S-wave elastic scattering of *o*-Ps from H_2 at low energy

J.-Y. Zhang,[1,2,3,*] M.-S. Wu,[1] Y. Qian,[4] X. Gao,[2] Y.-J. Yang,[5] K. Varga,[6] Z.-C. Yan,[1,7] and U. Schwingenschlögl[3,†]

[1]*State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China*

[2]*Beijing Computational Science Research Center, Beijing 100193, China*

[3]*Physical Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia*

[4]*Department of Computer Science and Technology, East China Normal University, Shanghai 200062, China*

[5]*Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China*

[6]*Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA*

[7]*Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3*

(Received 17 March 2019; published 3 September 2019)

The confined variational method is applied to investigate the low-energy elastic scattering of orthopositronium from H_2 by first-principles quantum mechanics. Describing the correlations with explicitly correlated Gaussians, we obtain accurate *s*-wave phase shifts and pickoff annihilation parameters for different incident momenta. By a least-squares fit of the data to the effective-range theory, we determine the *s*-wave scattering length $A_S = 2.02a_0$ and the zero-energy value of the pickoff annihilation parameter, $^1Z_{\rm eff} = 0.1839$. The obtained $^1Z_{\rm eff}$ agrees well with the precise experimental value of 0.186(1) [G. L. Wright *et al.*, J. Phys. B **16**, 4065 (1983)] and the obtained A_S agrees well with the value of $2.1(2)a_0$ estimated from the average experimental momentum-transfer cross section for positronium energy below 0.3 eV [F. Saito *et al.*, J. Phys. B **36**, 4191 (2003)].

DOI: 10.1103/PhysRevA.100.032701

I. INTRODUCTION

Scattering of positronium (Ps), i.e., a hydrogenlike atom composed of an electron and a positron, from atoms and molecules is fundamentally important for understanding the interaction between matter and antimatter [1–18]. Positronium can be in a spin singlet state [parapositronium (*p*-Ps)] or a spin triplet state [orthopositronium (*o*-Ps)]. Pickoff quenching is the process that the positron in the *o*-Ps is annihilated on collision with a molecular electron in the opposite spin state. The accuracy of the experimental determination of the pickoff annihilation parameter $^1Z_{\rm eff}$ of the *o*-Ps interaction with different targets such as H_2, CH_4, and CO_2 [1,2,14] is far higher than that achieved by theoretical methods. The experimental results therefore can be used to test the quality and efficiency of theoretical methods, in particular the accuracy of the generated scattering wave functions. The complicated short-range electron-positron and electron-electron correlations as well as the electron exchange between Ps and the target play key roles in the low-energy scattering of Ps. Theoretically, however, the accurate description of these interactions is very difficult and tedious due to the complex nature of a multicenter scattering system [19].

In this paper we present confined variational studies of the low-energy scattering properties of the experimentally studied *o*-Ps-H_2 system. This work extends the *ab initio* theoretical description of the scattering of a composite projectile from a one-center target to a multicenter target. The obtained zero-energy value of the pickoff annihilation parameter and the scattering length show good agreement with experiments [2,9], demonstrating the high accuracy of the confined variational method (CVM).

The CVM [20,21] was first developed by Mitroy and co-workers to accurately determine phase shifts of the low-energy elastic scattering of electrons (e^-) or positrons (e^+) from few-e^- atoms. It was further developed by Zhang *et al.* [22] to study the scattering of projectiles with internal structure, such as Ps. The CVM phase shifts for the *s*-wave e^--He scattering at wave number $k = 0.2a_0^{-1}$ and for the *s*-wave Ps-H elastic scattering at $k = 0.1a_0^{-1}$ and $k = 0.2a_0^{-1}$ have set a benchmark for other theoretical methods [16]. In addition, the CVM was used to generate basis sets of energy-optimized explicitly correlated Gaussian (ECG) functions for other collision calculation methods such as the stabilization method [21] and Kohn variational method [23].

The remainder of this paper is organized as follows. In Sec. II we briefly review the CVM using the e^+-atom scattering as an example. The reader is however referred to Refs. [20,22,24] for a full account. In Sec. III we numerically verify the CVM by calculating the phase shift and annihilation parameter of e^+ scattering from a H atom, giving also a comparison to other methods. Then the CVM is applied to study the scattering of *o*-Ps from H_2 at low energy in Sec. IV. Finally, we summarize in Sec. V.

