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# The adiabatic-diabatic approach to vibrational inelastic scattering: Theory and study of a simple collinear model

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The quantum mechanical problem of the vibrational excitation of a harmonic oscillator in one dimension is treated with an adiabatic basis set. The Smith transformation [Phys. Rev. **179**, 111 (1969)] is used to eliminate the dynamical coupling terms and leads to a new diabatic representation. The rate of convergence of calculated transition probabilities in the new diabatic representation is compared with calculations based on the usual asymptotic representation for a variety of different mass combinations and collision energies. These calculations revealed that: (i) the new diabatic potential matrix converges to the usual asymptotic one as the size of the adiabatic basis set becomes large enough; (ii) the transition probabilities converge much faster than the potential matrix elements and faster than those calculated by the usual method. Typically only about two states more than the upper state considered are required whereas in the usual representation many more states are needed, several of which are frequently closed.

## I. INTRODUCTION

Vibrational excitation in gas kinetic collisions is probably the most important of the energy transfer processes.<sup>1</sup> Since the energy per quantum is large and the relaxation is relatively slow, vibrational excitation and de-excitation is frequently a rate determining step in chemical reactions. A knowledge of vibrational relaxation rates is important for understanding chemical lasers, nozzle flows, shock waves, and sound propagation. Despite its importance, however, we are still far from being able to predict vibrationally inelastic cross sections. Quantum chemical theories are only able to predict the potential hypersurfaces for simple systems such as He-H<sub>2</sub> and Li<sup>+</sup>-H<sub>2</sub>. Very few molecular beam experiments with good resolution are available.<sup>2</sup> Even when available, their interpretation is not possible, because of the difficulties in scattering theory. Convergence in the calculations has been claimed for only a few realistic studies of the systems He-H<sub>2</sub>,<sup>3a,b</sup> Li<sup>+</sup>-H<sub>2</sub>,<sup>3c</sup> and Li-H<sub>2</sub>.<sup>3d</sup> However, the collision energies and transition probabilities in all cases were so low that a comparison with beam experiments was not possible. The main difficulty in the theory is the rapid nonlinear increase in computer time with increasing number of states and the need to take account of many rotational states. Recent approximations have been successful in considerably reducing the computing time for the rotational part of the problem.<sup>4</sup> For the vibrational part, experience gained in using conventional close coupling techniques applied to collinear systems indicates that many vibrational states including several closed channels, may be necessary.<sup>5</sup>

In view of this state of affairs we have embarked on a program to study alternative approaches. Previously Bowman and two of the present authors have examined the validity of the sudden approximation.<sup>6</sup> As expected, accurate results were only obtained in collisions of

light fast atoms from heavy slowly vibrating molecules. Since in most collisions of kinetic interest the vibrational periods are considerably shorter than the collision time, we have adopted an opposite approach in the present study, namely the adiabatic approach.

The adiabatic representation is a fundamental concept which is used when a collection of interacting particles can be divided into two groups of different time scales. The concept was introduced by Born and Oppenheimer<sup>7</sup> in the early days of quantum mechanics of molecular systems when they separated the treatment of the electronic part from the nuclear part making use of the fact that the electrons move much faster than the nuclei. The reason that the adiabatic representation has been largely overlooked in heavy particle scattering probably has to do with the fact that it is commonly thought that there is no obvious and general separation between "fast" and "slow" modes. However, near the classical turning point where vibrational transitions are expected to occur, the translational velocities become relatively small whereas the vibrational and rotational velocities remain almost unaffected. Our results support this idea and show that the adiabatic concept provides a powerful new approach for treating such processes.

The most obvious disadvantage in the adiabatic representation is the fact that the coupling among the various adiabatic (vibrational) states involves first derivatives which are not always easily handled. It is well known that the coefficients of these derivatives (the nonadiabatic coupling terms) behave in the vicinity of crossings (curves or points) in a very sharp way causing a numerical instability problem. However, in 1969 F. T. Smith,<sup>8</sup> while discussing electronic excitations in heavy particle collisions, suggested an orthogonal transformation which shifts the nonadiabatic coupling terms into the potential matrix. In this way a new set of equations is formed which is similar in form to the conventional set usually encountered in close coupling calculations. The new representation is called the *diabatic* representation. A few years later one of the present authors extended this method<sup>9</sup> and successfully applied it while

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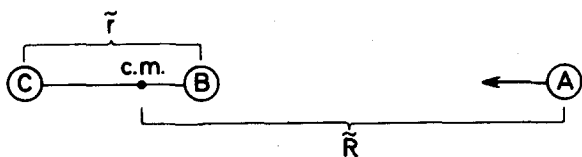


FIG. 1. The collinear collision geometry used in the present study.

treating electronic transitions taking place during a chemical reaction.<sup>10</sup>

As far as we are aware there have only been a few sporadic attempts at applying the adiabatic approach to vibrational or rotational excitation in heavy particle collisions. Levine *et al.*<sup>11</sup> were probably the first to discuss a two state adiabatic model for studying rotational excitation. Most recently Mullanney and Truhlar<sup>12</sup> studied rotational excitation in He-HF using the adiabatic approach but in a different way than presented here. For vibrational excitation Eno and Balint-Kurti<sup>13a</sup> applied an adiabatic basis set, but without the Smith transformation, for calculating vibrational transition probabilities within the Distorted Wave Born Approximation. In addition R. J. Cross<sup>13b</sup> has used a semiclassical perturbation theory based on an adiabatic expansion.

The paper starts with a brief description of how we adapt the formalism for electronically non-adiabatic transitions to the present problem. The calculation of the diabatic matrix elements for a model potential is discussed next. Analytic expressions for the matrix elements are derived in the two-state and three-state cases. In the following section we describe the techniques used to calculate the potential matrix elements numerically and how we solved the close coupling equations. Finally we compare the rate of convergence of the exact transition probabilities obtained with the new adiabatic approach with that obtained with the ordinary method. The paper closes with a discussion of the advantages of the adiabatic approach and the possibilities for using the adiabatic approach as a starting point for approximate procedures.

## II. THEORY

### A. Formalism for collinear collisions

Figure 1 shows a schematic diagram of the collision geometry. On introducing mass scaled vibrational  $r$  and translational  $R$  coordinates defined by<sup>14</sup>

$$r = \sqrt{\frac{\mu_{BC}}{\mu_{A,BC}}} \tilde{r}, \quad (1)$$

$$R = \sqrt{\frac{\mu_{A,BC}}{\mu_{BC}}} \tilde{R}, \quad (2)$$

the Schrödinger equation simplifies to

$$-\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial r^2} \right) \psi(R, r) + (V(R, r) - E) \psi(R, r) = 0. \quad (3)$$

If  $r = r_e(R)$  defines the minimum energy path then  $V(R, r)$  can be written

$$V(R, r) = V_0(R) + U(R, r) \quad (4)$$

where  $V_0(R) = V(R, r = r_e)$  and  $U(R, r = r_e) = 0$ .  $\mu$  is the reduced mass for the entire system

$$\mu = \sqrt{\frac{m_A m_B m_C}{m_A + m_B + m_C}}. \quad (5)$$

In the adiabatic approach we expand  $\psi(R, r)$  in the adiabatic basis set  $\phi_n(R, r)$ ,

$$\psi(R, r) = \sum_{n=0}^N \chi_n(R) \phi_n(R, r). \quad (6)$$

Substitution of the adiabatic expansion into the Schrödinger equation leads to coupling terms which are analogous to those which appear in the treatment of electronic curve crossing. Thus in the following we will follow closely the formalism developed for treating such problems in collinear collisions.

