Application of the Coordinate Rotation Method to Metastable Atom–Diatom Scattering Resonances

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Abstract

The procedure for applying the coordinate rotation device to the coupled-channel scattering equations is presented. Results of applications of the method to resonances occurring in low-energy atom–diatom collision processes are presented. In particular, rotational Feshbach resonances in model (homogeneous) potentials which have also been studied by Grabenstetter and Le Roy are examined within this novel approach.

1. Introduction

The so-called coordinate rotation method (CRM) [1] has been used successfully to study scattering resonances in electron–atom and electron–molecule collisions [2, 3]. More recently, it has also been used to study rotational predissociation in H_2^- [4]. In the present work, we report the first application of this technique to resonances which occur in closed-shell atom–diatom collisions. Unlike the H_2^- rotational predissociation problem, the three-atom situation addressed here involves motion on a three-dimensional potential energy surface (H_2^- involves only a one-dimensional curve). As a result, the diatom's internal (vibrational–rotational) energy and (rotational) angular momentum must be explicitly coupled to the corresponding quantities of the incident atom. The proper coupling of energy and angular momentum (asymptotic) basis functions yields the usual set of coupled-channel equations. These coupled differential equations, upon application of the coordinate rotation device, give rise to a set of coupled-complex differential equations for the components of the scattering wavefunction which correspond to various channels.

In Sec. 2 we obtain the set of coupled-channel differential equations for a closed-shell atom–diatom collision and we demonstrate how these equations are transformed upon coordinate rotation. In Sec. 3, we indicate how the resulting coupled-complex differential equations can be solved either by a finite difference method or by an expansion of the (radial) scattering wave amplitudes in terms of square-integrable basis functions. A method for identifying the desired metastable resonance energy (which is complex) and its accompanying wavefunction is also outlined in Sec. 3. Section 4 contains our concluding remarks.

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2. Coordinate Rotated Coupled-Channel Equations

In Figure 1 we display the set of lab-fixed coordinates which are used to describe the orientation (β,α) and bond length (R) of the diatom AB and the position (r,θ_0,ϕ_0) of the incident atom C relative to the center of mass of AB. In this coordinate system the Hamiltonian can be expressed as

$$H = -\frac{\hbar^2}{2\mu_{AB}}\nabla_{\mathbf{R}}^2 + U(R) - \frac{\hbar^2}{2\mu_{C,AB}}\nabla_{\mathbf{r}}^2 + V(r,\theta,R) \tag{1}$$

where μ_{AB} is the reduced mass of AB, $\mu_{C,AB}$ is the reduced mass of C relative to AB, and V is the atom–diatom interaction potential. Because ABC is a triatomic system, V can only depend on R, the angle θ between the AB axis and $\mathbf{r}$. There can be no ϕ dependence because of the axial symmetry of the system.

Because the total angular momentum (J) and one of its components commute with H, it is useful to couple the AB rotor states $Y_{jm}(\beta,\alpha)$ and the relative collisional angular momentum states $Y_{lM-m}(\theta_0,\phi_0)$ to give proper eigenstates [5] of J^2 and J_z:

$$\psi_{jl}^{JM} = \sum_m \langle lM-m,jm|JM\rangle\, Y_{j,m}(\beta,\alpha)Y_{l,M-m}(\theta_0,\phi_0) \tag{2}$$

In writing Eq. (2) we have assumed that the only angular momenta present are the diatom's rotational and the atom's collisional angular momenta; we thus have excluded open-shell electronic problems. The eigenfunctions of H which correspond to a fixed J,M can be expanded in terms of these angular momentum basis functions as

$$\Psi_{JM}(R\beta\alpha r\theta_0\phi_0) = \sum_{lj}\sum_{v} \psi_{jl}\phi_{jlv}^{JM}(r)H_{vj}(R) \tag{3}$$

where the $H_{vj}(R)$ are vibrational eigenfunctions of the diatom in its jth rotor level and the $\phi_{jlv}^{JM}(r)$ are amplitudes which describe the radial motion of C relative to AB. Substitution of the above eigenfunction into $(H-E)\Psi = 0$, fol-

