Two atoms scattering at low and cold energies

HASI RAY[1,2,3]

[1]National Institute of Technical Teachers' Training and Research Kolkata, Salt Lake City,
Kolkata 700 106, India
[2]New Alipore College, New Alipore, Kolkata 700 053, India
[3]Study Centre, S-1/407/6, B. P. Township, Kolkata 700 032, India
E-mail: hasi_ray@yahoo.com; hasi.ray1@gmail.com

Abstract. A modified static-exchange model is developed to study the collision of an atom with another atom. It includes the effect of long-range dipole–dipole van der Waals interaction between two atoms in addition to the exact effect of short-range force due to Coulomb exchange between two system electrons. Both these interactions dominate at colder energies. The system is treated as a four-centre problem in the centre-of-mass frame. The present *ab-initio* model is useful to study the two-atomic collisions at low energies, as well as cold energies. The new code is applied to study the scattering of positronium (Ps) by hydrogen (H), both in their ground states.

A modified static-exchange model (MSEM) is introduced to study the collision of an atom with another atom. The model includes the exact effect of short-range electron–electron exchange [1–6] and the effect of long-range dipole–dipole van der Waals interaction between two atoms [7,8]. Both these interactions gradually dominate as the system moves towards the colder energy region. The system was studied as a four-centre problem in the centre-of-mass (CM) frame. In the static-exchange model (SEM), the Schrödinger equation is solved by following the coupled-channel methodology [5,9] using angular momentum algebra, partial wave analysis and by considering all the Coulomb interaction terms exactly with exchange/antisymmetry between the system electrons. It is an exact and *ab-initio* model and is useful for studying low-energy atomic collision phenomena. But, the model includes no dipole–dipole interaction. In the present MSEM, the SEM is modified by including the effect of dipole–dipole van der Waals interaction between the atoms. The minimum value of interatomic separation (R_0) is an important parameter to

determine the strength of effective interatomic potential, as van der Waals interaction is defined as

$$V_{\text{van}}(R) = -\frac{C_W}{R^6},\tag{1}$$

where C_W is the van der Waals coefficient that mainly depends on the dipole polarizabilities of the two atoms [10] and R represents the interatomic distance.

Figure 1a presents the picture of two atoms with nuclei A and B attached with electrons 1 and 2, respectively. The corresponding picture of variation of the interatomic potential is shown in figure 1b. When two atoms are far apart, i.e. $R \to \infty$, the potential is almost zero indicating no interaction between the atoms. When they proceed to each other, i.e. R decreases, the potential starts becoming more and more negative and reaches a minimum value at $R = R_{\min}$, i.e. the attraction is maximum between the two atoms. The attraction gradually decreases when R is less than $R_{\min}$. So, the potential gradually increases, becomes zero when the interatomic separation is R_0. The interatomic potential starts to be sharply positive when R is less than R_0, where R_0 is the minimum value of the interatomic separation due to strong static Coulomb interaction between the atoms. So, the atoms begin repelling each other strongly and cannot proceed further towards each other.

Accordingly, the long-range van der Waals potential is defined as

$$\int d\vec{r}_{1A} \int d\vec{r}_{2B} \int d\hat{R} \int_{R=R_0}^{\infty} dR R^2 \left[\psi^*(\vec{R}, \vec{r}_{1A}, \vec{r}_{2B}) \left\{ -\frac{C_W}{R^6} \right\} \psi(\vec{R}, \vec{r}_{1A}, \vec{r}_{2B}) \right],\tag{2}$$