For simplicity we rewrite Eq. (6) as

$$\psi = \phi^* \chi. \quad (7)$$

Inserting Eq. (7) into Eq. (3) yields

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{d^2}{dR^2} + 2\tau^1 \frac{d}{dR} + \tau^2 \right) + \omega + V_0(R) - E \right] \chi = 0 \quad (8)$$

where the matrix  $\omega$  is diagonal,

$$\omega_{nm} = \epsilon_n(R) \delta_{nm}, \quad (9)$$

and  $\tau^1$  is an antisymmetric and  $\tau^2$  a symmetric matrix with the elements

$$\tau_{nm}^1(R) = \left\langle \phi_n \left| \frac{d}{dR} \right| \phi_m \right\rangle; \quad \tau_{nm}^2(R) = \left\langle \phi_n \left| \frac{d^2}{dR^2} \right| \phi_m \right\rangle \quad (10)$$

The coupling term  $\tau^1$  especially presents formidable computational problems as was discussed in the Introduction. These can be circumvented by introducing a new transformation first suggested by Smith<sup>6</sup> and applied by Baer<sup>9</sup> to collinear electronic excitation in atom-molecule collisions. The remainder of this Section is adapted directly from the work of Baer.<sup>9</sup>

A new adiabatic basis set  $\eta$  is introduced via the transformation matrix  $\mathbf{A}$ .

$$\phi = \mathbf{A}(R) \eta, \quad (11)$$

where we require that  $\mathbf{A}$  is only  $R$ -dependent. The same transformation is also applied to the translational function  $\chi$  such that

$$\chi = \mathbf{A}(R) \xi. \quad (12)$$

Consequently the total wave function in the new basis set becomes

$$\psi = \eta^* \mathbf{A}^* \mathbf{A} \xi. \quad (13)$$

As we shall see shortly the desired transformation matrix  $\mathbf{A}$  is orthogonal

$$\mathbf{A}^* \mathbf{A} = \mathbf{1}, \quad (14)$$

and therefore Eq. (13) simplifies to

$$\psi = \eta^* \xi. \quad (15)$$

Substitution of Eq. (12) into (8) yields

$$\left\{ -\frac{\hbar^2}{2\mu} \left[ \mathbf{A} \frac{d^2}{dR^2} + 2 \left( \frac{d\mathbf{A}}{dR} + \boldsymbol{\tau}^1 \mathbf{A} \right) \frac{d}{dR} + \frac{d^2 \mathbf{A}}{dR^2} + 2 \boldsymbol{\tau}^1 \frac{d\mathbf{A}}{dR} + \boldsymbol{\tau}^2 \mathbf{A} \right] + (\omega + V_0(R) - E) \mathbf{A} \right\} \boldsymbol{\xi} = 0. \quad (16)$$

This equation is simplified if  $\mathbf{A}$  is chosen to satisfy

$$\frac{d\mathbf{A}}{dR} + \boldsymbol{\tau}^1 \mathbf{A} = 0, \quad (17)$$

then it can be shown that  $\mathbf{A}$  is orthogonal (see Ref. 9) and, moreover, by further differentiating Eq. (17), (see Appendix B), we find

$$\frac{d^2 \mathbf{A}}{dR^2} + 2 \boldsymbol{\tau}^1 \frac{d\mathbf{A}}{dR} + \boldsymbol{\tau}^2 \mathbf{A} = 0. \quad (18)$$

Substituting Eqs. (17) and (18) into Eq. (16) and by taking advantage of the orthogonality of  $\mathbf{A}$ , Eq. (16) simplifies finally to

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \mathbf{W} + V_0(R) - E \right) \boldsymbol{\xi} = 0, \quad (19)$$

where

$$\mathbf{W} = \mathbf{A}^* \boldsymbol{\omega} \mathbf{A}. \quad (20)$$

It is seen that by introducing  $\mathbf{A}$  we have greatly simplified the Schrödinger equation, Eq. (8) and transformed it into the form encountered in the conventional treatments. Thus the dynamic couplings in Eq. (8) have been shifted into the potential matrix  $\mathbf{W}$ . In other words this transformation enables one to use the more efficient adiabatic representation and still avoid most of the deficiencies of this representation. The gain in simplicity is achieved at the expense of having to calculate  $\mathbf{W}$  by a more complicated procedure.

To calculate  $\mathbf{W}$  we have first to solve Eq. (17) for  $\mathbf{A}$ . The formal solution is given by<sup>15</sup>

$$\mathbf{A}(R) = \exp \left( - \int_{R_0}^R \boldsymbol{\tau}^1 dR \right), \quad (21)$$

where  $R_0$  is defined as some large  $R$ -value at which the basis set  $\phi(R, r)$  has its asymptotic form. Thus

$$\mathbf{A}(R_0) = \mathbf{1}. \quad (22)$$

To solve for  $\mathbf{A}$  we first diagonalize the argument in the exponent which is written for clarity as

$$\mathbf{B} = - \int_{R_0}^R \boldsymbol{\tau}^1(R) dR. \quad (23)$$

The transformation matrix is denoted by  $\mathbf{S}$

$$\mathbf{B}\mathbf{S} = \mathbf{S}\boldsymbol{\lambda}. \quad (24)$$

In Appendix A it is shown that since  $\mathbf{B}$  is antisymmetric,  $\mathbf{S}$  is unitary and the eigenvalues  $\lambda_{ij}$  are pure imaginary or zero. Once  $\mathbf{S}$  and  $\boldsymbol{\lambda}$  are determined  $\mathbf{A}$  takes the form

$$\mathbf{A} = \mathbf{S}\mathbf{E}\mathbf{S}^*, \quad (25)$$

where  $\mathbf{E}$  is a diagonal matrix

$$E_{ij} = \delta_{ij} \exp \lambda_{ij}. \quad (26)$$

## B. Diabatic matrix elements for a model potential

The calculation of the coupling matrix  $\boldsymbol{\tau}^1$  and the potential matrix  $\mathbf{W}(R)$  can be carried out analytically by

choosing the potential to be a perturbed harmonic oscillator

$$V(R, r) = V_0(R) + \frac{1}{2} k(R)(r - r_e(R))^2 \quad (27)$$

where  $V_0(R)$  is the potential describing the "elastic" interaction and  $k(R)$  and  $r_e(R)$  are the  $R$ -dependent adiabatic force constant and equilibrium distance respectively.