II. THEORY

Phase shifts are expressed in radians and atomic units throughout unless otherwise stated. Investigation of elastic scattering of e^+ from a spherical few-e^- atom with infi-

*jzhang@wipm.ac.cn

†udo.schwingenschlogl@kaust.edu.sa

nite nuclear mass essentially means solving the Schrödinger equation

$$H\Psi_i(\mathbf{r}) = E_i\Psi_i(\mathbf{r}), \quad E_i > 0, \tag{1}$$

where $\mathbf{r}$ represents the coordinate vectors of all the particles. Assuming that the interaction between e^+ and the atom becomes zero beyond a finite radius R_0, we may add a confining potential $V_{\rm CP}(\mathrm{r}_{e^+})$ on the positron to the Hamiltonian in Eq. (1) in order to convert a complicated problem of many-body continuum states into much easier problems of many-body discrete bound states, one-dimensional-potential bound states, and one-dimensional-potential scattering. The Schrödinger equation of the confined many-body system becomes

$$[H + V_{\rm CP}(\mathrm{r}_{e^+})]\Psi_i'(\mathbf{r}) = E_i\Psi_i'(\mathbf{r}). \tag{2}$$

The confining potential $V_{\rm CP}(\mathrm{r}_{e^+})$ is typically chosen in the form [20,24]

$$V_{\rm CP}(\mathrm{r}_{e^+}) = 0, \quad \mathrm{r}_{e^+} < R_0, \tag{3}$$

$$V_{\rm CP}(\mathrm{r}_{e^+}) = G(\mathrm{r}_{e^+} - R_0)^2, \quad \mathrm{r}_{e^+} \geqslant R_0, \tag{4}$$

where G is a positive number. Confining potentials of this type are chosen to avoid disturbing the e^+-atom interaction. Taking the discrete energies E_i and expectation values $\langle\Psi_i'(\mathbf{r})|V_{\rm CP}|\Psi_i'(\mathbf{r})\rangle$ as reference, we tune the auxiliary one-dimensional potential $V_{\rm aux}(\mathrm{r}_{e^+})$ by solving the Schrödinger equation

$$\left(-\frac{\nabla^2}{2} + V_{\rm aux}(\mathrm{r}_{e^+}) + V_{\rm CP}(\mathrm{r}_{e^+})\right)\Phi_i'(\mathbf{r}_{e^+}) = E_i'\Phi_i'(\mathbf{r}_{e^+}). \tag{5}$$

The boundary condition $V_{\rm aux}(\mathrm{r}_{e^+}) = 0$ has to be satisfied for $\mathrm{r}_{e^+} \geqslant R_0$. The purpose of the tuning is to achieve $E_i' = E_i$ and $\langle\Psi_i'(\mathbf{r})|V_{\rm CP}|\Psi_i'(\mathbf{r})\rangle = \langle\Phi_i'(\mathbf{r}_{e^+})|V_{\rm CP}|\Phi_i'(\mathbf{r}_{e^+})\rangle$. To this aim, $V_{\rm aux}(\mathrm{r}_{e^+})$ can be made flexible by inclusion of two or more parameters to adjust its shape and strength. For the elastic scattering of e^+ from a H atom, for example, it is chosen in this work in the form

$$\begin{aligned} V_{\rm aux}(\mathrm{r}_{e^+}) &= V_{\lambda_i,\alpha_i,\xi_i,\beta_i}(\mathrm{r}_{e^+}) \\ &= \lambda_i(1 + 1/\mathrm{r}_{e^+})\exp(-\alpha_i\mathrm{r}_{e^+}) + \xi_i\mathrm{r}_{e^+}^2\exp\left(-\beta_i\mathrm{r}_{e^+}^2\right), \end{aligned} \tag{6}$$

where λ_i, α_i, ξ_i, and β_i are the adjustable parameters. Equality of the energies means that the phase shift is the same and equality of the expectation values ensures that the normalization condition at the boundaries is the same. Finally, the phase shift is obtained by solving the Schrödinger equation

$$\left(-\frac{\nabla^2}{2} + V_{\rm aux}(\mathrm{r}_{e^+})\right)\Phi_i(\mathbf{r}_{e^+}) = E_i\Phi_i(\mathbf{r}_{e^+}). \tag{7}$$

