Extended Ore's positronium hydride wave function including ionic structures

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Abstract

We reported the computational results of extended Ore's positronium hydride wave function [Chukyo Univ. Bulletin of the School of International Liberal Studies 4(2), 23 (2012)]. The resulting binding energy of positronium and hydrogen atom is 0.117 eV, which is much smaller than the accurate computational value 1.067 eV. The present work attempts to improve the binding energy using the wave function including ionic structures Ps^+H^- and Ps^-H^+. Consideration of the ionic structures improves the binding energy by 0.010 eV. Further extension of Ore's wave function is also discussed.

The positronium hydride (PsH) is the prototype of positronium-atom complexes. There have been many quantum mechanical studies of PsH for the purpose of studying various positronium-atom complexes.[1–21] From the previous studies, it is known that consideration of the positron-electron correlation effects is very important. For particular, the quantum mechanical computations with explicitly correlated wave functions give very accurate results. Such computational methods are Hylleraas-type (Hylleraas) method, explicitly correlated Gaussian (ECG) method, etc.. The simplest explicitly correlated wave function may be valence bonding-like (VB-like) one calculated by Ore in 1951.[22] This wave function is written as

$$\Phi_{Ore} = S_{12}\chi_H(\boldsymbol{r}_1)\chi'_H(\boldsymbol{r}_2)\psi_{Ps}(\boldsymbol{r}_{02}), \tag{1}$$

with

$$\chi_H(\boldsymbol{r}_1) = \left(\frac{1}{\pi}\right)^{\frac{1}{2}}\exp(-r_1), \tag{2}$$

$$\chi_{\text{H}}'(\boldsymbol{r}_2) = \left(\frac{k}{\pi}\right)^{\frac{1}{2}} \exp(-kr_2), \tag{3}$$

and

$$\psi_{\text{Ps}}(\boldsymbol{r}_{02}) = \left(\frac{1}{8\pi}\right)^{\frac{1}{2}} \exp\left(-\frac{1}{2}r_{02}\right), \tag{4}$$

where 0 denotes the positron, 1 and 2 refer to the electrons, k is a variational parameter, and S_{12} is the symmetrizer with respect to exchange of 1 and 2. The binding energy of Ps and H obtained by Ore is 0.068 eV: Ore showed that PsH is energetically stable. However, this value is smaller than very accurate one 1.067 eV, which Hylleraas and ECG calculations give. On the other hand, the positron-electron pair annihilation rate value obtained by Ore is close to the accurate one. Although Hylleraas and ECG methods are powerful and useful, the application of them to many-electronic positronium-atom complexes is very difficult. Since Ore's wave function has simple form, it may be possible to apply Ore-type wave function to many-electronic positronium-atom complexes.

One of the disadvantages of Ore's wave function is the lack of flexibility. We removed this disadvantage by applying Gaussian function expansion of χ_{H}, χ_{H}', and ψ_{Ps} and a self-consistent field (SCF) method: we refer to this method as Ore-SCF. Ore-SCF calculation gave the Ps binding energy 0.117 eV.[23] This value is about a tenth of the accurate value. Therefore, further extension of Ore's wave function is needed. One possible further extension is to consider the ionic structures, i.e. Ps^+H^- and Ps^-H^+. Heitler and London improved the binding energy of hydrogen molecule by considering the ionic structures H^+H^- and H^-H^+.[24] Hence, it is expected that consideration of the ionic structures improves the energy of PsH. Another extension of Ore's wave function is to introduce electron-electron correlation effects. In this work, we attempt to improve the Ps binding energy by considering the ionic structures Ps^+H^- and Ps^-H^+.

Our wave function is written as

$$\Psi = C_1\Phi(\text{PsH}) + C_2\Phi(\text{Ps}^+\text{H}^-) + C_3\Phi(\text{Ps}^-\text{H}^+), \tag{5}$$

with

$$\Phi(\text{PsH}) = S_{12}\chi_{\text{H}}(\boldsymbol{r}_1)\chi_{\text{H}}'(\boldsymbol{r}_2)\psi_{\text{Ps}}(\boldsymbol{r}_{02}), \tag{6}$$

$$\Phi(\text{Ps}^+\text{H}^-) = S_{12}\chi_{\text{H}}(\boldsymbol{r}_1)\chi_{\text{H}}(\boldsymbol{r}_2)\xi(\boldsymbol{r}_0), \tag{7}$$

and

$$\Phi(\text{Ps}^-\text{H}^+) = S_{12}\psi_{\text{Ps}}(\boldsymbol{r}_{01})\psi_{\text{Ps}}(\boldsymbol{r}_{02})\chi_{\text{H}}'(\boldsymbol{r}_2), \tag{8}$$

