

Positronium collisions with O₂ and CO₂

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We calculate elastic and positronium (Ps) breakup cross sections for collisions of Ps with O₂ and CO₂ molecules in the fixed-nuclei approximation. We incorporate electron exchange and correlations for these processes by using the free-electron-gas model developed earlier for Ps scattering by rare-gas atoms and N₂ molecules. The results exhibit similarity between electron and Ps scattering when the cross section is plotted as a function of the projectile velocity, confirming experimental observations [S. J. Brawley *et al.*, *Science* **330**, 789 (2010)]. Below the Ps breakup threshold we observe resonance structures similar to those obtained earlier for Ps-N₂ scattering.

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I. INTRODUCTION

The similarity between electron and positronium (Ps) scattering discovered ten years ago [1] continues to attract the attention of experimentalists and theorists. Specifically, electron and Ps cross sections, when plotted as functions of the projectile velocity, exhibit a similar behavior and magnitude in a wide velocity range. A particularly interesting phenomenon is the recently observed resonant Ps-N₂ scattering [2] similar to resonant *e*-N₂ scattering (see Refs. [3,4] and references therein) which was confirmed by theory [5]. Scattering by the O₂ molecule and carbon dioxide (CO₂) presents a special interest in this regard. In contrast to N₂, O₂ contains two electrons in the unfilled π_g subshell. Although a low-energy Π_g resonance is observed in both *e*-N₂ and *e*-O₂ scattering, the latter resonance is extremely narrow [6,7] and can be observed only in experiments [8,9] with a very high energy resolution. In the case of CO₂ a sharp Π_u resonance exists in electron scattering from this molecule and there is an evidence of a resonance in Ps scattering as well [2,10].

Note, however, that there cannot be a one-to-one correspondence between electron-molecule and Ps-molecule scattering. First, in contrast to electron-molecule scattering, in the case of Ps-molecule scattering the electron in Ps does not possess a certain projection of angular momentum on the internuclear axis; therefore, the symmetry of the resonance is different in the two cases. In particular in the case of Ps-N₂ scattering, instead of one resonance of Π_g symmetry, we obtain three resonances of Σ_u , Π_u , and Δ_g symmetries [5]. Second, the long-range parts of electron-atom and electron-molecule interaction and Ps-atom and Ps-molecule interaction are different. In the former case it is dominated by the polarization potential decaying as the fourth power of the distance, and in the second case by the van der Waals potentials decaying as the sixth power of the distance. Therefore, in the

low-energy region electron and Ps scattering could exhibit different behavior.

The challenging aspect of the theoretical treatment of the Ps-atom and Ps-molecule interaction is an accurate inclusion of electron exchange and electron correlations. The exact treatment of these effects based on the close-coupling method [11–13] becomes very computationally expensive as the size of the target grows, and therefore so far this type of calculation has been carried out only for simple atomic systems like hydrogen and light rare-gas atoms. A few approximate methods for inclusion of exchange and correlation have been developed which include the pseudopotential method [14,15], methods based on many-body theory [16], and methods based on confined basis sets [17–20].

Recently we developed a method employing potentials based on the free-electron-gas (FEG) model for Ps-atom or Ps-molecule scattering [21]. These potentials were used to calculate elastic scattering cross sections for Ps-N₂ [5,22] and Ps-rare-gas-atom collisions [23]. The calculations were successful in the description of the relevant experiments, particularly in explanation of the resonance structure in the cross sections for Ps-N₂ scattering.

In what follows below we will describe our calculations of Ps-O₂ and Ps-CO₂ total scattering cross sections. As we showed in the past, the most important contribution to the total cross section for Ps scattering by a neutral target is given by elastic scattering and Ps ionization (fragmentation) or breakup. In Sec. II we describe our FEG potentials for the Ps-O₂ and Ps-CO₂ interactions which will be used to obtain elastic scattering cross sections. In Sec. III we describe our binary-encounter calculations of the Ps ionization cross section. In this section we also describe calculations of electron and positron scattering for these targets which are needed in the binary encounter model. We also employ FEG potentials in these calculations. In Sec. IV we present our total cross

sections for Ps scattering and in Sec. V we briefly discuss our attempts at including orthogonality using an orthogonalizing pseudopotential (OPP). Section VI is a brief conclusion. As it has become customary since the discovery of similarity between electron and Ps scattering [1], we plot all cross sections as functions of the projectile velocity. Atomic units are used throughout unless stated otherwise.

