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MECHANISM FOR COLLISION-INDUCED TRANSITIONS BETWEEN Λ-DOUBLETS IN $^1\Pi$ MOLECULES: REDUCTION TO A SINGLE SCATTERING POTENTIAL

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The theory is presented for rotational excitation of $^1\Pi$ molecules by collisions with rare gas atoms. It is shown that collision dynamics are described by the *two* electronic potential energy surfaces which correlate with the electronically degenerate Λ components (doublets) in the diatomic molecule. Because the ±Λ degeneracy can alternatively be described as being in the rotational rather than in the electronic degree of freedom, one can reformulate the collision dynamics in terms of a single *effective* electronic potential which then depends on Φ, the angle of rotation about the diatomic axis. The form of this Φ dependence is found to be identical to that postulated to explain experimental data for collisional transfer of laser-induced fluorescence.

1. Introduction

When an atom collides with a molecule, translational energy can be converted into internal energy (i.e., rotational, vibrational, or electronic energy) of the molecule. By measuring the probability (cross section) for such energy conversion processes one can, in principle, obtain information about the intermolecular forces which act during the collision. In practice, however, such studies have been hindered both by lack of detailed experimental data and also by inadequacies of the approximate theories used to relate cross sections to intermolecular potentials. Recently much progress has been made in overcoming the first obstacle for the case of electronically excited alkali molecules – Na_2, NaLi, and Li_2 – in collisions with rare gas atoms [1–8]. Many accurate cross sections have now been measured for collision-induced transitions between specific fine structure levels (Λ-doublets) in the $B\,^1\Pi$ state, revealing interesting and unanticipated results. For example, the probabilities for transition between neighboring Λ components of opposite electronic parity are generally different whereas the probabilities for transitions to neighboring components of the same electronic parity are equal within experimental error. This leads to the so-called "ΔJ asymmetry" in which the cross section for $\Delta J = +1$ transitions is not equal to $\Delta J = -1$, while $\Delta J = \pm 2$ are about the same*.

Progress towards understanding these collision processes in terms of intermolecular forces has not

* Each rotational level in a $^1\Pi$ state consists of two Λ components of opposite parity. For a homonuclear molecule collisions can only connect levels with the same parity. Since the overall parity changes with J as $(-1)^J$ it follows that $\Delta J = \pm 1$ transitions must change the electronic parity, i.e., must correspond to transitions between different Λ components, while $\Delta J = \pm 2$ transitions preserve the symmetry of the Λ components. For heteronuclear molecules all collision-induced transitions are permitted. See ref. [1].

kept pace with the experiments. Using various approximate scattering formalisms, it has been shown that many of the experimental results can be explained in terms of potentials which depend not only on P', the distance from the molecular center of mass to the projectile, and Θ', the angle between P' and the molecular axis, but also on Φ', the angle of rotation about the molecular axis. (see fig. 1; primes will be used to indicate coordinates measured relative to molecule-fixed axes.) The first workers [1] correctly realized that a Φ'-dependent potential was necessary to explain their energy transfer data and suggested that such a dependence arises from electronic-rotational coupling which orients the two Λ components (doublets) differently with respect to rotation of the molecule. Subsequently, Bergmann et al. [9] showed that the $\Delta J = \pm 1$ data for Na_2 could be fit within the framework of the Born scattering approximation by assuming a Φ'-dependent potential of the form $(e^{2i\Phi'} + e^{-2i\Phi'})$; Poppe [10] pointed out that the ΔJ asymmetry in this formulation arises from quantum interference and has no classical analog. Data for NaLi has been discussed in this same framework by Ottinger [7]. A more exact quantum formulation for scattering from this Φ'-dependent potential has been presented by Klar [11] within the framework of the helicity representation (close-coupling).

All of these theoretical analyses have evaded a crucial question: the origin of the Φ'-dependent potential. It should be recalled that in the fixed-nuclei (Born–Oppenheimer) approximation the electronic hamiltonian is invariant to rotation about the molecular axis. The diatomic wavefunctions – and hence their interaction with a projectile – are therefore expected to show cylindrical symmetry for excited states as well as for closed-shell ground states (where such symmetry is taken for granted). This apparent conflict can be resolved when one considers that these fine structure transitions involve two electronic potential energy surfaces so that a description in terms of scattering on a single surface cannot be directly employed. Indeed the multiple potential nature of the problem has been alluded to by Klar [11] and, more extensively by Ottinger [7] although neither of these authors actually considers scattering on the two potential surfaces. Using the analogy to collisions between ^2P alkali atoms and noble gas atoms, Bergmann and Demtröder [3] have also discussed two electronic potentials including a qualitative description of collision dynamics on these surfaces.

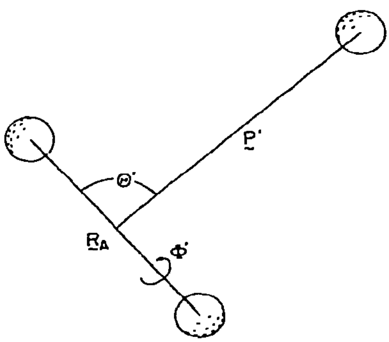

Fig. 1. Nuclear coordinate system used to describe the collision.

In this paper we will develop the scattering formalism for rotational excitation of $^1\Pi$ molecules. It will be shown that the two Λ components of each rotational level can be described alternatively as two electronic states or as one electronic state with two rotational modes. In a similar manner it will be shown that the two electronic potential energy surfaces for the collision can be reduced to a single "effective" potential surface. This is advantageous because methods for computing excitation cross sections on single surfaces are relatively well understood compared with the multiple surface problem. The Φ'-dependence of the effective potential arises naturally in this formulation. In essence we are mapping the (discrete) electronic degree of freedom onto the (continuous) coordinate which describes rotation about the internuclear axis; in this context we note that the Φ'-dependence will be responsible for transitions between electronic Born–Oppenheimer states.