The key point of the CVM is that the logarithmic derivatives of the wave functions $\Psi_i(\mathbf{r})$, $\Psi_i'(\mathbf{r})$, $\Phi_i'(\mathbf{r}_{e^+})$, and $\Phi_i(\mathbf{r}_{e^+})$ are exactly the same for the same energy E_i at $\mathrm{r}_{e^+} = R_0$, i.e.,

$$\Gamma_{\Psi_i} = \Gamma_{\Psi_i'} = \Gamma_{\Phi_i} = \Gamma_{\Phi_i'}, \tag{8}$$

with

$$\Gamma_{\Psi_i} \equiv \frac{1}{\Psi_i}\frac{d\Psi_i}{d\mathrm{r}_{e^+}}\bigg|_{R_0}. \tag{9}$$

As the phase shift is a function of the logarithmic derivative, the value obtained from solving Eq. (7) equals that of e^+-atom scattering.

The calculation of the annihilation parameters $Z_{\rm eff}$ for e^+ scattering and ${}^1Z_{\rm eff}$ for o-Ps scattering depends on the normalization of $\Psi_i'(\mathbf{r})$ to the scattering boundary condition. For e^+-H scattering, for example, the procedure for determining $Z_{\rm eff}$ is as follows. First, the expectation value of $\delta(\mathbf{r}_{e^-} - \mathbf{r}_{e^+})$ is computed with Ψ_i',

$$\langle\delta(\mathbf{r}_{e^-} - \mathbf{r}_{e^+})\rangle = \langle\Psi_i'(\mathbf{r}_{e^-}, \mathbf{r}_{e^+})|\delta(\mathbf{r}_{e^-} - \mathbf{r}_{e^+})|\Psi_i'(\mathbf{r}_{e^-}, \mathbf{r}_{e^+})\rangle. \tag{10}$$

Second, the ratio of $\Phi_i'(\mathbf{r}_{e^+})$ and the continuum radial wave function at R_0 is computed. For s-wave scattering this is $A_b = \Phi_i'(R_0)/\sqrt{4\pi}\sin(kR_0 + \delta_0)$. Then $Z_{\rm eff}$ is given by

$$Z_{\rm eff}(k) = \frac{\langle\delta(\mathbf{r}_{e^-} - \mathbf{r}_{e^+})\rangle}{A_b^2k^2}. \tag{11}$$

III. SCATTERING OF e^+ FROM A H ATOM

To demonstrate the accuracy of A_b in the CVM, we calculate δ_0, A_b, and $Z_{\rm eff}$ for the s-wave e^+-H scattering at $k = 0.2a_0^{-1}$, using two sets of basis functions: inner and outer. The inner basis functions are chosen as ECG functions

$$\phi_k = \exp\left(-\frac{1}{2}\sum_{ij} b_{k,ij}\mathbf{r}_i\cdot\mathbf{r}_j\right). \tag{12}$$

They are optimized using the stochastic variational method [25–27]. The outer basis functions are expressed in the form

$$\Psi_{\rm outer}^i = \psi^{\rm H}(\mathbf{r}_{e^-})\exp\left(-\tfrac{1}{2}\eta_i\mathbf{r}_{e^+}^2\right), \tag{13}$$

$$\psi^{\rm H}(\mathbf{r}_{e^-}) = \sum_j d_j\exp\left(-\frac{\mu_j\mathbf{r}_{e^-}^2}{2}\right). \tag{14}$$

The wave function of the H ground state, $\psi^{\rm H}(\mathbf{r}_{e^-})$, is written as a linear combination of 20 ECG functions with energy $E_{\rm H} = -0.499\,999\,999\,43$ hartree. Moreover, η_i is defined by the relation $\eta_i = 18.6/1.45^{i-1}a_0^{-2}$ for $1 \leqslant i \leqslant 40$. To take into account the polarization effect of H, $V_{\rm aux}(\mathrm{r}_{e^+})$ additionally includes the polarization potential

$$V_{\rm pol}(\mathrm{r}_{e^+}) = -\frac{\alpha_d}{2\mathrm{r}_{e^+}^4}\left[1 - \exp\left(-\mathrm{r}_{e^+}^6/\mathrm{r}_0^6\right)\right], \tag{15}$$

with the static dipole polarizability $\alpha_d = 4.5$ a.u. and cutoff parameter $\mathrm{r}_0 = 2.16a_0$.