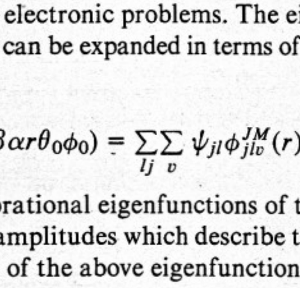

Figure 1. Lab-fixed coordinate system used in this work.

lowed by premultiplication by $\psi_{jl}^{JM*}H_{vj}^{*}$, and integration over β,α,R,θ_0, and ϕ_0 gives a set of coupled differential equations for the radial amplitudes ϕ_{jlv}^{JM}:

$$\delta_{l'l}\delta_{j'j}\delta_{v'v}\left\{-\frac{\hbar^2}{2\mu_{C,AB}}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)-\frac{l(l+1)}{r^2}\right]+\epsilon_{vj}-E\right\}\phi_{jlV}^{JM}$$
$$+\sum_{jlv}\langle\psi_{j'l'}^{JM}H_{v'j'}|V(r\theta R)|\psi_{jl}^{JM}H_{vj}\rangle\,\phi_{jlv}^{JM}=0 \quad (4)$$

where ϵ_{vj} is the vibrational–rotational energy of AB:

$$\left\{-\frac{\hbar^2}{2\mu_{AB}}\left[\frac{1}{R^2}\frac{d}{dR}\left(R^2\frac{d}{dR}\right)-\frac{j(j+1)}{R^2}\right]-\epsilon_{vj}+U(R)\right\}H_{vj}=0 \quad (5)$$

In practical application of the above coupled-channel [6] (CC) equations, the range of collision energies (E), together with the AB vibration–rotation energy level spacing, determines the range of the v and j quantum indices. The range of the interaction potential V together with the incident kinetic energy E determine the maximum value of the collisional angular momentum l. The form of V determines whether vibrational inelastic and/or rotational inelastic transitions will take place. If V is essentially independent of R, vibrational excitation will not occur; similarly V must depend on θ to achieve rotational excitation. Each specific scattering problem therefore requires careful consideration of the choices of j, l, and v as well as a consistent modeling of the interaction potential.

Before turning to the problem of coordinate rotating the above CC equations, the evaluation of the potential integral appearing in Eq. (4) requires further discussion. $V(r\theta R)$ is most naturally expressed in terms of the angle θ between the diatomic axis and the C atom. However, the angular momentum basis ψ_{jl}^{JM} is expressed in terms of the lab-fixed angles θ_0,ϕ_0. Therefore, to perform the integral over orientation which appears in Eq. (4), it is useful to express the $Y_{lM-m}(\theta_0,\phi_0)$ functions in terms of functions of the angles θ,ϕ $\{Y_{l\mu}(\theta,\phi)\}$:

$$Y_{l,M-m}(\theta_0,\phi_0)=\sum_{\mu}D_{M-m,\mu}^{l*}(\pi-\alpha,\beta,0)Y_{l\mu}(\theta,\phi) \quad (6)$$

where the transformation coefficients are elements of the rotation matrices connecting the two coordinate systems [5]. By inserting Eq. (6) into Eq. (4) and using well-known identities relating rotation matrices and 3-j symbols [5], the desired potential integral of Eq. (4) can be expressed as

$$V_{j'l'v',jlv}^{JM}=(-1)^{j+j'-l-l'}(2j+1)^{1/2}(2j'+1)^{1/2}\sum_{\mu}\begin{pmatrix} j' & l' & J \\ 0 & \mu & -\mu \end{pmatrix}\begin{pmatrix} j & l & J \\ 0 & \mu & -\mu \end{pmatrix}$$
$$\times\int Y_{l'\mu}^{*}(\theta,\phi)H_{v'j'}^{*}(R)V(r,\theta,R)Y_{l\mu}(\theta,\phi)H_{vj}(R)R^2\sin\theta\,dR\,d\theta\,d\phi \quad (7)$$

