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Classical limits to the sudden approximation

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We have examined the classical limits to the orbital and energy sudden approximations. It is shown that at large orbital and rotational quantum numbers the transformations which diagonalize the coupling matrix in the sudden limit also diagonalize the coupling matrix in the classical limit. The eigenvalues are no longer a delta function fixed in position during the collision but become a narrow wave packet moving with the classical velocity. The result is a uniform approximation valid in both the sudden and classical limits. A key feature of the theory is the use of the discrete-variable representation which allows an accurate counting of quantum states in the sudden representation. The theory should improve the accuracy of the sudden approximation while requiring little additional computer time.

I. INTRODUCTION

The sudden approximation has long been used in molecular scattering theory[1-4] because it allows a great simplification of the problem which can result in substantial savings in computer time for what is usually a very expensive calculation.[5] One typically removes some quantum number from the expression for the energy (or angular momentum) by replacing the quantum number with a constant. There is then a simple transformation which diagonalizes the Hamiltonian for the relevant quantum number. This diagonalization has the effect of freezing the angle variable conjugate to the quantum number (action variable) during the collision. For example, in the orbital sudden approximation[2] it is assumed that the range of l's coupled by the potential is small compared to l so that one can replace l by some averaged l_0 in the centrifugal energy term $l(l+1)/R^2$. A simple transformation involving a Clebsch–Gordan coefficient takes the problem from the space-fixed representation into the body-fixed representation where the orbital motion is completely diagonal.[6] The cost in computer time of solving a large set of N coupled differential equations scales roughly as N^3. Breaking the set into n sets of N/n equations then saves a factor of n^2 in computer time. The classical effect of the orbital sudden approximation, as will be shown below, is to neglect the change of the polar scattering angle $\theta(t)$ during the collision. At large l (large impact parameter) this angle changes by 180° during the collision, and the orbital sudden approximation fails.

A second and related approach is the classical limit.[7] When the orbital and/or the rotational quantum numbers become sufficiently large, it may be possible to find a transformation which will diagonalize the coupling matrix. This appears to be the case when the scattering problem is formulated in terms of a classical trajectory and may be more general. In this case the conjugate angle variable is not frozen but moves with the classical motion during the collision. This approximation is not as commonly used nor as clearly formulated as the sudden approximation. It is closely related, however to Miller's semiclassical mechanics[8] which involves this same action-angle transformation and a classical phase. Clearly, both the sudden and classical limits are related since they both transform the problem to an infinitely narrow wave packet which remains stationary or moves with a classical velocity during the collision. There must also be a close relationship between these methods and the various wave-packet methods of Heller and others[9] which express the wave function in terms of Gaussian wave packets which propagate along classical trajectories.

The purpose of this paper is to develop the classical limits to the transformations used in the sudden approximation. By doing this carefully it will be shown that these transformations also correspond to the classical limiting diagonalizing transformations. The method gives a uniform procedure for treating the scattering which is valid in both the sudden and classical limits rather than two separate procedures for each case. In the case of the energy sudden approximation we make extensive use of the discrete-variable representation (DVR) formulated by the Light group.[10] The DVR allows the use of a finite transformation from N states in the energy representation to N states in the sudden, position representation. The more traditional approach requires the use of infinite basis sets in both representations. Not only is this unrealistic in that states of very high energy are being coupled into the problem, but it introduces serious problems in counting quantum states properly. All these problems are avoided by using the DVR.

In principle, the basic transformation theory developed here can be applied to a wide variety of scattering problems using several different approaches to the underlying scattering theory. To demonstrate the method we will use the simple case of an atom colliding with a rigid linear rotor with no electronic complications like spin or electronic angular momentum. The sudden approximation can be applied directly to the Schrödinger equation. The classical limit is not so easily applied, and so we use a set of coupled differential equations in time. We assume that the trajectory is determined by some spherically symmetric potential $V_0(R)$. The rest of the potential $\Delta V(R,r) = V - V_0$ serves as a time-dependent perturbation acting on the orbital and internal degrees of freedom. By expressing the total wave function in

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terms of the complete basis set of orbital and internal states, a set of coupled differential equations in time is obtained. The derivation is closely modeled after the one in most text books treating time-dependent perturbation theory.[11]

The method in this paper can easily be used for any time-dependent scattering theory of this type or any theory derived from this such as a perturbation theory, an exponential perturbation theory,[12,13] or the more recent sudden perturbtion theory.[4] With somewhat more difficulty it can be extended to more complex scattering problems or to different types of scattering theory.

The outline of the paper is as follows. In the next section the time-dependent scattering theory is developed. In Sec. III the theory is developed for the orbital sudden approximation. Most of these results have been previously shown,[13] so only a summary will be given. In Sec. IV and V the theory will be applied to the energy sudden approximation in two forms, first when the orbital sudden approximation is valid (the coupled states case), and then for the more general case. Section VI is a discussion.

II. TIME-DEPENDENT SCATTERING THEORY

The development of a time-dependent inelastic scattering theory closely follows the standard derivation of time-dependent perturbation theory.[11] The main difference is that we wish to include the orbital angular momentum along with the internal molecular energy states. At the level of a perturbation theory the results can be obtained quite easily as a semiclassical approximation to a quantum mechanical scattering theory. In any event, the details of the theory are of secondary importance. We assume that the potential can be decomposed into a spherically symmetric part $V_0(R)$ and the remainder ΔV, where $R(t)$ is the distance between the centers of mass of the two colliding molecules. Given V_0 we can calculate a trajectory,

$$t = \mp (\mu/\hbar)\int_{R_c}^{R} \frac{dR}{p}, \tag{1}$$

$$\theta = \pm (l+1/2)\int_{R_c}^{R} \frac{dR}{R^2 p}, \tag{2}$$

$$p(R)^2 = k^2 - (2\mu/\hbar^2)V_0(R) - (l_0+1/2)^2/R^2. \tag{3}$$

Equation (1) gives the classical time as a function of R. The top sign holds for the incoming half of the trajectory and the bottom sign for the outgoing half. R_c is the classical turning point where the radial momentum $\hbar p = 0$. Equation (2) gives the deflection angle; μ is the reduced mass of the colliding molecules, and $k^2 = 2\mu E_{\text{trans}}/\hbar^2$. Throughout the paper, we will assume that l is large enough that we can use $l(l+1) = (l+1/2)^2$.