II. PS SCATTERING POTENTIALS

For elastic Ps-O₂ and Ps-CO₂ scattering we determine the scattering potentials in the same way as was done for Ps-N₂ scattering [5]. In Ref. [21] we derived expressions for the exchange and correlation energies as functions of the Fermi energy. In order to introduce the dependence of these energies on the projectile position relative to the target we determine the Fermi energy in terms of the charge density of the O₂ or CO₂ ground state. The Ps-molecule scattering potentials obtained in this way are then expanded in Legendre polynomials. In all of our scattering calculations the static potential and all FEG potentials depend on the ground-state electronic charge density. The charge density for O₂ was obtained by performing the restricted Hartree-Fock (RHF) calculations [24] implemented in the GAUSSIAN 03W suite of programs [25]. The 6-31G* basis set [24] was employed for the RHF geometry optimization of the O₂ molecule. The charge density for CO₂ was determined from the molecular orbitals of Yoshimine and McLean [26].

The correlation potential at large distances is matched to the van der Waals potential with a cutoff of the form

$$V_W(\mathbf{R}) = -\frac{C_0 + C_2 P_2(\cos \chi)}{(R^2 + R_c^2)^3}, \quad (1)$$

where R is the position of the center of Ps relative to the center of mass of the molecule. χ is the angle between \mathbf{R} and the internuclear axis, and R_c is a cutoff radius. The van der Waals coefficients C_0 and C_2 were calculated from the London formula using the molecular and Ps polarizabilities.

For O₂ we use the polarizabilities $\alpha_0 = 10.6$ a.u. and $\alpha_2 = 4.77$ a.u., giving $C_0 = 91.5$ a.u. and $C_2 = 41.2$ a.u. In order for the correlation potential to match smoothly to the asymptotic form we have chosen a cutoff radius of $R_c = 1.19$ a.u. and for the spherical component $\lambda = 0$ switched from the correlation potential to the asymptotic form at $R = 3.4$ a.u.

For CO₂ we use the polarizabilities $\alpha_0 = 17.76$ a.u. and $\alpha_2 = 9.49$ a.u., giving $C_0 = 160.5$ a.u. and $C_2 = 85.8$ a.u. In order for the correlation potential to match smoothly to the asymptotic form we have chosen a cutoff radius of $R_c = 0.3$ a.u. and for the spherical component $\lambda = 0$ switched from the correlation potential to the asymptotic form at $R = 4.58$ a.u.

In Fig. 1 we show the lowest two components ($\lambda = 0, 2$) of the Legendre expansion for the total potential (exchange plus correlation) for a Ps velocity of 0.01 a.u. and compare them with the potentials for Ps-N₂ scattering [5]. The potentials for O₂ and N₂ are very similar, but the Ps-O₂ potential is more attractive for intermediate values of R . For Ps-CO₂ the $\lambda = 0$ component is much more attractive near $R = 0$ due to the presence of the carbon atom at the origin. The potential for CO₂ is generally more attractive than for O₂ and N₂ at

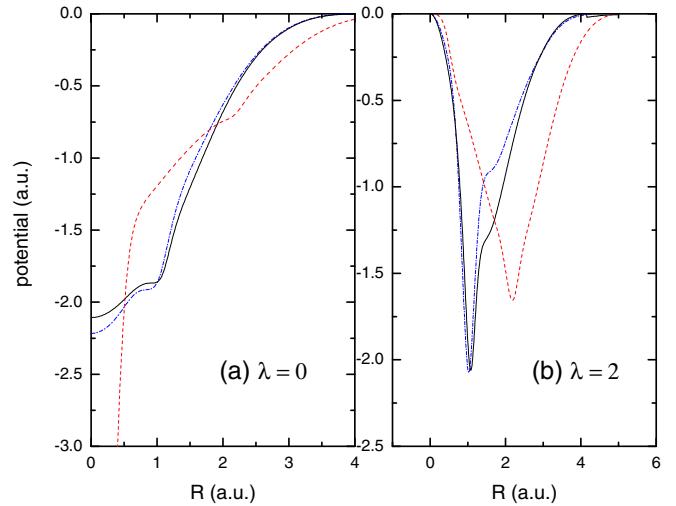


FIG. 1. First two Legendre components ($\lambda = 0, 2$) of the total FEG potentials (exchange plus correlation) for Ps-O₂ (solid lines), for Ps-CO₂ (red dashed lines), and for Ps-N₂ (blue dash-dotted lines).

larger values of R , partly due to the stronger van der Waals interaction for CO₂, but mostly due to the larger internuclear separation.

We solve the Schrödinger equation with these potentials using the integral equation method of Ref. [27] to obtain elastic Ps scattering cross sections. These elastic cross sections will be presented in Sec. IV along with our total cross sections.

III. IONIZATION

Apart from elastic scattering, the largest contribution to the total cross section for positronium collisions is expected to be Ps ionization (fragmentation) or breakup. In the present paper we employ the binary encounter approximation to calculate cross sections for Ps ionization [28,29]. We have previously applied this approximation to calculate Ps ionization cross sections in collision with rare gas atoms Ar, Kr, and Xe [15] which were in good agreement with previous calculations using the impulse approximation [30]. The binary encounter approximation for Ps ionization was extended to nonspherical interactions and applied to Ps-N₂ scattering in Ref. [5].