The effective interaction potential is related in a straightforward manner to the two original electronic potential energy surfaces. Thus one can obtain the effective interaction within the framework of ab initio calculations which have been extensively developed for computing electronic potential energies. The form of the Φ'-dependence is found to be identical to that assumed in previous studies.

We will present the quantum scattering formalism in section 2 and indicate a natural expansion solution in terms of the correct asymptotic states. The asymptotic forms for an atomic projectile and a $^1\Pi$ diatomic target will be discussed in section 3. In section 4 the interaction potential and matrix elements will be considered and it will be shown how these are related to electronic potential energy surfaces of the combined target–projectile molecule. Finally, in section 5 we will make some general comments on approximate scattering formalisms which are appropriate to the systems for which data is available.

2. Scattering theory

Because the collisions under consideration involve more than one electronic state, it is appropriate to use a quantum mechanical scattering formalism for which we need the hamiltonian of the total system – target plus projectile. For collisions in which the structural identity (i.e., nuclei and number of electrons) of target and projectile remains unchanged, it is convenient to write the total hamiltonian (in space-fixed coordinates) as

$$\mathcal{H} = \mathcal{H}_A(\boldsymbol{R}_A) + \mathcal{H}_B(\boldsymbol{R}_B) + T(\boldsymbol{P}) + V(\boldsymbol{R}_A, \boldsymbol{R}_B, \boldsymbol{P}) . \quad (2.1)$$

$\mathcal{H}_A(\boldsymbol{R}_A)$ and $\mathcal{H}_B(\boldsymbol{R}_B)$ are hamiltonians for the separate target and projectile and depend only on their respective internal (i.e., nuclear and electronic) coordinates. $T(\boldsymbol{P})$ is the kinetic energy of relative motion and depends only on the collision coordinate $\boldsymbol{P}$, the vector from the target center of mass to the projectile. The interaction potential V depends, in general, on the internal coordinates $\boldsymbol{R}_A$ and $\boldsymbol{R}_B$ as well as on $\boldsymbol{P}$ and becomes negligible for sufficiently large $\boldsymbol{P}$.

The quantum scattering problem, in the time-independent formulation, consists of solving the Schrödinger equation for the total wavefunction at energy E:

$$[\mathcal{H}(\boldsymbol{R}_A, \boldsymbol{R}_B, \boldsymbol{P}) - E]\, \Psi(\boldsymbol{R}_A, \boldsymbol{R}_B, \boldsymbol{P}) = 0 . \quad (2.2)$$

Because the system must asymptotically approach target and projectile states as $\boldsymbol{P} \to \infty$, it is natural to expand the total wavefunction as

$$\Psi(\boldsymbol{R}_A, \boldsymbol{R}_B, \boldsymbol{P}) = \sum_{ij} \psi_i^A(\boldsymbol{R}_A)\, \psi_j^B(\boldsymbol{R}_B) f_{ij}(\boldsymbol{P}) , \quad (2.3)$$

where

$$[\mathcal{H}_A(\boldsymbol{R}_A) - E_i^A]\, \psi_i^A(\boldsymbol{R}_A) = 0 , \quad (2.4a)$$

and

$$[\mathcal{H}_B(\boldsymbol{R}_B) - E_j^B]\, \psi_j^B(\boldsymbol{R}_B) = 0 , \quad (2.4b)$$

are Schrödinger equations for separate target and projectile. Information about the collision is then contained entirely in the radial functions $f_{ij}(\boldsymbol{P})$. On substituting eqs. (2.1), (2.3), and (2.4) into (2.2) it is apparent that only the interaction V has off-diagonal matrix elements and is thus "responsible" for causing collision-induced transitions.

3. Asymptotic forms

For an atomic projectile the internal hamiltonian is just the electronic energy

$$\mathcal{H}_B(\boldsymbol{R}_B) = \mathcal{H}_B^{el} = \sum_i [\tfrac{1}{2}\nabla_i^2 - Z_B/r_i + \sum_{j>i} 1/|r_i - r_j|] \quad (3.1)$$

where sums are over the electrons in the projectile, B, r_i are electron coordinates measured from the nucleus and parallel to space-fixed axes, and Z_B is the nuclear charge. Atomic units* are used here and throughout the rest of the paper. The atomic wavefunctions then correspond to the usual spectroscopic states. Because $\mathcal{H}_B^{el}$ is invariant to rotations about the nucleus, angular momentum will be a good quantum number. We restrict our attention to rare gas atoms so that electron spin and orbital angular momenta are zero in the ground state. Consequently we are able to ignore internal angular momentum of the projectile.

The target hamiltonian and wavefunction are more complicated than the atomic case since the internal coordinates include nuclear as well as electronic degrees of freedom. It is convenient to write the hamiltonian as the sum of three parts

$$\mathcal{H}_A = \mathcal{H}_A^{el} + \mathcal{H}_A^{vib} + \mathcal{H}_A^{rot} , \quad (3.2)$$

where $\mathcal{H}_A^{el}$ describes the kinetic energy of the electrons and the potential energy of the electrons and nuclei; $\mathcal{H}_A^{vib}$, the radial motion of the nuclei; and $\mathcal{H}_A^{rot}$, the rotational motion of the nuclei. To obtain molecular wavefunctions one normally makes the Born–Oppenheimer approximation of independent nuclear and electronic motions (fixed-nuclei approximation). Then the total wavefunction is a product

* 1 au energy = 1 hartree ≈ 27.21 eV.