The Hamiltonian for the problem becomes

$$H = H_{\text{int}}(r) + [L^2 - (l_0+1/2)^2\hbar^2]/(2\mu R^2) + \Delta V(R,r), \tag{4}$$

where $\mathbf{r}$ is the collection of internal and orbital variables, L is the orbital angular momentum operator, and l_0 is the orbital angular momentum quantum number used for the classical trajectory. Note that by using the classical trajectory, we must remove the radial kinetic energy, orbital motion, and V_0 from H. We can now expand the total, time-dependent wave function in terms of the eigenfunctions of H_{int}, $\phi_n(r)$ and the eigenfunctions of L^2 and L_z, $Y_{lm}(\Theta,\Phi)$,

$$\Psi = \Sigma a_{nlm}\phi_n Y_{lm} \exp[-iE_n t/\hbar + i(l-l_0)\theta(t)], \tag{5}$$

where $\dot{\theta} = -(l_0+1/2)\hbar/\mu R^2$. We then insert Eq. (5) and its derivative into the time-dependent Schrödinger equation, left multiply by $\phi_{n'}^* Y_{l'm'}^*$, and integrate over all space. This gives

$$\begin{aligned}\dot{a}_{n'l'm'} &= -(i/\hbar)\Sigma\langle n'l'm'|A|nlm\rangle a_{nlm} \\ &= -(i/\hbar)\Sigma\langle n'l'm'|\Delta V|nlm\rangle \\ &\quad\times\exp(i\omega_{n'n}t - i\Delta l\theta)a_{nlm},\end{aligned} \tag{6}$$

where $\omega = (E_{n'} - E_n)/\hbar$ and $\Delta l = l' - l$.

If the perturbation is small enough, then we can approximate Eq. (6) to first order. The transition probability is

$$P_{n'nl'lm'm} = \hbar^{-2}\left|\int_{-\infty}^{\infty}\langle n'l'm'|A|nlm\rangle dt\right|^2. \tag{7}$$

Variants on this approach include an exponential perturbation theory.[12,13] If Eq. (7) is derived from more formal scattering theory, one can use a different V_0 for each quantum state. In this case Eq. (6) includes a term in the exponential giving the difference in the V_0's.[4] If one neglects the $\Delta l\theta$ term, Eq. (7) is identical to the usual time-dependent perturbation theory, since one does not usually include orbital angular momentum in such a calculation. Note that this term has roughly the same effect as the ωt term in that it reduces the transition probability for large Δl. The orbital sudden approximation is obtained by ignoring $\Delta l\theta$ or, equivalently, setting $\theta = 0$. The energy sudden approximation is obtained by setting $\omega = 0$. We will then use Eq. (6) and make various transformations on the coupling matrix $\mathbf{A}$ so that the equations are decoupled.

III. THE ORBITAL SUDDEN APPROXIMATION

In the case of an atom and a rigid linear rotor, the potential depends only on $\mathbf{R}$ and γ the angle between R and the molecular axis. We can express $\Delta V(R,\gamma)$ in a series of Legendre polynomials,

$$\Delta V(R,\gamma) = \Sigma v_\lambda(R)P_\lambda(\cos\gamma). \tag{8}$$

The coupling matrix becomes[14,15]

$$\begin{aligned}&\langle j'm_j'l'm_l'|A|jm_jlm_l\rangle \\ &\quad= \sum_{\lambda=0}^{\infty} v_\lambda(R)(-1)^{\mu}\left\{\frac{[l][j]}{[l'][j']}\right\}^{1/2} \\ &\qquad\times C(j\lambda j';000)C(l\lambda l';000)C(j\lambda j';m_j\mu m_j') \\ &\qquad\times C(l\lambda l';m_l-\mu m_l')\exp(i\omega t - i\Delta l\theta),\end{aligned} \tag{9}$$

where $[x] = 2x+1$ and C is a Clebsch–Gordan coefficient.

We can partially diagonalize $\mathbf{A}$ by coupling the orbital and rotational angular momenta,

$$|JMjl\rangle = \sum_{m_j} C(jlJ;m_jm_lM)\,Y_{jm_j}(\theta_m,\phi_m)Y_{lm_l}(\Theta,\Phi), \tag{10}$$

where (θ_m,ϕ_m) is the orientation of the molecular axis and (Θ,Φ) is the orientation of $\mathbf{R}$. The coupling matrix is then

diagonal in J and M and independent of M. The diagonalization works, of course, because the total angular momentum must be conserved. The coupling matrix in the new representation is given by

$$\langle j'l'|A\,|jl\rangle_J = \sum_\lambda v_\lambda(R)(-1)^{j-l'-J}\{[l][j]\}^{1/2} \times C(j\lambda j';000)C(l\lambda l';000)\begin{Bmatrix} J & l & j \\ \lambda & j' & l' \end{Bmatrix} \times \exp(i\omega t - i\Delta l\theta), \quad (11)$$

where $\{\ \}$ is a $6-j$ symbol. There are two useful semiclassical approximations that can be made on Eq. (11). For small j,λ and large l, we can use an approximation to various C's in Eqs. (9) and (10),[16]

$$C(l\lambda l';m\mu m') = d^\lambda_{\mu\Delta l}(\theta_l) \quad (l \gg \lambda), \quad (12)$$

$$\cos\theta_l = m/(l+1/2), \quad (13)$$

where d is the central part of a rotation matrix. The formula comes from Edmonds,[15] but I have used Rose's[14] phase convention for d. For this limit Eq. (9) becomes

$$\langle j'l'|A\,|jl\rangle_J = \sum_\lambda v_\lambda(R)\left\{\frac{[j]}{[j']}\right\}^{1/2} C(j\lambda j';000) \times C(j\lambda j';\delta-\Delta l\delta')(-1)^{\Delta l} d^\lambda_{0\Delta l}(\pi/2) \times \exp(i\omega t - i\Delta l\theta), \quad (14)$$