Now that V and the angular momentum functions are expressed in terms of a common coordinate system, this integral can, in principle, be done. To do so would, in general, require a two-dimensional numerical integration for each value of the r coordinate. Because such numerical integrations are not usually practical, it is quite common to introduce an explicit functional form for the potential V. The most commonly used expression involves writing V as a sum of terms each having a different θ dependence:

$$V = \sum_{L=0}^{L_{\max}} V_L(r,R)P_L(\cos\theta) \tag{8}$$

By separating out the angular dependence of V, one can perform the θ and ϕ integrals appearing in Eq. (7), thereby reducing the V integral to

$$\begin{aligned} V^{JM}_{j'l'v',jlv} = {} & (-1)^{j+j'-l-l'}[j]^{1/2}[j']^{1/2}[l]^{1/2}[l']^{1/2} \sum_L \sum_\mu \begin{pmatrix} j' & l' & J \\ 0 & \mu & -\mu \end{pmatrix} \begin{pmatrix} j & l & J \\ 0 & \mu & -\mu \end{pmatrix} \\ & \times (-1)^\mu \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & L \\ \mu & -\mu & 0 \end{pmatrix} \int H^*_{v'j'}(R)V_L(r,R)H_{vj}(R)R^2dR \end{aligned} \tag{9}$$

which now requires only a one-dimensional integration over R. Further simplification of this coupling integral requires explicit choices for the $V_L(r,R)$. We shall not pursue this matter further in the present section; such discussions are better left to the following section which deals with the application of the methods outlined here.

In the so-called complex coordinate rotation method, one multiplies, in the relevant Schrödinger equation, the spatial coordinate of the scattered particle by the complex quantity $\exp(i\eta)$. The resultant complex-scaled Hamiltonian is known to possess the same bound-state energies as the original Hamiltonian plus additional square-integrable eigenstates which have complex eigenenergies $E = E_r - i\Gamma/2$ and which correspond to the sought-after metastable resonance states. The fact that the resonance states become square integrable upon coordinate rotation implies that one can locate such resonances accurately by approximating (expanding) the eigenfunctions of the rotated Hamiltonian in a basis set consisting of square-integrable functions. Basis sets which are appropriate to the atom–diatom scattering problem considered here will be discussed briefly below.

The replacement of r, the C-to-AB distance, by $r\exp(i\eta)$ results in the following set of coordinate-rotated (CR) coupled-channel equations

$$\begin{aligned} & \delta_{j'j}\delta_{l'l}\delta_{v'v}\left\{\exp(-2i\eta)\frac{-\hbar^2}{2\mu_{c,AB}}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{l(l+1)}{r^2}\right] + \epsilon_{vj} - E\right\}\phi^{JM}_{jlv} \\ & \qquad + \sum_{jlv}\langle\psi^{JM}_{j'l'}H_{v'j'}|V(r\exp(i\eta),\theta,R)|\psi^{JM}_{jl}H_{vj}\rangle\phi^{JM}_{jlv} = 0 \end{aligned} \tag{10}$$

Of course, the coupling matrix elements can be further simplified, as in Eq. (9), by introducing the expansion for $V(r,\theta,R)$ shown in Eq. (8). In addition, the complex scaling of V is greatly facilitated if one chooses functional forms for $V(r,\theta,R)$ or $V_L(r,R)$ in which the r dependence is homogeneous [1]. For example, the Lennard–Jones function $V_2(r,R) = a_2(R)\,r^{-12} - b_2(R)\,r^{-6}$ scales easily under $r \rightarrow r\exp(i\eta)$ to become $V[r\exp(i\eta),R] = a_2 r^{-12}\exp(-12i\eta) -$

$b_2 r^{-6} \exp(-6i\eta)$. However, the Morse function $D\{1 - \exp[-(r - r_e)]\}^2$ does not scale homogeneously. The value of using a functional form which scales homogeneously is obvious. In this case, the integral displayed in Eq. (9) reduces to a sum of integrals which are η independent (and, hence, evaluated once and for all) multiplied by various powers of $\exp(-i\eta)$. As a result, the evaluation of the η dependence of the CC differential equation is greatly simplified.