The ionization amplitude in the binary encounter approximation is expressed through the body-frame T -matrix elements in the fixed-nuclei approximation for electron and positron scattering by the target. To calculate the scattering matrices we have solved the Schrödinger equation for electron and positron scattering using the integral equation method [27] in the static-exchange plus polarization approximation [31] using the potentials described below. We emphasize that, in this section, our goal is to obtain scattering matrices for electron and positron scattering that produce cross sections in as good agreement with experimental data as possible using potentials that do not use any adjustable parameters. These scattering matrices then serve as input in the binary encounter approach that allows us to calculate Ps ionization cross sections. For comparative purposes we have also tried using a semiempirical correlation-polarization potential for e⁺-O₂ scattering.

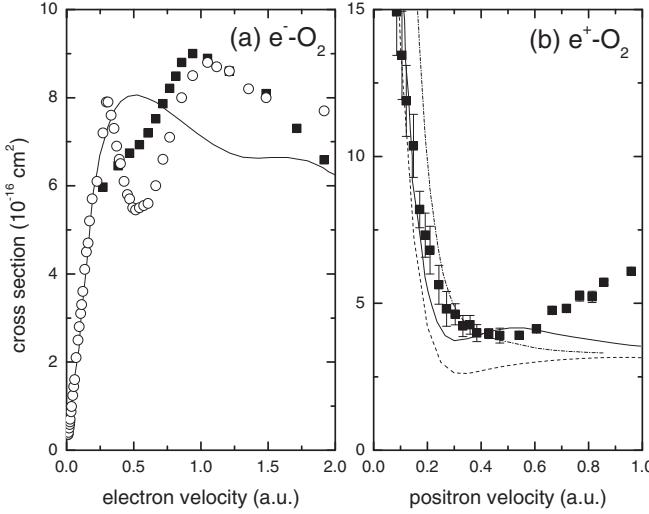


FIG. 2. (a) Elastic e^- -O₂ cross sections as functions of electron velocity. Solid line, present calculation; squares, recommended elastic cross sections of Itikawa [34]; circles, elastic cross sections compiled by Murphy [35]. (b) Total elastic e^+ -O₂ cross section as a function of positron velocity. Solid line, present calculation including Σ , Π , and Δ symmetries and using semiempirical polarization of Eq. (2); dashed line, present calculations using correlation potential of O'Connell and Lane [33]; dot-dashed line, calculations of Tenfen *et al.* [36]; squares, measured total cross sections of Chiari *et al.* [37].

For e^- -O₂ elastic scattering the static potential is attractive. We also use the Hara free-electron-gas approximation (HFEGE) for the exchange potential [32]. For the correlation-polarization potential we use the FEG model of O'Connell and Lane [33] which was successfully applied by them to electron scattering by rare-gas atoms. In this model the long-range polarizability is enforced by switching to the long-range form at the distance at which it intersects with the FEG correlation potential.

In Fig. 2(a) we show our calculated elastic e^- -O₂ cross sections compared with the recommended elastic cross sections of Itikawa [34] and the measurements of Murphy [35] which extend to very low velocities. The agreement between our calculated cross sections and the measurements of Murphy [35] at low velocities is very good. At higher velocities the present calculations are slightly smaller than the experimental values, but overall the agreement is good. At low velocities our cross section disagrees with the R -matrix results of Higgins *et al.* [7], which do not exhibit a strong downturn towards lower energies (velocities) observed in our calculations and confirmed by Murphy's measurements [35]. As explained in Ref. [7] this is probably due to the omission of long-range polarization effects in the expansion of the scattering wavefunction in the R -matrix calculation. We also do not detect a very narrow Π_g resonance obtained in the R -matrix calculations at $E = 0.0554$ Ry (velocity 0.235 a.u.). We note that the structure in the experimental data due to the Π_g resonance is prominent in the vibrational excitation data, but not as much in elastic scattering [34]. Last, as shown in the R -matrix calculations of Higgins *et al.* [7] the resonance structure is very sensitive to the internuclear separation. When we use only the static potential for e^- -O₂ elastic scattering

we do observe a Π_g resonance structure, but when we add exchange and correlation it disappears. It could be possible that our model potential is too attractive, and the resonance position is shifted towards lower energies, where it becomes even narrower, or even towards negative energies; however, we believe that the general agreement of our results with experimental measurements should provide a good estimate of the Ps ionization cross section.