where $\delta = J - l$ and $\delta' = J - l'$. The equation is convenient because it expresses Δl as a projection quantum number. The d matrix can be expressed as a spherical harmonic, and the two Clebsch–Gordan coefficients can be expressed as the integral of three spherical harmonics to give

$$\langle j'l'|A\,|jl\rangle = \sum_\lambda v_\lambda(R)\frac{4\pi}{[\lambda]}(-1)^{\Delta l}Y_{\lambda\Delta l}(\pi/2,\pi-\theta) \times \langle j'\delta'|Y_{\lambda-\Delta l}(\theta_m,\phi_m)|j\delta\rangle\exp(i\omega t) \quad (15)$$

$$= \langle j'\delta'|\Delta V(R(t),\beta(t)|j\delta\rangle\exp(i\omega t), \quad (16)$$

where $\beta(t)$ is the angle between (θ_m,ϕ_m) and $[\pi/2,\pi-\theta(t)]$.

When both l and j are large we can use a semiclassical expression for the 6-j symbol in Eq. (11),[15]

$$\begin{Bmatrix} J & l & j \\ \lambda & j' & l' \end{Bmatrix} = \frac{(-1)^{J+l'+j}}{\{[j][l]\}^{1/2}} d^\lambda_{-\Delta l\Delta j}(\theta_J), \quad (17)$$

$$\cos\theta_J = \frac{(J+1/2)^2-(j+1/2)^2-(l+1/2)^2}{2(j+1/2)(l+1/2)}. \quad (18)$$

Comparing Eq. (12) and Eq. (17) we see that we can replace the 6-j coefficient in Eq. (11) with

$$\begin{Bmatrix} J & l & j \\ l & j' & l' \end{Bmatrix} = \frac{(-1)^{J+l+j}}{\{[j][l]\}^{1/2}} C(j\lambda j';\delta-\Delta l\delta'), \quad (19)$$

$$\delta = \frac{(J+1/2)^2-(j+1/2)^2-(l+1/2)^2}{2(l+1/2)}. \quad (20)$$

Then, if we use Eq. (12) for $C(l\lambda l';000)$ we obtain Eq. (14) except for a factor of $\{[j]/[j']\}^{1/2}$ which is approximately one at large j. Thus, Eqs. (15) and (16) is a uniform approximation valid at large and small j if Eq. (20) is used for δ.

In the orbital sudden approximation we can diagonalize the coupling matrix with the transformation,[6]

$$|jv\rangle_J = \sum_l \left\{\frac{[l]}{[J]}\right\}^{1/2} C(ljJ;0vv)(-1)^{l-j}|jl\rangle_J. \quad (21)$$

In the orbital sudden case this transforms the coupling matrix to

$$\langle j'v'|A\,|jv\rangle_J = \sum_{\lambda=0}^\infty v_\lambda(R)\left\{\frac{[j]}{[j']}\right\}C(j\lambda j';000) \times C(j\lambda j';v0v)\exp(i\omega t)\delta_{v'v}. \quad (22)$$

The use of Eq. (12) converts Eq. (21) into[13]

$$|jv\rangle_J = \sum_\delta (-1)^{l-j}D^j_{\delta v}(0,-\pi/2,0)|jl\rangle_J. \quad (23)$$

The effect of Eq. (23) is to rotate the molecular axis by 90°. This transforms Eqs. (15) and (16) to

$$\langle J'v'|A\,|jv\rangle_J = \langle j'v'|\Delta V[R(t),\alpha(t)]|jv\rangle\exp(i\omega t) \quad (24)$$

$$= \sum_\lambda v_\lambda(R)\left\{\frac{4\pi[j]}{[\lambda][j']}\right\}^{1/2} \times (-1)^{\Delta v}C(j\lambda j';000)C(j\lambda j';v\Delta vv') \times Y_{\lambda-\Delta v}[\theta(t),\pi/2]\exp(i\omega t), \quad (25)$$

where $\alpha(t)$ is the angle between (θ_m,ϕ_m) and $[\theta(t),\pi/2]$. In the orbital sudden limit, $\theta(t) = 0$ and the spherical harmonic in Eq. (25) becomes $\{[\lambda]/4\pi\}^{1/2}\delta_{v'v}$ and Eq. (25) becomes identical to Eq. (22). Thus Eq. (25) is a uniform approximation valid in the orbital sudden limit for all l and j and valid in the classical limit of large l when the orbital sudden limit does not apply. I have been unable to find a classical limit valid for large j and l analogous to Eq. (23). It should be noted, however, that the orbital sudden approximation is generally good for small l where the collision is hard and of short duration (θ is small). At large l it breaks down, but Eq. (25) is still valid.

IV. ENERGY SUDDEN APPROXIMATION (ORBITAL SUDDEN CASE)

In the energy sudden approximation the coupling matrix is basically ΔV.[1–3] The diagonalizing transformation takes the matrix of ΔV in the energy representation and transforms it back into the original position representation where it is diagonal. This is the reverse process of taking the matrix elements of ΔV which takes the function ΔV in the position representation and converts it into a matrix in the energy representation. In the original treatments of the sudden approximation the transformation matrix is the original wave function $\phi_i(x)$. For a problem like the rigid rotor, there are a countably infinite number of basis functions. The position variable (quantum number) is a continuous function which therefore has an uncountably infinite number of values. These infinities not only make it difficult to count states and thus normalize the various transformations, but they also cause problems in computation. All of these problems are avoided by using the discrete-variable representation (DVR) of Light and co-workers.[10] Consider the evaluation of a matrix element of $V(x)$ using a Gaussian numerical quadrature,

$$\langle i|V|j\rangle = \int \phi_i^*(x)V(x)\phi_j(x)w(x)dx$$

$$\cong \sum_{\alpha=1}^{N} \phi_i^*(x_\alpha) V(x_\alpha) \phi_j(x_\alpha) w_\alpha, \tag{26}$$

where x_α are the points in the quadrature and w_α are the associated weights. We can then define a unitary matrix

$$\langle i|T|\alpha\rangle = \phi_i^*(x_\alpha) w_\alpha^{1/2} \tag{27}$$

which transforms the N quantum states i to the N positions x_α.

