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Complex scattering lengths in multi-channel atom–molecule collisions

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Abstract

It is shown that in the presence of inelastic scattering, zero energy elastic and inelastic scattering can be characterized by a complex scattering length, the imaginary part of which is related directly to the total inelastic scattering cross section. Collisions between H atoms and vibrationally excited H_2 molecules are investigated. Zero energy cross sections for all vibrational states of H_2 and the corresponding complex scattering lengths are reported using accurate quantum mechanical calculations. We obtain large values of the elastic cross sections which we attribute to s -wave bound and quasi-bound states of $H \cdots H_2(v)$. The energies and lifetimes of the quasi-bound states are extracted from the complex scattering lengths. © 1997 Elsevier Science B.V.

The experimental realization of Bose–Einstein condensation (BEC) of ultracold atoms and the associated theoretical developments have revived interest in low energy atomic and molecular scattering. The temperature regimes achieved in these experiments allow the use of the scattering length to describe the properties of the condensates and considerable attention has been given to its determination in single channel scattering for which only elastic scattering is possible. For multi-channel scattering with more than one open channel, the scattering length becomes a complex quantity. The inclusion of complex scattering lengths in the solution of the Gross–Pitaevskii equation for the description of Bose–Einstein condensates would be potentially very useful because the imaginary part of the scattering length gives the rate of decay of the condensate. Though the need for the use of complex scattering phases for multi-channel problems is recognized, no simple formulation

has been presented that accurately characterizes complex scattering lengths.

As part of the continuing research on BEC, several schemes have been proposed for the creation of aggregates of ultracold molecules [1–4]. Because many of the suggested schemes involve vibrationally excited molecules as intermediate species, details of their quenching in collisions with cold atoms have become an important issue. In a preceding paper, we have addressed [5] this problem by examining inelastic collisions of H with vibrationally excited H_2 molecules using accurate quantum mechanical calculations. The inelastic cross sections and the corresponding rate coefficients were found to be very large for high vibrational levels of H_2 . In this Letter, we consider low energy elastic collisions between H and vibrationally excited H_2 and show how the total inelastic cross section may be used to construct the imaginary part of the scattering length for the incom-

ing channel. The imaginary part of the scattering length describes the loss of flux from the initial channel in the limit of zero kinetic energy and is a measure of the efficiency of quenching collisions. In the zero energy limit the elastic cross sections approach constant values. For the system considered here, the limiting values are large, of the order of 10^{-13} cm² for the first several vibrational states of H₂. Such large values for the elastic cross sections were not anticipated for this system. We find that a weakly bound H...H₂ complex corresponding to an s-wave bound state supported by the shallow van der Waals well exists and has a pronounced effect on the elastic cross sections. We show that from the complex scattering lengths, the positions and energy widths of the quasi-bound states can be predicted.

We restrict our analysis to s-wave scattering which dominates at very low kinetic energies. From the analytical properties of the S-matrix and for an interaction potential which vanishes more rapidly than R^{-4} where R is the atom–molecule separation, the scattering amplitude may be written

$$f(k) = \frac{1}{g(k^2) - ik}, \quad (1)$$

where $g(k^2)$ is an analytical even function of the momentum k . For single channel scattering, $g(k^2)$ is a real function of the collision energy, but for multi-channel scattering it has real and imaginary parts.

A Taylor series expansion of $g(k^2)$ has the form

$$g(k^2) = -\frac{1}{a} + \frac{1}{2}r_0k^2 + \dots \quad (2)$$

where a is the scattering length and r_0 is the effective range. The scattering length is real when only elastic scattering collisions may occur and complex for multi-channel scattering.

The singularities of the scattering amplitude $f(k)$ correspond to the energies of bound states or positions of resonances. An estimate of the bound state energy is obtained by solving the spectral equation $g(k_n^2) = ik_n$ which is applicable for both elastic and inelastic scattering. For low k , the equation reduces to

$$\frac{1}{2}r_0\kappa_n^2 - \kappa_n + \frac{1}{a} = 0, \quad (3)$$

where $k_n = i\kappa_n$ and the bound state energy is then

given by $E_n = -\hbar^2\kappa_n^2/2\mu$ where μ is the reduced mass of the collision system.

We show that where Wigner's threshold laws [6] apply, it is possible to characterize low energy multi-channel scattering by scattering lengths that are complex numbers. We consider as an example vibrational relaxation of a diatomic molecule by collision with an atom. The molecule is initially in a vibrationally excited state, labeled by the vibrational quantum number v , and the velocity of the incoming wave for this channel is very small so that only s-wave scattering is present in the entrance channel. For s-wave scattering, only the spherical component in the Legendre expansion of the interaction potential given by $U(R, r, \theta) = \sum_{\lambda=0}^{\infty} U_{\lambda}(R, r) P_{\lambda}(\cos \theta)$ is important where r is the vibrational coordinate of the molecule, R is measured from the center of mass of the molecule, and θ is the angle between R and the molecular axis.