ψ represents the system wavefunctions. Here, $\vec{r}_{1A}$ and $\vec{r}_{2B}$ represent position vectors of the atomic electrons from their corresponding nuclei A and B, respectively; $\vec{R}$ is the interatomic separation. How to determine the value of R_0 is an important question to evaluate the potential. No information is available in literature. In hydrogen molecule, the internuclear separation is 1.48 a.u. [11], but, the molecule formation is possible only when the two electrons are in singlet (antiparallel spins) state. According to the definition of Lennard–Jones (LJ) 6-12 potential, the LJ parameter σ should be equal to R_0 and it is 5.3 a.u. [12] for H–H system. However, in a cold atomic system, when the atoms are very slow, the density and temperature of the atoms in the system seem to control the value of R_0.
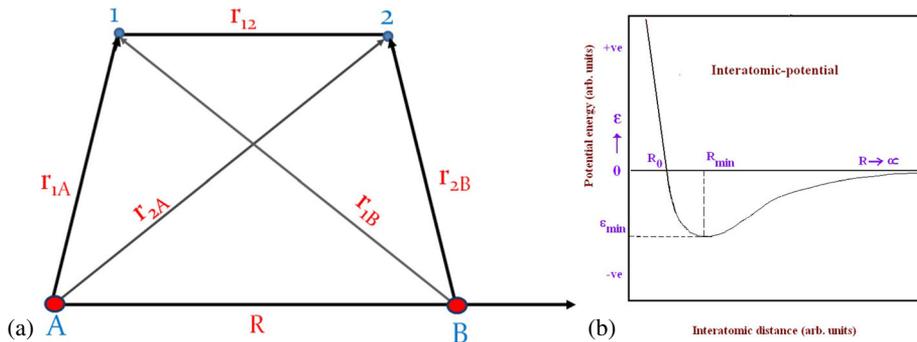

Figure 1. (**a**) A two-atomic system. (**b**) The form of interatomic potential.

Barker and Bransden [7] described the van der Waals interaction of such two-atomic systems as

$$V_{\text{van}}(R) = 0, \quad \text{if } R < R_0$$

and

$$V_{\text{van}}(R) = -\frac{C_W}{R^6}, \quad \text{if } R \geq R_0 \text{ when } R_0 \to 0. \tag{3}$$

At higher energies (i.e. normal temperatures), the atoms move much faster. Accordingly, they acquire greater kinetic energies to overcome the interatomic repulsive barrier and move closer to each other. As a result, the minimum distance between the two atoms (R_0) can be almost equal to zero. But at cold environment, e.g. in upper atmospheres or in cold atomic systems in the laboratory, the atoms are very slow having less kinetic energies. At the same time, their densities are very poor as in optical lattices or upper atmosphere. So, it is not possible for R_0 to become zero and it should vary with the temperature (e.g. the kinetic energy) and the density (e.g. the average interatomic separation) of the medium in addition to atomic properties of the atoms. The effective interatomic potential following Lennard–Jones 6-12 potential contains the short-range repulsive electron–electron exchange correlation part $\sim R^{-12}$ and the long-range attractive dipole–dipole interaction part $\sim R^{-6}$. In principle, the short-range electron–electron exchange force is repulsive, if the electron spins form a triplet state ($S = 1$) and it is attractive if the spins form a singlet state ($S = 0$). Very recently, the scientific community realizes the need of quantum control of isolated atomic system with nanoscale localization [13] instead of the collective motion of atoms as new possibilities of quantum control of ultracold atoms [14].

In this study, the present SEM and MSEM codes (considering them as a four-centre problem) were applied to study the collision of positronium (Ps) with hydrogen (H), both are in ground states. Here, Ps has a very high polarizability (eight times higher than H) to make van der Waals interaction stronger. Earlier, Ray *et al* [5] studied the system exactly using the static-exchange approximation in the CM frame considering it as a three-centre problem; as Ps is a very light atom, it is a very good assumption. The detailed theory about the SEM is available in ref. [5].

The initial and final channel wave functions are defined as

$$\psi_i = e^{i\vec{k}_i \cdot \vec{R}} \phi_{1s}(r_{1A}) \phi_{1s}(r_{2B}), \tag{4}$$

$$\psi_f = (1 \pm P_{12}) e^{i\vec{k}_f \cdot \vec{R}} \phi_{1s}(r_{1A}) \phi_{1s}(r_{2B}). \tag{5}$$

Here $\phi_{1s}(r_{1A})$ and $\phi_{1s}(r_{2B})$ are ground-state wave functions of the two atoms and P_{12} is the exchange (or antisymmetry) operator.

