Diatomic molecule-like configuration interaction wave functions of positronium-atom systems

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Abstract

A positronium-atom system can be considered as a diatomic molecule. From this perspective, diatomic molecule-like configuration interaction (CI) wave functions of positronium-atom systems are constructed. The diatomic molecule-like CI wave functions have forms corresponding to Hartree-Fock and CI wave functions of diatomic molecules. The diatomic molecule-like CI wave functions are examined for positronium fluoride (PsF), and their advantages are discussed in this work.

1. INTRODUCTION

The positron is the anti-particle of the electron and the bound state it makes with the electron is called positronium (Ps), which is a hydrogen-like atom. The positronium makes bound states with various atoms, which are referred to as positronium-atom systems.

Quantum mechanical calculations of positronium-atom systems have been carried out since the 1950's, have noted the incorporation of inter-particle correlation effects into the wave functions. In particular, the inclusion of positron-electron correlation effects is very important. The simplest positronium-atom system is positronium hydride (PsH), which is a three-body system in Coulomb potential field of the proton. Hence, the calculations of wave functions with inter-particle distances are feasible. These wave functions are Hylleraas-type functions, explicitly correlated Gaussian functions, and so on, and these are known to give very accurate results. However, it is very difficult to calculate such wave functions for many-electronic positronium-atom systems.

For many-electronic positronium-atom systems, the Hartree-Fock (HF) method[1–3], configuration interaction (CI) method[4–8], variational perturbation theory[9,10], and Quantum Monte Carlo[11] are used. In particular, the CI method is a standard method for quantum mechanical calculations of

atomic systems, and it is suitable for many-electronic positronium-atom systems. Unfortunately, the convergence of CI wave functions is very slow, because the effects of higher angular momentum λ of orbitals and of the many-body excitation are large. This is a disadvantage for the CI method. However, it is usually used due to the simple form of the CI wave function. As an approximation to the complete CI calculations, multireference singly and doubly excited CI (MRSDCI) may be useful.

CI calculations of positronium-atom systems are usually performed taking the systems as atoms, i.e. one-center expanded wave functions are calculated. A positronium-atom system is considered as a diatomic molecule of Ps and an atom (X), denoted as PsX. CI wave functions for PsX can be estimated using the method adopted for diatomic molecules. Quantum mechanical calculations for diatomic molecules are performed using two-center expanded wave functions. For diatomic molecules, first HF calculations are performed, and then singly and doubly excited CI (SDCI) calculations are carried out. Further, the singly, doubly, triply, and quadruply excited CI (SDTQCI) method or multireference SDCI (MRSDCI) method, which is an approximation to SDTQCI, is employed. This work provides CI wave functions for PsX as diatomic molecular wave functions, i.e. diatomic molecule-like CI wave functions. Moreover, the wave functions for positronium fluoride (PsF) are examined.

The next section provides diatomic molecule-like CI wave functions of PsX. The third section sets out details of the test calculations for the diatomic molecule-like CI wave functions. The fourth section summarizes and discusses the results of the test calculations.

2. WAVE FUNCTIONS

To express the given CI wave functions for PsX, two excitation operators are defined. The first one is the n-electron excitation operator T_n^-, and the second is the n-body (one-positron and $(n-1)$-electron) excitation operator T_n^+; for example, T_1^+ and T_2^+ are one-positron and positron-electron pair excitation operators, respectively.

A PsX wave function corresponding to a diatomic molecular HF wave function includes only positron-electron correlation effects. We refer to this wave function as the positron-electron correlated HF (pec-HF) one, and it is written as

$$\Psi_{pec\text{-HF}} = (1 + T_2^+)\Phi_0 , \qquad\qquad (1)$$

Here, Φ_0 is a wave function consisting of variationally optimized occupied orbitals. These optimized occupied orbitals include positron-electron correlation effects. The binding energy (BE)

for *pec*-HF calculations is estimated as follows:

$$\text{BE} = E\,(\text{Ps}) + E_{\text{HF}}\,(\text{X}) - E_{pec\text{-HF}}\,(\text{PsX})\,, \tag{2}$$

where $E(\text{Ps})$ is the energy of positronium (-0.25 hartree), $E_{\text{HF}}\,(\text{X})$ is the HF energy of atom X, and $E_{pec\text{-HF}}\,(\text{PsX})$ is the *pec*-HF energy.