First we calculate the matrix elements of  $\boldsymbol{\tau}^1$ . If  $|n, R\rangle$  is the  $n$ th harmonic oscillator wave function at some value of  $R$  then  $|n, R\rangle$  can be written as

$$|n, R\rangle = \left( \frac{\mu \omega(R)}{\hbar} \right)^{1/4} |\bar{n}\rangle, \quad (28)$$

where  $\omega(R)$  is the (adiabatic) frequency and  $|\bar{n}\rangle$  is the solution of the equation

$$\frac{1}{2} \left( y^2 - \frac{d^2}{dy^2} \right) |\bar{n}\rangle = (n + \frac{1}{2}) |\bar{n}\rangle. \quad (29)$$

Here  $y$  stands for

$$y = \sqrt{\frac{\mu \omega(R)}{\hbar}} (r - r_e(R)). \quad (30)$$

To calculate  $\boldsymbol{\tau}^1$  [see Eq. (10)] we need the derivatives of  $|n, R\rangle$  with respect to  $R$ . Equations (28) and (30) yield

$$\begin{aligned} \frac{d}{dR} |n, R\rangle &= \frac{1}{4\omega} \frac{d\omega}{dR} \left( 1 + 2y \frac{d}{dy} \right) |n, R\rangle \\ &\quad - \sqrt{\frac{\mu \omega}{\hbar}} \frac{dr_e}{dR} \frac{d}{dy} |n, R\rangle. \end{aligned} \quad (31)$$

To continue, use is made of the annihilation and creation operators  $\mathbf{a}$  and  $\mathbf{a}^*$  defined as

$$\mathbf{a} = \frac{1}{\sqrt{2}} \left( y + \frac{d}{dy} \right), \quad (32)$$

$$\mathbf{a}^* = \frac{1}{\sqrt{2}} \left( y - \frac{d}{dy} \right). \quad (33)$$

From Eq. (32) and (33) we obtain

$$\frac{d}{dy} = \frac{1}{\sqrt{2}} (\mathbf{a} - \mathbf{a}^*), \quad (34)$$

$$1 + 2y \frac{d}{dy} = \mathbf{a}^2 - (\mathbf{a}^*)^2. \quad (35)$$

With help of these operators  $\boldsymbol{\tau}^1$  can be simplified to read

$$\boldsymbol{\tau}^1 = \boldsymbol{\tau}_\omega f_\omega - \boldsymbol{\tau}_{r_0} f_{r_0}, \quad (36)$$

where

$$\boldsymbol{\tau}_\omega = \mathbf{a}^2 - (\mathbf{a}^*)^2, \quad (37)$$

$$\boldsymbol{\tau}_{r_0} = \mathbf{a} - \mathbf{a}^*, \quad (38)$$

and

$$f_\omega = \frac{1}{4\omega} \frac{d\omega}{dR}, \quad (39)$$

$$f_{r_0} = \sqrt{\frac{\mu \omega}{2\hbar}} \frac{dr_e}{dR}. \quad (40)$$

The  $\boldsymbol{\tau}_{r_0}$  and  $\boldsymbol{\tau}_\omega$  are antisymmetric matrices of the form

$$\tau_{r_0} = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \\ -\sqrt{1} & 0 & \sqrt{2} & 0 & 0 \\ 0 & -\sqrt{2} & 0 & \sqrt{3} & 0 \\ 0 & 0 & \ddots & \ddots & \ddots \end{pmatrix} \quad (41)$$

$$\tau_{\omega} = \begin{pmatrix} 0 & 0 & \sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{6} & 0 \\ -\sqrt{2} & 0 & 0 & 0 & \sqrt{12} & 0 \\ 0 & -\sqrt{6} & 0 & 0 & 0 & \ddots \\ 0 & 0 & \ddots & \ddots & \ddots & \ddots \end{pmatrix} \quad (42)$$

Next, to find **A** we need the matrix **B** which is defined in Eq. (23) and is conveniently expressed in the following way

$$\mathbf{B} = \tau_{r_0} F_{r_0} - \tau_{\omega} F_{\omega}, \quad (43)$$

where

$$F_{\omega} = \int_{R_0}^R f_{\omega} dR = \frac{1}{4} \ln \frac{\omega(R)}{\omega(R_0)}, \quad (44a)$$

$$F_{r_0} = \int_{R_0}^R f_{r_0} dR = \int_{R_0}^R \sqrt{\frac{\mu \omega(R)}{2\hbar}} \frac{dr_e(R)}{dR} dR. \quad (44b)$$

The integral for  $F_{r_0}$  cannot be performed unless  $\omega(R)$  and  $r_e(R)$  are explicitly given. Assuming, however, that  $\omega(R)$  is a slowly varying function of  $R$ , we find

$$F_{r_0} \cong \sqrt{\frac{\mu \bar{\omega}}{2\hbar}} (r_e(R) - r_e(R_0)), \quad (45)$$

where  $\bar{\omega}$  is some average value of  $\omega(R)$  in the interval  $(R, R_0)$ .

From the theory given in the previous section it can be seen that in order to have vibrational excitation it is important that **B** will have large off-diagonal terms (the diagonal elements are identically zero). From the results presented so far, it is apparent that the magnitudes of these elements depend on the curvature of the minimum energy path [i.e.,  $(r_e(R) - r_e(R_0))$ ] as well as on the relative variations of  $\omega(R)$  as a function of  $R$ . Although the effect due to the curvature enters only in  $F_{r_0}$  whereas the effect due to the variations in  $\omega(R)$  enters in both,  $F_{r_0}$  and  $F_{\omega}$ , it seems that the curvature is more important for vibrational excitation. This can be seen in the following way: first we notice that a zero curvature yields  $F_{r_0} = 0$  and a constant  $\omega$  yields  $F_{\omega} = 0$  but  $F_{r_0} \neq 0$ . In the **B** matrix  $F_{r_0}$  is located next to the diagonal [at  $(i, i \pm 1)$ ] whereas  $F_{\omega}$  is located further out [at  $(i, i \pm 2)$ ]. Since the importance of matrix elements is larger the closer they are to the diagonal we notice that the vanishing of  $F_{\omega}$  (i.e., constant  $\omega$ ) will have a smaller effect on the excitation than the vanishing of  $F_{r_0}$  (i.e., zero curvature).

### C. Analytic expressions for potential matrix elements

For the model potential adopted here it is possible to calculate the potential matrix analytically. We treat

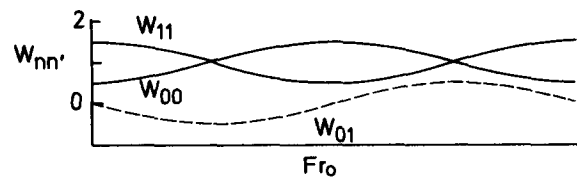


FIG. 2. The diabatic potential energy curves for the two state case and assuming  $\omega(R) = \text{constant}$  is shown schematically as a function of  $F_{r_0}$ , which is the only interaction parameter in the two state case. The diabatic coupling term  $W_{01}$  is shown at the bottom as a dashed line.

only the two simplest cases, namely the two-state and the three-state cases. The calculation for larger basis sets can be carried out similarly.