For positron scattering the static potential is repulsive instead of attractive. We can add to it a semiempirical polarization potential of the form

$$V_{\text{pol}}(r) = \left[-\frac{\alpha_0}{2r^4} - \frac{\alpha_2}{2r^4} P_2(\cos \theta) \right] C(r), \quad (2)$$

where

$$C(r) = 1 - \exp[-(r/r_c)^p] \quad (3)$$

is a cutoff function and r_c is an adjustable cutoff parameter. For the polarization potential we use $\alpha_0 = 10.6$ a.u. and $\alpha_2 = 4.77$ a.u. which are also the values used in the recent e^+ -O₂ calculations of Tenfen *et al.* [36]. In order to get good agreement with the experimental values of Chiari *et al.* [37] we use $p = 1$, but have had to choose different values of r_c depending on the scattering symmetry. For gerade symmetries (Σ_g , Π_g , Δ_g) we have used $r_c = 2.3$ a.u. and for ungerade symmetries (Σ_u , Π_u , Δ_u) we have used $r_c = 1.29$ a.u. We show our calculated total elastic e^+ -O₂ cross section in Fig. 2(b) and compare it with the experimental results of Chiari *et al.* [37] and the calculations of Tenfen *et al.* [36].

It is often quite difficult to obtain a good fit to the experimental cross section for positron scattering by varying the parameters of the semiempirical potential and we have not been able to obtain a good fit for all velocities up to the Ps formation threshold for e^+ -CO₂ scattering. Therefore, we have tried using the correlation-polarization potential of Ref. [33] for positron scattering by both molecular targets as well. We show the resulting elastic cross section in this case for e^+ -O₂ scattering in Fig. 2(b).

In Fig. 3(a) we show our results for the e^- -CO₂ total elastic scattering cross section using the HFEGE exchange potential and the FEG correlation potential of O'Connell and Lane [33]. Our cross sections are generally a little larger than the recommended values [38] and the calculations of Morrison *et al.* [39]. We emphasize, however, that those calculations employed the semiempirical polarization potential, whereas our calculations, which use the correlation potential of Ref. [33], do not employ an adjustable cutoff parameter. Also the calculations of Ref. [39] include only Σ and Π scattering symmetries whereas ours include Δ symmetries as well. The sharp rise of the cross section at low velocities and the position of the Π_u resonance that has also been seen in other theoretical studies [39,43,44] is well reproduced by this model.

In Fig. 3(b) we show our results for e^+ -CO₂ scattering. As mentioned above, we could not find a set of parameters for Eq. (2) that gave good agreement with the measurements of Zecca *et al.* [40] or of Hoffman *et al.* [41] over the entire velocity range; therefore, we have used only the correlation model of O'Connell and Lane [33] here. As for O₂ this model of correlation gives e^+ -CO₂ cross sections that are slightly

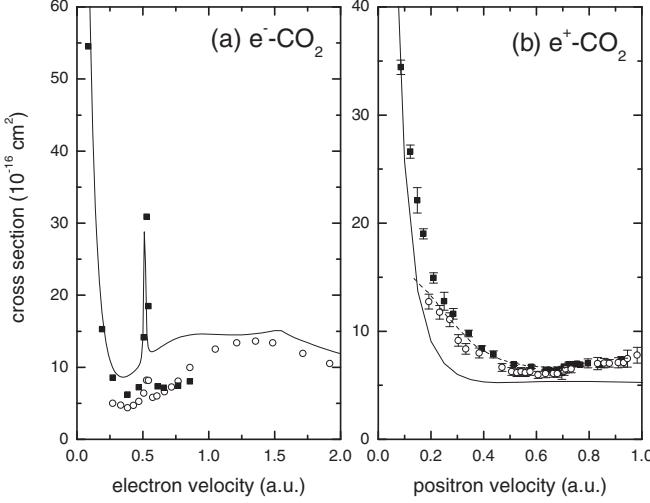


FIG. 3. (a) Elastic e^- -CO₂ cross sections as functions of electron velocity. Solid line, present calculation; circles, recommended elastic cross sections of Itikawa [38]; squares, elastic cross sections calculated by Morrison *et al.* [39]. (b) Total elastic e^+ -CO₂ cross section as a function of positron velocity. Solid line, present calculation including Σ , Π , and Δ symmetries and using FEG correlation potential of Ref. [33]; squares, measured total cross sections of Zecca *et al.* [40]; circles, measured cross sections of Hoffman *et al.* [41]; dashed line, BF-VCC calculations of Ref. [42].

smaller than the experimental values. Other calculations agree better with experiment at intermediate energies (velocities) [42,45,46]. As an example we show the body-frame vibrational close-coupling (BF-VCC) calculations of Gianturco and Mukherjee [42] in Fig. 3(b). As discussed by Morrison *et al.* [47], for the case of e^+ -H₂ scattering, the polarization potential for positrons should be more attractive at intermediate distances than for electrons due to the attraction between the positron and the electron cloud of the target molecule. By using the same correlation-polarization potential as for electron scattering we are neglecting this effect, and its inclusion in the FEG model of correlation for positron scattering might improve the agreement with experiment. On the other hand, our calculations agree well with the sharp rise in the experimental data for low velocities and again we feel that they should provide a good estimate of the Ps-CO₂ ionization cross section.