Table I addresses the convergence of our calculations for s-wave e^+-H scattering and gives a comparison with other methods. We obtain $k = \sqrt{2(E_3 - E_{\rm H})}$ from the third eigenenergy E_3 of the e^+-H system confined in the potential $V_{\rm CP}(\mathrm{r}_{e^+}) = G(\mathrm{r}_{e^+} - R_0)^2$, where $G = 2.732\,96 \times 10^{-5}$ and $R_0 = 21.0a_0$. For increasing size of the inner basis, G is tuned gradually, so k approaches $0.2a_0^{-1}$. Then, using k and $\langle\Psi_3'(\mathbf{r})|V_{\rm CP}|\Psi_3'(\mathbf{r})\rangle$ as reference, we determine the parameters of $V_{\rm aux}(\mathrm{r}_{e^+})$ in Eq. (6). Keeping $\lambda_i = 0.999\,50$, $\alpha_i = 2.0a_0^{-1}$, and $\beta_i = 0.230a_0^{-2}$ fixed for calculations including the 40 outer basis functions, the requirement $\langle\Psi_i'(\mathbf{r})|V_{\rm CP}|\Psi_i'(\mathbf{r})\rangle = \langle\Phi_i'(\mathbf{r}_{e^+})|V_{\rm CP}|\Phi_i'(\mathbf{r}_{e^+})\rangle$ can be satisfied by tuning only ξ_i. The

TABLE I. Convergence of the results for s-wave e^+-H scattering at $k = 0.2a_0^{-1}$ as a function of the number N of ECG functions. Here k denotes the wave number, δ_0 the phase shift, and $Z_{\rm eff}$ the annihilation parameter.

N	k (a_0^{-1})	δ_0 (rad)	$Z_{\rm eff}$
$N_{\rm inner}$			
200	0.200 001 85	0.187 536	5.482
300	0.200 000 36	0.187 630	5.536
400	0.200 000 11	0.187 646	5.545
500	0.200 000 09	0.187 648	5.554
$N_{\rm inner} + N_{\rm outer}$			
240	0.200 000 72	0.187 608	5.480
340	0.200 000 12	0.187 646	5.535
440	0.200 000 02	0.187 653	5.545
540	0.200 000 00	0.187 654	5.553
COP [28]	0.200	0.1877	5.538
KV [29,30]	0.200	0.1875	
HNV [31]	0.200	0.1876	
TM [32,33]	0.200	0.1868	5.5394

operator $\delta(\mathbf{r}_{e^-} - \mathbf{r}_{e^+})$ does not commute with the Hamiltonian, so there are no common eigenstates. During the optimization, many sets of nonlinear parameters may give the same energy but they generate different expectation values $\delta_{ep} = \langle\delta(\mathbf{r}_{e^-} - \mathbf{r}_{e^+})\rangle$. Therefore, the energy is variationally minimized, while δ_{ep} is variationally maximized.

The convergence of k is accelerated by augmenting the outer basis. As a consequence, the convergence of δ_0, which is related to k, is also accelerated. However, this procedure makes δ_{ep} slightly smaller than when calculated with only the inner basis. Both k and δ_0 show very good convergence. We obtain $\delta_0 = 0.187\,65$ rad. This result agrees well with the extrapolated value (0.1877 rad) of the correlated optical potential (COP) calculation by Bhatia *et al.* [34], with the value (0.1875 rad) of the Kohn variational (KV) calculation by Humberston *et al.* [30], and with the value (0.1876 rad) of the Harris-Nesbet variational (HNV) calculation by Gien [31]. On the other hand, it is 4.6‰ larger than the value (0.1868 rad) of the 21-state close-coupling approach [32]. As the COP result (5.538 [28]) and the T-matrix (TM) result (5.5394 [32,33]) are close to the value calculated with 300 ECG functions (5.536), the CVM final result of $Z_{\rm eff} = 5.553$ is more accurate than the results of the COP and TM methods. It turns out that $Z_{\rm eff}$ increases monotonically with the number of ECG functions but converges slowly. We estimate that the exact value of $Z_{\rm eff}$ falls within the range from 5.554 to 5.559. We note that a calculation with only a large inner basis has the capacity to generate accurate values for δ_0 and $Z_{\rm eff}$.