### The two-state case

In the two-state case the effects due to the dependence of  $\omega(R)$  on  $R$  are, as we can see from Eq. (42), automatically excluded. Therefore  $\tau^1$  becomes

$$\tau^1 = - \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} f_{r_0}. \quad (46)$$

Consequently, the unitary transformation **S** is

$$\mathbf{S} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \\ -i & 1 \end{pmatrix}, \quad (47)$$

and the two corresponding eigenvalues are

$$\lambda_{\pm} = \pm i F_{r_0}. \quad (48)$$

Accordingly **A** takes the form

$$\mathbf{A} = \begin{pmatrix} \cos F_{r_0} & \sin F_{r_0} \\ -\sin F_{r_0} & \cos F_{r_0} \end{pmatrix} \quad (49)$$

Finally the two diabatic potential curves are given by

$$W_{00} = \left(\frac{1}{2} + \sin^2 F_{r_0}\right) \hbar \omega(R), \quad (50)$$

$$W_{11} = \left(\frac{3}{2} - \sin^2 F_{r_0}\right) \hbar \omega(R),$$

and the diabatic coupling term by

$$W_{01} = -\frac{1}{2} \sin(2F_{r_0}) \hbar \omega(R). \quad (51)$$

Figure 2 shows the diabatic potentials as well as the diabatic coupling as a function of the interaction strength parameter  $F_{r_0}$ . For simplicity  $\omega(R)$  is assumed to be constant and independent of  $R$ .

### The three-state case

In the three-state case both  $f_{\omega}$  and  $f_{r_0}$  are incorporated. The  $\tau^1$  matrix has the form

$$\tau^1 = - \begin{pmatrix} 0 & f_{r_0} & -\sqrt{2} f_{\omega} \\ -f_{r_0} & 0 & \sqrt{2} f_{r_0} \\ \sqrt{2} f_{\omega} & -\sqrt{2} f_{r_0} & 0 \end{pmatrix}, \quad (52)$$

and consequently **S** becomes

$$\mathbf{S} = \begin{pmatrix} -\frac{g}{g_0} \sqrt{\frac{2}{3}} + \frac{i}{\sqrt{6}} & -\frac{g}{g_0} \sqrt{\frac{2}{3}} - \frac{i}{\sqrt{6}} & \frac{\sqrt{2}}{g_0} \\ \frac{1}{g_0} \sqrt{\frac{3}{2}} & \frac{1}{g_0} \sqrt{\frac{3}{2}} & \frac{g}{g_0} \sqrt{2} \\ -\left(\frac{g}{g_0} \frac{1}{\sqrt{3}} + \frac{i}{\sqrt{3}}\right) & -\left(\frac{g}{g_0} \frac{1}{\sqrt{3}} - \frac{i}{\sqrt{3}}\right) & \frac{1}{g_0} \end{pmatrix}, \quad (53)$$

where

$$g = \frac{F_\omega}{F_{r_0}}; \quad g_0 = \sqrt{3 + 2g^2}. \quad (54)$$

The three eigenvalues are

$$\lambda = 0; \pm i\rho, \quad (55)$$

where  $\rho = \sqrt{3F_{r_0}^2 + 2F_\omega^2}$ .  $\mathbf{A}$  is then found to be

$$\mathbf{A} = \frac{1}{g_0^2} \begin{pmatrix} \frac{1}{3} [(4g^2 + g_0^2) \cos \rho + 6] & -2 \left[ g \cos \rho + \frac{g_0}{2} \sin \rho - g \right] & \frac{\sqrt{2}}{3} [(2g^2 - g_0^2) \cos \rho + 3g_0 g \sin \rho + 3] \\ -2 \left[ g \cos \rho - \frac{g_0}{2} \sin \rho - g \right] & 3 \cos \rho + 2g^2 & \sqrt{2} [-g \cos \rho - g_0 \sin \rho + g] \\ \frac{\sqrt{2}}{3} [(2g^2 - g_0^2) \cos \rho - 3gg_0 \sin \rho + 3] & \sqrt{2} [-g \cos \rho + g_0 \sin \rho + g] & \frac{2}{3} [(g^2 + g_0^2) \cos \rho + \frac{3}{2}] \end{pmatrix}, \quad (56)$$

Of some interest are the two limiting cases when either  $F_\omega$  or  $F_{r_0}$  are zero. In the first case ( $F_\omega = 0$ ) we have for  $\mathbf{A}$

$$\mathbf{A} = \begin{pmatrix} \frac{1}{3} (\cos \delta + 2) & -\frac{\sin \delta}{\sqrt{3}} & \frac{\sqrt{2}}{3} (1 - \cos \delta) \\ \frac{\sin \delta}{\sqrt{3}} & \cos \delta & -\sqrt{\frac{2}{3}} \sin \delta \\ \frac{\sqrt{2}}{3} (1 - \cos \delta) & \sqrt{\frac{2}{3}} \sin \delta & \frac{1}{3} (1 + 2 \cos \delta) \end{pmatrix}. \quad (57)$$

where

$$\delta = \sqrt{3} F_{r_0}. \quad (58)$$

For this case we also calculated  $W_{00}$ ,  $W_{11}$ ,  $W_{22}$ , and  $W_{01}$ ,  $W_{12}$ , and  $W_{02}$

$$\begin{aligned} W_{00} &= \left\{ \frac{1}{2} + \frac{1}{3} [3 \sin^2 \delta + 4(1 - \cos \delta)^2] \right\} \hbar \omega, \\ W_{11} &= \left( \frac{3}{2} + \frac{\sin^2 \delta}{3} \right) \hbar \omega, \\ W_{22} &= \left[ \frac{3}{2} + \frac{1}{3} (8 \cos \delta + \cos 2\delta) \right] \hbar \omega, \\ W_{01} &= -\frac{\sin \delta}{3\sqrt{3}} (4 - \cos \delta) \hbar \omega, \\ W_{02} &= -\frac{\sqrt{2}}{9} (1 - \cos \delta)^2 \hbar \omega, \\ W_{12} &= -\frac{1}{3} \sqrt{\frac{2}{3}} \sin \delta (2 + \cos \delta) \hbar \omega. \end{aligned} \quad (59)$$

In the other case ( $F_{r_0} = 0$ ) we have for  $\mathbf{A}$

$$\mathbf{A} = \begin{pmatrix} \cos \chi & 0 & \sin \chi \\ 0 & 1 & 0 \\ -\sin \chi & 0 & \cos \chi \end{pmatrix}, \quad (60)$$

where

$$\chi = \sqrt{2} F_\omega. \quad (61)$$

From Eq. (60) we see that when  $F_{r_0} = 0$  neither the first nor the third state are coupled to the second state. This result applies also for larger basis sets in the sense that when  $F_{r_0} = 0$  the odd states are not coupled with the even states.