The effective range theory correlates the s-wave elastic phase shift (δ_0) and the incident energy ($\sim k^2$) with the scattering length and range of the potential according to the relation:

$$k \cot \delta_0 = -\frac{1}{a} + \frac{1}{2} r_0 k^2. \tag{6}$$

So, one can easily determine the scattering length (a) and effective range (r_0) from the $k \cot \delta_0$ vs. k^2 plot.

A highly efficient computer code was developed using the non-relativistic Schrödinger theory and FORTRAN programing. The code can calculate the elastic phase shift and cross-section for both the singlet ($S = 0$) and the triplet ($S = 1$) channels, using a partial wave analysis, e.g. $L = 0$ indicates s-wave, $L = 1$ indicates p-wave, etc. In addition, an augmented Born approximation was used to include the contribution of higher partial waves as accurately as possible to calculate integrated/total elastic cross-sections. Here all the SEM data [5] are reproduced using the present code; all of them are exactly the same. Different values of R_0 were chosen to vary the effective interatomic potential in the MSEM code to study the variation of scattering length (a) and the range (r_0) at the cold energy region. The most accurate value of the van der Waals coefficient reported by Mitroy *et al* [10] was used to include the van der Waals potential. The s-wave elastic phase shift (δ_0) and the corresponding cross-section (amplitude-square) were computed using the present new code. Both the singlet ($S = 0$) and triplet ($S = 1$) channels were studied here. According to literature, the singlet ($+$) channel is responsible for the molecule formation [15] and the ($-$) channel is responsible for the BEC formation [16].

In figure 2, the s-wave (i.e. putting angular momentum $L = 0$ in partial wave analysis) elastic phase shifts (δ_0) are presented for the singlet ($+$) and triplet ($-$) channels of Ps–H scattering by varying the collision energy (E) for $R_0 = 2.5, 3, 4, 5, 7$ and 10 a.u. These
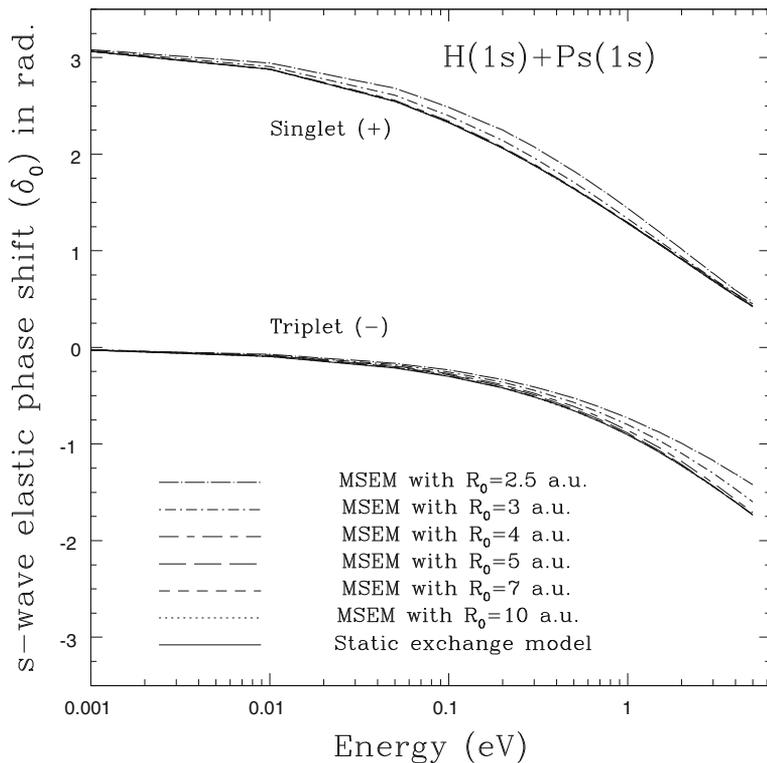

