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Improving polarization description in positron-molecule scattering: a model potential approach

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ABSTRACT

In the present article we have proposed and tested a new polarization scheme within the Schwinger Multichannel method based on a model potential to describe positron-molecule polarization and correlation. For this test, we have calculated integral and differential cross sections for the elastic scattering of positrons by pyrazine and compared these results with the existing theoretical and experimental data. Furthermore, in order to evaluate the possible bound state, we have also obtained the scattering lengths. Our current results greatly improved previous ab-initio calculations showing a significantly better agreement between the theoretical results and experimental results, particularly at low angles for the differential cross sections.

Introduction

Understanding positron interactions with matter is of fundamental significance to many applications. For instance, positron annihilation is a core concept in positron emission tomography (PET) scan for diagnostics in medicine¹,², in positron annihilation spectroscopy for identification of defects in solids (specially in semiconductors)³,⁴, and for the study of some astrophysical phenomena⁵,⁶. In order to correctly describe these processes, accurate data related to positron scattering, positronium formation, positron annihilation and bound states⁷,⁸ are required.

As of recent years, ab initio methods developed to describe positron scattering by molecules have struggled to describe existing experimental data (integral cross sections, differential cross sections and bound state energies when relevant), particularly for nonpolar molecules. The main problems in these results are in the low energy regime (below 20 eV), in which the calculated data significantly underestimates the experimental results even when the Ps formation channel is closed¹⁹,²⁷. This can be also associated with a lower than expected intensity of the calculated differential cross sections in lower angles²⁵,²⁷.

In the description of the calculated bound states, it is also possible to notice that the calculated energies are also lower than experimentally observed²⁴. These problems are possibly related to an insufficient description of the interaction between the incident positron and the electrons of the molecular target with the current polarization schemes, as recently discussed in the work of Graves and Gorfinkiel²⁶,²⁷. This raises the question: could we have reached the limit in the ab initio description of correlation and polarization effects?

In order to properly address this matter, Swann and Gribakin²⁸,³¹ expanded the work that Mitroy and Ivanov have performed for atoms in order to obtain better calculations for bound states and scattering cross sections. Their work used a model potential to describe the correlation and polarization interactions between the incoming positron and the target. This semiempirical potential employed has one free parameter that can be adjusted either to reproduce bound states or scattering calculations. What is interesting, however, is that the adjusted parameter for positron-H scattering was applied to positron-methane scattering with good results. However, in the case of positron-molecule scattering, the authors could only compare the s-wave eigenphase obtained with a model potential and a state-of-the-art scattering calculations.

Hence, in face of these systematic difficulties to describe positron scattering from nonpolar molecules with ab initio methods and the success of Swann and Gribakin to reproduce s-wave eigenphase in positron scattering and positron-molecule bound states, we have opted to include the same model potential in the SMC method. By doing so, we can investigate if the earlier mentioned problems could be solved by a change in the description of polarization, which previously used virtual excitations of the target molecule. The main advantage of the current implementation is that we are able to obtain not only s-wave eigenphase, but also integral and differential cross sections for whichever target we choose. Furthermore, this implementation dramatically reduces computational costs and time and can allow calculations for more complicated systems.

In order to test this new implementation, we have chosen pyrazine as our main target since it has experimental data for both
integral and differential cross sections by positron impact. Besides, our own group have previously performed an extensive \textit{ab initio} calculation, having reached the limit of our computational facility to do so. Furthermore, this molecule was also studied by different \textit{ab initio} and semiempirical methods. Hence, this symmetric nonpolar molecule is ideal to analyze how the current treatment of polarization can improve our description of correlation and polarization interaction.

\textbf{Theory and Computational Details}

The Schwinger multichannel method\textsuperscript{32,36} has already been described in detail in other works, in such a way that we will only review the most important aspects of the method. The resulting scattering amplitude of the Schwinger multichannel method for positron scattering has the following form:

\begin{equation}
    f(\vec{k}_f, \vec{k}_i) = -\frac{1}{2\pi} \sum_{\mu,\nu} \langle S_{k_i} | V | \chi_\mu \rangle (d^{-1})_{\mu \nu} \langle \chi_\nu | V | S_{k_f} \rangle
\end{equation}

where

\begin{equation}
    d_{\mu \nu} = \langle \chi_\mu | \hat{Q} \hat{H} + PV - V G_p^{(+) \dagger} V | \chi_\nu \rangle
\end{equation}

In the above expressions, $P$ is the projection operator onto energetically open electronic states of the target, $Q$ is the projection operator onto energetically closed electronic states of the target, $\hat{H}$ is the collision energy minus the full scattering Hamiltonian, $G_p^{(+) \dagger}$ is the free-particle Green’s function projected on the $P$ space, $| S_{k_i(f)} \rangle$ is a solution of the unperturbed Hamiltonian $H_0$ and is given by the product of a target state and a plane wave with momentum $\vec{k}_i(f)$, $V$ is the interaction potential between the incident positrons and the electrons and nuclei of the target. Finally, $| \chi_\mu \rangle$ is an $(N+1)$-particles ($N$ electrons and one positron) variational trial basis.