If the entrance channel is the vibrational level v , the open channels in the limit of zero incoming energy are the vibrational levels $v' \leq v$. The total inelastic cross sections σ_v^{in} may be written as the sum

$$\sigma_v^{\text{in}} = \frac{\pi}{k^2} \sum_{v' < v} S_{vv'}^2 = \frac{\pi}{k^2} \{1 - |S_{vv}|^2\}, \quad (4)$$

where $S_{vv'}$ is the element of the scattering matrix S_v connecting the initial and final vibrational levels and the elastic cross section is given by

$$\sigma_v^{\text{el}} = \frac{\pi}{k^2} |1 - S_{vv}|^2. \quad (5)$$

The scattering phase shift $\delta_v(k)$ for the incoming channel is obtained from the definition $S_{vv} = \exp(2i\delta_v(k))$ and the complex scattering length $a_v = (\alpha_v - i\beta_v)$ is the limit as $k \rightarrow 0$ of $-\delta_v(k)/k$. Expanding S_{vv} in powers of k , we write

$$S_{vv} \approx 1 + 2i\delta_v(k) = 1 - 2ik(\alpha_v - i\beta_v). \quad (6)$$

The imaginary part ($-\beta_v$) of the scattering length must be negative to ensure that $\sum_{v'} |S_{vv'}|^2 \leq 1$. From Eqs. (4) and (6), we obtain in the limit of vanishing k

$$\beta_v = k\sigma_v^{\text{in}}/4\pi, \quad (7)$$

consistent with Wigner's threshold law [6]. We have recently demonstrated [5] by explicit numerical cal-

culations that the individual inelastic cross sections $\sigma_{v'}$ exhibit an inverse velocity dependence at near zero incident energy.

The complex scattering length can be expressed alternatively in the form

$$a_v = |a_v| \exp(-i\gamma_v), \quad 0 \leq \gamma_v \leq \pi, \quad (8)$$

where

$$|a_v| = (\alpha_v^2 + \beta_v^2)^{1/2}, \quad (9)$$

and

$$\gamma_v = \arctan(\beta_v/\alpha_v). \quad (10)$$

The angle γ_v is a measure of the relative contribution of the inelastic and elastic scattering to the total cross section. For single channel collisions $\gamma_v = 0$ and for inelastic scattering with complete absorption $\gamma_v = \pi/2$. For small k , the scattering amplitude $f(k)$ can be written

$$f(k) = -|a_v| \frac{\cos\gamma_v - i(\sin\gamma_v + k|a_v|)}{1 + 2k|a_v|\sin\gamma_v + k^2|a_v|^2}, \quad (11)$$

from which in the limit $k \rightarrow 0$ we obtain $\sigma_v^{\text{el}} = 4\pi|a_v|^2$.

Estimates of the position and width of any resonance that exists in the entrance channel are given by the real and imaginary parts of the energy E where

$$E = -\frac{\hbar^2}{2\mu|a_v|^2} (\cos 2\gamma_v + i \sin 2\gamma_v) = E_v - \frac{i}{2} \Gamma_v. \quad (12)$$

The energy E is real only for single channel scattering where $\sin 2\gamma_v = 0$. For multi-channel scattering, the level is either quasi-bound or unbound (virtual) and it will decay into lower levels with a lifetime $\tau_v = \hbar/\Gamma_v = \mu|a_v|^4/(2\hbar\alpha_v\beta_v)$.

Consider the specific case of vibrationally inelastic collisions between H and $\text{H}_2(v)$ in which the molecule is assumed to be initially and finally in the $j=0$ rotational state. In the numerical calculations, we employed the most recent H_3 ab initio potential energy surface of Boothroyd et al. [7]. The quantum scattering calculations were performed by solving the fully coupled Schrödinger equation within the total angular momentum representation of Arthurs and Dalgarno [8]. The vibrational basis for obtaining the coupled equations was constructed by an expansion

in Hermite polynomials [5]. The coupled channel equations were solved using the inelastic scattering program MOLSCAT [9] in which the modified quasi-adiabatic log derivative method of Manolopoulos [10] was used to propagate the coupled equations.

In Table 1, we show the real and imaginary parts of the scattering lengths for all bound vibrational states of H_2 as well as the zero energy elastic cross sections. As in Ref. [5], the calculations were performed by coupling all the bound vibrational levels of H_2 but neglecting coupling to the closed vibrational continuum which may be important for $v > 5$ [11]. The accuracy of the results is also limited by the neglect of reactive scattering. The inelastic cross sections for vibrational de-excitation collisions for $v < 5$ of H_2 are small and so are the imaginary parts of the scattering lengths. They become comparable in magnitude to the real parts for $v > 10$. The large values of the zero energy cross sections are attributed to the shallow van der Waals well which supports an s-wave bound state for $v = 0$ and quasi-bound states for $v > 0$. The real and positive scattering length for $v = 0$ indicates the presence of a near zero energy bound state. The spherically symmetric part of the interaction potential $U_0(R)$ in the van der Waals well region averaged over the $v = 0$ vibrational wave function and the corresponding s-wave