If one were to use an *ab initio* potential energy surface for $V(r,\theta,R)$ in Eq. (7), one would be forced to compute, as Morokuma and George [7] did for HeH^{2+}, the "electronic energy" V using *ab initio* quantum chemical tools at the "geometry" $[r \exp(i\eta),\theta,R]$. This, of course, requires the evaluation of complex electron–nucleus interaction integrals and the location of a complex "electronic energy." It is, in fact, our intent to eventually perform such calculations in connection with our investigation of the dissociative lifetimes of electronically excited metastable states of triatomic molecules. However, for the immediate future, we intend to explore the utility of the coordinate rotation method in atom–diatom resonance situations which involve potentials having homogeneous r dependence and which have already been examined by other methods in the literature. That is, we want to check the results of our approach against those which have been obtained by others using well-established techniques of scattering theory. Clearly, our goal is to reproduce the existing results with less computational effort and to then move on to more difficult problems such as arise in using *ab initio* nonseparable forms for $V[r \exp(i\eta),\theta,R]$.

3. Solution of the CRCC Equations

According to the philosophy of the coordinate rotation method, we should expand the amplitudes $\{\phi_{jlv}(r)\}$ (the fixed index J,M is suppressed for convenience) in a square-integrable basis $\{b_n(r)\}$ and then look for the (complex) eigenvalues $E_\mu(\eta)$ of the resulting secular equations. These eigenvalues will, of course, depend on the "rotation angle" η. By plotting the complex $E_\mu(\eta)$ ($E_\mu = E_{\mu,r} - i\Gamma_\mu/2$) as η is varied, we can then obtain so-called η trajectories for each of the eigenenergies $E_\mu(\eta)$.

The desired resonance eigenvalue is the one which, for $\eta > \tan^{-1}(\Gamma_\mu/2E_{\mu,r})$, is relatively independent of η.

The primary difficulties involved in implementing the process outlined above have to do with basis set choice and the efficient identification of the resonance eigenvalue. If N basis functions are used to expand the ϕ_{jlv}, one obtains an $N\cdot d_l\cdot d_j\cdot d_v$-dimensional secular problem, where d_l, d_j, and d_v are the number of l, j, and v quantum numbers included. Clearly, this overall dimension can become quite large even for relatively "simple" three-atom systems. For these reasons, it is of utmost importance that square-integrable basis functions be chosen very judiciously (to span the important region of r space) and that numerical methods be used which permit one to find eigenvalues of the (complex symmetric) secular problem within rather narrow energy ranges. That is, methods which locate either all or the lowest few roots of the secular problem are not practical. Procedures such as the inverse iteration scheme must be used to search for eigenenergies, which are then checked for η independence, within a range of energies (as dictated by the energy range of the incident colliding atom).

In the initial prototype calculations which we are presently undertaking, we are exploring the use both of Gaussian basis functions having different "centers" r_n and exponents $\alpha_n\{b_n(r) = \exp[-\alpha_n(r - r_n)^2]\}$, and of "unit square" basis functions $[S_n(r)]$ which can be expressed as differences between Heaviside functions $\{S_n(r) = \theta[r - (n+1)a] - \theta(r - na),\ 0 \le n \le N\}$ where a is the step unit along the r axis. The use of these $S_n(r)$ basis functions gives rise to the familiar set of finite-difference equations which arise from Eqs. (10):

$$\delta_{j'j}\delta_{l'l}\delta_{v'v}\left[\exp(-2i\eta)\,\frac{-\hbar^2}{2\mu_{c,AB}}\,a^{-2}\left(\bar{\phi}_{n+1} + \bar{\phi}_{n-1} - 2\bar{\phi}_n - \frac{l(l+1)}{n^2}\bar{\phi}_n\right) + \epsilon_{vj}\bar{\phi}_n - E\bar{\phi}_n\right] + \sum_{ljv} \langle \psi_{j'l'}H_{v'}|V(na\exp(i\eta),\theta,R)|\psi_{jl}H_v\rangle\bar{\phi}_n = 0 \quad (11)$$

where $\bar{\phi}_n \equiv \phi(na)$ and the indices J,M,j,l,v have been suppressed.