The matrix  $\mathbf{A}$  given in Eq. (60) yields the following  $\mathbf{W}$  elements

$$\begin{aligned} W_{00} &= \left( \frac{1}{2} + 2 \sin^2 \chi \right) \hbar \omega, \\ W_{11} &= \frac{3}{2} \hbar \omega, \\ W_{22} &= \left( \frac{5}{2} - \sin^2 \chi \right) \hbar \omega, \\ W_{01} &= W_{12} = 0, \\ W_{02} &= -\sin 2\chi \hbar \omega. \end{aligned} \quad (62)$$

### III. NUMERICAL RESULTS

As in the conventional approach the size of the vibrational basis set will have a profound effect on the accuracy of the results. We examine the rate of convergence from two different points of view. In the first subsection we study how the potential matrix elements due to the new diabatic states depend on the size of the basis set. Then we examine the convergence of the transition probabilities as we increase the basis set in solving the Schrödinger equation, Eq. (19).

#### A. Calculation of potential matrix elements

Although as demonstrated in the previous section the potential matrix can be calculated analytically for an arbitrarily large basis set, in practice it is easier to calculate the potential matrix numerically. For simplicity we assume that the force constant  $k$  of Eq. (27) is independent of  $R$ . The collision reduces then to the well-known forced oscillator problem which is characterized by a linear time dependent force. In the stationary state treatment this problem is equivalent to the coupling introduced by  $r_e(R)$ . For clarity we introduce a dimensionless parameter  $\gamma$  defined by [see Eq. (45)]

$$\gamma \equiv F r_0 = \sqrt{\frac{\mu \omega}{2\hbar}} (r_e(R) - r_0). \quad (63)$$

It is also convenient to introduce the root mean square width  $\Delta r$  of the harmonic oscillator in its ground state

$$\Delta r = \sqrt{\frac{\hbar}{2\mu\omega}}, \quad (64)$$

consequently  $\gamma$  becomes

$$\gamma = \frac{1}{2\Delta r} (r_e(R) - r_0) = \frac{1}{2} \frac{\Delta r_e(R)}{\Delta r}. \quad (65)$$

Thus  $\gamma = \frac{1}{2}$  implies that the shift in the potential minimum is equivalent to the root mean square amplitude of the oscillator.

In Fig. 3 we examine how the potentials for the two lowest diabatic states  $W_{00}$  and  $W_{11}$  as well as the diabatic coupling term  $W_{01}$  depend on the size of the basis set  $N$ . Shown are the results for  $N=2, \dots, 7$  each as a function of  $\gamma$ . In addition the solid line shows the corresponding matrix elements for the fully converged results. From Fig. 3 we observe that the size of the basis set needed for convergence depends on the interaction parameter  $\gamma$ . For example for  $\gamma \leq 1.0$  ( $\Delta r_e(R) \geq 2\Delta r$ ) convergence is achieved for  $N=5$ , whereas for  $\gamma=1.5$

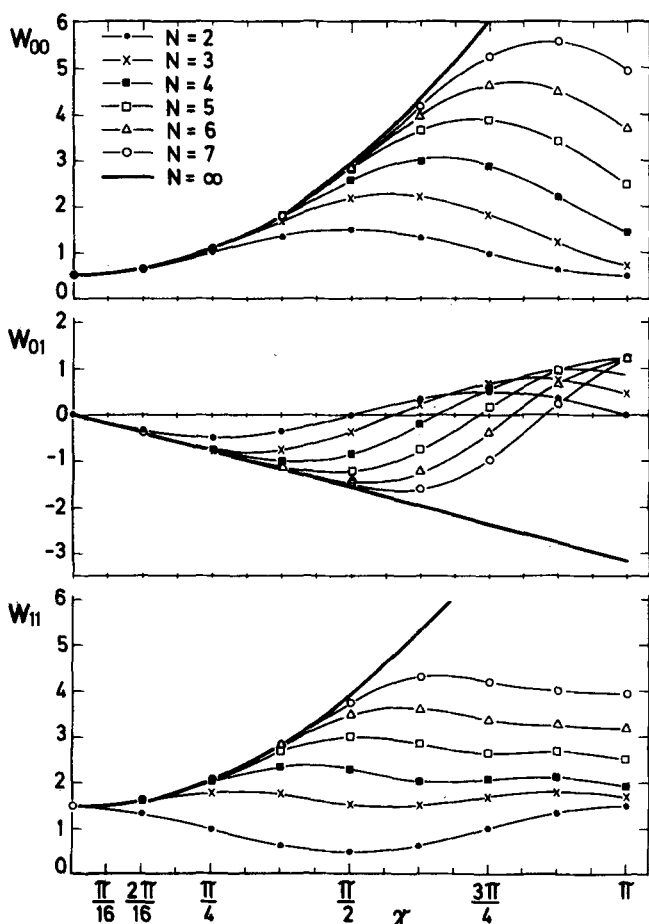


FIG. 3. The diabatic potential coupling terms are plotted as a function of the potential parameter  $\gamma$  for different size basis sets  $N$ . Shown are the results for  $N=2, \dots, 7$  and for the fully converged matrix elements. The potentials are in units of  $\hbar\omega$ .

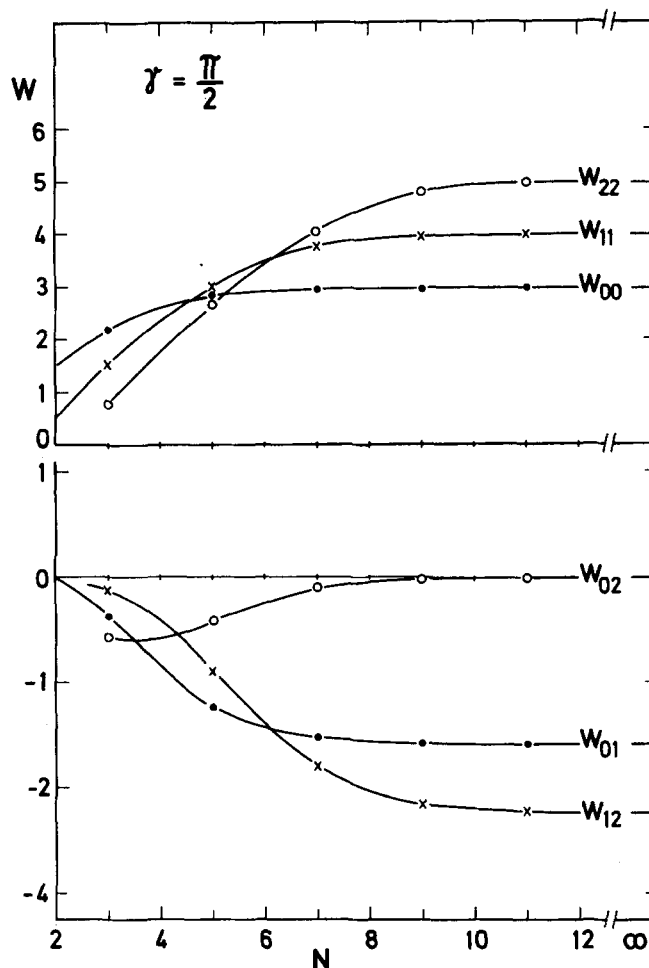


FIG. 4. The dependence of the first potential matrix elements is shown as a function of the size of the basis set  $N$  for a given value of the potential parameter  $\gamma = \pi/2$ . The potentials are in units of  $\hbar\omega$ . The converged results are indicated by the long horizontal lines at the far right.