In constructing a Gaussian quadrature[16] one finds a set of polynomials orthogonal over the space of interest and which have the appropriate weighting function $w(x)$. The positions x_α are the N zeros of the Nth polynomial, and the associated weights are obtained from the properties of the Nth and $(N-1)$th polynomial. For the rigid rotor in state $v=0$ we use the standard Gauss–Legendre quadrature where the associated polynomials are the Legendre polynomials $P_l(\cos\theta_\alpha)$. For the more general case we use a set of polynomials proportional to the spherical harmonics,[14,17]

$$\begin{aligned} Z_l^m(x) &= (-1)^m (1-x^2)^{-m/2} P_l^m(x) \\ &= \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right]^{-1/2} \\ &\quad \times (1-x^2)^{-m/2} Y_{lm}(\theta,0), \end{aligned} \tag{28}$$

where $x=\cos\theta$. The Z's are related to the Chebechev polynomials.[17] The equations derived are appropriate to nonegative m. The case of negative m may be obtained by using symmetry rules for the spherical harmonics.[14,15]

To implement the method we need a classical limit to the spherical harmonic. This is provided by Brusaard and Tolhoek,[18]

$$\begin{aligned} Y_{lm}(\theta,\phi) &= \pi^{-1} e^{im\phi} [1-\mu^2-x^2]^{-1/4} \\ &\quad \times \sin[(l+1/2)g(\mu,x) + m\pi/2 + \pi/4], \end{aligned} \tag{29}$$

where

$$g(\mu,x) = \pi/2 - \int_0^x \frac{[1-\mu^2-z^2]^{1/2}}{(1-z^2)}\,dz, \tag{30}$$

$\mu = m/(l+1/2)$, and $x=\cos\theta$. Equation (29) is valid in the classically allowed region defined by $[1-\mu^2-x^2]>0$. The integral can be done to give

$$\begin{aligned} g(\mu,x) &= \arccos\left[\frac{x}{(1-\mu^2)^{1/2}}\right] \\ &\quad + \mu \arcsin\left[\frac{\mu x}{\{[(1-\mu^2)(1-x^2)]\}^{1/2}}\right]. \end{aligned} \tag{31}$$

Note that for $\mu=0$, $g=\theta$. In the Appendix it is shown that approximate roots for $Y_{L,v}$ are given by

$$\theta_\alpha = \pi/2 + y, \tag{32}$$

$$y = \frac{(2\alpha - L + v - 1)\pi}{(2L+1)(1-\mu^2)^{1/2}} \quad [\alpha = 1,2,\ldots,(L-v)]. \tag{33}$$

A more accurate set of roots is given by

$$\theta_\alpha = \pi/2 + y + \frac{\mu^2}{2(1-\mu^2)^{1/2}}(\tan y - y). \tag{34}$$

A further increase in accuracy can be obtained by replacing m^2 by $m^2 - 1/4$. With this substitution, Eq. (34) is almost as accurate as an iterated solution of Eq. (29). The roots for small v/L are generally accurate to 10^{-3} rad. The accuracy degrades somewhat for larger v/L but remains good to less than about 10^{-2} rad. In the Appendix it is also shown that the classical limit to the transformation matrix is given by

$$\begin{aligned} \langle jv|T|\alpha v\rangle &= [2/(L+1/2)]^{1/2} \sin\theta_\alpha (\sin^2\theta_\alpha - \mu_L^2)^{-1/4} \\ &\quad \times (\sin^2\theta_\alpha - \mu_j^2)^{-1/4} \sin[(j+1/2) \\ &\quad \times g(\mu_j,\theta_\alpha) + v\pi/2 + \pi/4], \end{aligned} \tag{35}$$

where L is the order of the quadrature, $\mu_L = v/(L+1/2)$, and $\mu_j = v/(j+1/2)$. For the case $v=0$, $\mu_L = \mu_j = 0$ and $g=\theta_\alpha$, and Eq. (35) simplifies drastically.

The classical limit to the sudden coupling matrix is obtained by applying the transformation of Eq. (35) to Eq. (22) or to Eq. (25). We will use both forms since the expression for the orbital sudden approximation is simpler than the general case and quite useful. First, we take the orbital sudden case. Since we are using a classical limit, we can approximate the Clebsch–Gordan coefficients in Eq. (22) by using Eq. (12). This gives

$$\begin{aligned} \langle \alpha' v|A|\alpha v\rangle_J &= \sum_{\lambda jj'} \langle \alpha' v|T|j' v\rangle d^{\lambda}_{0\Delta j}(\pi/2) d^{\lambda}_{0\Delta j}(\theta_j) \\ &\quad \times v_\lambda(R) \exp(i\omega_{jj} t) \langle jv|T^\dagger|\alpha v\rangle, \end{aligned} \tag{36}$$

where $\cos\theta_j = \mu_j = v/(j+1/2)$. The lower limits on j and j' are given by the edge of the classically allowed region of $Y_{jv}(\theta_\alpha,0)$ which occurs when $\sin\theta_\alpha = \pm\mu_j$ or $j_{\min} + 1/2 = |v|/\sin\theta_\alpha$. The upper limit is $j_{\max} = L-1$. For large j,

$$\omega_{jj} = 2(j+1/2)\Delta j\hbar^2/2I = \Delta j\omega_0.$$

That is, at large j the rotational energy levels become approximately equally spaced. We can also express the d matrices in Eq. (36) as spherical harmonics. Note that Δj appears as a magnetic quantum number and that $\omega t = \Delta j \omega_0 t$ so that $\omega_0 t$ becomes the azimuthal argument to one of the spherical harmonics; ω_0 is the classical angular velocity, and thus $\omega_0 t$ is simply the rotation of the molecule during the collision. Putting the various pieces together gives

$$\begin{aligned} \langle \alpha' v|A|\alpha v\rangle_J &= \sum_{\lambda jj'} v_\lambda(R) \frac{16\pi}{[L][\lambda]} \sin\theta_{\alpha'} \sin\theta_\alpha [(\sin^2\theta_{\alpha'} - \mu_L^2)(\sin^2\theta_\alpha - \mu_L^2)(\sin^2\theta_{\alpha'} - \mu_{j'}^2)(\sin^2\theta_\alpha - \mu_j^2)]^{-1/4} \\ &\quad \times \sin[(j'+1/2)g(\mu_{j'},\theta_{\alpha'}) + v\pi/2 + \pi/4] \sin[(j+1/2)g(\mu_j,\theta_\alpha) + v\pi/2 + \pi/4] Y_{\lambda\Delta j}(\pi/2,\omega_0 t) \\ &\quad \times Y^*_{\lambda\Delta j}(\theta_j,0). \end{aligned} \tag{37}$$