By arranging the set of amplitudes $\{\bar{\phi}_{jlv}\ (r = na),\ n = 0, 1, \ldots, N\}$ into a column vector Φ which is partitioned into its jlv components, the above equations can be expressed in matrix form as

$$(\mathbf{H} + \mathbf{V} - E)\bar{\phi} = \delta_{j'j}\delta_{l'l}\delta_{v'v}(\mathbf{H}_l + \epsilon_{vj} - E)\Phi_{jlv} + \sum_{jlv} \mathbf{V}_{j'l'v',jlv}\Phi_{jlv} = 0 \quad (12)$$

where the identification of the **H** and **V** matrices from Eq. (11) is clear. This set of coupled (for the various j,l,v channels) finite-difference equations can be solved for the (complex) eigenenergies E_μ and the corresponding amplitude $\{\bar{\phi}_{\mu,jlv}(na)\}$. By examining the trajectories of the E_μ as η is varied, one can identify the desired resonance roots.

To illustrate how the above-described procedures are carried out in practice, we report here the first results of applying the CRCC method to a model atom–diatom collision which has been investigated independently by Grabenstetter and Le Roy [8] using another approach. In these calculations, the interaction potential $V(R,r,\theta)$ is taken to be a sum of a spherical part $V_0(r)$ and an anisotropic part $V_2(r)\,P_2(\cos\theta)$ with V_0 and V_2 given in the Lennard–Jones form:

$$V_{0,2} = 4\epsilon[b_{0,2}(\sigma/r)^{12} - a_{0,2}(\sigma/r)^6] \quad (13)$$

The numerical values of these potential parameters and all other information needed to specify the model are given in Table I.

Because V is assumed to be independent of R, we are explicitly excluding vibrational inelastic events from consideration. Thus, we remove the vibrational quantum states (v,v') from our basis and concentrate on the coupling of rotational and translational motion.

The Gaussian basis set chosen for use in these calculations consists of 15 functions $\{\exp[-d(r - r_j)^2]\}$ all having exponent $d = 20$ and centers $r_j = 3.3 + j \times 0.372$ Å $(0 \le j \le 14)$. These positions span the region of r space in which V is significant $(3 < r < 8$ Å$)$. The exponent was chosen to permit substantial overlap between neighbor Gaussians.

TABLE I. Parameters characterizing the model system and the computed resonance energies.

μ (amu)	1.981
B_d (cm^{-1})	60.551
ϵ (cm^{-1})	60.408
σ (Å)	3.4745
a_0	1.00
a_2	0.09
b_0	1.00
b_2	0.5

	Resonance energy (cm^{-1})	Resonance width (cm^{-1})
Grabenstetter and Le Roy [8]	338.13	0.16
Present work	342.93	0.25

In the collision energy range examined by Grabenstetter and Le Roy, only the $j = 0$ and $j = 2$ states of the (presumed homonuclear) diatom are likely to play an important role (the $j = 0 \rightarrow j = 2$ excitation energy is 363.306 cm^{-1}).

In examining the $J = 0$ channel, we are then restricted to collisional angular momenta (l) of $l = 0$ and $l = 2$. Hence, our two coupled channels are labeled $j = l = 0$ and $j = l = 2$. These two channels combine with our chosen 15 basis functions to yield matrices in Eq. (10) of dimension 30.