$$\psi_A(R_A) = \psi_A^{el}(r_i;R)\,\psi_A^{vib}(R)\,\psi_A^{rot}(R)\,, \qquad (3.3)$$

where r_i are electron coordinates and R is the internuclear coordinate. Upon substituting (3.3) into (3.2) and ignoring various nuclear–electronic cross terms, the wavefunctions for the different degrees of freedom can be obtained separately. The electronic wavefunction satisfies a Schrödinger equation

$$\Big\{\sum_i\Big(\tfrac{1}{2}\nabla_i^2 - Z_a/|r_i + [M_b/(M_a+M_b)]R| - Z_b/|r_i - [M_a/(M_a+M_b)]R| + Z_aZ_b/|R| + \sum_{j>i} 1/|r_i - r_j|\Big) - E_A^{el}(R)\Big\}\,\psi_A^{el}(r_i;R) = 0\,, \qquad (3.4)$$

and is seen to depend parametrically on the internuclear distance $R = R_a - R_b$ because of the Coulomb interaction between the nuclei a, b of charges Z_a, Z_b and masses M_a, M_b and the electrons i, where r_i is measured with respect to space-fixed axes from the molecular center of mass. The vibrational wavefunction satisfies the radial Schrödinger equation

$$[\tfrac{1}{2}\mu_A\nabla_R^2 + E_A^{el}(R) + E_A^{rot}(R) - E_A]\,\psi_A^{vib}(R) = 0\,, \qquad (3.5)$$

where μ_A is the reduced mass of the molecule and $E_A^{rot}(R)$ represents the centrifugal potential,

$$E_A^{rot}(R) = \langle\psi_A^{rot}(R)|B(R)O^2|\psi_A^{rot}(R)\rangle\,. \qquad (3.6)$$

Here $B(R) = (2\mu_A R^2)^{-1}$, and O is the rotational angular momentum operator of the nuclei, which may be expressed in terms of the total angular momentum J, the electronic orbital angular momentum L, and the electronic spin angular momentum S as

$$O = J - L - S\,. \qquad (3.7)$$

Molecular electronic wavefunctions (or approximations thereto) are generally obtained in a molecule-fixed (i.e., a rotating) coordinate system with origin at the center of mass and, for diatomics, with the z' axis conventionally along the internuclear axis. (We will designate rotating, molecule-fixed coordinates by primes.) The electronic wavefunctions belong to irreducible representations of the space symmetry group of the nuclei – $C_{\infty v}$ for heteronuclear and $D_{\infty h}$ for homonuclear diatomics. Because the molecule does not have spherical symmetry, the electronic orbital angular momentum cannot be a good quantum number. However, its projection on the internuclear axis is a constant of the motion and is designated by Λ. States with $\Lambda \neq 0$ are doubly degenerate corresponding to momentum in opposite senses about the axis. It can be shown that the electronic functions in rotating molecule-fixed coordinates have the form [12]

$$\psi_{el} \sim f_{|\Lambda|}(r_1', \theta_1'; r_2', \theta_2'; \varphi_2' - \varphi_1'; \;...; r_N', \theta_N'; \varphi_N' - \varphi_1') \times \exp(\pm i\Lambda\varphi_1')\,, \qquad (3.8)$$

so that the charge distribution can be viewed as a "rigid cloud" whose rotation about the internuclear axis – and hence the electronic angular momentum – is expressed entirely in the factor $\exp(\pm i\Lambda\varphi_1')$. In this form it is explicitly clear that, within the fixed-nuclei approximation, the electronic wavefunctions have cylindrical symmetry, changing by at most a phase factor under rotation about the axis.

The vibrational wavefunctions are eigenfunctions of a one-dimensional hamiltonian eq. (3.5) and can therefore always be obtained, at least numerically. Scattering theory for a vibrating rotor is a straightforward extension of that for a rigid rotor [13,14]. We will henceforth simplify our notation and discussion by ignoring vibrational transitions and consider only a rigid rotor.

In the presence of electron orbital or spin angular momentum, nuclear rotational angular momentum is no longer a good quantum number. Therefore, the rotational wavefunctions, $\psi_A^{rot}(R)$ differ from the electronic and vibrational functions in that they do not in general satisfy a Schrödinger equation. Instead one chooses representations for $\psi_A^{rot}(R)$ which are eigenfunctions of the most important part of the rotational hamiltonian. For singlet molecules $O = J - L$ so that

$$\mathcal{H}_A^{rot}(R) = B(R)(J-L)^2 = B(R)(J^2 - J_{z'}^2) + B(R)(J_+L_- + J_-L_+) + \tfrac{1}{2}B(R)(L_+L_- + L_-L_+)\,, \qquad (3.9)$$

where $J_{z'} = L_{z'}$, since O is perpendicular to the internuclear axis by definition. We choose to work in Hund's case (a) where the rotational wavefunctions $\psi_{J\Lambda M}(\alpha\beta\gamma)$ are eigenfunctions of the first term in eq. (3.9) and are recognized to be the symmetric top wavefunctions with projection M on the space-fixed z axis and projection Λ on the body-fixed z' axis.

Thus

$$\psi_{J\Lambda M}(\alpha\beta\gamma) \sim \mathcal{D}^{J*}_{M\Lambda}(\alpha\beta\gamma)\,, \tag{3.10}$$

and $E^{\rm rot}_{\rm A}$ in eq. (3.6) is given by

$$E^{\rm rot}_{\rm A}(R) = \langle\psi_{J\Lambda M}|B(R)\,O^2|\psi_{J\Lambda M}\rangle = B(R)[J(J+1)-\Lambda^2]\,, \tag{3.11}$$

where the expectation value of the second term in eq. (3.9) vanishes and we neglect the (homogeneous perturbation) contribution from the third term. The Euler angles $\alpha\beta\gamma$ which appear in $\psi_{J\Lambda M}$ relate space-fixed and molecule-fixed axes. The angle γ, which measures rotation about the z' axis is arbitrary for a diatomic molecule and we adopt the convention $\gamma = 0$ [15]. The electronic-rotation functions are then

$$\begin{aligned}\lambda_\pm &\sim f_{|\Lambda|}[\exp({\rm i}\Lambda\varphi_1')\mathcal{D}^{J*}_{M\Lambda}(\alpha\beta 0)\\ &\quad\pm\exp(-{\rm i}\Lambda\varphi_1')\mathcal{D}^{J*}_{M-\Lambda}(\alpha\beta 0)]\\ &\equiv f_{|\Lambda|}[\mathcal{D}^{J*}_{M\Lambda}(\alpha\beta\varphi_1')\pm\mathcal{D}^{J*}_{M-\Lambda}(\alpha\beta\varphi_1')]\,,\end{aligned} \tag{3.12}$$

where we have taken a linear combination of the degenerate $\pm\Lambda$ states so that $\lambda_\pm$ also have well defined parity. The electronic-rotation wavefunctions must have definite parity because the target hamiltonian, $\mathcal{H}_{\rm A}$, is invariant to the inversion of all coordinates through the origin. We note that *the identity in eq. (3.12) allows us to interpret the $\pm\Lambda$ degeneracy as being alternatively in either the electronic or the rotational wavefunction*, a point to which we will return later.