Similarly, the wave function of PsX corresponding to a diatomic molecular SDCI wave function has configurations which one-positron, one-electron, and two-electron excited from the *pec*-HF wave function. We refer to this wave function as the positron-electron correlated SDCI (*pec*-SDCI) and it is written as

$$\Psi_{pec\text{-SDCI}} = (1 + T_1^- + T_1^+ + T_2^-)\,\Psi_{pec\text{-HF}}\,. \tag{3}$$

One-positron excitation describes the effect equivalent to the change of the nuclear distance of diatomic molecules. Eq.(3) can be rewritten using Eq.(1) as follows:

$$\Psi_{pec\text{-SDCI}} = (1 + T_1^- + T_1^+ + T_2^- + T_2^+ + T_3^+ + T_4^+)\,\Psi_{pec\text{-HF}} \tag{4}$$

$$= (1 + T_1^- + T_1^+ + T_2^- + T_2^+)\,\Phi_0 + (T_3^+ + T_4^+)\,\Phi_0\,. \tag{5}$$

The first parenthesis part on the right hand side of Eq.(5) is the same as the SDCI wave function of the HF reference configuration, i.e. the ordinary SDCI. The *pec*-SDCI wave function is equivalent to the ordinary SDCI with the addition of three- and four-body excitations including one-positron excitation. The binding energy for *pec*-SDCI calculations is given by

$$\text{BE} = E\,(\text{Ps}) + E_{\text{SDCI}}\,(\text{X}) - E_{pec\text{-SDCI}}\,(\text{PsX})\,, \tag{6}$$

where $E_{\text{SDCI}}\,(\text{X})$ is the SDCI energy of X and $E_{pec\text{-SDCI}}\,(\text{PsX})$ is the energy estimated from the *pec*-SDCI wave function.

The wave function corresponding to SDTQCI of diatomic molecules is given by the positron-electron correlated SDTQCI (*pec*-SDTQCI) wave function:

$$\Psi_{pec\text{-SDTQCI}} = \Psi_{pec\text{-SDCI}} + (T_3^- + T_4^-)\,\Psi_{pec\text{-HF}} \tag{7}$$

$$= \Psi_{pec\text{-SDCI}} + (T_3^- + T_4^- + T_5^+ + T_6^+)\,\Phi_0\,. \tag{8}$$

Five- and six-body excitations (including one-positron excitation) appear in the *pec*-SDTQCI wave function and it is difficult to calculate such many-body excited wave functions. Hence, as an approximation to *pec*-SDTQCI, *pec*-MRSDCI wave functions are considered. The binding energy for *pec*-SDTQCI is written as

$$\text{BE} = E(\text{Ps}) + E_{\text{SDTQCI}}(\text{X}) - E_{pec\text{-SDTQCI}}(\text{PsX}) , \tag{9}$$

where $E_{\text{SDTQCI}}(\text{X})$ is the SDTQCI energy of X and $E_{pec\text{-SDTQCI}}(\text{PsX})$ is the pec-SDTQCI energy.

3. COMPUTATIONAL ASPECTS

In this work, we carried out pec-HF and pec-SDCI calculations for positronium fluoride (PsF). We employed HF wave function as Φ_0 in pec-HF calculations. To include the relaxation effects of positronic and electronic orbitals, we calculated pec-HF wave functions considering only the single excitations. These wave functions are the ordinary SDCI wave functions without two-electron excitations.

