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A route to inversion for rotational collisions using hard shape potentials [1]

J.C. Belchior, J.P. Braga

Departamento de Química, ICEx, Universidade Federal de Minas Gerais, Pampulha, 31270 Belo Horizonte, MG, Brazil

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Abstract

The collision energy and the semiaxes of the hard ellipsoid are related by an analytical expression to obtain the parameters K, and either the range of the potential, α, or the anisotropy of the potential, δ, for the potential model $V(r, \theta) = Ke^{-\alpha r}(1 + \delta^2 \cos^2\theta)$. The hard shape theory has been used to optimize the semiaxes of the ellipsoid by fitting cross sections to quantum results. This inversion procedure showed an average error of 7% in the α or δ parameter and about 15% in the K parameter.

1. Introduction

Generally, the main aim for studying atom–diatomic rotational collisions is to obtain information about the intermolecular potential. It is well recognized that inelastic cross sections can provide such information.

Most of the studies in rotational scattering often are for obtaining accurate inversion procedures, i.e., from the experimental data the potential parameters might be obtained. For an atom–atom elastic collision such a procedure can generally provide potentials with high accuracy [1–3]. However, for more complicated systems, the available methods involve a trial and error procedure.

For atom–diatomic molecule collisions rotational scattering has been studied using different approaches [4–6]. For example, applying the IOS method, Schinke [7] has obtained accurate results by fitting rotational cross sections for He–Na_2. However, this was carried out for a single collision energy. For several energies, Gislason et al. [8] have determined the spherical part of the interaction potential for Li^+–N_2 and Li^+–CO collisions. They compared the inversion results with other works and the spherically symmetric part of the potential agreed well with the experiments of Botter et al. [9] and Eastes and co-workers [10].

Treating collisions within a hard potential impulsive model, Bosanac and Petrovic [11] have proposed a new approach called hard shape quantum theory. Murrell and Bosanac [12] have applied such a method for fitting state-to-state atom–diatomic rotational cross sections with high accuracy. Such a method has been also applied to atom–polyatomic symmetric

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top molecule collisions [13] and satisfactory results were achieved. Recently Belchior and Murrell [14] have proposed an inversion procedure applied to atom–heteronuclear diatomic molecule collisions using hard shape potentials for quantum mechanical calculations. They showed that one can map out the repulsive soft potential, which can define hard shape surfaces, at different collision energies. Their inversion method showed, for the softest derived potential ($\alpha = 4$ Å^{-1}), an error of about 10% for the cross sections, which is small compared with experimental errors. For example, for Ar–HF, Rawluk and coworkers [15] have recently found, measuring differential cross sections with state resolved inelastic scattering, errors between 10–30%.

This paper aims to obtain the parameters of the interaction potential (K, α or δ) by optimizing the hard shape potential. However, a full fitting to cover the whole set of parameters is not possible in this approach and therefore one chooses either α or δ. For completeness we have chosen the spherical parameters, namely K and α, although one could choose K and δ instead.

As either experimental or theoretical data are not available for a wide range of collision energies we will carry out the inversion procedure assuming a soft repulsive potential model to calculate state-to-state quantum cross sections. These data will be taken as the experimental results. Our successful procedure will be those that the outcome fitted parameters turn out to be the same as those previously chosen for the spherically symmetric potential model.

2. Theoretical model

For an atom–diatomic rotational collision using a soft repulsive potential of the type

$$V(r, \theta) = V(r)(1 + \delta^2 \cos^2\theta), \tag{1}$$

where

$$V(r) = K\mathrm{e}^{-\alpha r} \tag{2}$$

the classical turning point for the above potential (Eq. (1)) at $\theta = 0$ (r_A) and $\theta = \pi/2$ (r_B) is given by

$$r_A = \frac{-1}{\alpha}\ln\left(\frac{E}{K(1+\delta^2)}\right) \tag{3}$$

and

$$r_B = \frac{-1}{\alpha}\ln\left(\frac{E}{K}\right). \tag{4}$$

Korsch and Schinke [16] showed that, in the hard ellipsoid model with main semiaxes A(major) and B(minor), the following shape can be obtained:

$$r(\theta) = B\left(1 + \tfrac{1}{2}\epsilon^2 \cos^2\theta\right), \tag{5}$$

where

$$\epsilon = \frac{(A^2 - B^2)^{1/2}}{A}. \tag{6}$$

For systems with small eccentricity ϵ, the classical turning point surfaces can be written as

$$r_c(\theta) = B - E\delta^2(\partial r/\partial V)_{V=E}\cos^2\theta. \tag{7}$$