IV. SCATTERING OF o-Ps FROM H_2

We employ the fixed nucleus approximation with an internuclear distance of $R_{H_2} = 1.45a_0$, which is almost the equilibrium distance $1.448a_0$. Here $E_{H_2} = -1.174\,057\,038$ hartree, as calculated by Rychlewski *et al.* [35] with 300 ECG functions, is adopted for the ground-state energy of H_2. The Hamiltonian for o-Ps-H_2 scattering is

$$H = -\sum_{i=1}^{4}\frac{\nabla_i^2}{2} + \sum_{j>i=1}^{4}\frac{q_i\,q_j}{|\mathbf{r}_j - \mathbf{r}_i|} + \sum_{i=1}^{4}\left\{\frac{q_i}{|\mathbf{r}_i - \mathbf{R}/2|} + \frac{q_i}{|\mathbf{r}_i + \mathbf{R}/2|}\right\}, \quad (16)$$

where $\mathbf{r}_i$ is the coordinate of the ith particle ($e^{\pm}$) relative to the midpoint of the H_2 molecular axis and q_i is its charge. The vectors $\pm\mathbf{R}/2$ represent the displacements of the two protons from the midpoint. The basis for the interaction region has the form

$$\phi_k = \hat{P}\exp\left(-\frac{1}{2}\sum_{i=1}^{4}b_{k,i}|\mathbf{r}_i - \mathbf{S}_{k,i}|^2\right) \times \exp\left(-\frac{1}{2}\sum_{i=1}^{3}\sum_{j=i+1}^{4}a_{k,ij}|\mathbf{r}_i - \mathbf{r}_j|^2\right). \quad (17)$$

The vector $\mathbf{S}_{k,i}$ displaces the center of the ECG function for the ith particle to a point on the internuclear axis. The operator $\hat{P}$ ensures that the basis has Σ_g symmetry. The confining potential is added in the center-of-mass coordinate $\boldsymbol{\rho}_i = (\mathbf{r}_{e^+} + \mathbf{r}_i)/2$ so that the potential acting on the center of mass of e^+ and the ith e^- of the target is not reasonable. However, this effect declines for increasing R_0 [22]. Following previous experience with the s-wave elastic scattering of Ps from a H atom [22], $R_0 = 24a_0$ is used for the o-Ps-H_2 scattering. As o-Ps experiences, during the scattering, a van der Waals potential, we choose the auxiliary potential as

$$V_{\lambda_i,\alpha_i}(\rho) = \lambda_i\exp(-\alpha_i\rho) - \frac{C_6}{\rho^6}\left[1 - \exp\left(-\rho^6/\rho_0^6\right)\right], \quad (18)$$

with the cutoff parameter $\rho_0 = 6.0a_0$ and dispersion coefficient $C_6 = 49.3$ a.u. [36]. The parameters λ_i and α_i in Eq. (18) are adjusted to satisfy the conditions $E_i' = E_i$ and $\langle\Psi_i'(\mathbf{r})|V_{\rm CP}|\Psi_i'(\mathbf{r})\rangle = \langle\Phi_i'(\boldsymbol{\rho})|V_{\rm CP}|\Phi_i'(\boldsymbol{\rho})\rangle$. When another value of ρ_0 is used, λ_i and α_i are modified to keep the conditions satisfied. Both the phase shift and scattering amplitude determined with different ρ_0 (e.g., $\rho_0 = 3a_0$) do not change as long as there is no overlap of the Ps and H_2 particle clouds. Only the inner basis is used, because the outer basis is too complicated in this case. Similar to the case of e^+-H scattering, we expect that accurate scattering parameters can be obtained with a large inner basis. In the following text, we use a superscript T to indicate the triplet spin character of the pickoff annihilation. Due to the complexity of the multicenter scattering system, variational optimization of the energy and δ_{ep}^T together is very time consuming. Hence, only the energy is optimized by adjusting the nonlinear parameters of the ECG functions.