convergence requires  $N=7$ . Examination of Fig. 3 provides insight into the relative rate of convergence for systems with different reduced masses  $\mu$ , but identical potentials. For small values of  $\mu$   $\Delta r$  is large and convergence can be achieved with a relatively reduced basis set. For large values of  $\mu$   $\Delta r$  is small and we expect a slower convergence.

In Fig. 4 we examine more closely the dependence of the first three diagonal elements  $W_{10}$ ,  $W_{11}$ , and  $W_{22}$  and the corresponding coupling terms  $W_{01}$ ,  $W_{02}$ , and  $W_{12}$  as a function of the size of the basis set  $N$  for a given value of the strength parameter  $\gamma = \pi/2$ . It is seen that for  $N \geq 10$  all six matrix elements are well converged. These converged results can be compared with the matrix elements occurring in the conventional potential matrix. To see this we consider the ordinary close coupling equations

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} - E \right) \psi_n + \sum_m U_{nm} \psi_m = 0, \quad (66)$$

where  $U_{nm}$  is given by

$$U_{nm} = \langle \bar{n} | \frac{1}{2} k(r - r_e(R))^2 - \frac{1}{2} k(r - r_0)^2 | \bar{m} \rangle + (n + \frac{1}{2}) \hbar\omega \delta_{nm}. \quad (67)$$

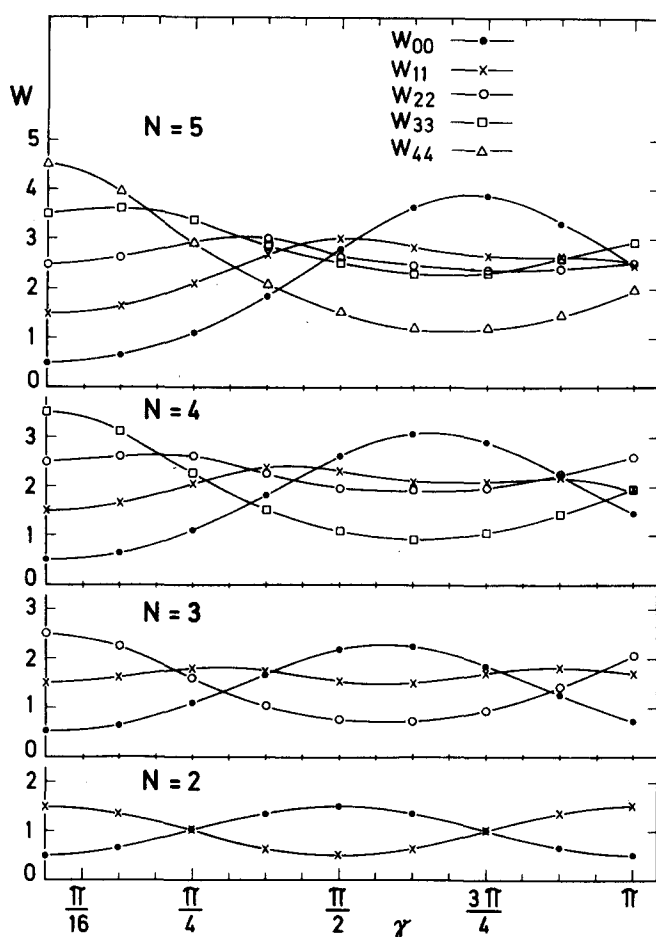


FIG. 5. The diabatic states for different size of the basis set  $N$  are shown as a function of  $\gamma$ . The potentials are in units of  $\hbar\omega$ .

Since  $k$  is assumed to be independent of  $R$  it can be shown that

$$U_{nm} = -\sqrt{n \pm 1} k(r_e(R) - r_0) \sqrt{\frac{\hbar}{2\mu\omega}} \delta_{mn \pm 1} + \left[ \frac{1}{2} k(r_e(R) - r_0)^2 + (n + \frac{1}{2}) \hbar\omega \right] \delta_{nm}. \quad (68)$$

Recalling

$$k = \mu\omega^2, \quad (69)$$

we get

$$U_{nm} = [-\sqrt{n \pm 1} \delta_{mn \pm 1} \gamma + (\gamma^2 + n + \frac{1}{2}) \delta_{nm}] \hbar\omega. \quad (70)$$

Equation (70) is easily evaluated and the results are shown on the far right-hand side in Fig. 4. The comparison with converged results reveals that these are indeed identical. Agreement with the ordinary asymptotic representation potential matrix elements was found for all values of  $\gamma$  for which converged diabatic potentials were obtained (see, e.g., Fig. 3). This result demonstrates that in the limit of convergence the matrix elements in the adiabatic equations [Eq. (19)] are identical to those in the conventional close coupling equations. This also implies that in this limit the wave functions have to be identical as well. Thus the adiabatic approach provides new insight into the dynamics only

when  $N$  is less than that needed for full convergence. We will see in the next section that indeed the adiabatic approach is capable of yielding converged  $S$  matrix elements even with only a few diabatic states and with potential matrix elements which are far from being converged. This is the true merit of the adiabatic approach. It yields exact converged transition probabilities without requiring convergence with regard to the diabatic potential matrix elements.

Of particular interest is Fig. 5, where we show the variations of a few of the lower diabatic states as a function of the size of the basis employed in the treatment. There are many curve crossings. Starting from  $\gamma = 0$  we note a certain systematic behavior which is independent of  $N$ . The first crossing of the ground state is with the highest state, the next crossing is with the next lower state and so forth until the first excited state is encountered. Thus for instance in the case of  $N=5$  the  $(0, 0)$  state crosses the  $(1, 1)$  state following three other crossings and consequently, in the Landau-Zener<sup>16</sup> sense, the two states, for most practical cases, won't interact directly. Still this doesn't mean that the  $0 \rightarrow 1$  transition probability is necessarily small because the  $(4, 4)$  curve in this case can serve as a "carrier" of the transition probability.

Another fact to be noticed is the steady motion of the crossing points towards larger  $\gamma$  with increasing  $N$ . Again, in the Landau-Zener<sup>16</sup> sense, this shift is required in order to decrease the interaction among neighboring states which otherwise would become too large due to the existence of a larger number of newly formed crossing points.