Figure 2. The variation of s-wave elastic phase shift for the singlet ($+$) and triplet ($-$) channels using SEM and MSEM for $R_0 = 2.5, 3, 4, 5, 7$ and 10 a.u.
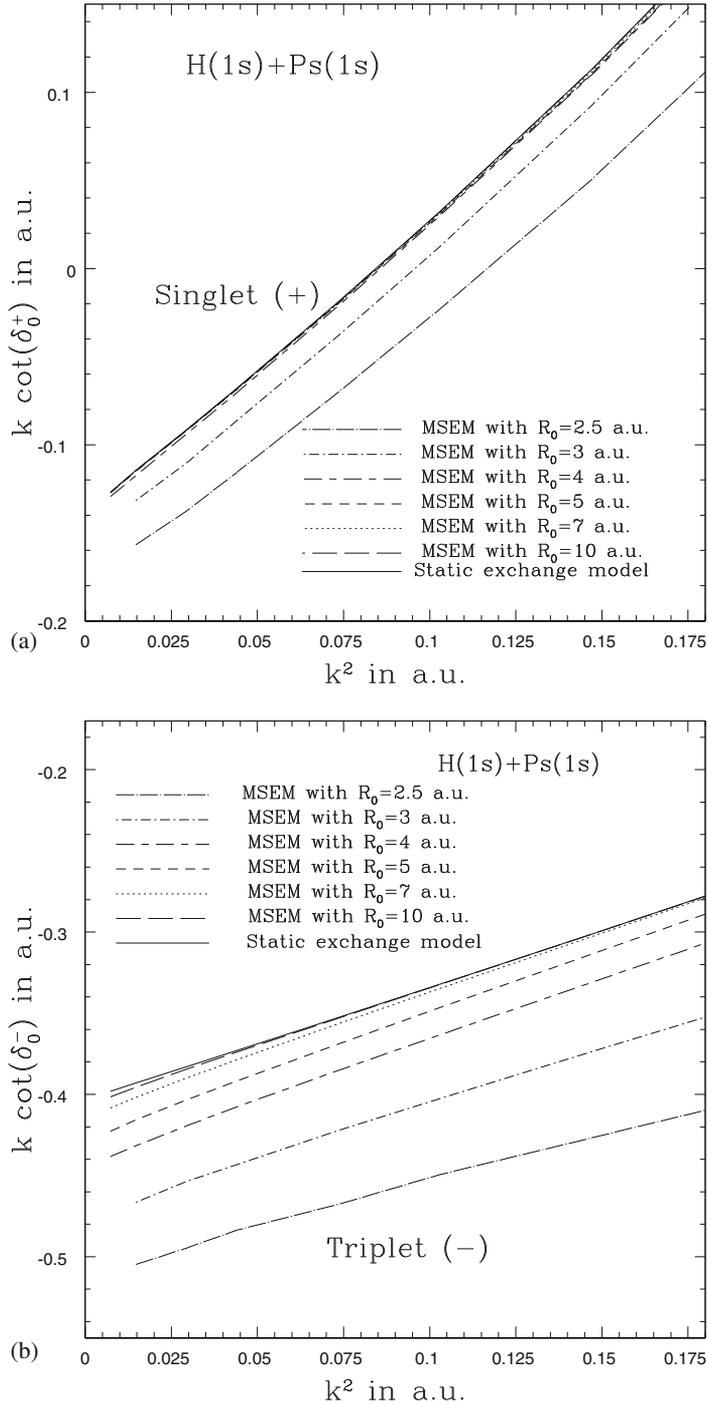
Figure 3. The variation of $k \cot \delta_0$ vs. k^2 using SEM and MSEM for $R_0 = 2.5, 3, 4,$ 5, 7 and 10 a.u. **(a)** for the singlet $(+)$ channel and **(b)** for the triplet $(-)$ channel.