We now consider the effect of the two terms in eq. (3.9) which were ignored. $L_+L_- + L_-L_+$ is a homogeneous perturbation which can only connect electronic states with the same Λ. Consequently, this has the effect of slightly shifting an entire potential energy curve, so that it is generally undetectable by spectroscopic means; because no symmetry is changed, it will also be unimportant for collision dynamics. The heterogeneous perturbation term, $J_+L_- + J_-L_+$, which arises from coriolis interaction, is readily seen to connect states that differ by one unit in Λ. For a Π state this gives rise to a splitting between Λ components when account is taken of the interaction with neighboring Σ states. A Σ state has definitive parity (Σ^+ or Σ^-) and the perturbation will connect it with only one of the parity components of the Λ doublet, shifting its energy relative to the unaffected component of opposite parity. Like the homogeneous perturbation term, this term does not change the symmetry of the electronic-rotational wavefunctions and does not therefore significantly alter collision dynamics. The energy splitting caused by this term will, of course, affect the collisional energy transfer; however, this splitting is negligible compared with thermal collision energies, and thus the Λ splitting can be neglected.

We show now that the electron density in the two Λ components forms lobes as noted by Ottinger et al. [1]. These lobes are directed along J or perpendicular to J, and in both cases perpendicular to the internuclear axis in the high J limit (J large compared to Λ). The electron density distribution, when averaged over the rotational motion of the nuclei, becomes

$$\int\lambda_\pm^*\lambda_\pm\sin\beta\,{\rm d}\beta\,{\rm d}\alpha \sim |f_1|^2[1\pm\cos 2\varphi_1'\,S(J,M)]\,, \tag{3.13}$$

where

$$S(J,M) = [(2J+1)/4\pi]\int_0^{2\pi}{\rm d}\alpha\int_0^{\pi}\sin\beta\,{\rm d}\beta \times\mathcal{D}^{J}_{M1}(\alpha\beta 0)\mathcal{D}^{J*}_{M-1}(\alpha\beta 0)\,. \tag{3.14}$$

According to the vector model, the angular momentum J precesses about the space-fixed z axis making a projection M upon it. For $M = 0$, J must therefore be in the (x,y) plane. However, in the high J limit, J must also be perpendicular to the internuclear axis and hence must lie in the (x',y') plane. Thus J is along the line of nodes (i.e., the y' axis) for $M = 0$. In this case $S(J,0) = -1$ (see appendix) so that eq. (3.13) becomes

$$\int\lambda_\pm^*\lambda_\pm\sin\beta\,{\rm d}\beta\,{\rm d}\alpha \sim |f_1|^2(1\mp\cos 2\varphi_1') \sim |f_1|^2\begin{Bmatrix}\sin^2\varphi_1'\\ \cos^2\varphi_1'\end{Bmatrix}\,. \tag{3.15}$$

Since φ' is measured from the x' axis and J lies along y' for $M = 0$, we see from the above that the $\lambda_\pm$ charge distribution forms lobes directed parallel and perpendicular to J, respectively. For $M = J$, J approaches the z axis and hence the (y',z') plane coincides with the (x,y) plane in the limit of high J; thus J is along the x' axis. In this case, $S(J,J) = J/(J+1)$ (see appendix) and in the high J limit eq. (3.13) becomes

$$\int \lambda_\pm^* \lambda_\pm \sin\beta\, d\beta\, d\alpha \sim |f_1|^2 (1 \pm \cos 2\varphi_1') \sim |f_1|^2 \begin{Bmatrix} \cos^2\varphi_1' \\ \sin^2\varphi_1' \end{Bmatrix} \quad (3.16)$$

Here again the $\lambda_\pm$ charge distribution forms lobes directed parallel and perpendicular to J, respectively. For intermediate M values, the description of the classical motion is more complicated; however, it can be shown that eq. (3.13) always reduces to $\cos^2 g$ and $\sin^2 g$ distributions where the angle g is measured from the precessing J vector.

This typical situation can be described in an alternate manner. Rather than consider $\lambda_\pm$ as two differently oriented electronic states, we can consider instead a single electronic function by allowing for rotation about two orthogonal axes. Thus we will arbitrarily fix the electron lobes along the x' axis

$$\bar{\lambda}_{el} \sim f_{|\Lambda|} \cos\Lambda\varphi_1' , \quad (3.17)$$

and use the near-symmetric top rotational functions which describe (in the high J limit) rotation about the x' and y' axes

$$\bar{\lambda}_{rot} \sim \mathcal{D}^{J*}_{M\Lambda}(\alpha\beta\gamma) \pm \mathcal{D}^{J*}_{M-\Lambda}(\alpha\beta\gamma) . \quad (3.18)$$

Thus the total electronic-rotation wavefunctions become

$$\bar{\lambda}_\pm \sim f_{|\Lambda|} \cos\Lambda\varphi_1' [\mathcal{D}^{J*}_{M\Lambda}(\alpha\beta\gamma) \pm \mathcal{D}^{J*}_{M-\Lambda}(\alpha\beta\gamma)] . \quad (3.19)$$

Note that the body-fixed axes in eq. (3.17) are not identical to our previous definition, but must now be chosen along the principal moments of inertia so that we may use the rotational wavefunctions for the near-symmetric top. We must also then reintroduce γ into the rotational wavefunction. Eqs. (3.12) and (3.19) give two representations, $\lambda_\pm$ and $\bar{\lambda}_\pm$, for the electronic-rotational motion which are equivalent; they give idenidentical probability distributions and matrix elements.