The product of sines can be resolved into a term with the sum of the two frequencies, a frequency proportional to $(j+j')$, and

a term with the difference of the two frequencies, a frequency proportional to Δj. We can neglect the sum term because it has no region of stationary phase. We can expand the argument of the difference term and keep only the first-order part,

$$\sin[\ ]\sin[\ ] = 1/2\cos\left\{(j+1/2)[g(\mu_j,\theta_{\alpha'})-g(\mu_j,\theta_\alpha)]+\Delta j g(\mu_j,\theta_{\alpha'})+(j+1/2)\Delta j\frac{\partial q}{\partial\mu}\frac{\partial\mu}{\partial(j+1/2)}\right\}, \tag{38}$$

$$\frac{\partial q}{\partial\mu} = \arcsin\left[\frac{\mu x}{[(1-\mu^2)(1-x^2)]^{1/2}}\right]. \tag{39}$$

Evaluating the various derivatives in Eq. (38) gives

$$\sin[\ ]\sin[\ ] = 1/2\cos\{(j+1/2)[g(\mu_j,\theta_{\alpha'})-g(\mu_j,\theta_\alpha)]+\Delta j\delta\}, \tag{40}$$

where

$$\delta = \arccos\left[\frac{\cos\theta_\alpha}{(1-\mu^2)^{1/2}}\right]. \tag{41}$$

If $\alpha'\neq\alpha$, then the cosine in Eq. (40) will oscillate rapidly as j is summed to give zero. Thus the off-diagonal elements will be small compared to the diagonal elements, and the transformation diagonalizes the coupling matrix in the classical limit as well as in the sudden limit. Expressing the cosine as the sum of two imaginary exponentials, converts Eq. (40) to

$$\langle\alpha'v|A\,|\alpha v\rangle_J = \sum_{\lambda j\Delta j} v_\lambda(R)\frac{4\pi}{[L\,][\lambda\,]}\sin^2\theta_\alpha(\sin^2\theta_\alpha-\mu_L^2)^{-1/2}$$
$$\times(\sin^2\theta_\alpha-\mu_j^2)^{-1/2}[\,Y_{\lambda\Delta j}(\pi/2,\omega_0 t+\delta)+Y_{\lambda\Delta j}(\pi/2,\omega_0 t-\delta)\,]\,Y^*_{\lambda\Delta j}(\theta_j,0)\delta_{\alpha'\alpha}. \tag{42}$$

The sum over Δj can be evaluated by using the spherical harmonic addition theorem to give

$$\langle\alpha'v|A\,|\alpha v\rangle_J = \sum_{\lambda j} v_\lambda(R)[L\,]^{-1}\sin^2\theta_\alpha(\sin^2\theta_\alpha-\mu_L^2)^{-1/2}(\sin^2\theta_\alpha-\mu_j^2)^{-1/2}[P_\lambda(\cos\gamma_+)+P_\lambda(\cos\gamma_-)]\delta_{\alpha'\alpha} \tag{43}$$

$$= \sum_j [L\,]^{-1}\sin^2\theta_\alpha\{(\sin^2\theta_\alpha-\mu_L^2)(\sin^2\theta_\alpha-\mu_j)\}^{-1/2}[\Delta V(R,\gamma_+)+\Delta V(R,\gamma_-)]\delta_{\alpha'\alpha}, \tag{44}$$

where $\gamma_\pm$ is the angle between $(\pi/2,\omega_0 t\pm\delta)$ and $(\theta_j,0)$. A simple expression for $\gamma_\pm$ is obtained by using $\lambda=1$,

$$\cos\gamma_\pm = \cos(\omega_0 t)\cos\theta_\alpha \mp \sin(\omega_0 t)(\sin^2\theta_\alpha-\mu_j^2)^{1/2}. \tag{45}$$

In the energy sudden limit, the IOS case, $\omega_0=0$ and $\gamma_+=\gamma_-=\theta_\alpha$. The sum over j can be done explicitly. We replace the sum by an integral over $(j+1/2)$. The coupling matrix becomes

$$\langle\alpha'v|A\,|\alpha v\rangle_J = \sum_\lambda v_\lambda(R)P_\lambda(\cos\theta_\alpha)\delta_{\alpha'\alpha}$$
$$= \Delta V(R,\theta_\alpha)\delta_{\alpha'\alpha}. \tag{46}$$

This is, of course, the same result which is obtained by applying Eq. (27) to Eq. (22) without any assumption of a classical limit. Equations (43) and (44) is then a uniform approximation valid in both the sudden and classical limits. It is valid for all j when $\omega=0$ and for large j when $\omega\neq 0$.

A second useful special case is the case where $v=0$. Here $\mu_L=\mu_j=0$ and Eq. (45) becomes $\gamma_\pm=\theta_\alpha\pm\omega_0 t$. The coupling matrix becomes

$$\langle\alpha'0|A\,|\alpha 0\rangle_J = 1/2[\Delta V(R,\theta_\alpha+\omega_0 t)$$
$$+\Delta V(R,\theta_\alpha-\omega_0 t)]. \tag{47}$$

In other words, the molecule starts out at $t=0$ with the orientation θ_α and rotates in either direction in the x–z plane (note that $v=0$). In the general case, the molecule also starts at θ_α and rotates, but now the plane of the rotation is at an angle with respect to the z axis so that the description is more complicated. The plane of the rotation also depends on j so that the sum over j cannot be done as easily as in the two cases described above.