The reference configuration for the pec-SDCI wave function comprises of natural orbitals (NOs) obtained from pec-HF calculations. As NOs are not calculated variationally, these pec-SDCI calculations do not give variational energies. We estimated the pec-SDCI energy by adding the energy lowering of pec-SDCI to the pec-HF energy calculated with occupied HF orbitals. The pec-SDCI calculations must be carried out with the reference space consisting of all configurations of pec-HF wave function. However, these calculations are not feasible. In this work, we carried out pec-SDCI calculations with the reference space consisting of configurations having weight greater than 10^{-4}.

An atomic orbital with angular momentum λ can be written using the radial function $P_{n\lambda}(r)$ and the spherical harmonics $Y_\lambda^m(\theta, \phi)$ as follows:

$$\psi_{n\lambda m}(\text{r}, \theta, \phi) = r^{-1} P_{n\lambda}(r) Y_\lambda^m(\theta, \phi) . \tag{10}$$

In this work, all radial functions expressed as linear expansions with the B-splines. The B-splines of order K, $\{ B_{i,K} \}$, are piecewise polynomials of degree $K - 1$ on a knot sequence in a cavity of radius R[12,13]. The knot sequence $\{ t_i \}$ is a set of points defined on an interval $0 \le r \le R$. Several methods that generate the knot sequence are proposed by Gilbert and Bertoncini[14]. In atomic calculations, the knot sequence that concentrates near the nucleus is required because the atomic orbitals rapidly change near the nucleus. Hence, an exponential[14] or a geometric series[15] knot sequence is suitable for atomic calculations. This work employed an exponential knot sequence. The radial function $P_{n\lambda}(r)$ is expanded with the B-splines and enforces the boundary conditions $P_{n\lambda}(0) = 0$ and $P_{n\lambda}(R) = 0$. Since the first and the last terms of the B-splines with K-fold multiple knots are nonzero at $r = 0$ and at $r = R$, respectively, they are removed from the basis function to satisfy the boundary conditions. $P_{n\lambda}$ is expanded with the N-term B-spline set $(B_{2,K}, \cdots, B_{N+1,K})$. This work used a 100-term B-spline

set with $K = 9$, $R = 60$ au, and $R_1 = 10^{-3}$ au for all calculations, where R_1 is the initial interval of the knot sequence.

The orbital sets used are listed in TABLE 1. *pec*-HF calculations employed the HF orbitals for the electronic orbitals $1s$, $2s$, and $2p$ and the positronic orbital $1s_+$. Further, NOs obtained from *pec*-HF calculations were employed for correlating orbitals. All orbitals used for *pec*-SDCI calculations were the NOs obtained for *pec*-HF calculations.

TABLE 1. Orbital sets used in all calculations. λ_{max} is the maximum angular momentum value of orbital sets.

λ_{max}	Orbital set
1	$30s30p$
2	$30s30p30d$
3	$30s30p30d30f$
4	$30s30p30d30f20g$
5	$30s30p30d30f20g20h$
6	$30s30p30d30f20g20h20i$
7	$30s30p30d30f20g20h20i10k$
8	$30s30p30d30f20g20h20i10k10l$
9	$30s30p30d30f20g20h20i10k10l10m$

4. RESULTS AND DISCUSSION

We performed *pec*-HF calculations for PsF by using orbital sets listed in TABLE 1. These calculations are denoted as *pec*-HF(λ_{max}), where λ_{max} is the maximum angular momentum of the orbital set used. TABLE 2 summarizes the *pec*-HF energies $E_{pec\text{-}HF}$ (PsF) and the binding energies (BE) values. The BEs were calculated using E_{HF} (F) = −99.409349 hartree[16]. The energy contribution from the orbitals having angular momentum greater than 9 ($E_{\lambda>9}$) were estimated using an extrapolation method. FIG.1 shows the energy contribution from the respective λ-NOs, on a log-log scale. It reveals that the energy contribution by adding λ-NOs (ΔE_{λ}) converges linearly at $\lambda \geq 6$. This correlation can be expressed as