4. Interaction potential

The interaction between target and projectile, V, depends in general on the internal coordinates $\boldsymbol{R}_A$ and $\boldsymbol{R}_B$ as well as on the collision coordinate $\boldsymbol{P}$. Because V has matrix elements between target and projectile functions a common coordinate system is desirable, and, for the systems under consideration, it is easiest to use the rotating, molecule-fixed diatomic target coordinates (see fig. 1). In this frame, the projectile is at $\boldsymbol{P}' = (P', \Theta', \Phi')$ where it is apparent that $P' = P$ and that $\Theta'\Phi'$ and $\Theta\Phi$ are related by the rotation $R(\alpha\beta\gamma)$ which rotates space-fixed into molecule-fixed axes [i.e., the Euler angles can be identified with those in eq. (3.10)].

The largest interactions between a diatomic molecule and an atom are electrostatic interactions; indeed other interactions are not important for the systems under comsideration. The Coulomb interaction will have off-diagonal matrix elements to excited electronic states of both target and projectile, and these will depend parametrically on nuclear coordinates. Thus, despite the fact that only single electronic states of target and projectile are of interest – i.e., we do not consider electronically inelastic processes – the collision proceeds through *virtual* electronic excitations of both target and projectile, and these excited states must be included in the expansion of the total wavefunction, eq. (2.3). The problem can be greatly simplified by constructing a potential which acts only in the space of the nuclear coordinates but which implicitly accounts for the excited electronic states of target and projectile. This is accomplished as usual by a unitary transformation on the basis set to diagonalize or partially diagonalize the offending operator. A similar approach for atom–atom collisions has been named the "perturbed stationary state" (PPS) method [16], and we adopt this nomenclature. In this treatment

$$\mathcal{H}_{PSS} = \mathcal{H}^{el}_A(r_A;\boldsymbol{R}_A) + \mathcal{H}^{el}_B(r_B) + V(\boldsymbol{R}_A,\boldsymbol{R}_B,\boldsymbol{P}) \quad (4.1)$$

is just the electronic (Born–Oppenheimer) hamiltonian for the composite A–B "molecule". Then $\mathcal{H}_{PSS}$ has a complete set of electronic states (potential energy surfaces in the space of the nuclear coordinates) which spans the same space as the complete sets of $\mathcal{H}^{el}_A$ and $\mathcal{H}^{el}_B$; indeed these two sets are related by the unitary transformation which diagonalizes V.

As noted in section 2 the interaction can "induce" transitions to other states, so that one wants to work in a representation in which the initial state is strongly coupled by V to as few other states as possible; in the PSS representation coupling to other electronic levels is suppressed. At first glance, it may appear that the PSS representation has suppressed *all* coupling among target levels; this is not so because $\mathcal{H}^{\mathrm{rot}}_{\mathrm{A}}(R_{\mathrm{A}})$ is not, in general, diagonal in this representation and will cause transitions amongst PSS states. One might be tempted to go one step further and diagonalize $\mathcal{H}_{\mathrm{A}}(R_{\mathrm{A}}) + \mathcal{H}_{\mathrm{B}}(R_{\mathrm{B}}) + V(R_{\mathrm{A}}, R_{\mathrm{B}}, P)$ instead of just the electronic parts. The difficulty here is that this transformation will introduce complicated coupling terms in the kinetic energy operator, $T(P)$. Note that carrying this process one step further and diagonalizing the total hamiltonian is of course just equivalent to *solving* the scattering problem. The point we are trying to make here is that one wants to choose a representation for the full hamiltonian which is a compromise between simplicity of evaluating matrix elements and ease of handling the collision dynamics.

The problem of computing the interaction potential is now reduced to obtaining Born–Oppenheimer electronic potential energy surfaces for the triatomic molecule, a tractable problem which has been extensively studied. In discussing these PSS electronic wavefunctions it is convenient to introduce a second set of molecule-fixed coordinates, r''. To facilitate comparison with the asymptotic states, we choose r'' to coincide as nearly as possible with r'. Thus we choose a common origin and we define the z'' axis to coincide with the z' axis; however, we choose atom B to lie in the $x''z''$ plane. Thus the PSS coordinates r'' are obtained from the diatomic coordinates r' by the rotation Φ' about z' so that

$$\varphi' = \Phi' + \varphi'' . \tag{4.2}$$

The PSS electronic wavefunctions will belong to irreducible representations of the space symmetry group of the nuclei. Whereas the diatomic target has infinitely many planes of symmetry, the triatomic has in general only one ($\mathrm{C_s}$ symmetry group) and this reduction in symmetry will play an important role in the scattering dynamics. The PSS wavefunctions can be labeled A' or A'' according to whether they are even or odd under reflection in the plane of the nuclei ($x''z''$ plane).

Because collision cross sections refer only to the asymptotic behavior of a system, the nature of the PSS electronic states as $P' \to \infty$ will be important. The doubly degenerate diatomic states (Λ doublets) must split under the lower $\mathrm{C_s}$ symmetry (which has no degenerate representations) into states that are even or odd with respect to reflection in the $x''z''$ plane (which transforms φ'' to $-\varphi''$). The former will correlate with A' and the latter with A'' PSS states. For an asymptotic target state with electronic momentum Λ about the diatomic axis, the A' state must transform as $\cos\Lambda\varphi''$ and the A'' state as $\sin\Lambda\varphi''$. This symmetry splitting is quite analogous to Λ-doubling where the diatomic symmetry is removed by nuclear rotation which also defines a unique plane through the nuclei. It is important to note, however, that the Λ-doublets and the PSS asymptotic states refer to *spatially* different planes of symmetry: The PSS state to $x''z''$ and the Λ-doublets to $x'z'$. These two sets are, of course, related by a unitary transformation which depends on the relation between r' and r'' coordinates, and it is this fact which will lead to an apparent Φ'-dependent interaction potential.