Equating Eqs. (5) and (7) and rearranging the results one obtains

$$(\partial V/\partial r)_{V=E} = \frac{E\delta^2}{B - A}. \tag{8}$$

It can be shown, using Eq. (2), that the range of the potential is given by

$$-\frac{1}{E}(\partial V/\partial r)_{V=E} = \alpha. \tag{9}$$

It can be observed that the range of the potential, α, and the anisotropic parameter, δ, are related by a constant value if Eqs. (8) and (9) are compared. Therefore, for a given δ or α, either Eq. (8) or (9) can be used to calculate the values of the first derivative of the potential. For our initial propose, i.e., to obtain the spherical parameters K and α, the hard shape radii can be used to calculate the range of the potential [14].

It can be shown, using Eq. (2) at the classical turning point, that the amplitude is given by

$$K = E\mathrm{e}^{\alpha r_h}, \tag{10}$$

where r_h is defined as the hard shape radius [14].

Taking N_2–Ne system for testing the procedure and assuming the following soft repulsive potential model

$$V(r, \theta) = 0.69\mathrm{e}^{-3.39r}(1 + 0.3\cos^2\theta), \tag{11}$$

state-to-state total cross sections can be evaluated by solving the multichannel equations. To fit such cross

sections the following hard shape potential has been used

$$V(r)=\infty, \quad \text{if } r\leqslant f(E,\theta),$$
$$V(r)=0, \quad \text{if } r>f(E,\theta). \tag{12}$$

The hard shape function, $f(E,\theta)$, is written as

$$f(E,\theta)=M(E)+N(E)\cos^2\theta, \tag{13}$$

where $M=B$ and

$$N=\frac{B}{2A^2}(A^2-B^2). \tag{14}$$

3. The basic equations for the hard shape model

Although the hard shape theory is well detailed in Refs. [11,13], the key equations to calculate the hard shape state-to-state cross sections will be given below. First it is necessary to solve a set of linear coupled equations

$$\sum_{jm}F^{Jm_o}_{j_om_o;jm}\sum_l i^{l+1}(2l+1)C(ljJ;0m)\times C(ljJ;0m')W^+_{jl;j'm'}+\frac{1}{k_{j_o}}\sum_l i^l(2l+1)C(lj_oJ;0m_o)\times C(lj_oJ;0m')W^-_{j_ol;j'm'}=0, \tag{15}$$

where

$$W^+_{jl,j'm'}=\int \mathrm{d}\Omega\,\left(r^j_h\right)^{1/2}Y^*_{j'm'}H^{(1)}_{l+1/2}\left(r^j_h\right)Y_{jm'}, \tag{16}$$

and

$$W^-_{j_ol,j'm'}=\int \mathrm{d}\Omega\,\left(r^{j_o}_h\right)^{1/2}Y^*_{j'm'}J_{l+1/2}\left(r^{j_o}_h\right)Y_{j_om'}, \tag{17}$$

where

$$r^j_h=f(E,\theta)k_j, \tag{18}$$

and $J_{l+1/2}$ and $H^{(1)}_{l+1/2}$ are respectively the spherical Bessel and Hankel functions [13].

The total cross sections are calculated after solution of (15) which will provide the $F^{JM}_{jm,j'm'}$, coefficients. Summing over final m_j values and averaging over initial m_j gives the total cross section

$$\sigma_{j,j'}=\frac{4\pi}{2j+1}\frac{k_{j'}}{k_j}\sum_J\sum_{m=-j}^{j}\sum_{l'=|J-j'|}^{J+j'}\times(2l'+1)\left|\sum_{m'=-j'}^{j'}F^{JM}_{jm,j'm'}C(l'j'J;0m')\right|^2. \tag{19}$$

4. Discussion

Although the soft potential model (Eq. (1)) chosen to calculate state-to-state rotational cross sections is one of the simplest models, one can argue that in some circumstances simple models can provide qualitative informations concerning the interaction of the colliding particles. It is the case for systems with small anisotropy such as He–H_2 collisions. It is also accepted that rotational excitation is generally governed by the repulsive part of the interaction. Therefore this inversion procedure, using the potential model, Eq. (11), might give details for understanding inversion data.