Table II shows the convergence of the results for Σ_g o-Ps-H_2 scattering at $k = 0.1a_0^{-1}$ when the number of ECG functions increases. We have $k = 2\sqrt{(E_1 - E_{\rm Ps} - E_{H_2})}$, where E_1 is generated with the confining potential parameter $G = 1.7717 \times 10^{-4}$ (obtained from the optimization of the nonlinear parameters) and $E_{\rm Ps} = -0.25$ hartree is the exact energy of the Ps ground state. In Eq. (18), λ_i and α_i have to be tuned together for each basis to satisfy the requirements to k and

TABLE II. Convergence of the results for Σ_g o-Ps-H_2 scattering at $k = 0.1a_0^{-1}$ as a function of the number N of ECG functions. Here k denotes the wave number, $\delta_{ep}^T = \langle \delta^T(\mathbf{r}_{e^-} - \mathbf{r}_{e^+})\rangle$, δ_0 is the phase shift, and $^1Z_{\rm eff}$ is the pickoff annihilation parameter.

N	k (a_0^{-1})	δ_{ep}^T	δ_0 (rad)	$^1Z_{\rm eff}$
2800	0.100 033	8.4671×10^{-6}	−0.1860	0.165 83
3200	0.100 016	8.4769×10^{-6}	−0.1854	0.166 28
3600	0.100 003	8.4710×10^{-6}	−0.1849	0.166 41
4000	0.099 993	8.4677×10^{-6}	−0.1846	0.166 52

$\langle \Phi_1'(\boldsymbol{\rho})|V_{\rm CP}|\Phi_1'(\boldsymbol{\rho})\rangle$. For a basis with 3600 ECG functions, for example, we obtain $\lambda_i \simeq -0.382\,964$ and $\alpha_i \simeq 0.553a_0^{-1}$. Both k and δ_0 show good convergence for an increasing number of ECG functions, in contrast to δ_{ep}^T and $^1Z_{\rm eff}$ (though they vary monotonically).

Table III presents results of our CVM calculations for three values of k. We focus our attention on scattering with $k \leqslant 0.1a_0^{-1}$ for two reasons. First, the most reliable experimental information comes from annihilation experiments of thermal o-Ps. Second, the collision can be treated as s-wave scattering and thus the molecular aspects of the asymptotic wave function can be neglected. By fitting δ_0 from Table III to the effective-range theory [37]

$$k\cot(\delta_k) = -\frac{1}{A_S} + \frac{1}{2}r_0k^2 - \frac{4\pi C_6}{15A_S^2}k^3 - \frac{16C_6}{15A_S}k^4\ln(k), \tag{19}$$

the scattering length $A_S = 2.02a_0$ and effective range $r_0 = -8.16a_0$ are obtained.

In addition, we estimate δ_0 and $^1Z_{\rm eff}$ for Σ_g o-Ps-H_2 scattering with k up to $0.5a_0^{-1}$ using the stabilization method (SM) [21] with 4400 ECG functions and 15 external basis functions constructed from products of the wave functions of Ps and H_2 with connecting Gaussians

$$\Psi_{\rm ext}^i = \psi^{\rm H_2}(\mathbf{r}_1,\mathbf{r}_2)\psi^{\rm Ps}(\mathbf{r}_3-\mathbf{r}_4)\exp\left[-\frac{1}{2}\eta_i\left(\frac{\mathbf{r}_3+\mathbf{r}_4}{2}\right)^2\right], \tag{20}$$

TABLE III. Confining potential parameter G, $\delta_{ep}^T = \langle \delta^T(\mathbf{r}_{e^-} - \mathbf{r}_{e^+})\rangle$, phase shift δ_0, and pickoff annihilation parameter $^1Z_{\rm eff}$ for Σ_g o-Ps-H_2 scattering at different k. Experimental values of $^1Z_{\rm eff}$ are listed for comparison. Numbers in parentheses give the uncertainty in the last digit.

k (a_0^{-1})	G	δ_{ep}^T	δ_0 (rad)	$^1Z_{\rm eff}$
0.060 94	2.15×10^{-6}	1.7876×10^{-6}	−0.1196	0.1736
0.082 75	2.27×10^{-6}	4.7048×10^{-6}	−0.1527	0.1688
0.099 993	1.7717×10^{-4}	8.4677×10^{-6}	−0.1846	0.1665
0.0	Effective-range theory			0.1839
Experiment at 77.4 K [1]				0.197(3)
Experiment at 250 K [1]				0.195(5)
Experiment at 293 K [1]				0.193(5)
Experiment at 293 K [2]				0.186(1)