As noted, the PSS states asymptotically approach diatomic states whose electronic wavefunctions (for $|\Lambda| = 1$) depend on the azimuthal angle as

$$A' \xrightarrow[P' \to \infty]{} \cos\varphi'' , \quad A'' \xrightarrow[P' \to \infty]{} \sin\varphi'' . \tag{4.3}$$

On the other hand, the electronic part of the target functions has the asymptotic form [eq. (3.8)]

$$A_+ \xrightarrow[P' \to \infty]{} \mathrm{e}^{\mathrm{i}\varphi'} , \quad A_- \xrightarrow[P' \to \infty]{} \mathrm{e}^{-\mathrm{i}\varphi'} . \tag{4.4}$$

Using the relation between PSS and target coordinates, eq. (4.2), it is easy to find a unitary transformation between the asymptotic functions in eqs. (4.3) and (4.4), viz.

$$\begin{pmatrix} A_+ \\ A_- \end{pmatrix} = 2^{-1/2} \begin{pmatrix} \mathrm{e}^{\mathrm{i}\Phi'} & \mathrm{i}\mathrm{e}^{\mathrm{i}\Phi'} \\ \mathrm{e}^{-\mathrm{i}\Phi'} & -\mathrm{i}\mathrm{e}^{-\mathrm{i}\Phi'} \end{pmatrix} \begin{pmatrix} A' \\ A'' \end{pmatrix} . \tag{4.5}$$

In the $A_\pm$ basis, matrix elements of $\mathcal{H}_{\mathrm{PSS}}$ are

$$\langle A_+ | \mathcal{H}_{\mathrm{PSS}} | A_+ \rangle = \langle A_- | \mathcal{H}_{\mathrm{PSS}} | A_- \rangle = \tfrac{1}{2}(E' + E'') = q_0 , \tag{4.6a}$$

$$\langle A_+ | \mathcal{H}_{\mathrm{PSS}} | A_- \rangle = \langle A_- | \mathcal{H}_{\mathrm{PSS}} | A_+ \rangle^* = \tfrac{1}{2}\mathrm{e}^{-2\mathrm{i}\Phi'}(E' - E'') = q_2 , \tag{4.6b}$$

where E^i, the electronic energy of PSS state A^i, is a function of P' and Θ'. We have made an identification of these matrix elements with the q_λ given by Klar [11], thus specifying an explicit method for obtaining his parameters in terms of the PSS electronic potential energy surfaces.

We obtain our final expansion wavefunctions $\epsilon_\pm$ by associating the appropriate rotational functions with the $A_\pm$ electronic functions so that we have a basis which goes asymptotically to the proper target electronic-rotation states. By analogy with eq. (3.12) we have

$$\epsilon_\pm = 2^{-1/2}[A_+\mathcal{D}^{J*}_{M1}(\alpha\beta 0) \pm A_-\mathcal{D}^{J*}_{M-1}(\alpha\beta 0)] . \qquad (4.7)$$

This transformation is *not* identical to that discussed by Klar due to the presence of the target rotational functions. Matrix elements of $\mathcal{H}_{\mathrm{PSS}} + \mathcal{H}^{\mathrm{rot}}_{\mathrm{A}}$ in the $\epsilon_\pm$ basis are

$$\langle\epsilon_\pm|\mathcal{H}_{\mathrm{PSS}} + \mathcal{H}^{\mathrm{rot}}_{\mathrm{A}}|\epsilon_\pm\rangle = E^{\mathrm{rot}}_{\mathrm{A}} + q_0 \pm \tfrac{1}{2}S(J,M)(q_2 + q_{-2}) , \qquad (4.8a)$$

$$\langle\epsilon_\pm|\mathcal{H}_{\mathrm{PSS}} + \mathcal{H}^{\mathrm{rot}}_{\mathrm{A}}|\epsilon_\mp\rangle = \pm\tfrac{1}{2}S(J,M)(q_{-2} - q_2) , \qquad (4.8b)$$

where $S(J,M)$ is the rotational overlap integral defined in eq. (3.14).

Although we have identified the matrix elements of Klar with the two electronic energy surfaces, it is not yet apparent how these are related to "the potential ... in the body-fixed system" discussed by him. Indeed, Klar does not appear to make this connection. By analogy with our treatment of the Λ-doublet electronic-rotation functions, $\lambda_\pm$, we now seek an alternate description, analogous to $\bar{\lambda}_\pm$, which has a single electronic function and two rotational states. We note first that the linear combination $(A_+ + A_-)$ asymptotically approaches $\cos\varphi'$ while $(A_+ - A_-)$ asymptotically approaches $\sin\varphi'$. We thus consider the functions

$$\epsilon_x = \tfrac{1}{2}(A_+ + A_-)[\mathcal{D}^{J*}_{M1}(\alpha\beta\gamma) + \mathcal{D}^{J*}_{M-1}(\alpha\beta\gamma)] , \qquad (4.9a)$$

$$\epsilon_y = \tfrac{1}{2}(A_+ - A_-)[\mathcal{D}^{J*}_{M1}(\alpha\beta\gamma) + \mathcal{D}^{J*}_{M-1}(\alpha\beta\gamma)] . \qquad (4.9b)$$

Finally we use the identity

$$\epsilon_y = \tfrac{1}{2}(A_+ - A_-)[\mathcal{D}^{J*}_{M1}(\alpha\beta\gamma) + \mathcal{D}^{J*}_{M-1}(\alpha\beta\gamma)]$$
$$= \tfrac{1}{2}(A_+ + A_-)[\mathcal{D}^{J*}_{M1}(\alpha\beta\gamma + \pi/2) - \mathcal{D}^{J*}_{M-1}(\alpha\beta\gamma + \pi/2)] . \qquad (4.10)$$