## B. Solution of the close coupling equations

To study numerically the convergence of the close coupling equations the perturbed oscillator potential Eq. (27) was used with  $k(R) = \text{constant}$ . This potential contains two  $R$ -dependent variables  $V_0(R)$  and  $r_e(R)$ . These were determined by a fit with the Jackson-Mott potential,<sup>17</sup> traditionally used in studies of this type.<sup>5</sup> The Jackson-Mott potential is defined in terms of reduced units (indicated by a  $\sim$ ), which are different from the ones used up to now in the present work, by

$$U(\hat{R}, \hat{r}) = \frac{1}{2} \hat{r}^2 + e^{-\alpha(\hat{R} - \hat{r})}, \quad (71)$$

where the energies are measured in units of  $\hbar\omega$  and all distances in units of  $\sqrt{\hbar/\mu_{BC}\omega}$ .  $r_e(R)$  is extracted from the relationship

$$\left. \frac{\partial U}{\partial \hat{r}} \right|_{\hat{r}=\hat{r}_e} = 0 \quad (72)$$

with the result

$$\hat{r}_e(\hat{R}) = -\alpha e^{-\alpha(\hat{R} - \hat{r}_e)}. \quad (73)$$

$V_0(R)$  is determined by equating Eq. (27) with Eq. (71) in the new reduced units with result

$$V(\hat{R}) = \frac{1}{2} \hat{r}_e^2 - \frac{\gamma_e}{\alpha}. \quad (74)$$

From here on we will use these traditional reduced potential parameters and units in describing the calculations of this section.



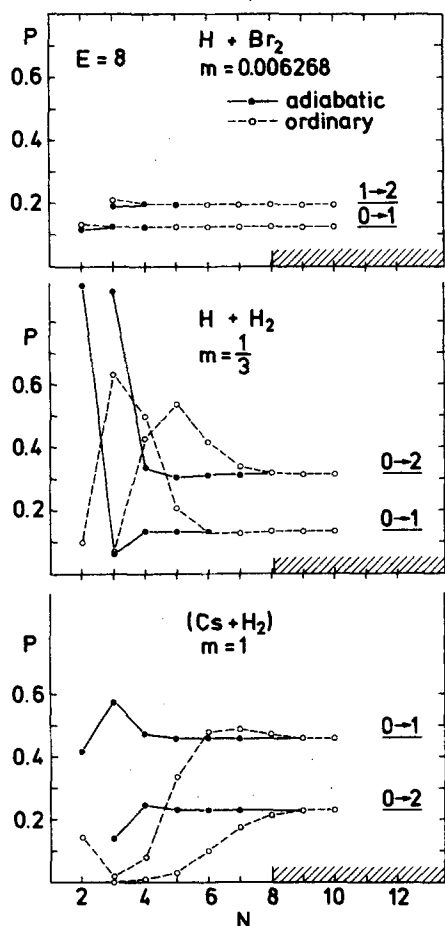


FIG. 6. The convergence of transition probabilities as a function of the size of the basis set is compared for the ordinary asymptotic with the present adiabatic approach for two low lying transitions. Three representative systems with widely varying mass parameters were chosen at a fixed total energy of  $8\hbar\omega$ . The converged results are marked at the far right of the figure. The region of energetically closed channels is indicated by the shaded region.

With the perturbed oscillator potential the Schrödinger equation in the asymptotic representation Eq. (66) and in the adiabatic representation Eq. (19) were solved. In both cases a standard Predictor-Corrector Numerov Method was used. The actual integrator used was adapted from one written by W. E. Baylis.<sup>18</sup> The calculation of the S matrix and transition probabilities was performed as described in reference.<sup>19</sup>

To compare the convergence of both methods we have plotted in Fig. 6 transition probabilities for two low lying transitions as a function of the size of the basis set. Three representative systems with widely varying mass parameters at a fixed energy of  $8\hbar\omega$  were chosen:  $\text{H} + \text{Br}_2$ ,  $m = 0.006268$ ;  $\text{H} + \text{H}_2$ ,  $m = 0.3333$ ; and  $\text{Cs} + \text{H}_2$ ,  $m = 1$ . In all cases the potential parameter  $\alpha$  was chosen in accordance with the recommendation made by Secrest and Johnson.<sup>5a</sup> For  $\text{H} + \text{Br}_2$  we find that both methods converge rapidly. The results imply that in this situation only one channel in addition to the minimum number is required. This system can be regarded as representing a typical "sudden" type of collision where the collision time is very short compared to the vibrational

period. Previously it has been shown that the much simpler sudden approximation provides very accurate results in this extreme case.<sup>6</sup>

In the case of  $\text{H} + \text{H}_2$  we see large differences in the rate of convergence of the two methods. The asymptotic representation converges slowly and requires a basis set with at least  $N=8$  for the probability of the transition  $0 \rightarrow 1$  denoted by  $P_{01}$ . This includes all open states. For  $P_{02}$  one additional closed state is needed and thus  $N=9$ . Since we are interested in  $P_{01}$  and  $P_{02}$  we have to include, at least, three states and thus  $N=3$  is the minimal size of the basis set in the adiabatic representation. The ordinary treatment requires 9 states, which is 6 states more than the minimal size we conclude that the adiabatic treatment yields a much faster convergence rate; by adding only one state above the minimum size the results are already close to the converged ones. The inclusion of one further state then brings the transition probabilities within a few percent of the converged results. A similar improvement in the rate of convergence is observed in the  $\text{Cs} + \text{H}_2$  case. Here again the ordinary asymptotic representation requires  $N=9$ , whereas the adiabatic representation requires only two states more than the minimal basis set. Thus for  $N=4$ ,  $P_{01}$  agrees within a few percent with the converged result and so does  $P_{02}$  for  $N=5$ .

In Fig. 7 we examine the effect of different energies on the rate of convergence of both methods. Here we have chosen another system namely  $\text{He} + \text{H}_2$  ( $m = \frac{2}{3}$ ) which lies midway between the two systems  $\text{H} + \text{H}_2$  and  $\text{Cs} + \text{H}_2$  shown in Fig. 6. At the lowest energy  $E = 4\hbar\omega$  we see that the adiabatic approach yields nearly exact results with only the minimal basis set. This is quite encouraging especially when we realize that the transition probability is quite large. The same holds also at  $E = 6\hbar\omega$ . In both cases the ordinary asymptotic approach converges very slowly. At larger energies the convergence of the adiabatic approach is somewhat slower, but as found in Fig. 6 again only two states beyond the minimal basis set are sufficient for a high accuracy. From Fig. 6 and 7 we conclude that the number of states needed for convergence with our new treatment is less than about one half the number of states required with the ordinary asymptotic approach.

The relative rates of convergence for a large number of different transitions is compared for  $\text{He} + \text{H}_2$  at  $E = 6\hbar\omega$  in Table I. As can be seen the results here confirm the conclusions reached in connection with Fig. 6 and 7. The convergence of the adiabatic approach is very rapid in every case. Especially for the transitions among high lying states, e.g.,  $P(n=3 \rightarrow 4)$  the minimal basis set yields results which already lies within about 25% of the exact results.

