A diffusion Monte Carlo accurate interaction potential between H and PsH

Massimo Mella\textsuperscript{a)} and Gabriele Morosi\textsuperscript{b)}

\textsuperscript{a)}Dipartimento di Chimica Fisica ed Elettrochimica, Universita’ degli Studi di Milano, via Golgi 19, 20133 Milano, Italy

\textsuperscript{b)}Dipartimento di Scienze Chimiche, Fisiche e Matematiche, Universita’ dell’Insubria, polo di Como, via Lucini 3, 22100 Como, Italy

(Received 20 September 1999; accepted 17 November 1999)

The interaction potential between H and PsH, and between H and H\textsuperscript{−} have been calculated using the diffusion Monte Carlo method. As far as the H−H\textsuperscript{−} system is concerned, our results appear to be the most accurate published so far. The potential functions show the H−PsH system to be bound with respect to the H\textsubscript{2}+Ps dissociation channel for nuclear distances larger than 3.5 bohr, while the H\textsubscript{2}−e\textsuperscript{−} threshold lies 0.25 hartree above for all the distances studied. Moreover, the H−PsH potential curve presents a minimum located at 5.2 bohr that can be attributed to the van der Waals interaction between the two fragments. The relevancy of these results for the low energy scattering of Ps on H\textsubscript{2} and for the exchange reaction of H with Ps is discussed.  © 2000 American Institute of Physics. [S0021-9606(00)31303-4]

During the last few years, the Positronium atom Ps = (e\textsuperscript{+}, e\textsuperscript{−}) has been used as a probe to collect valuable information in many branches of physics and chemistry. For instance, this light atom allows to study the free-volume holes in polymers,\textsuperscript{1} the surface of ionic crystals,\textsuperscript{2} and the spin conversion in metal-ligand complexes.\textsuperscript{3} Although the use of Ps as an analytical probe is spreading quickly, only few theoretical studies\textsuperscript{4–10} have been carried out to understand the complex interaction between this species and the surrounding matter.

Differently from any other atom, the light mass of Ps forbids the use of the Born–Oppenheimer approximation, forcing one to resort to nonadiabatic methods to study its complexes with atoms and molecules.\textsuperscript{4,5} Nevertheless, some attempts have been made to study the scattering of this species with light atomic and molecular targets.\textsuperscript{6–10}

Among the most recent studies we quote the work by McAlinden, MacDonald, and Walters,\textsuperscript{8} where the scattering between Ps and the two atomic targets He and Ar was considered. In that work, the problem was simplified by allowing only elastic scattering for the two targets, and neglecting the exchange interaction between the electrons of the atoms and of the Ps.

The total and elastic cross section in Ps scattering on a positively charged target was studied by Sur, Adhikari, and Ghosh\textsuperscript{7} for the H\textsuperscript{+}, Li\textsuperscript{+}, and Na\textsuperscript{+} systems. They used a coupled static close-coupling approximation for low and medium energies, obtaining results that are relevant for the Ps scattering on the surface of ionic crystals containing alkali metals.

As far as theoretical studies on molecular targets are concerned, we notice the work on the Ps–H\textsubscript{2} scattering by Comi, Prosperi, and Zecca;\textsuperscript{8} they studied both the elastic scattering and the vibrational excitation of H\textsubscript{2}, showing that, for kinetic energies of the Ps below its excitation threshold, the contribution of the inelastic scattering to the total cross section is three orders of magnitude smaller than the elastic one. For the same system, Biswas and Ghosh,\textsuperscript{9} and Biswas and Adhikari\textsuperscript{10} pointed out the necessity of including both the excitation and the dissociation channels of the Ps and the possible electronic excitation of H\textsubscript{2} in computing the cross section for kinetic energies larger than the Ps dissociation threshold. Although a direct comparison of the three cited studies on Ps–H\textsubscript{2} is made complex by the different methods and approximations used, the results show that all the studied components of the inelastic cross section can play an important role in defining the total cross section for these systems in the explored energy range.

