=2.99$ bohrs, are too great to allow any interpretation of Ps_2 as a "triangular pyramid" [2].

C. Dipositronium excited states

Bound states of dipositronium, Ps_2, must lie below the lowest-energy dissociation products, in this case 2Ps or $-\frac{1}{2}E_H$. States above this limit lie in the continuum. Optimization of the lowest A_2, B_1, B_2 and E states as well as the first exited A_1 state of Ps_2 led to unbound states.

In Table III we report expectation values for the first excited state of A_1 symmetry, labeled $2A_1$, with an energy of $-0.499\,5262E_H$, and for the B_1 symmetry state with an energy of $-0.499\,4428E_H$. It appears that these energy values are both approaching the energy of two separated positronium atoms, $-\frac{1}{2}E_H$, (Ps+Ps). The large values of $\langle r_1\rangle=\langle R_{12}\rangle$ and $\langle r_{23}\rangle=\langle R_{34}\rangle$ confirm this separated-atom picture.

In Table IV the energy value $-0.312\,1195E_H$ and the large values of $\langle r_1\rangle$ and $\langle r_{23}\rangle$ for the A_2 symmetry state again suggest a separated-atom picture. In this case the energy is approaching that of a positronium atom together with a positronium atom in its first excited state, $-0.3125E_H$, (Ps+Ps*), where Ps* is the 2*s* or 2*p* state of positronium.

In Tables IV and V we report expectation values for the B_2 and E (projector e_{11}^E) symmetry states, respectively. Values of $\langle r_i\rangle$ and $\langle r_{ij}\rangle$ for these two states are of the same order of magnitude as those for the ground state. We believe these states are low-lying metastable or resonance states embedded in the continuum of Ps_2. They are bound relative to the separated 1*s*,2*p* states of 2Ps with which they correlate. Our calculations gave an

TABLE V. Dipositronium E excited-state expectation values (in a.u.) based on the single projector e_{11}^{E}.

Expectation value	140 terms
$\langle -\frac{1}{2}\nabla_1^2\rangle=\langle -\frac{1}{2}\nabla_2^2\rangle=\langle -\frac{1}{2}\nabla_3^2\rangle$	0.165 2404
$\langle -\nabla_1\cdot\nabla_2\rangle$	−0.066 3557
$\langle -\nabla_1\cdot\nabla_3\rangle$	−0.101 8909
$\langle -\nabla_2\cdot\nabla_3\rangle$	0.003 0063
$\left\langle \frac{1}{r_1}\right\rangle=\left\langle \frac{1}{r_{23}}\right\rangle$	0.138 7798
$\left\langle \frac{1}{r_2}\right\rangle=\left\langle \frac{1}{r_{13}}\right\rangle$	−0.246 6392
$\left\langle \frac{1}{r_3}\right\rangle=\left\langle \frac{1}{r_{12}}\right\rangle$	−0.222 4043
η	0.999 3434
Energy	−0.330 0469
$\langle r_1\rangle=\langle r_{23}\rangle$	9.562 9397
$\langle r_2\rangle=\langle r_{13}\rangle$	8.379 1048
$\langle r_3\rangle=\langle r_{12}\rangle$	7.974 4810
$\langle r_1^2\rangle=\langle r_{23}^2\rangle$	112.553 22
$\langle r_2^2\rangle=\langle r_{13}^2\rangle$	101.362 61
$\langle r_3^2\rangle=\langle r_{12}^2\rangle$	87.530 474
$\left\langle \frac{1}{r_1^2}\right\rangle=\left\langle \frac{1}{r_{23}^2}\right\rangle$	0.029 4832
$\left\langle \frac{1}{r_2^2}\right\rangle=\left\langle \frac{1}{r_{13}^2}\right\rangle$	0.183 6203
$\left\langle \frac{1}{r_3^2}\right\rangle=\left\langle \frac{1}{r_{12}^2}\right\rangle$	0.137 3456
$\langle \delta(r_1)\rangle=\langle \delta(r_{23})\rangle$	0.000 1411
$\langle \delta(r_2)\rangle=\langle \delta(r_{13})\rangle$	0.013 2287
$\langle \delta(r_3)\rangle=\langle \delta(r_{12})\rangle$	0.009 1250

energy value of $-0.314\,4520E_H$ for the A_2 symmetry state, and $-0.330\,020E_H$ for the doubly degenerate E symmetry state. These results appear to improve the energy estimates and the symmetry classification of states previously found by Ho [41] at $-0.313E_H$ and $-0.3294E_H$ by a complex coordinate rotation method and given a "just tentative" classification as resonant singlet and triplet spin states.

VII. CONCLUSIONS AND DISCUSSION

Correlated Gaussian basis functions were used to achieve an improved upper bound, $-0.515\,9767$ a.u., for the ground-state energy of dipositronium. The best previous energy estimate lies $0.000\,87E_H$ or 0.024 eV above the present value. By including charge-reversal symmetry, the correlated Gaussian basis has surpassed an even larger Hylleraas basis. An improved description of spatial distribution in Ps_2 is achieved using $\langle R_{ij}\rangle$ and $\langle R_{ij}^2\rangle$ and the correct charge-reversal symmetry.

We estimate that more than 90% of the correlation energy has been accounted for in the present method. If the lithium atom example is used to calibrate our method, the exact ground state of dipositronium lies near $-0.5173E_H$.

Dipositronium lifetimes can be estimated from computed values of $\langle \delta(r_{13})\rangle$, the probability density of an electron at the position of a positron. We have done this using the following formula [42] without radiative corrections and assuming the two-photon process only:

$$\frac{1}{t}=\frac{\pi\alpha^4 c4P}{a_0}\langle \delta(r_{13})\rangle \;, \tag{64}$$

where the factor 4 arises from the four possible electron-positron pairs in Ps_2, and P is the probability that the annihilating pair will be singlet spin coupled (para). For the bound A_1 ground state and the resonance state B_2, the spin-free wave function is symmetric under interchange of the two electrons and also symmetric under interchange of the two positrons. It follows from the required antisymmetry under simultaneous space and spin permutations that the spin factor must be a spin singlet for the pair of electrons and a spin singlet for the pair of positrons. When the spins are recoupled to find spin states for electron-positron pairs, say S_{13} and S_{24}, then one finds a probability of $P=\frac{1}{4}$ for $S_{13}=0$. The resonant E-state spin couplings are more-complicated mixtures of singlet and triplet, but again one finds $P=\frac{1}{4}$. In this way we find lifetimes of positronium states $t(A_1)=0.906$ ns, $t(B_2)=1.83$ ns, and $t(E)=1.5$ ns.

The correlated Gaussian basis used here has computational advantages and disadvantages. Explicit inclusion of interparticle distances r_{ij} makes the basis more rapidly convergent than a conventional orbital product with configuration interaction. Hamiltonian integrals are very simple in this basis. Coulomb cusps are poorly represented and tend to slow the rate of convergence. Each basis function has six nonlinear variational parameters so that complete optimization costs grow excessively with the basis size.

Approaches to improve the basis can be suggested. Premultipliers of the form r_{ij}^n might improve the cusp properties and convergence rate. Other nonspherical premultipliers can give higher angular momentum states. New optimization strategies should be explored, analytic formulas for derivatives with respect to nonlinear parameters should be implemented, and tempering schemes should be studied.

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