$$-\Delta E_{\lambda} = a\lambda^{-b} , \qquad\qquad (11)$$

where a and b are the fitting parameters. We obtained a=0.566023 and b=3.452499. The value of b is large. It shows that positron-electron correlation energies against λ converge very slowly. The energy contribution $E_{\lambda>9}$ was estimated as

$$E_{\lambda>9} = \sum_{\lambda=10}^{\infty} \Delta E_\lambda \,, \tag{12}$$

and $E_{\lambda>9} = -0.000920$ hartree was obtained.
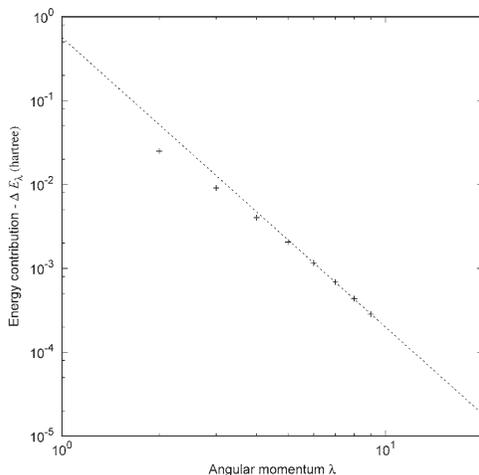

FIG. 1. Energy contribution from the respective λ orbitals.

TABLE 2. Total energies ($E_{pec\text{-HF}}$) and binding energies (BE) of PsF given by *pec*-HF calculations. λ_{max} is the maximum angular momentum value of orbital sets.

$\lambda_{\max}$	$E_{pec\text{-HF}}$ (hartree)	BE (eV)
1	−99.651643	−0.2097
2	−99.676657	0.4710
3	−99.685723	0.7177
4	−99.689755	0.8274
5	−99.691818	0.9150
6	−99.692976	0.9337
7	−99.693664	0.9456
8	−99.694099	0.9533
9	−99.694384	0.9533
∞	−99.695304[a]	0.9784

[a] Extrapolated value.

Let us discuss the relaxation effects of orbitals due to positron-electron correlation effects. FIG.2 shows the 1*s*-, 2*s*-, 2*p*-, and NOs obtained from *pec*-HF(9) calculations together with the HF orbitals. One can infer from FIG.2 that the $1s_+$ orbital shrinks. The shapes of the electronic orbitals have also changed, and their change is smaller than that of the positronic orbital. To see these changes in detail, the charge density difference $\Delta\rho$ of each orbital given below has been plotted in FIG.3,

$$\Delta\rho(\rho) = \rho_{pec\text{-HF}}(r) - \rho_{HF}(r), \tag{13}$$

where $\rho_{pec\text{-HF}}(r)$ and $\rho_{HF}(r)$ are the charge densities of orbitals obtained from pec-HF and HF calculations, respectively.