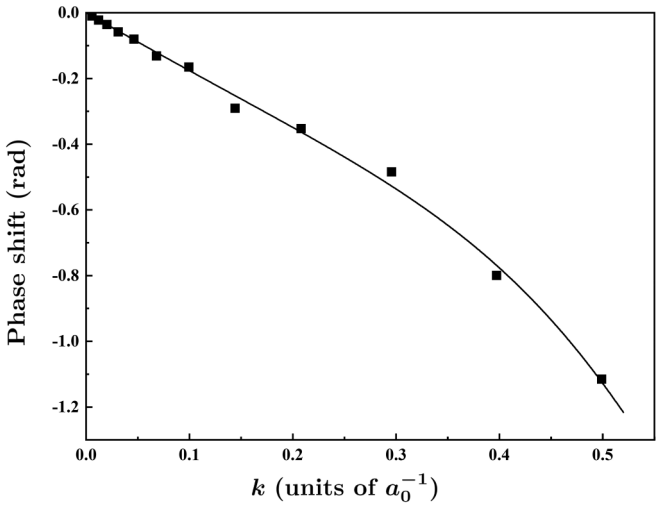

FIG. 1. Plot of the s-wave phase shift δ_0 for Σ_g o-Ps-H_2 scattering as a function of k. The line represents an effective range fit using Eq. (21).

where $\eta_i = 1/1.45^{2i-2}a_0^{-2}$. The ground state $\psi^{\rm H_2}(\mathbf{r}_1,\mathbf{r}_2)$ is represented by a linear combination of 120 ECG functions with an energy of $-1.174\,056\,790$ hartree, which is only 2.5×10^{-7} hartree higher than the close-to-exact value of $-1.174\,057\,038$ hartree [35]. The ground state $\psi^{\rm Ps}(\mathbf{r}_3-\mathbf{r}_4)$ is represented by a linear combination of 12 ECG functions with an energy of $-0.249\,999\,95$ hartree. For individual pseudostates the phase shifts are shown in Fig. 1 together with an effective range fit to the expression

$$k\cot(\delta_k) = -\frac{1}{A_S} + \frac{1}{2}r_0k^2 + Bk^3, \tag{21}$$

which is more suitable than Eq. (19) for data including larger k values. The SM value of the scattering length ($1.78a_0$) is almost 14% smaller than the more accurate CVM value. As r_0 is sensitive to the effective range expansion and momentum fitting range, the SM ($-0.72a_0$) and CVM ($-8.16a_0$) values deviate strongly. The value $A_S = (2.1 \pm 0.2)a_0$ estimated from the average experimental momentum-transfer cross section σ_m for Ps energy below 0.3 eV agrees well with the CVM result [9]. Using Doppler broadening spectroscopy, Skalsey *et al.* [10] obtained $\sigma_m = (3.8 \pm 0.8)\pi a_0^2$ over an incident energy range from 0.39 to 3.00 eV. Garner *et al.* [4] found in their o-Ps beam experiments that the total cross section rises from $5.3\pi a_0^2$ at 10 eV to a maximum of $10.3\pi a_0^2$ at about 25 eV, declines to $6.02\pi a_0^2$ at about 60 eV, and hardly changes from 60 eV to 110 eV. Our CVM result for the s-wave cross section at $k = 0.1a_0^{-1}$ ($13.59\pi a_0^2$) is much larger than that of the three-Ps-state coupled-channel method ($3.79\pi a_0^2$) [7] (obtained by tuning the parameter of the exchange potential to fit the experimental data by Garner *et al.* [4] and Skalsey *et al.* [5]). Moreover, the scattering length of the pseudopotential method is much smaller when taking into account the van der Waals interaction ($0.64a_0$) [17], while otherwise it is only a bit larger ($2.06a_0$) than the CVM value ($2.02a_0$). The large spread in the experimental results of Garner *et al.* [4], Saito *et al.* [9], and Skalsey *et al.* [10] indicates that the Ps-H_2 total cross section (and/or σ_m) probably has a strong energy dependence