Table 1. The s-wave elastic scattering lengths (a) and effective ranges (r_0) in atomic units for electron spin singlet ($+$) and triplet ($-$).

Parameters	SEM data	MSEM data						Data of others
		$R_0 = 10a_0$	$R_0 = 7a_0$	$R_0 = 5a_0$	$R_0 = 4a_0$	$R_0 = 3a_0$	$R_0 = 2.5a_0$	
$a(+)$	7.25	7.22	7.19	7.14	7.04	6.17	5.32	4.5[a], 5.22[b], 5.20[c], 5.84[d], 3.49[e], 4.30[f]
$r_0(+)$	3.79	3.78	3.77	3.75	3.74	3.73	3.48	2.2[a], 2.90[d], 2.08[f]
$a(-)$	2.49	2.45	2.43	2.36	2.27	2.12	2.02	2.36[a], 2.41[b], 2.45[c], 2.32[d], 2.46[e], 2.2[f]
$r_0(-)$	1.42	1.41	1.40	1.38	1.34	1.28	1.19	1.31[a]

[a]Stabilization calculation of Drachman and Houston [15].
[b]Close-coupling calculation of Sinha *et al* [19].
[c]R-matrix calculation of Blackwood *et al* [20].
[d]Kohn variational calculation of Page [21].
[e]Variational calculation of Adhikari and Mandal [22].
[f]Stochastic variational calculation of Ivanov *et al* [23].

were compared with the SEM data in the energy range 10^{-3} to 10^0 eV in the same figure. The results are in good agreement. At $R_0 = 10$ a.u., the phase shift data using the MSEM exactly coincide with the SEM data (the solid and the dotted curves). It indicates that there is a negligible effect of dipole–dipole interaction on interatomic potential, if there is no possibility for the two atoms to be closer than 10 a.u. When $R_0 = 7$ a.u., we observed all the *s*-wave elastic phase shifts to be slightly greater than static-exchange data. It indicates the presence of dipole–dipole van der Waals interaction on SEM potential. Similar trends are observed in all the data, i.e. the phase shifts are always greater as we increase the strength of dipole–dipole interaction, e.g. when R_0 decreases as 5, 4, 3 and 2.5 a.u. Again the triplet channels are more sensitive to dipole–dipole long-range interaction than the corresponding singlet channels. The effect of dipole–dipole interaction is seen even when $R_0 = 1000$ a.u.; there is very little increase in phase shift on 5th or 6th decimal places. All the observed facts are consistent with the existing physics [3,17,18]. The corresponding amplitude squares (cross-section) also show a similar consistency in agreement but are not presented here. If readers are interested, these are available at author's contribution in arXiv:1308.1939, maintained by Cornell University Library, USA.

To evaluate the scattering lengths, the effective range theory is useful. $k \cot \delta_0$ is plotted against k^2 to evaluate $-1/a$ in figure 3a for singlet channel and in figure 3b for triplet channel. The scattering length (a) varies systematically by varying R_0 as $2.5a_0$, $3a_0$, $4a_0$, $5a_0$, $7a_0$ and $10a_0$. The variation of the computed scattering lengths and ranges using different values of R_0 are presented in table 1 and compared with the SEM data and available data [15,17–21]. When $R_0 = 10a_0$ or greater, all the data almost coincide with the SEM data. There is always a very small difference between the SEM data and MSEM data, almost upto $R_0 = 50a_0$, indicating the long-range behaviour of the potential. Here, all the scattering lengths are positive, indicating the possibility of binding and the presence of Feshbach resonances. The variation of triplet scattering length is more sensitive to long-range interaction than to singlet scattering length.

In conclusion, the author introduced a modified static-exchange model (MSEM) and constructed a computer code successfully to study two-atomic interactions by considering it as a four-centre problem. The code is highly efficient to provide valuable basic information on the interatomic potential and forces at low and cold energies.

Acknowledgement

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