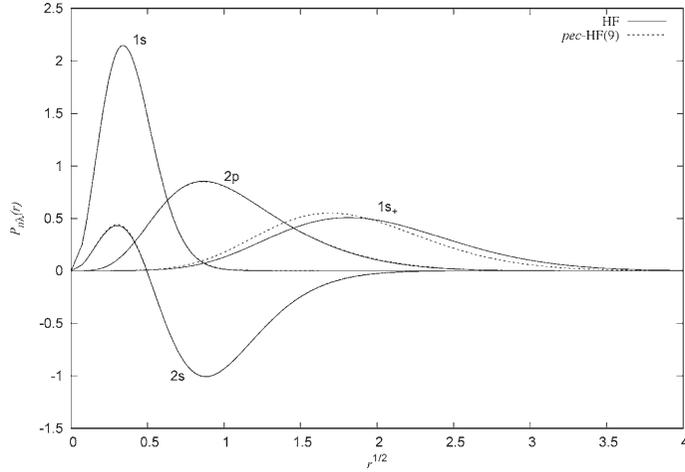FIG. 2. HF orbitals and *pec*-HF natural orbitals.
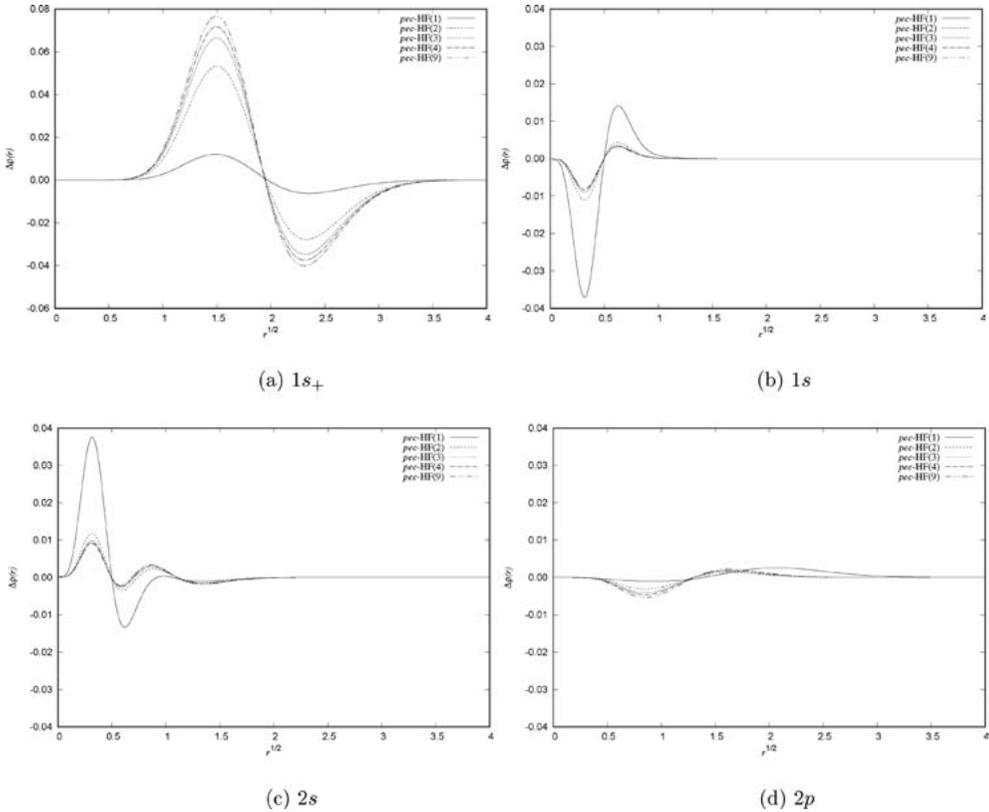

(a) $1s_+$

(b) $1s$

(c) $2s$

(d) $2p$

FIG. 3. Charge density differences of natural orbitals from HF orbitals.

A large change in the charge density of $1s_+$ is noted. The value of $1s_+$ charge density increases at $r = 1.92$ au, and it decreases at $r = 6.35$ au. This change is large for calculations with orbitals having higher angular momentum. This indicates that the introduction of positron-electron correlation effects is important. As evident from FIG.2, *pec*-HF calculations must use orbitals having $\lambda \geq 3$ in order to calculate charge density of $1s_+$ as correctly as possible.

The differences in electronic charge densities are smaller compared to the positronic charge density difference. For $1s$ and $2s$, the *pec*-HF(1) calculation gives a larger change in the charge densities. The charge densities obtained from *pec*-HF(2) change smaller than those obtained from *pec*-HF(1) wave function. The *pec*-HF(1) calculation gives incorrect charge densities of $1s$ and $2s$ orbitals. Thus, it is important to introduce the angular correlation effects again.