The converged cross sections as a function of collision energy are obtained by integrating the coupled equations following Arthurs and Dalgarno's method [17] and are given in Table 1. These data have been taken to be the experimental cross sections. For each collision energy the hard shape parameters, M and N, were calculated using a standard least-squares approximation with equal weights for the data points and the hard shape theory. The optimized cross sections and the optimum semiaxes of the ellipsoid or the hard shape parameters as a function of collision energy are given in Table 2.

Table 1
CC inelastic cross sections from the potential (11)

E_c (meV)	$\sigma_{0j'}$ (Å^2)		
	$j'=2$	$j'=4$	$j'=6$
46.0	1.152	0.0897	0.0
66.0	1.159	0.1302	0.007
86.0	1.121	0.1576	0.012
106.0	1.071	0.1740	0.017

Table 2
Optimized cross sections and the optimum A and B semiaxes of the ellipsoid and the hard shape parameters $M = B$ and N

E_c (meV)	$\sigma_{0j'}$ (Å^2)			M (Å)	N (Å)	A (Å)
	$j' = 2$	$j' = 4$	$j' = 6$			
46.0	1.152	0.0897	0.0	1.127	0.0872	1.226
66.0	1.159	0.1302	0.007	1.013	0.0849	1.110
86.0	1.121	0.1576	0.012	0.941	0.0818	1.035
106.0	1.071	0.1740	0.017	0.891	0.0728	0.981

Table 3 compares the parameters A and B with the analytical results given by Eqs. (3) and (4). Small differences between the actual data and the inverted ones are observed. Such differences can be first attributed to the expansion which ends up to Eq. (5) that is considered for small ϵ. However, to provide rotational excitation (torque), it is necessary to balance the latter parameter. Such errors can be also attributed to that previously pointed out in Ref. [14].

It is recognized that the hard shell model has limitations such as to overestimate the differential cross section in the backward direction and to underestimate it in the forward direction. These limitations are mainly due to the tail of the potential or the tunnel effect and both are certainly not present in the hard shape model.

The tunnel effect was analyzed in terms of the phase shift for spherical potential models as [18]

$$\delta = \tan^{-1}\left(-\epsilon^{1/3}\frac{\mathrm{Ai}(-\epsilon^{2/3})}{\mathrm{Ai}'(-\epsilon^{2/3})}\right) - \varepsilon - kA, \qquad (20)$$

where

$$\epsilon = k/\alpha, \qquad (21)$$

and k is the wavenumber, Ai is the Airy function and Ai′ its derivative. It was concluded that the slow convergence (roughly as $\alpha^{-1/3}$) of the elastic phase shift is mainly due to the importance of the tunnelling into the soft potential.

Recently, however, Belchior and Murrell have re-analyzed the tunnel effect and the tail of the potential for a hetero-nuclear diatomic molecule [14] and they showed that using hard shape potentials one has usually a shift in the hard shape radii, r_h. They showed for a repulsive potential that the tunnelling effect pushes back the wave function, decreasing the $l = 0$ phase shift, while the tail of the potential pulls out the wave function, increasing the $l = 0$ phase shift. The conclusion was that, on balance, the tail of the potential has a bigger influence than the tunnel effect. Because of the great influence of the tail of the potential, which is not present in the hard shape model, they have argued that the hard shape radii should always be greater than the equivalent soft potential contour. Therefore they have found better results by subtracting a quantity from the elastic part of the hard shape radii.

Fig. 1 compares the soft repulsive potential at $\theta = 0$, Eq. (11), with the hard shape parameter N and the parameters A and B. The same kind of shift as discussed above can be seen.