Within the Schwinger multichannel method, the positron-molecule interactions can be treated in the static (S) and static plus polarization (SP) approximations. In the S approximation the target molecule is only described by its Hartree-Fock ground state, while in the SP approximation virtual excitations of the target are also included in order to account for the polarization interaction between the incident positron and the electrons of the target molecule. As previously discussed, however, the SP approximation has proven inefficient.

The model potential used by Swann and Gribakin\textsuperscript{28} to describe correlation and polarization interactions between a positron and the electrons of a molecule is given by:

\begin{equation}
    V_{\text{cor}}(\vec{r}) = -\sum_A \frac{\alpha_A}{2 |\vec{r} - \vec{r}_A|^4} \left[ 1 - \exp \left( \frac{|\vec{r} - \vec{r}_A|^6}{\rho_A^6} \right) \right]
\end{equation}

where $A$ is the index representing the atoms of the molecule, $\alpha_A$ are the hybrid polarizabilities of atom $A$ as according to the work of Miller\textsuperscript{37} and $\rho_A$ is a cutoff radius, an empirical parameter for each atom that defines the strength and range of the correlation potential. As stated in\textsuperscript{28}, the value of $\rho_A$ may look arbitrary, but anything in between 1.5 – 3.0 a.u. can be considered physical.

So far, to determine the optimal values of $\rho_A$, Mitroy and Ivanov compared calculated positron $s$-wave eigenphases and compared with accurate theoretical data for positron scattering by He\textsuperscript{38} and Ar\textsuperscript{39}. In case of positron-H scattering, $\rho_A$ was obtained by comparing the scattering length with close-coupling calculations\textsuperscript{40}. For Mg and Be, they obtained the cutoff parameter to obtain the same binding energy than a stochastic-variational calculation\textsuperscript{41}. Swann and Gribakin followed their work\textsuperscript{42} and used, for a series of target such as H$_2$, N$_2$ and CH$_4$, the same value of $\rho_A$ obtained for H with good results for scattering calculations.

In the new version of the SMC method with this implementation, we have incorporated the model potential $V_{\text{cor}}$ described in equation (3) with the potential $V$ already present in equations (1) and (2), resulting in the same expressions with $V \rightarrow V + V_{\text{cor}}$. Since the model potential $V_{\text{cor}}$ is being used to explicitly describe short-range correlation and polarization, we have not included virtual excitations of the target in our calculations. Through out this work, this procedure will be refered as static plus correlation model potential (S+V$_{\text{cor}}$).

We have performed similar calculations for the $s$-wave eigenphase for the hydrogen (H$_2$), nitrogen (N$_2$) and methane (CH$_4$) molecules as was previously done by Swann and Gribakin in\textsuperscript{30}. This was done in order to verify if our calculations in the S+V$_{\text{cor}}$ approximation yields results consistent with those of Swann and Gribakin. Although not the most optimal basis set to be
Figure 1. Comparison between the s-wave eigenphase calculated by Swann and Gribakin, and as calculated by the S+V_{cor} approximation with the 12s8p8d basis set for the hydrogen molecule (top panel) and nitrogen molecule (middle panel), and the 12s8p8d/8s basis set for methane (bottom panel). Integral and differential calculations in [44].

Figure 2. Molecular structure of pyrazine. Grey spheres represent carbon atoms, white spheres represent hydrogen atoms and blue spheres represent nitrogen atoms.

used with the Schwinger Multichannel method, these test calculations were done with the same basis sets used by Swann and Gribakin to describe the molecules, the 12s8p8d for the hydrogen and nitrogen molecules, and the 12s8p8d/8s for methane. The differences between the calculations relies not only on the codes used, but also on the basis used to describe the positron. In the work of [30], a separate 12 s basis functions was used, whilst in this work the positron scattering orbital was described by bound and virtual orbitals. However, as can be seen in Figure (1), we have an excellent agreement between the results calculated in the S+V_{cor} approximation and those calculated by Swann and Gribakin.

To take the implementation to further scrutiny, we investigated the case of pyrazine molecule, a non-polar simple molecule with recent experimental integral and differential cross section data. The geometry of the ground state used in the scattering calculations presented in this article was the same from the work of Moreira and Bettega [25], and is shown in Figure (2).

The scattering calculations were done in the S+V_{cor} approximation with the basis sets TZV++(3d,3p), using the cutoff distance $\rho = 2.051$ a.u. for all atoms. We have made this choice following the procedure done by Swann and Gribakin in [30]. It was not in our interest in this first calculation to obtain the best value of $\rho_A$ for this particular system, since the major goal in this work is to determine if and how the model potential can improve our description of the low-energy scattering process. It is important to note that the sum of all hybrid atomic polarizabilities of pyrazine gives a value of 60.846 a.u. for the polarizability of pyrazine, which is in good agreement with the ones obtained from high level calculations [43].

Results and Discussion

In Figure (3) we present a comparison for the "folded" differential cross sections (FDCS) at some energies of interest, calculated in previous works with the SMC method (specially the one calculated with the best ab-initio polarization scheme, namely
Figure 3. "Folded" differential cross sections for positron scattering from pyrazine at some energies of interest.