where ξ is the positronic orbital, C_1, C_2, and C_3 are variational coefficients. χ_{H}, χ_{H}', ψ_{Ps}, and ξ are

represented as linear expansion with 20-term Gaussian functions. The linear expansion coefficients of χ_H, χ'_H, and ψ_{Ps} are determined by Ore-SCF calculation of $\Phi(PsH)$. The positronic orbital ξ is determined by the variational calculation of $\Phi(Ps^+H^-)$ with fixed χ_H. We calculated the Ps binding energy by the variational calculation of Eq.(5), and also evaluated the energy lowering due to each ionic effect.

Our results are summarized in Table 1 together with other values. The wave function including the two ionic structures gave the Ps binding energy 0.177 eV. The ionic structure effects lower the Ps binding energy by 0.01 eV. The effects of Ps^+H^- and Ps^-H^+ structures lower the Ps binding energy by 0.003 eV and 0.005 eV, respectively. It is considered that the effect of Ps^+H^- structure is small because $\Phi(PsH)$ includes component of H^-. To summarize, we found that the effect of the two ionic structures is small. The Ps binding energy is 0.94 eV smaller than the accurate value. Therefore, other extensions of wave function are needed.

Table 1.　Total energies E and Ps binding energies BE of PsH.

Method	Reference	E (hartree)	BE (eV)
Ore-SCF	Ref. 23	−0.754304	0.117
Ore-SCF+Ps^+H^-+Ps^-H^+	This work	−0.754653	0.127
Ore-SCF+Ps^+H^-	This work	−0.754430	0.121
Ore-SCF+Ps^-H^+	This work	−0.754492	0.122
Ore	Ref. 22	−0.75251	0.068
Hylleraas	Refs. 13 and 18	−0.789197	1.067
ECG	Ref. 14	−0.789197	1.067

A further extension is to introduce the electron-electron correlation effect. To this end, it is suitable to employ the configuration interaction (CI) method. CI wave functions constructed with orthonormal orbitals is easy to compute. Thus, we orthogonalize Ore's wave function $\Phi(PsH)$. Non-orthogonal orbitals χ_H and χ'_H are orthogonalized as follows[25]:

$$\chi_H = \frac{1}{\sqrt{a^2 + b^2}} (a\phi_1 + b\phi_2) \tag{9}$$

and

$$\chi'_H = \frac{1}{\sqrt{a^2 + b^2}} (a\phi_1 - b\phi_2), \tag{10}$$

where ϕ_1 and ϕ_2 are mutually orthonormal orbitals. Substituting Eqs.(9) and (10) into Eq.(6), Eq.(6) is transformed as follows:

$$
\begin{aligned}
\Phi(\text{PsH}) = \frac{1}{a^2 + b^2} S_{12} [& a^2 \phi_1(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2) + ab\phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) \\
& - ab\phi_2(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2) - b^2 \phi_2(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2)]\psi_{\text{Ps}}(\boldsymbol{r}_{02}).
\end{aligned}
\tag{11}
$$

Therefore, using an orthonormal set $\{\phi_i\}$, the CI expansion of $\Phi(\text{PsH})$ is written as

$$
\Phi(\text{PsH}) = \sum_{i,j} S_{12}\, C_{ij}\phi_i(\boldsymbol{r}_1)\phi_j(\boldsymbol{r}_2)\psi_{\text{Ps}}(\boldsymbol{r}_{02}).
\tag{12}
$$

Moreover, we impose the strong orthogonality condition on ψ_{Ps}:
$$
\langle \phi_i(\boldsymbol{r}_2)|\psi_{\text{Ps}}(\boldsymbol{r}_{02})\rangle = 0 .
\tag{13}
$$
In actual calculations, the weak orthogonality condition is imposed instead of the strong orthogonality one to reduce the number of many-electron integrals. The strong orthogonality condition is imposed as
$$
[1 - p(\boldsymbol{r}_2)]\psi_{\text{Ps}}(\boldsymbol{r}_{02}),
\tag{14}
$$
where $p(\boldsymbol{r}_2) = \sum_i |\phi_i(\boldsymbol{r}_2)\rangle\langle\phi_i(\boldsymbol{r}_2)|$. The weak orthogonal function is the function expanded Eq.(14) with the basis functions used to expand ψ_{Ps}.[26] We are going to use this CI wave function to improve on Ore's results. Furthermore, we are planning to apply it to many-electronic positronium-atom complexes.

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