The 30 complex eigenvalues of the resulting secular problem were obtained at many values of the rotation angle (η). In fact, η was permitted to assume complex values $[\exp(i\eta) = \alpha \exp(i\theta)]$ where the amplitude α is thought of as being related to the "usual" scaling of wavefunctions arising in, for example, treatment of the virial theorem, and θ is the "true angle" of rotation in the complex plane. By examining θ trajectories of all 30 eigenvalues $\alpha = 0.85, 0.90, 1, 1.075, 1.080, 1.083, 1.085, 1.087$, and 1.10, several of which are shown in Figure 2, in steps of $\Delta\theta = 1 \times 10^{-3}$ rad, we were able to identify one energy level which became relatively stable (θ independent) for $\theta \gtrsim 13 \times 10^{-3}$ rad. The value of α which gave the most stable θ trajectory was $\alpha = 1.085$. The so-called stability "cusp" (see Fig. 2) in the optimum θ trajectory occurred at $\theta = 14 \times 10^{-3}$ rad, at which the complex eigenvalue was $E = (342.93 - i0.124)$ cm^{-1}. For this same model potential, Grabenstetter and Le Roy found the resonance energy to be 338.13 cm^{-1} and to have a width ($\Gamma = -2 \operatorname{Im}E$) of $\Gamma = 0.16$ cm^{-1}. Our results, which required about 1 min of CPU time per θ value on the Utah DEC 2060 computer, are thus in reasonably good agreement with those of Le Roy et al.

In examining the nature of the eigenvector of Eq. (10) corresponding to the above resonance eigenenergy, we find the $j = l = 2$ components to be considerably larger than those for $j = l = 0$, thereby indicating the rotational Feshbach nature of this scattering resonance.

Based on the results of this initial work, we are encouraged about the potential utility of the coordinate rotation method in treating atom–diatom collision

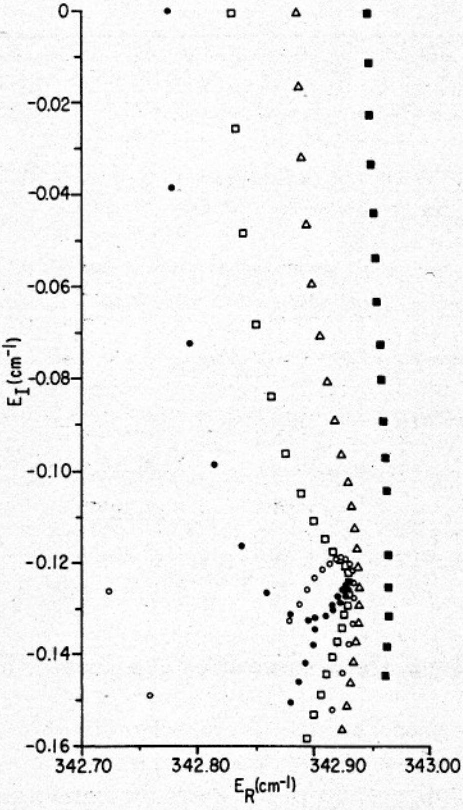

Figure 2. A collection of θ trajectories. The θ increment is 1×10^{-3} rad, beginning at $\theta =$ 0.0 rad; $\alpha =$ (○) 1.087, (●) 1.085, (□) 1.083, (△) 1.080, (■) 1.075.

resonances. We are presently applying this device to other "model" problems treated by Grabenstetter and Le Roy which involve significantly more anisotropic potentials. In the next phase of our work on this project, we plan to study lifetimes both of metastable van der Waals' complexes such as Ar—HCl and of predissociating (excited electronic) states of triatomic molecules such as HCN.

Certainly these coordinate rotation calculations do not provide the same wealth of detail about the scattering process as is obtained in full quantal solutions of the coupled-channel equations with proper boundary conditions; the present method is *designed* to evaluate lifetimes and resonance energies. On the other hand, these first results do indicate the practicality of the approach and do suggest that this tool might be a valuable means to obtaining information about lifetimes for systems which would not permit full solutions of the scattering differential equations and relevant boundary conditions.

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