SP3)\(^{25}\), the R-Matrix method\(^{26,27}\), the IAM-SCAR+I method\(^{26}\), with the differential cross sections calculated for the present article in the S+V\(_{corr}\) approximation; plus the experimentally measured differential cross sections of Edwards \textit{et al.}\(^{26}\).

The reason to start with the FDCS is that its features are usually harder to describe and the correct description of the process is better evaluated in this comparison. As stated in previous works\(^{26,27}\), SMC previous data\(^{25}\) and R-matrix calculation agrees almost perfectly among them, both considerably missing the experimental forward - \(\theta \leq 45^\circ\) (backward \(180 - \theta\)) - scattering angle peak, but agreeing very well with higher angles. The experimental trend at low angles is observed in the IAM-SCAR+I method\(^{26}\), but there is not a good agreement with the experimental results. The calculation in the S+V\(_{corr}\) approximation is able to capture the trend at low angles and also agrees particularly well at higher angles for energies above 3.0 eV.

This is a remarkable result since we are using a cutoff distance optimized for the Hydrogen atom and only for \(s - wave\). In a way, this is significant since an optimal value of \(\rho\) can be used for different systems, providing reliable cross sections. Also, as stated in previous work by Mitroy and Ivanov, it would be best if a different \(\rho\) is obtained for a different \(l - wave\). This was not done in this work and could explain the discrepancy observed particularly at 1.30 and 2.0 eV.

In Figure (4) we present the same a comparison as in the FDCS, but for the integral cross sections. From the comparison of the calculated cross sections in the SMC method (in the SP approximation), the R-Matrix method and the S+V\(_{corr}\) approximation, a higher intensity of the calculated integral cross section in the S+V\(_{corr}\) approximation is noticed. This behaviour is linked to the higher intensity of the calculated differential cross sections at lower angles with the S+V\(_{corr}\) approximation. The bigger difference with the IAM-SCAR method arises from their inclusion of the real Ps formation channel, which seems to be overestimated. Even though both IAM-SCAR and our current model uses model polarization potential, the former consider independent atoms and makes further correction to account for the full target while ours considers the molecule target as one.

Once again, this overestimation can be attributed to using the same cut off parameter for all angular momenta scattering wave. However, it is striking how the magnitude of the ICS increases in the current calculation when compared to previous \textit{ab-initio} calculations from both SMC and R-Matrix methods, even though both calculations were among the best and more expensive ever made for positron scattering. This probably indicates that the \textit{ab-initio} way to describe target polarization in positron scattering is not enough to correctly reproduce what happens in reality.

Another result that points toward this direction comes from the comparison between the \(s\)-wave eigenphase calculated with the SMC method in the SP3 polarization scheme and in the S+V\(_{corr}\) approximation, which is presented in Figure (5). While in the SP3 polarization scheme there is a Ramsauer-Townsend minimum around 1.7 eV, such a minimum is not manifested in the calculation done with the S+V\(_{corr}\) approximation, indicating that the description of polarization in the S+V\(_{corr}\) approximation is
much more attractive than that of the SP3 polarization scheme. It is also possible to notice that the s-wave eigenphase in the S+V_{corr} approximation also tends to $\pi$ radians, a behaviour linked to the existence of a bound state.

The bound state energy calculated with the SMC method in the SP3 polarization scheme was $\varepsilon_b = 12.6$ meV, with the R-Matrix method (only the highest result calculated for the bound state energy is being shown) was $\varepsilon_b = 2.6$ meV, and with the S+V_{corr} approximation $\varepsilon_b = 84.3$ meV. As can be seen, the bound state energy calculated in the S+V_{corr} approximation is much higher than that of the other calculated results. Unfortunately, there is no experimental data on it, but the current result is much closer to the experimental bound state energy of benzene $\varepsilon_b = 150$ meV, a proximity that should be expected for a molecule such as pyrazine.

Although some improvements may still be required for a better agreement between calculation and experiment, it seems that the polarization scheme in the S+V_{corr} approximation is able to generally account better for the long and short-range interactions between positron and the molecule, not able to be achieved by any \textit{ab-initio} methods thus far.

**Summary**

In this article we have proposed and tested a novel polarization scheme within the SMC method framework, the S+V_{corr} approximation. With the S+V_{corr} approximation we were able to greatly improve the agreement between the theoretical and experimental results for positron elastic scattering from pyrazine in both ICS and FDCS. We associate this improvement due to a more accurate description of the long and short range positron interaction with the molecule, not feasible in any \textit{ab-initio} methods. These are no doubt encouraging results that goes into the direction of producing reliable integral and differential cross sections for several targets.
Data Availability

All data generated or analysed during this study are included in this published article (and its Supplementary Information files).

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**Author contributions statement**

A. de S. B. and S. d’A. S. conceived and supervised the study, F. F. F. conducted the calculations, all authors analysed the results and reviewed the manuscript.

**Competing interests**

The author(s) declare no competing interests.
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