Using the T matrices corresponding to the above-described elastic scattering calculations we have used the binary encounter method [5] to calculate the Ps ionization cross sections. In Fig. 4 we show our Ps-O₂ and Ps-CO₂ binary-encounter ionization cross sections and compare them with our previous calculations for N₂. For CO₂ we use the FEG correlation potential of Ref. [33] in the calculation of the positron contribution while for O₂ we present results employing both the FEG correlation potential and semiempirical potential of Eq. (2).

We see that the CO₂ cross section is largest and O₂ is smallest. Generally, this mirrors the overall size of the cross sections for electron and positron scattering by these molecules. We note, however, that for O₂ the ionization cross section is slightly smaller if we use Eq. (2) in the calculation

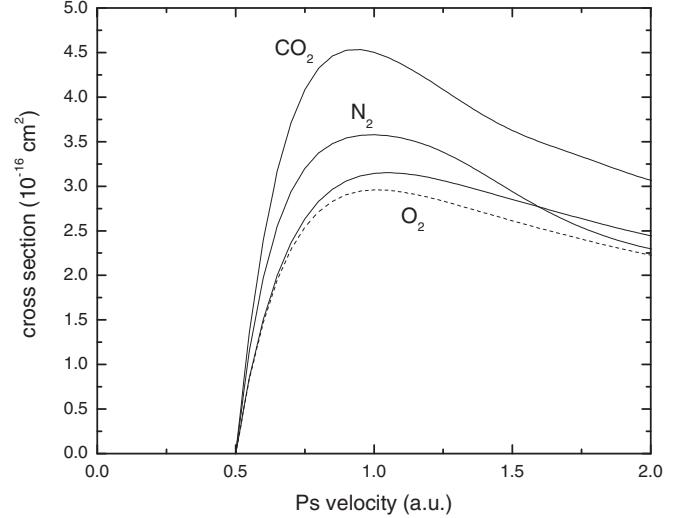


FIG. 4. Ps ionization (fragmentation) cross sections calculated using the binary-encounter approximation for Ps-CO₂, Ps-N₂, and Ps-O₂, in order of decreasing magnitude at a Ps velocity of 1 a.u. Solid lines are calculated using the FEG correlation potential of Ref. [33] for both the electron and positron contributions. The dashed line represents the Ps-O₂ ionization cross section using the semiempirical correlation potential of Eq. (2) for the positron contribution.

of the positron contribution. This is despite the e^+ -O₂ cross section being larger in this case and shows that there is not an entirely direct correlation between the size of the elastic electron and positron cross sections and the Ps ionization cross section. The ionization cross section is directly related to the differential cross section for electron and positron scattering, not to the total elastic cross section.

IV. ELASTIC AND TOTAL CROSS SECTIONS

In Fig. 5 we present the calculated elastic and total cross sections for Ps-O₂ scattering. At higher velocities the total cross section (elastic plus ionization) agrees quite well with experiment. At low velocities, below the Ps-ionization threshold ($v = 0.5$ a.u.) the calculated cross sections exhibit resonance structures. These resonances are similar to those seen for Ps-N₂ scattering [5] except they are shifted to slightly lower velocities and are slightly narrower. This might not be unexpected since, as we can see from Fig. 1, the Ps-O₂ potentials are generally more attractive than the Ps-N₂ potentials, particularly for intermediate values of R .

In Fig. 6 we show the partial cross sections for all Ps-O₂ scattering symmetries included in the present elastic cross sections. We see that the sharp resonance peaks are mainly due to resonances in the Δ_g and Π_u symmetries, but there are also resonances in the Σ_u and Δ_u symmetries. We have seen previously similar features in all of these symmetries for Ps-N₂ scattering when using the FEG potentials (see Fig. 7 of Ref. [5]). These resonances are just “pulled” to lower velocities by the more attractive Ps-O₂ interaction.