Following Belchior and Murrell's method we therefore should subtract the factor corresponding to

Table 3
Comparison of the optimized parameters A and B with their respective values subtracting α^{-1} and the analytical parameters r_A (Eq. 3) and r_B (Eq. 4)

E_c (meV)	A (Å)	B (Å)	$(A-\alpha^{-1})$ (Å)	$(B-\alpha^{-1})$ (Å)	r_A (Å)	r_B (Å)
46.0	1.226	1.127	0.896	0.797	0.876	0.799
66.0	1.110	1.013	0.786	0.689	0.770	0.692
86.0	1.035	0.941	0.722	0.628	0.692	0.614
106.0	0.981	0.891	0.681	0.591	0.630	0.553

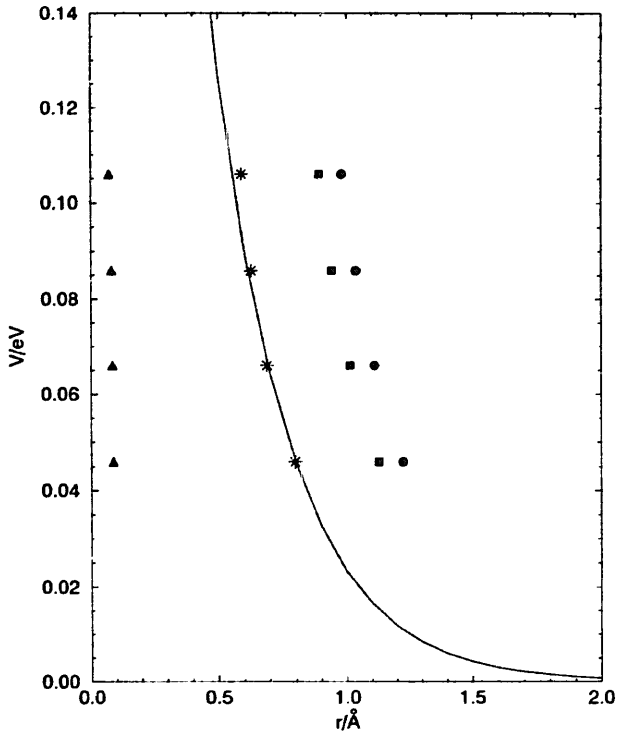

Fig. 1. The soft repulsive potential, Eq. (11), at $\theta = 0$ (full line) compared with the hard shape parameter N (black triangles), with the ellipsoid parameters A (black dots) and B (black boxes), and $A - \alpha^{-1}$ (stars).

the main contribution to the shift which is the tail of the potential. According to their procedure it is $1/\alpha'$.

For obtaining the amplitude of the potential Eq. (10) was used with α' previously determined as described above and the results are shown in Table 4. Taking the average for all α one finds 3.16 Å^{-1} which can be considered satisfactory compared with the exact value 3.39 Å^{-1}. A very accurate result can also be obtained for the average $K = 0.80$ eV compared to 0.69 eV.

Table 4
Range of the potential, α, obtained from (9) and K obtained from (10); the exact values are $\alpha = 3.39$ Å^{-1} and $K = 0.69$ eV

E_c (meV)	α (Å^{-1})	$r_h = (M+N)$ (Å)	K (eV)
46.0	3.03	0.884	0.67
66.0	3.09	0.774	0.72
86.0	3.19	0.710	0.83
106.0	3.33	0.669	0.98
average	3.16		0.80

5. Conclusion

We have shown that the above procedure produces at least qualitative results for the parameters of the potential model and therefore it might be used in a simple way to invert experimental data since one takes into account that the system should have small anisotropy.

The state-to-state rotational cross sections recently obtained according to Ref. [14], using the inverted potential, showed an average error of 10%. The amplitude of such an inverted potential could not be compared with the initial parameter because in their procedure it was necessary to minimize the fitted data. Although the hardness parameter (α) was also optimized they have obtained an average error for the soft potential about 3%, but for the hardest potential model ($\alpha = 7$ Å^{-1}) their average error was about 18%. Our results were obtained analytically (Eqs. (9) and (10)) and therefore the relative error is 7% for the hardness factor and 16% for the amplitude of the interaction potential.

It should also be pointed out that the procedure described in this work provides the parameters of the potential analytically while the inverted potential obtained by Belchior and Murrell was carried out by an optimization of the inverted data.

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