V. ENERGY SUDDEN APROXIMATION (GENERAL CASE)

In the general case the derivation is similar except that now v can change. The molecule will rotate during the collision, but the orbital motion also changes, and this complicates the description of the collision. One final difficulty is that we must apply yet another transformation to diagonalize the v quantum number. This is done using an action-angle type transformation.[7] We start by applying the transformation given by Eq. (35) to Eq. (25). As before we make use of the semiclassical limit of the Clebsch–Gordan coefficient given by Eq. (12). The result is

$$\langle\alpha'v'|A\,|\alpha v\rangle_J = \sum_{\lambda j j'} v_\lambda(R)\frac{16\pi}{[L\,][\lambda\,]}\sin\theta_\alpha\sin\theta_{\alpha'}[(\sin^2\theta_{\alpha'}-\mu_L'^2)(\sin^2\theta_\alpha-\mu_L^2)(\sin^2\theta_{\alpha'}-\mu_{j'}'^2)(\sin^2\theta_\alpha-\mu_j^2)]^{-1/4}$$
$$\times\sin[(j'+1/2)g(\mu_{j'}',\theta_{\alpha'})+v'\pi/2+\pi/4]\sin[(j+1/2)g(\mu_j,\theta_\alpha)+v\pi/2+\pi/4](-1)^{\Delta v}Y_{\lambda\Delta j}(\pi/2,0)$$

$$\times d^{\lambda}_{\Delta j \Delta \nu}(\theta_j) Y_{\lambda -\Delta\nu}(\theta, -\pi/2)\exp(i\Delta j\omega_0 t). \tag{48}$$

The first spherical harmonic comes from the semiclassical expression of the first Clebsch–Gordan coefficient in Eq. (25). The d matrix comes from the second C coefficient. As before, we resolve the product of sines into a rapidly oscillating term which is neglected and into a slowly oscillating term:

$$\sin[\ ]\sin[\ ] = 1/2\cos\Big\{(j+1/2)[g(\mu_{j\nu},\theta_{\alpha'\nu}) - g(\mu_{j\nu},\theta_{\alpha\nu})] + \Delta j g(\mu_{j\nu},\theta_{\alpha'\nu}) + (j+1/2)\Delta j \frac{\partial q}{\partial \mu}\frac{\partial \mu}{\partial j} + (j+1/2)\frac{\partial q}{\partial \mu}\frac{\partial \mu}{\partial \nu}\Delta\nu + \Delta\nu\pi/2\Big\}, \tag{49}$$

$$= 1/2\cos\{(j+1/2)[g(\mu_{j\nu},\theta_{\alpha'\nu}) - g(\mu_{j\nu},\theta_{\alpha\nu})] + \Delta j\delta + \Delta\nu\delta' + \Delta\nu\pi/2\}, \tag{50}$$

where

$$\delta' = \arcsin\left[\frac{\mu_j\cos\theta_a}{(1-\mu_j^2)^{1/2}\sin\theta_\alpha}\right]. \tag{51}$$

As before, when we sum over a range of j's the cosine will oscillate rapidly unless $\theta_{\alpha'} = \theta_\alpha$. Note however that, if $\nu' \neq \nu$, then $\alpha' \neq \alpha$ when the two θ's are equal. As before, we express the cosine as a sum of two imaginary exponentials and put the various arguments into the azimuthal angles of the spherical harmonics and rotation matrices. The result is

$$\begin{aligned}\langle \alpha'\nu'|A|\alpha\nu\rangle_J = \sum_{\lambda j\Delta j}\frac{4\pi}{[L\,][\lambda\,]}\sin^2\theta_\alpha(\sin^2\theta_\alpha - \mu_L^2)^{-1/2} \\ \times(\sin^2\theta_\alpha - \mu_j^2)^{-1/2}\{Y_{\lambda\Delta j}(\pi/2,\omega_0 t+\delta)D^{\lambda}_{\Delta j\Delta\nu}(0,\theta_j,-\pi/2-\delta') \\ + Y_{\lambda\Delta j}(\pi/2,\omega_0 t-\delta)D^{\lambda}_{\Delta j\Delta\nu}(0,\theta_j,\pi/2+\delta')\}Y^*_{\lambda\Delta\nu}(\theta,-\pi/2)\delta(\theta_{\alpha'}-\theta_\alpha),\end{aligned} \tag{52}$$

where D is a rotation matrix.[14] The sum over Δj simply rotates the coordinates of $Y_{\lambda\Delta j}$.

We must now find a transformation which will diagonalize the ν quantum number. In the classical limit the coupling matrix depends largely on $\Delta\nu$ and only weakly on ν itself. In this case we can use an action-angle type transformation to diagonalize the coupling matrix. The transformation is given by [7(a)]

$$\langle\beta|T_1|\nu\rangle = N^{-1/2}\exp(2\pi i\beta\nu/N) \tag{53}$$

$$= N^{-1/2}\exp(i\phi_\beta\nu), \tag{54}$$

where N is the number of ν's present, $\nu,\beta = 0,1,2,\ldots,N-1$, and $\phi_\beta = 2\pi\beta/N$ is the angle variable conjugate to the quantum number ν. If a function $f_{\Delta\nu}$ depends only on $\Delta\nu$ and is independent of ν itself, then the transformed function becomes

$$\langle\beta'|f|\beta\rangle = \delta_{\beta'\beta}\sum_{\Delta\nu} f_{\Delta\nu}\exp(i\phi_\beta\Delta\nu). \tag{55}$$

If we apply Eq. (54) to Eq. (52) we obtain

$$\begin{aligned}\langle\alpha'\beta'|A|\alpha\beta\rangle_J = \sum_{\substack{\lambda j\Delta j\\ \nu\Delta\nu}}\frac{4\pi v_\lambda}{[L\,][\lambda\,]N_\nu}\sin^2\theta_\alpha(\sin^2\theta_\alpha-\mu_L^2)^{-1/2}(\sin^2\theta_\alpha-\mu_j^2)^{-1/2}\delta(\theta_{\alpha'}-\theta_\alpha)\delta_{\beta'\beta}Y^*_{\lambda\Delta\nu}(\theta,-\pi/2-\phi_\beta) \\ \times\{Y_{\lambda\Delta j}(\pi/2,\omega_0 t+\delta)D^{\lambda}_{\Delta j\Delta\nu}(0,\theta_j,\pi/2-\delta') + Y_{\lambda\Delta j}(\pi/2,\omega_0 t-\delta)D^{\lambda}_{\Delta j\Delta\nu}(0,\theta_j,-\pi/2+\delta')\}.\end{aligned} \tag{56}$$