In Fig. 7 we present the calculated elastic and total cross sections for Ps-CO₂ scattering. The results are similar to those obtained for Ps-O₂ scattering. Again we see good agreement with experiment above the Ps-ionization threshold. There is

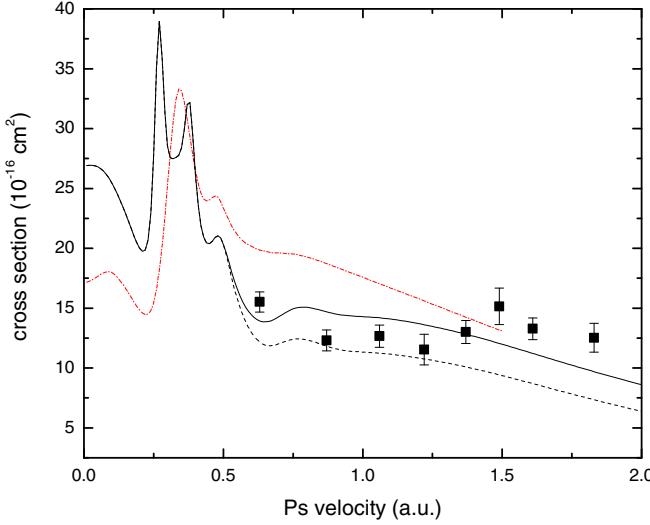


FIG. 5. Cross sections for Ps scattering with O₂. Solid line, theory, total cross section; dashed line, theory, elastic cross section; squares, measurements of Brawley *et al.* [1]. For comparison the dash-dotted red line is the total Ps-N₂ cross section of Ref. [5].

some indication of a resonance at $v = 0.6$ a.u. in the experimental data, but overall the theoretical resonance structure is more pronounced than in measured results for both CO₂ and N₂. In Fig. 8 we show the partial cross sections for Ps-CO₂ scattering. Once again we see similar resonance structures as for O₂. In Fig. 9 we compare our total Ps cross section with experiment and recommended values of the total e^- -O₂ and e^- -CO₂ scattering cross sections. We see that above the Ps-ionization threshold the electron and Ps cross sections become similar which confirms the experimental observations. Below the threshold the electron and Ps cross sections are quite different. This might not be unexpected since the long-range correlation is quite different in the two cases.

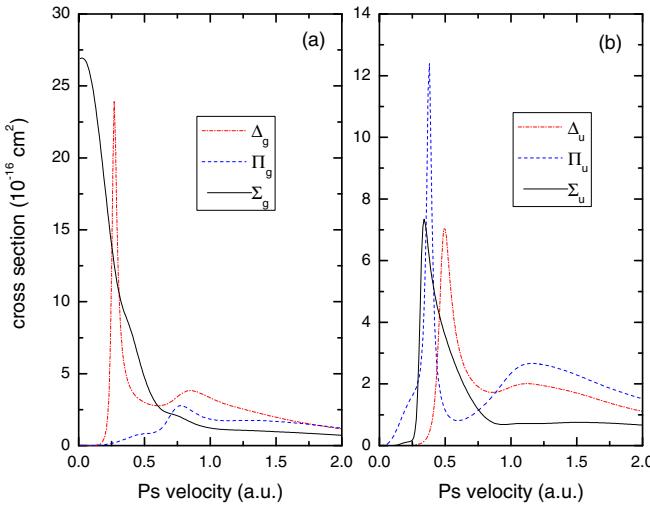


FIG. 6. Partial cross sections for Ps-O₂ elastic scattering: (a) even (gerade) scattering symmetries and (b) odd (ungerade) scattering symmetries.

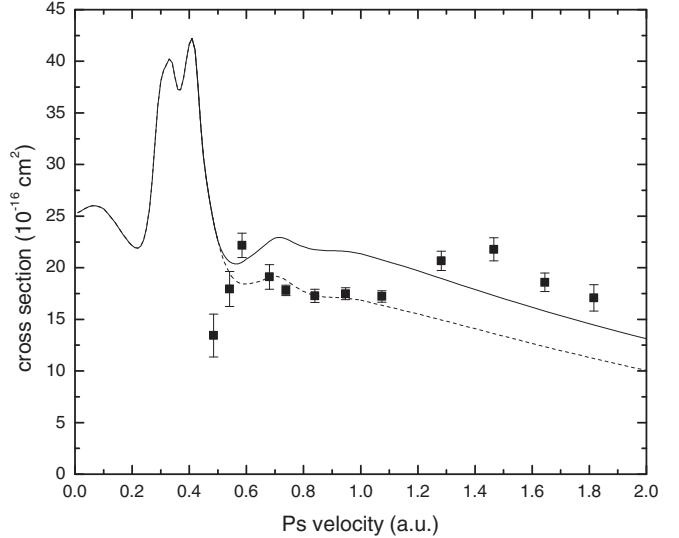


FIG. 7. Cross sections for Ps scattering with CO₂. Solid line, theory, total cross section; dashed line, theory, elastic cross section; squares, measurements of Brawley *et al.* [10].