A different way of looking at this problem is given by considering the H+H+Ps three body collision system as a prototypical model for the matter–antimatter interaction and collision, and employing a chemical frame of mind to study the possible reactions,

\begin{align*}
\text{Ps} + \text{H}_2 &\rightarrow \text{H} + \text{PsH}, \\
\text{Ps} + \text{H}_2 &\rightarrow \text{H} + \text{Ps}, \\
\text{Ps} + \text{H}_2 &\rightarrow \text{H}_2 + e^+ \rightarrow \text{H} + \text{H}^- + e^+, \\
\text{PsH} + \text{H} &\rightarrow \text{H} + \text{PsH}.
\end{align*}
Here, reaction (1) represents the exchange reaction between H and its lighter isotopic analog Ps.

The possibility to produce PsH atoms in a methane-positron crossed molecular beam, as shown by Schrader and co-workers,\textsuperscript{11} opens up the chance to study directly the reaction between this exotic atom and the ordinary matter. Differently from the similar H+H+e\textsuperscript{−} problem, the theoretical analysis of these systems requests the use of nonstandard numerical tools that allow one to correctly describe all the important features of the positron–electron interaction in molecular systems.

In our previous works, we showed the ability of quantum Monte Carlo (QMC) to cope with these systems, and to compute accurate values for various properties.\textsuperscript{5} With the goal to understand the reactions reported above, in this study we computed the potential energy surface for the two systems H–PsH and H–H\textsuperscript{−} using the diffusion Monte Carlo method in the fixed node approximation (FN-DMC). Since all the QMC methods are well described in the literature,\textsuperscript{12} we restrict ourselves to present only few important details, referring the reader to our previous works for further information.

For the two studied systems we approximate the ground state wave function by the analytical model,\textsuperscript{5}

\[ \Psi_f(R) = A[C_{symm} \prod_{\mu=1}^{N_P} U(r_{\mu}, k_{\mu}) | \Theta_p \Theta_p] \]  

where A is the antisymmetrization operator, C_{symm} is an operator used to fix the spatial symmetry of the state, \( \Theta_p \) and \( \Theta_p \) are the spin eigenfunctions for electrons and positron. In Eq. (5) the index \( \mu \) runs over the \( N_P \) interparticle distances \( r_{\mu} \), and the term \( U(r_{\mu}, k_{\mu}) \) is a Padé factor whose analytical form is

\[ U(r_{\mu}, k_{\mu}) = \exp \left[ \frac{k_{\mu,1}r_{\mu} + k_{\mu,2}r_{\mu}^2}{1 + k_{\mu,3}r_{\mu}^2} \right] \]  

\( k_{\mu} \) is a vector of three nonlinear parameters for the \( \mu \)th distance of the exponential term. The parameters of the trial wave function were optimized for all the distances studied in this work minimizing the variance of the local energy over a fixed set of walkers in configuration space. Since diffusion Monte Carlo is able to compute exactly the total energy of a nodeless system, the unique approximation in our calculation is due to the choice to use the nodal surface of our model function as the correct one. Nevertheless, comparing the energy values in our previous work with the accurate results obtained by means of a linear expansion in terms of explicitly correlated Gaussians, we found optimal agreement between the values obtained with the two methods even for the H–H\textsuperscript{−} system.

The parameters of the trial wave function are available from the authors upon request. We present the diffusion Monte Carlo results for the H–H\textsuperscript{−} and the H–PsH interactions in Table I and Table II, respectively.

As far as \( H_2^− \) is concerned, the most accurate results published so far are the ones obtained by Senekowitsch et al.\textsuperscript{13} by means of the coupled electron pair approximation (CEPA). These results are reported in Table I together with the Monte Carlo ones for comparison. Although their results were obtained using a large basis set and a multiconfigurational procedure, from Table I it is possible to see that they lay 1 mhartree above the Monte Carlo results, therefore showing the accuracy of the nodal structure of our model functions. A more stringent test of the accuracy of the nodal surfaces is given by comparing our results with the CEPA ones\textsuperscript{13} after shifting them by −0.797 mhartree, i.e., the difference between the CEPA asymptotic value of the energy, \( −1.026\,954 \) hartree, and the exact one,\textsuperscript{14} \( −1.027\,751 \) hartree. This shift can give the exact energies for every nuclear distance only if the difference between the exact and CEPA values remains constant on going towards shorter bond lengths. Even after the shift, the diffusion Monte Carlo results lay below the CEPA values, the difference being approximately 0.1 mhartree. Remembering that Monte Carlo results are strictly upper bounds to the exact energy, the comparison between the CEPA and our results evidences the good quality of the nodal surface of our wave function.