If we change the overall phase of ϵ_y by $\pi/2$ we have our desired basis set,

$$\bar{\epsilon}_\pm = \tfrac{1}{2}(A_+ + A_-)[\mathcal{D}^{J*}_{M1}(\alpha\beta\gamma) \pm \mathcal{D}^{J*}_{M-1}(\alpha\beta\gamma)] . \qquad (4.11)$$

We have thus accomplished our desired simplification of reformulating the problem in terms of a single electronic function,

$$2^{-1/2}(A_+ + A_-) \equiv A'\cos\Phi' - A''\sin\Phi' , \qquad (4.12)$$

with two rotational states. The rotational functions are identical to those for the K-doublets of a near-symmetric top with $K = 1$. The interaction potential in this model is just the electronic energy which is readily found to be

$$\bar{V}(P',\Theta',\Phi') = \tfrac{1}{2}\langle A_+ + A_-|\mathcal{H}_{\mathrm{PSS}}|A_+ + A_-\rangle$$
$$= \tfrac{1}{2}(E' + E'') + \tfrac{1}{4}(E' - E'')(e^{2i\Phi'} + e^{-2i\Phi'}) . \qquad (4.13)$$

The Φ' dependence enters naturally in this picture and is seen to have the form postulated by Bergmann et al. [9] to account for the ΔJ asymmetry†.

The above analysis has led to an effective Φ'-dependent potential despite our emphasis on the cylindrical symmetry of the diatomic target. To conclude this section we will try to provide some more physical insight into the origin of this phenomenon. The crucial part of the analysis is the separation of rotational and electronic motions and the subsequent ability to choose a representation for these motions which involves a single electronic state. This is possible only in the high J limit where the Λ components can be described as electron lobes aligned parallel or perpendicular to the nuclear rotation vector, or, alternatively, as electron lobes fixed in the molecular frame with rotation parallel or perpendicular to the lobes. In the latter picture one expects the interaction with a closed-shell atom to depend on Φ', the azimuthal angle of the projectile relative to the electron lobes; for example one expects the interaction to be more repulsive if the projectile approaches in the plane of the electron lobes than if the approach is perpendicular to this plane. Thus the A'' PSS state is expected to be energetically lower, in general, than the A' state. Since we have only two electronic "stationary state" potential surfaces, we expect the collision to take place

† If one ignores excitation to electronic states of different Λ, the expansion of the $^1\Pi$ interaction potential in spherical harmonics $Y_{lm}(\Theta,\Phi)$ has a range of l values determined by the shape of E' and E'', but m takes on only the values 0 and 2. This is in contradistinction to the case of a general (near) symmetric top where the range of m as well as of l is determined by the three-dimensional shape of the potential surface. (See, e.g., Verter and Rabitz [17].)

adiabatically along the lower A'' potential surface in the absence of nuclear rotation. However, in the rotating molecule, J is firmly oriented relative to the electron lobes; as the projectile adiabatically approaches it tries to align the electron lobes perpendicular to the direction of approach, which is equivalent to exerting a torque on J. Thus the projectile does not follow an adiabatic surface, but rather forms a diabatic "superposition" state which is seen from eq. (4.12) to be just the *geometric projection* of the A' and A'' states on the molecule-fixed Λ-doublet lobes (see fig. 2). Hence the Φ'-dependent effective potential arises from the conflict between electronic-rotational coupling which tries to align the electron lobes relative to the space-fixed direction of J and interaction with the projectile which tries to align the electron lobes relative to its direction of approach.

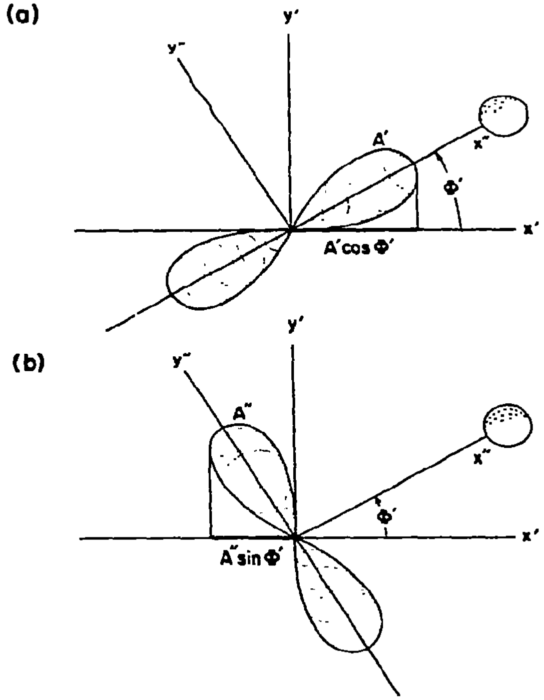

Fig. 2. "Diabatic" superposition state as a projection of stationary states on the Λ-doublet lobes which are fixed along the x' axis: (a) projection of the A' state, (b) projection of the A'' state. The internuclear axis is perpendicular to the plane of the figure.

5. Collision dynamics

The quantum scattering formulation employed in the preceeding theoretical development leads naturally to the close-coupling [18] method for collision dynamics; indeed eq. (2.1) embodies the basic expansion technique of close-coupling. Despite recent breakthroughs in numerical techniques for solving the close-coupling equations, this method is tractable – even with the largest available computers – only for collisions which involve less than about a dozen of the lowest rotational levels. The available alkali data, however, involve rotational levels $J = 10$–100, and it is not currently possible to perform close-coupling calculations for such systems. Fortunately, one expects other, more approximate techniques to become valid for such cases. In this section we will comment briefly on the suitability of methods which have been employed or which might reasonably be employed for those systems where data are available.