V. ORTHOGONALITY

In electron-atom and electron-molecule scattering, use of the static-exchange approximation leads to overlap terms between the target orbitals and the scattering wavefunction [31]. These terms are due to the antisymmetric character of the total many-electron wavefunction. When the static-exchange equations are solved exactly using the full nonlocal exchange kernel the scattering wavefunction is ensured to be orthogonal to the occupied target orbitals for closed-shell targets [48,49]. When local approximations to the exchange potential are made orthogonality is no longer ensured. The effect of including orthogonality in the local calculations has been studied for electrons by rare-gas atoms using a Lagrange multiplier technique [33] and was found to be small.

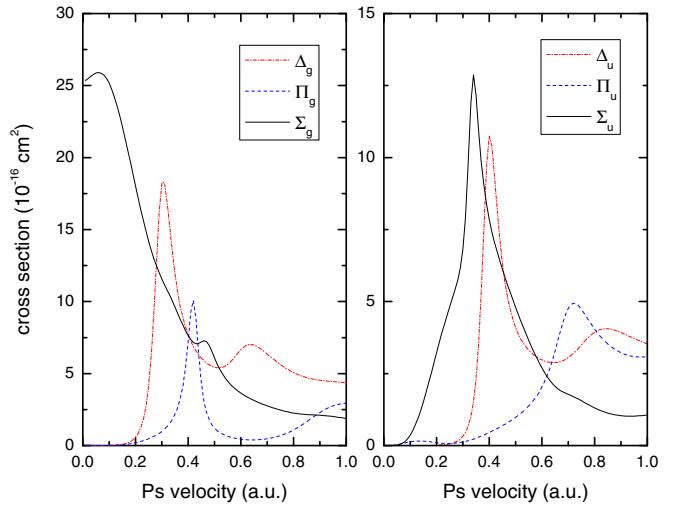


FIG. 8. Partial cross sections for Ps-CO₂ elastic scattering: (a) even (gerade) scattering symmetries and (b) odd (ungerade) scattering symmetries.

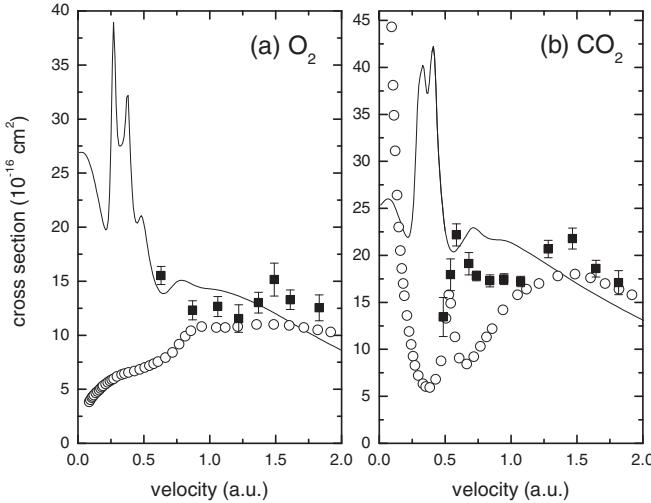


FIG. 9. Total scattering cross sections for Ps and e^- scattering by (a) O_2 and (b) CO_2 . Solid lines, present results; squares, Ps experiment, O_2 [1] and CO_2 [10]; circles, recommended e^- total scattering cross sections for O_2 [34] and CO_2 [38].

To incorporate orthogonality in electron and Ps scattering calculations the OPP method has been suggested [50,51]. In this method a nonlocal repulsive potential containing a strength parameter γ is added to the electron-molecule Hamiltonian. The strength parameter is made large enough so that orthogonality is enforced and the scattering calculations are converged in the sense that further increase of γ leads to a negligible change in the phase shifts and cross sections.

Our application of this method to Ps scattering by rare gas atoms [23] turned out to be successful, but all attempts to add OPP to Ps interaction with molecules led to Hamiltonians which appear to be too repulsive to describe resonances in these systems. This is illustrated for Ps- N_2 collisions in Fig. 10. We see here that inclusion of the OPP removes all resonance structure. Furthermore, we encounter severe numerical difficulties which affects convergence when iterative methods are used to solve the coupled integro-differential equations especially as the strength parameter is increased.

In this connection we note that Mitroy *et al.* [50,51] made the following observations regarding the OPP method:

(1) In their one state calculation [51] of Ps-He scattering the phase shift showed no sign of stabilizing as the strength parameter γ was increased. They concluded that a Ps basis with only one scattering state does not have the flexibility to give a zero overlap with the $1s$ core orbital. A previous investigation of the application of the OPP to bound-state problems also revealed that the quality of the basis did have an impact on the ability of the calculation to achieve a zero overlap and this could have an impact upon the computed energy and rate for positron annihilation [50].