We have kept the sum over ν because A depends weakly on ν. The sum over Δj causes a rotation of the spherical harmonic $Y_{\lambda\Delta j}$ to give a new spherical harmonic. The sum over $\Delta\nu$ is then spherical harmonic addition theorem and gives the sum of two Legendre polynomials,

$$\begin{aligned}\langle\alpha'\beta|A|\alpha\beta\rangle_J = \sum_{\lambda j\nu}\{[L\,]N_\nu\}^{-1}\sin^2\theta_\alpha(\sin^2\theta_\alpha-\mu_L^2)^{-1/2}(\sin^2\theta_\alpha-\mu_j^2)^{-1/2}\delta(\theta_{\alpha'}-\theta_\alpha)\delta_{\beta'\beta}v_\lambda(R) \\ \times\{P_\lambda(\cos\gamma_+) + P_\lambda(\cos\gamma_-)\},\end{aligned} \tag{57}$$

$$\langle\alpha'\beta'|A|\alpha\beta\rangle = \sum_{j\nu}\{[L\,]N_\nu\}^{-1}\sin^2\theta_\alpha(\sin^2\theta_\alpha-\mu_L^2)^{-1/2}(\sin^2\theta_\alpha-\mu_j^2)^{-1/2}\delta(\theta_{\alpha'}-\theta_\alpha)\delta_{\beta'\beta}$$

$$\times\{\Delta V(R,\gamma_+)+\Delta V(R,\gamma_-)\}. \tag{58}$$

An expression for $\cos\gamma_\pm$ can be obtained by evaluating the case of $\lambda=1$,

$$\cos\gamma_\pm=\sum_{\Delta j\Delta\nu}(4\pi/3)Y_{1\Delta j}(\pi/2,\omega_0 t\pm\delta)D^1_{\Delta j\Delta\nu}(0,\theta_j,\mp\pi/2\mp\delta')Y^*_{1\Delta\nu}(\theta,-\pi/2-\phi_\beta), \tag{59}$$

$$\begin{aligned}\cos\gamma_\pm&=\sin\theta_j\cos\theta\cos(\omega_0 t\pm\delta)\mp\cos\theta_j\sin\theta\cos(\omega_0 t\pm\delta\pm\delta'+\phi_\beta)\\&=\cos\theta\cos(\omega_0 t)\cos\theta_\alpha\mp\cos\theta\sin(\omega_0 t)(\sin^2\theta_\alpha-\mu_j^2)^{1/2}\\&\quad+\frac{\sin\theta\cos\theta_j}{\sin^2\theta_j\sin\theta_\alpha}\{\mp\cos(\omega_0 t+\phi_\beta)\cos\theta_\alpha(\sin^2\theta_\alpha-\mu_j^2)^{1/2}\\&\quad\times(1-\mu_j)+\sin(\omega_0 t+\phi_\beta)(\sin^2\theta_\alpha-\mu_j^2+\mu_j\cos^2\theta_\alpha)\}.\end{aligned} \tag{60}$$

Except for the sum over $\Delta\nu$ Eqs. (57) and (58) are identical to Eqs. (43) and (44). The definition of $\gamma_\pm$ given by Eq. (60) clearly reduces to Eq. (45) in the orbital sudden limit when $\theta=0$. The main differences between the general result given by Eqs. (58)–(60) and the orbital sudden case of Eqs. (43)–(45) is that the description of the rotation is more complicated in the general case. In the orbital sudden case $\theta=0$ so that the atom is along the polar axis. In the general case the atom moves off $\theta=0$ so that the orbital and rotational motions are taking place simultaneously in different planes.

VI. DISCUSSION

We have shown that the same transformation matrix which diagonalizes the coupling matrix for inelastic scattering in the sudden limit will also diagonalize it in the classical limit of large rotational and orbital quantum numbers. In the sudden limit, the eigenvalues of the coupling matrix are the potential energy evaluated at selected points in space. The molecular motion is frozen during the collision. In the classical limit the eigenvalues are the potential energy evaluated at these same points in space, except now the molecule rotates and the direction of the vector between the centers of mass moves with a classical angular velocity during the collision. The approximations obtained here are uniform in that the same equation works in both the sudden and classical limits. The approximations will fail if the system is not correctly described by either limit. This will occur, for example, if the rotational quantum numbers are small and yet the energy separations between quantum states are large. It is quite common, however, that the lower j states have small enough energy spacings to be treated by the sudden approximation, while the larger j states are effectively classical. For the case where $\nu=0$ the results are intuitively obvious. The quadrature points θ_α are equally spaced. The transformation matrix given by Eq. (35) becomes

$$\langle j\nu|T|\alpha\nu\rangle=\{4/[L]\}^{1/2}\sin[(j+1/2)\theta_\alpha+\pi/4]. \tag{61}$$

This is an action-angle transformation since θ_α is proportional to α; θ_α is the angle variable conjugate to the quantum number j [action variable $(j+1/2)\hbar$].

The theory was developed in the context of a time-dependent scattering theory. This is not necessary for the sudden approximation which can be obtained directly from Schrödinger's equation without recourse to a classical path. The classical limit, however, requires a classical time to describe the rotation. This classical time does require a classical trajectory. For example, it is not even defined inside the classical turning point. For a case close to the sudden limit, one could set up a quantal scattering theory and make reference to a classical trajectory only to describe the small molecular motions which constitute the deviations from the sudden approximation. The basic quantal scattering theory would not have to be severely compromized by a semiclassical treatment of the radial motion.