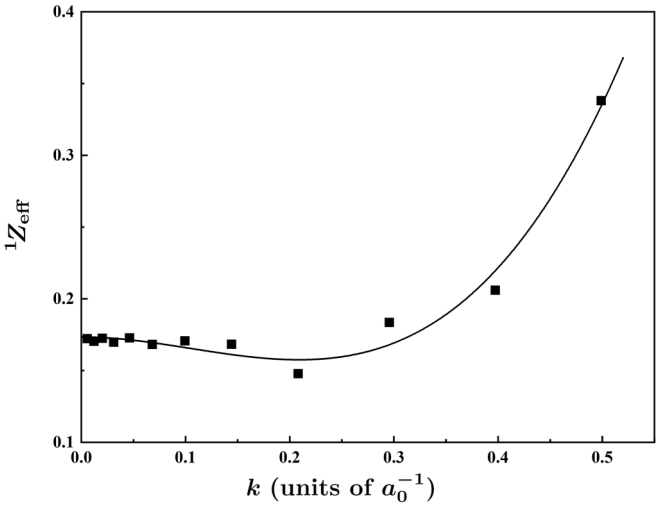

FIG. 2. Plot of the s-wave pickoff annihilation parameter $^1Z_{eff}$ for Σ_g o-Ps-H_2 scattering as a function of k. The line represents an effective range fit using Eq. (22).

at low energy (similar to intermediate energy), which has to be investigated further by both experiment and theory.

Using the effective-range theory expansion [38]

$$^1Z_{eff}(k) = {}^1Z_{eff}^{(0)} + {}^1Z_{eff}^{(1)}k^2 + {}^1Z_{eff}^{(2)}k^3, \tag{22}$$

fitting the CVM value of $^1Z_{eff}$ leads to $^1Z_{eff}^{(0)} = 0.184$, while a 6% smaller and less accurate value ($^1Z_{eff}^{(0)} = 0.173$) is obtained by fitting the SM value of $^1Z_{eff}$ (see Fig. 2). Experimental values of 0.197(3) [1], 0.195(5) [1], 0.193(5) [1], and 0.186(1) [2] from weighted least-squares fits of observed decay rates at low H_2 gas densities and temperatures of 77.4, 250, 293, and 293 K, respectively, indicate that the low-density $^1Z_{eff}^{(0)}$ is independent of the temperature (at the level of accuracy of the experimental data). The fit of Ref. [1] was constrained to a vacuum annihilation rate of $\Gamma_{vac} = 7.24\ \mu s^{-1}$, which is almost 3% larger than the accurate experimental value of $7.0401(7)\ \mu s^{-1}$ [39]. Using no such constraint, a better value of $\Gamma_{vac} = 6.95(8)\ \mu s^{-1}$ was determined in Ref. [2]. The very good agreement with the experimental value of $^1Z_{eff}^{(0)} = 0.186(1)$ [2] demonstrates the high quality of the CVM near-zero-energy wave functions and hence indicates that the CVM phase shifts and scattering length are accurate at the level of $^1Z_{eff}^{(0)}$ (about 1%).

V. SUMMARY

The CVM is a powerful method that fully utilizes the advantages of studying bound states of atoms and molecules to determine phase shifts and normalization constants of asymptotic wave functions for collisions. We have verified the accuracy of the CVM normalization constant for e^+-H scattering by comparison with other methods. The CVM result of $Z_{eff} = 5.553$ for s-wave e^+-H scattering at $k = 0.2a_0^{-1}$ is a significant improvement in accuracy since the COP value of $Z_{eff} = 5.538$ was reported [28]. For o-Ps-H_2 scattering we have reported accurate values of δ_0 and $^1Z_{eff}$ for three different incident momenta. The CVM results of $^1Z_{eff}^{(0)}$ and A_S, extracted by means of the effective-range theory, show excellent agreement with precise experimental data [2,9]. As the studied problem was intractable for a long time, we believe that the present work will inspire new experimental and theoretical efforts on the low-energy o-Ps scattering from few-body targets.

ACKNOWLEDGMENTS

J.-Y.Z. was supported by the "Hundred Talents Program" of the Chinese Academy of Sciences. Z.-C.Y. was supported by the NSERC of Canada and in part by the CAS/SAFEA International Partnership Program for Creative Research Teams. The research reported in this paper was supported by funding from King Abdullah University of Science and Technology. The authors are thankful for the computational resources provided by the ACEnet of Canada.

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