(2) The use of excessively large γ degrades the quality of the wave function as it attempts to satisfy a condition that is increasingly difficult to fulfill with a finite basis.

(3) The OPP operator is best used in situations where it is feasible to use a sufficiently large channel space so that the expectation value of the OPP operator can be sufficiently close to zero.

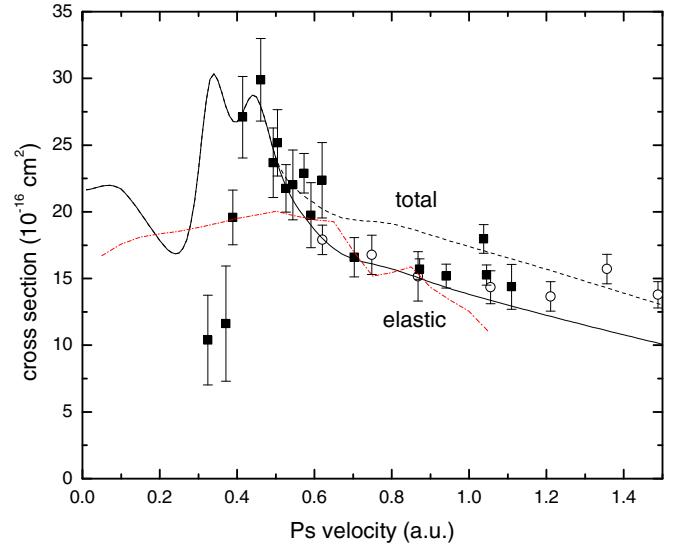


FIG. 10. Cross sections for Ps scattering with N_2 . Solid line, theory, total cross section; dashed line, elastic cross section obtained by using FEG potentials [5]; red dash-dotted line, elastic cross section including OPP; squares, experiment, Brawley *et al.* [1]; open circles, Shipman *et al.* [2].

We have also attempted to apply the OPP method to electron-molecule scattering and show our results in Fig. 11 for e^- - H_2 elastic scattering, including only FEG potentials as well as including the OPP. In this case we see once again that the FEG potentials by themselves give good agreement with experiment, while inclusion of the OPP destroys this agreement at low velocities.

To conclude, the OPP can sensibly be applied to the scattering of two composite objects, but it is important to ensure that the wave function is sufficiently flexible so that the expectation of the OPP operator can be made sufficiently

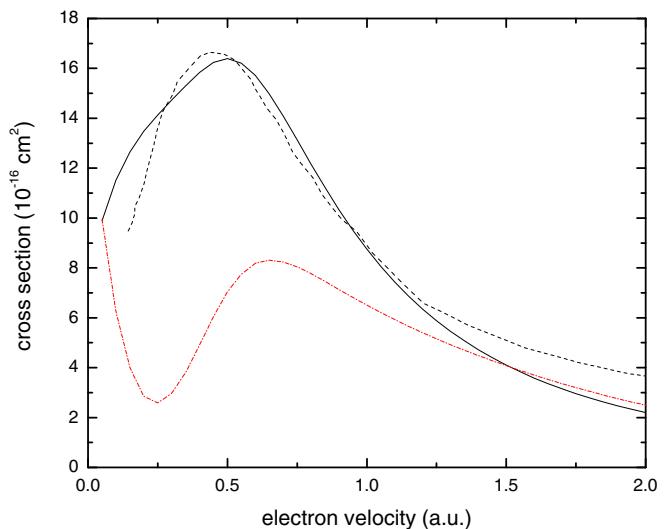


FIG. 11. Cross sections for electron scattering with H_2 . Solid line, present elastic cross section using FEG potentials; red dash-dotted line, present elastic cross section including OPP; dashed line, total cross section of Kauppila and Stein [52].

small and therefore does not influence the phase shifts in a manner other than the reason for which it was originally introduced. We have found that these requirements are not satisfied in e^- -molecule and Ps-molecule problems with the exchange and correlation potentials we are employing; therefore, the OPP method has not been used further in the present calculations.

VI. CONCLUSION

We have studied the application of local FEG potentials to electron, positron, and Ps scattering by O₂ and CO₂. In general the agreement with experiment is good in all cases, including for O₂ which is an open-shell target.

For Ps scattering our total cross sections, including elastic scattering and ionization, agree well with experiment for velocities above the ionization threshold. Below the threshold our calculations show a rich resonance structure. Similar resonances have been observed experimentally near the threshold

for N₂ and CO₂. However, it appears that our cross sections below the threshold are quite larger than the experimental values. This implies that more theoretical and experimental study is needed in this region.

We have also attempted to include orthogonality effects using an OPP and found that this is not entirely appropriate for e^- -molecule or Ps-molecule scattering. It might be possible to generalize the Lagrange multiplier method of including orthogonality to Ps collisions in order to further study these effects.

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