There are no fundamental reasons why the theory is restricted to the case of an atom and a rigid linear rotor. It is easily seen how to generalize to the case of two linear rotors. The case of nonlinear rotors is more complicated but should be possible. Vibration is not normally in the sudden or classical range since the vibrational spacings are large and only low v states are needed. However, at very high energies, small-angle vibrationally inelastic scattering[19] should be easily treated by a theory similar to the one derived here. One would use a Gauss–Hermite quadrature[17] based on the Hermite polynomials for the discrete-variable representation. The classical limit to the vibrational wave function is easily obtained. The diagonalizing transformation will, presumably, diagonalize the coupling matrix in both the sudden and classical limits. The eigenvalues in the sudden limit will be the potential evaluated at the points given by the Gauss–Hermite quadrature. In the classical limit the bond distance will change as the molecule vibrates during the collision.

The methods of this paper should be only slightly more difficult to apply than the use of the sudden approximation, since the coupling matrix is still diagonal. The results should be more accurate because the theory includes the changes in energy and orbital angular momentum during the collision. Equivalently, the molecule is allowed to rotate during the collision.

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APPENDIX: DERIVATION OF THE QUADRATURE POINTS, WEIGHTS, AND THE TRANSFORMATION MATRIX

The theory of Gaussian quadrature[16] states that the points of the quadrature θ_α are given by the N roots of the Nth orthogonal polynomial. In this case we look for the N roots of $Y_{L\nu}(\theta_\alpha,0)$. The asymptotic form of Y is given by Eq. (29). The roots occur when the argument of the sine is an integral multiple of π. We must then solve

$$h(\mu,\theta) = (L+1/2)g(\mu,\theta) + \nu\pi/2 + \pi/4 - (\alpha+\nu)\pi = 0. \tag{A1}$$

Equation (A1) is set up so that $\alpha = 1,2,3,\ldots,(L-\nu)$ give $(L-\nu)$ distinct roots. Equations (30) and (31) give an expression for g. For $\nu=\mu=0$, $g=\theta$. For nonzero values of μ we can expand g about $\pi/2$ to get

$$g(\mu,\theta) = \pi/2 + (1-\mu^2)^{1/2}(\theta-\pi/2) + O[(\theta-\pi/2)^3]. \tag{A2}$$

If we keep only the linear term we obtain Eqs. (32) and (33). The roots in θ, but not in $x=\cos\theta$, are equally spaced. From Eq. (30) we see that g depends only on even powers of μ. By differentiating Eq. (30) with respect to μ^2 and setting $\mu=0$ we obtain

$$\left.\frac{\partial q}{\partial \mu^2}\right|_{\mu^2=0} = 1/2\cot\theta. \tag{A3}$$

By adding in this term we can correct Eq. (A1) to give

$$h = (L+1/2)\{y[1-(1-\mu^2)^{1/2}] - (\mu^2/2)\tan y\} + \cdots. \tag{A4}$$

Since the correction introduced by Eq. (A3) is small, we can extrapolate to the root of Eq. (A4) using Newton's method. Without the cotangent term,

$$\frac{\partial h}{\partial\theta} = (L+1/2)(1-\mu^2)^{1/2}, \tag{A5}$$

and the corrected root is given by Eq. (34).

In an actual calculation, one needs to calculate the roots only once. This is not a major part of the calculation, and can easily be done exactly without having to use a semiclassical approximation. However, the calculation of the exact roots is done by Newton's method. When L is large, they are closely spaced, and, if the original guess for the root is not accurate enough, roots are missed, and duplicate ones are found. Equation (34) then gives a good initial approximation to start Newton's method. An asymptotic expansion of the Legendre function[17] suggests the replacement of ν^2 with $\nu^2-1/4$, and this turns out to improve the accuracy for all ν including $\nu=0$. Comparison was made with numerical calculations of the exact roots. From the construction of the approximation, it is obvious that the largest errors occur for $\alpha=1$, $(L-\nu)$, the roots furthest from $\pi/2$ and for larger ν. For $\nu=0$ the maximum error is roughly $4\times10^{-3}/L$. The largest error for all ν seems to occur at $\nu=L-3$ and is roughly $3\times10^{-4}L^{1/2}$.

The weights for the quadrature are given by[16]

$$w_\alpha = A_L\gamma_{l-1}/\{A_{L-1}Z_L^{\nu\prime}(x_\alpha)Z_{L-1}^{\nu}(x_\alpha)\}, \tag{A6}$$

where $x_\alpha=\cos\theta_\alpha$, and the polynomials used are given by Eq. (28). A_L is the coefficient of the leading power of the polynomial, and γ_L is the normalization,

$$\int Z_L^{\nu}(x)Z_{L'}^{\nu}(x)w(x)dx = \gamma_L\delta_{L'L}. \tag{A7}$$

The properties of the Legendre functions are well known[17] and give

$$\gamma_L = 2(L+\nu)!/\{(2L+1)(L-\nu)!\}, \tag{A8}$$

$$A_L = (2L)!/\{2^L L!(L-\nu)!\}. \tag{A9}$$

Also of use is the recursion relation,[17]

$$(1-x^2)Z_L^{\nu\prime}(x) = -LxZ_L^{\nu}(x) + (L+\nu)Z_{L-1}^{\nu}(x). \tag{A10}$$

We then have

$$w_\alpha = 2(L+\nu)!/\{(L-\nu)!(1-x_\alpha^2)[Z_L^{\nu\prime}(x_\alpha)]^2\}. \tag{A11}$$

Using the derivative of Eq. (29) to get Z' gives

$$w_\alpha = (1-x_\alpha^2)^{\nu+1}\pi(L+1/2)^{-1}(1-x_\alpha^2-\mu^2)^{-1/2}. \tag{A12}$$

The weights are usually accurate to a few percent or better. From Eq. (27) we obtain the transformation matrix,

$$\langle j\nu|T|\alpha\nu\rangle = Y_{j\nu}(\theta_\alpha,0)w_\alpha^{1/2}(1-x_\alpha^2)^{-\nu/2}(2\pi)^{1/2}. \tag{A13}$$

The factor of $(4\pi)^{1/2}$ enters because the Y's are normalized over 4π sr, while we are integrating only over θ. The factor of $(1-x_\alpha)^{-\nu/2}$ is the square root of the weighting function $w(x)$ of the Z polynomials. Using Eq. (29) for Y gives Eq. (35) for the transformation matrix. It is easily seen to be unitary and hence properly normalized.

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