Table 1

Real and imaginary parts of the scattering length, zero energy elastic cross sections and lifetimes of $\text{H} \cdots \text{H}_2(v)$ species as a function of the vibrational levels of H_2

v	α_v (10^{-8} cm)	β_v (10^{-8} cm)	σ_v^{el} (10^{-16} cm ²)	τ (s)
0	19.87	0.0	4964	∞
1	15.73	2.89×10^{-7}	3110	7.1×10^{-4}
2	13.48	1.24×10^{-6}	2284	1.0×10^{-4}
3	11.97	4.57×10^{-6}	1799	2.0×10^{-5}
4	10.73	2.42×10^{-4}	1447	2.7×10^{-7}
5	9.58	2.59×10^{-2}	1152	1.8×10^{-9}
6	8.56	1.26×10^{-1}	920	2.6×10^{-10}
7	8.12	3.74×10^{-1}	830	7.6×10^{-11}
8	9.02	1.37	1045	3.0×10^{-11}
9	7.45	6.09×10^{-1}	701	3.6×10^{-11}
10	3.54	6.67×10^{-1}	162	3.8×10^{-12}
11	1.14	1.35	39	3.3×10^{-13}
12	2.41	6.97	686	9.3×10^{-12}
13	1.50	5.54	415	6.9×10^{-12}
14	4.42	1.48	272	3.8×10^{-12}

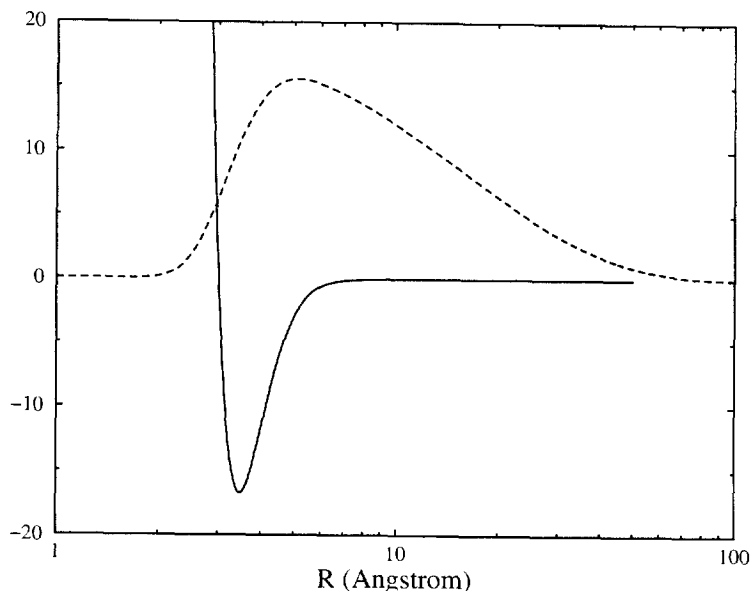


Fig. 1. Solid line: spherically symmetric part of the interaction potential in units of cm^{-1} in the region of the van der Waals well averaged over the $v = 0$ vibrational wave function of the molecule ($U_{\text{eff}}(R) = \langle \phi_0(r) | U_0(R, r) | \phi_0(r) \rangle$); dashed line: the corresponding normalized bound state wave function. The wave function amplitude is given in units of $\text{\AA}^{-1/2}$, magnified by a factor of 50 for convenience of plotting.

bound state wave function are shown in Fig. 1. The bound state has a binding energy of 0.0984 cm^{-1} and H lies at a mean distance of 3.48 \AA from the center of mass of H_2 . The existence of the bound state of H_3 is a consequence of the potential energy surface of Boothroyd et al. [7]. Its binding energy is sensitive to the details of the potential energy surface. Our calculations showed no other bound states, but we found either quasi-bound or virtual states associated with each of the vibrational levels of H_2 whose lifetimes are obtained from the imaginary parts of the scattering lengths and are listed in Table 1. The lifetimes are substantially larger than the

vibrational period of the molecule which indicates that the quasi-bound states are well defined.

A stringent test for the validity of the scattering length description is to predict accurately the bound state energies using the effective range expansion. In Table 2 we give the binding energies for $v = 0$ to 3 obtained from the bound state calculations and the scattering calculation using the effective range expansion. For $v = 0$ and 1 the agreement between the two calculations is very good. The agreement deteriorates for higher v levels because the scattering calculations are performed by coupling all vibrational levels whereas the bound state calculations are done using the individual vibrationally averaged potentials.

To summarize, we have demonstrated that complex scattering lengths for the elastic channel in a multi-channel problem can be readily constructed from the inelastic cross sections, and we have shown that the large values for the zero energy elastic cross sections for $\text{H} + \text{H}_2(v)$ scattering we obtained are the consequence of a near zero energy s-wave bound state for $v = 0$ and s-wave quasi-bound states for $v > 0$.

Table 2

Effective ranges and bound state energies in cm^{-1} of $\text{H} \cdots \text{H}_2(v)$

v	$r_0(10^{-8} \text{ cm})$	E_r^a	E_r^b
0	6.45	-0.1002	-0.0984
1	6.00	-0.1833	-0.1782
2	5.85	-0.2969	-0.2700
3	5.50	-0.4247	-0.3770

^a From effective range theory (Eq. (3)).

^b From bound state calculation.

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