The interaction of the positron and the $2p$-electron is large because the $2p$ electron is in the outermost shell. However, the $2p$ charge density difference is smaller than that of $1s$ and $2s$. The charge density obtained from the *pec*-HF(9) calculation increases at $r = 2.70$ au. The $2p$ charge density difference obtained from the *pec*-HF(1) attains a maximum value at $r = 4.28$ au. The *pec*-HF(1) also gives an incorrect charge density of $2s$ orbital. Therefore, accurate calculations of the *pec*-HF need the orbital set of $\lambda_{max} \geq 2$.

From the above results, we can infer that it is desirable to develop a self-consistent field method (SCF) of *pec*-HF wave functions because the relaxation effects of positronic and electronic orbitals are large. This SCF method is employed to variationally optimize only occupied orbitals, i.e. a restricted multiconfigurational SCF method. The *pec*-SDCI calculation was carried out with the reference space consisting of NOs with $\lambda_{max} = 9$. This calculation is denoted by *pec*-SDCI(9). The dimension of the reference space and of the wave function is respectively 18 and 4,204,291 in this calculation. The resulting energy lowering from the *pec*-HF calculation with occupied NOs is −0.364877 hartree. The *pec*-SDCI(9) energy is estimated by adding the *pec*-HF(9) energy and the energy lowering. As a result, $E_{pec\text{-SDCI}} = -100.058712$ hartree is obtained. This value is due to the introduction of two-electron excitations into *pec*-HF(9) wave function. Namely, correlation effects of four-body consisting of one-positron and three-electron is very important.

TABLE 3 lists the binding energies (BE) obtained in this work together with other works. The BE of *pec*-HF(9) is 33 % of the experimental value[17]. The *pec*-SDCI(9) calculation gives 2.480 eV of the BE, and it is 86 % of the experimental BE value. This shows the necessity of electron-electron correlation effects. The BE value of 2.480 eV obtained from the *pec*-SDCI(9) calculation is lower than that of SDCI[5], and this value is almost the same as that of MRSDCI[7]. This is due to the correlation effects of four-body consisting of one-positron and three-electron. Although MRSDCI calculations

considers four-electron excited effects, the *pec*-SDCI calculation neglects those effects. The *pec*-SDCI calculation is the same as the SDCI calculation of diatomic molecules. Hence, it is very important to consider four-body including one-positron effects for CI calculations of PsX.

Configurations having two-electron excitations $2p^2 \rightarrow 3p^2$ and $2p^2 \rightarrow 3p4p$ have large weight in the *pec*-SDCI wave function. Including these configurations, four-electron correlation effects can be introduced to wave functions. Calculations of such wave functions may give more accurate BE values, and therefore *pec*-SDTQCI calculations need to be

TABLE 3. Binding energies (BE) of PsF.

	BE (eV)
This work	
pec-HF(9)	0.9533
pec-HF(9) + higher λ	0.9784
pec-SDCI(9)	2.455
pec-SDCI(9) + higher λ	2.480
Other works	
HF[a]	−0.440
SDCI[b]	2.070
MRSDCI[c]	2.445
FCI limit[c]	2.778
FCI limit + higher λ[c]	2.806
DMC[d]	1.98 ± 0.17
Experiment[e]	2.9 ± 0.5

[a]Cade and Farazdel (Ref.1)
[b]Saito (Ref.5); *B*-spline orbital set with $\lambda_{max} = 8$.
[c]Saito (Ref.7); *B*-spline orbital set with $\lambda_{max} = 8$.
[d]Schrader et al. (Ref.11)
[e]Tao and Green (Ref.17)

carried out. However, *pec*-SDTQCI wave functions must be calculated approximately, because they include up to six-body excited configurations. Therefore, it may be practically important to perform *pec*-MRSDCI calculations with reference spaces consisting of principal configurations of the *pec*-SDCI wave functions.

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