A number of proposals have appeared recently for reducing the dimensionality of computations within the close-coupling formulation so that current numerical techniques could handle a significantly larger number of rotational levels [19–21]. All of these rely on approximate angular momentum coupling to partially decouple the equations. The utility of such methods for the systems under consideration depends on the sensitivity of the interesting "propensity rules" to these approximations in angular momentum coupling. Preliminary calculations (on other systems) using the method of Rabitz [19] indicate that unacceptable errors may be introduced this way. Although these or similar techniques may ultimately prove useful, it will be necessary to carefully check their validity for the systems of interest.

One of the most commonly used quantum scattering techniques is the Born approximation. Although extremely simple, it gives remarkably accurate results for some systems. It is particularly useful for weak, long-range interactions and also for high collision energies. Unfortunately, its validity is at best marginal for excitation of alkali molecules at thermal energies. On the other hand, being an approximate solution – albeit in zeroth order – to the full close-coupling equations, the Born approximation is expected to reflect at least the qualitative features of these collisions. It is not surprising therefore, that Bergmann et al. [9] were able to reproduce many trends in the experimental data on the basis of a parameterized Born treatment. One does not, however, expect that the parameters obtained this way are quantitatively related to the actual interaction potential, since they must also contain information about higher-order effects ignored in the scattering approximation. Indeed, Ottinger [7] has indicated that the potential parameters obtained this way do not in fact correspond to reasonable potentials.

At energies where many quantum levels are accessible, one expects classical mechanics to become a valid description. Indeed classical trajectory calculations are known to adequately describe many aspects of molecular rotational excitation in thermal collisions. However, such calculations cannot, in general, reproduce propensity rules since these reflect quantum mechanical interference effects [22,23]. This fact has been noted by Poppe [10] in connection with alkali diatomic systems. Fortunately, one does not have to entirely abandon the simplifications of classical mechanics in order to calculate propensity rules. Rather, one can adopt a semi-classical description. Miller has discussed a semi-classical treatment wherein quantum mechanics is used only to account for interference effects between different classical trajectories [24]. Other semi-classical formalisms are also possible. For example, one can treat the relative collision motion classically while retaining a purely quantum description of the internal target states [25]. We believe the most promising approach for calculating cross sections for collision-induced rotation-fine structure transitions would be a semi-classical description of the collision process.

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Appendix

Consider the integral

$$S(J,M) = [(2J+1)/4\pi] \int_0^{2\pi} \mathrm{d}\alpha \int_0^{\pi} \sin\beta \, \mathrm{d}\beta \times \mathcal{D}^J_{M1}(\alpha\beta 0)\, \mathcal{D}^{J*}_{M-1}(\alpha\beta 0) . \tag{A.1}$$

In (A.1) the $\mathcal{D}$-functions are rotation matrices [26], given by

$$\mathcal{D}^J_{MN}(\alpha\beta 0) = \exp(-iM\alpha)\, d^J_{MN}(\beta) , \tag{A.2}$$

with the normalization

$$[(2J+1)/4\pi] \int_0^{2\pi} \mathrm{d}\alpha \int_0^{\pi} \sin\beta \, \mathrm{d}\beta \times \mathcal{D}^{J*}_{MN}(\alpha\beta 0)\, \mathcal{D}^J_{MN}(\alpha\beta 0) = 1 . \tag{A.3}$$

The $d^J_{MN}(\beta)$ are polynomials in powers of $\sin\beta/2$ and $\cos\beta/2$ having the form

$$d^J_{MN}(\beta) = [(J+M)!\,(J-M)!/(J+N)!\,(J-N)!]^{1/2} \times \sum_S (-1)^{J-M-S} \binom{J+N}{J-M-S} \binom{J-N}{S} \times (\cos\beta/2)^{2S+M+N} (\sin\beta/2)^{2J-2S-M-N} , \tag{A.4}$$

where the sum is over all values of S for which the binomial coefficients

$$\binom{X}{Y} = \frac{X!}{(X-Y)!\,Y!} \tag{A.5}$$

lead to non-negative factorials. Substituting (A.4) and (A.2) into (A.1) and performing the integration over $\mathrm{d}\alpha$ we obtain

$$S(J,M) = [(2J+1)/2]\, [(J+M)!(J-M)!/(J+1)!\,(J-1)!] \times \sum_S \sum_T (-1)^{S+T} \binom{J+1}{J-M-S} \binom{J-1}{S} \binom{J-1}{J-M-T} \binom{J+1}{T} \times \int_0^{\pi} (\cos\beta/2)^{2S+2T+2M} (\sin\beta/2)^{4J-2S-2T-2M} \sin\beta \, \mathrm{d}\beta . \tag{A.6}$$

With the help of the identity [27]

$$\int_0^{\pi} (\cos\beta/2)^{2A} (\sin\beta/2)^{2B} \sin\beta \, \mathrm{d}\beta = 2A!B!/(A+B+1)! \tag{A.7}$$

where A and B are non-negative integers, (A.6) becomes

$$S(J,M) = [(J+M)!\,(J-M)!/(J+1)!\,(J-1)!]$$
$$\times \sum_S \sum_T (-1)^{S+T} \binom{J+1}{J-M-S} \binom{J-1}{S}$$
$$\times \binom{J-1}{J-M-T} \binom{J+1}{T} \Big/ \binom{2J}{M+S+T}. \qquad (A.8)$$

Eq. (A.8) can be evaluated in closed form to give

$$S(J,M) = -1 + \frac{|M|(2J+1)}{J(J+1)}. \qquad (A.9)$$

For the special case $M = J$, $S(J,J) = J/(J+1)$; this can be obtained trivially from eq. (A.8) since the double summation reduces to a single term. For the special case, $M = 0$, $S(J,0) = -1$; this can be obtained most simply by noting that $D^J_{01} = -D^{J*}_{0-1}$ and using the normalization relation to evaluate eq. (A.1).

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