As far as H–PsH is concerned, comparing the Monte Carlo results in Tables I and II one can see that the total energy for H–PsH lies almost 0.25 hartree below the \( H_2^− \) plus a free positron energy, i.e., the positron affinity of \( H_2^− \) is roughly equal to the Ps ground state energy. We feel that this result reflects the differences of the leptonic structure in the two systems, i.e., the existence in the H–PsH system of the Ps moiety polarized by the two H atoms. The other possibility could be to have a positron bound to the H–H\textsuperscript{−} system by means of the Coulomb interaction, but in this case the positron affinity should be twice as large as the one we com-

\begin{table}[h]
\centering
\caption{DMC and CEPA ground state energy (hartree) for the H$_2^-$ system.}
\begin{tabular}{lrr}
\hline
R (bohr) & \( E_{\text{DMC}} \) & \( E_{\text{CEPA}} \) \\
\hline
5.0 & $-1.0435 \, 25(1)$ & $-1.042 \, 325$ \\
4.8 & $-1.044 \, 28(1)$ & \\
4.6 & $-1.045 \, 30(1)$ & \\
4.4 & $-1.046 \, 48(1)$ & \\
4.0 & $-1.048 \, 97(1)$ & $-1.048 \, 009$ \\
3.5 & $-1.052 \, 65(3)$ & $-1.051 \, 603$ \\
3.25 & $-1.055 \, 02(1)$ & $-1.054 \, 062$ \\
3.2 & $-1.055 \, 71(1)$ & \\
3.0 & $-1.058 \, 87(2)$ & $-1.057 \, 900$ \\
2.98 & $-1.059 \, 32(1)$ & \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{DMC ground state energy (hartree) for the H–PsH system.}
\begin{tabular}{lrr}
\hline
R (bohr) & \( E_{\text{DMC}} \) \\
\hline
3.5 & $-1.2874(3)$ \\
3.8 & $-1.2892(3)$ \\
4.0 & $-1.2906(2)$ \\
4.2 & $-1.2923(2)$ \\
4.5 & $-1.2936(2)$ \\
5.0 & $-1.2954(3)$ \\
5.5 & $-1.2950(2)$ \\
6.0 & $-1.2935(2)$ \\
6.5 & $-1.2933(3)$ \\
7.0 & $-1.2926(1)$ \\
8.0 & $-1.2904(2)$ \\
\hline
\end{tabular}
\end{table}
As far as the reverse process is concerned, our results show that the collision between Ps and a vibrationally excited H₂ might result in H and PsH. Specifically, if one compares the energy difference between the minimum of the H₂+Ps potential energy and the energy of the crossing point between the two curves, i.e., 0.1371(3) hartree, with the 2p→1s excitation energy of 0.1875 hartree for the Ps, it clearly appears that even in the Ps elastic collision regime this process is energetically allowed. Therefore, with the goal to better understand the collision dynamic of the Ps on H₂ and to explore the possibility to induce the Ps–H exchange reaction, we think it is worthwhile to expand the study by Comi et al. introducing higher vibrational excitations in H₂ in order to compute the cross sections for the various allowed processes. A similar work was carried out by Bardsley and Wadephra for the H+H+e⁻ system, showing that the dissociation of H₂ induced by the collision with the electron is quite important, as well as the excitation to higher vibrational states.

Concluding, in this work we carried out the most accurate calculation for the H–H⁻ system for various H–H distances, as well as the first calculation of the potential energy curve for the H–PsH system using the diffusion Monte Carlo method. Our energy results allowed us to discuss the difference in the leptonic structure between the two systems as well as the possible dissociation patterns during a collisional event. Future work might address the potential energy between excited states of both the H and PsH systems.

The authors would like to thank Matteo Malgrati for the help in carrying out some of the calculations on H₂. Financial support by the Universita’ degli Studi di Milano is gratefully acknowledged. The authors are indebted to the Centro CNR per lo Studio delle Relazioni tra Struttura e Reattività’ Chimica for grants of computer time. Also, this work has benefited from a Postdoctoral fellowship of M.M.