Tables II, III, and IV summarize all the converged results obtained with the adiabatic approach for the perturbed oscillator potential.

In previous exact calculations for collinear collisions the largest value of  $m$  studied was  $m = 3.737$ .<sup>5b</sup> The lack of calculations for larger  $m$  values is attributed to the very slow convergence of the asymptotic method for large

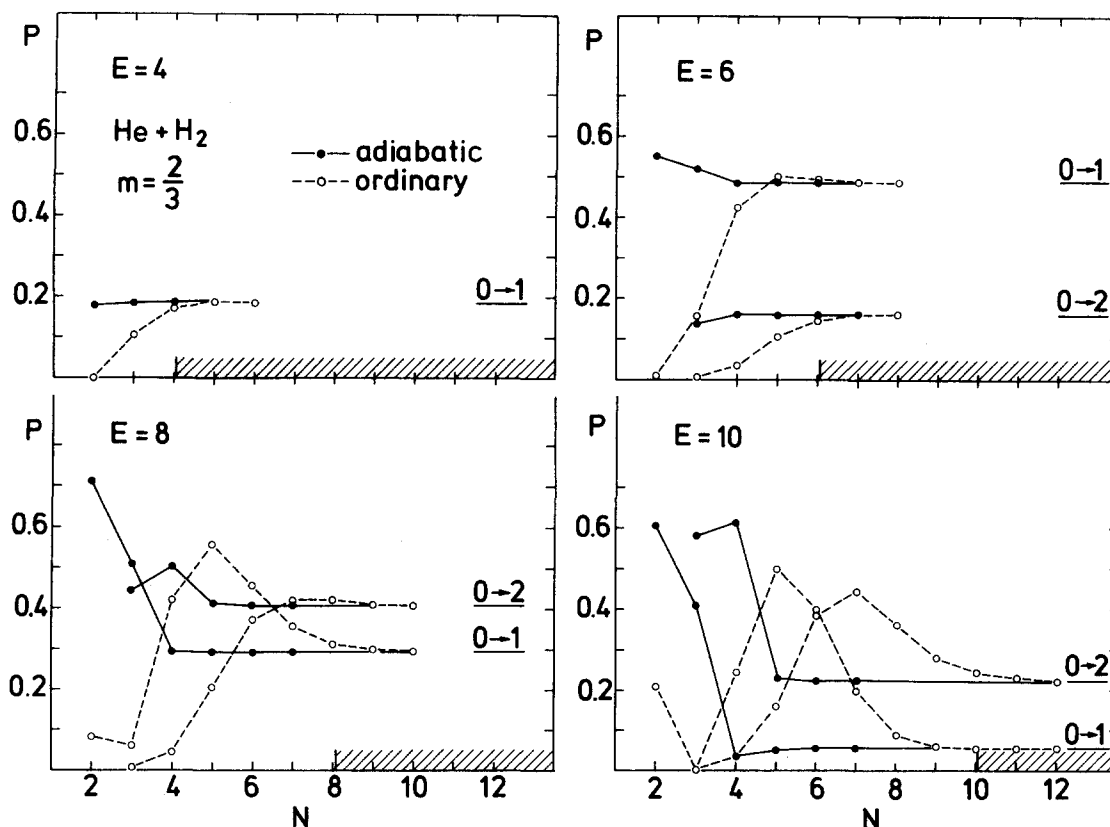


FIG. 7. The convergence of transition probabilities as a function of the size of the basis set is compared for the ordinary asymptotic with the present adiabatic approach for the system  $\text{He} + \text{H}_2$  at total energies of 4, 6, 8, and  $10 \hbar\omega$ . The converged results are marked at the far right of the figure. The region of energetically closed channels is indicated by the shaded region.

$m$  values (see Fig. 6) and the need to include an increasing number of closed channels with increasing  $m$ . In Table IV we present the first results for the model system  $\text{Ne} + \text{HBr}$  with  $m = 15.9642$  made possible with the adiabatic approach. This system shows much the same trends as found for the systems with smaller  $m$  values. There is no evidence of resonances related to "chatter" found in the classical calculations.<sup>20</sup> For low energies the transition probabilities are very small, they rise

slowly with increasing  $E$  and attain sizable values only at  $E \geq 20\hbar\omega$ . Comparison with the results in Fig. 7 suggests that the energy value at which the transition probabilities reach a maximum increases with  $m$ .

#### IV. DISCUSSION

The previous section demonstrated that the adiabatic approach converges much more rapidly than the asymp-

TABLE I. The transition probabilities for various transitions  $i \rightarrow f$  using the present adiabatic approach (upper value) are compared with corresponding values based on the ordinary asymptotic approach for different size basis sets  $N$ . The system is  $\text{He} + \text{H}_2$  ( $m = 2/3$ ,  $\alpha = 0.314$ ) at a fixed total energy of  $6\hbar\omega$ .

$N$	$P_{i \rightarrow f}$	0-1	0-2	0-3	1-2	1-3	2-3	2-4	3-4
2		$5.47-1^a$	...	...	...	...	...	...	...
		$1.01-2$	...	...	...	...	...	...	...
3		$5.20-1$	$1.39-1$	...	$4.16-1$	...	...	...	...
		$1.57-1$	$4.69-3$	...	$2.87-3$	...	...	...	...
4		$4.88-1$	$1.61-1$	$1.02-2$	$3.93-1$	$8.56-2$	$3.10-1$	...	...
		$4.28-1$	$3.43-2$	$4.95-4$	$1.79-1$	$3.06-3$	$6.34-4$	...	...
5		$4.87-1$	$1.59-1$	$1.24-2$	$3.85-1$	$9.30-2$	$3.20-1$	$1.99-2$	$1.37-1$
		$5.00-1$	$1.04-1$	$4.29-3$	$3.59-1$	$2.56-2$	$1.50-1$	$9.10-4$	$5.62-5$
6		$4.87-1$	$1.59-1$	$1.24-2$	$3.85-1$	$9.27-2$	$3.20-1$	$1.89-2$	$1.33-1$
		$4.94-1$	$1.45-1$	$9.67-3$	$3.88-1$	$6.91-2$	$2.84-1$	$8.31-3$	$7.57-2$
7		$4.85-1$	$1.61-1$	$1.36-2$	$3.79-1$	$1.01-1$	$3.30-1$	$2.46-2$	$1.24-1$

<sup>a</sup>— $n$  denotes  $10^{-n}$ .

TABLE II. Converged transition probabilities at a fixed total energy of  $8\hbar\omega$  are compared for the three systems  $\text{H} + \text{Br}_2$  ( $m = 0.006268$ ,  $\alpha = 0.1278$ ),  $\text{H} + \text{H}_2$  ( $m = 1/3$ ,  $\alpha = 0.314$ ) and  $\text{Cs} + \text{H}_2$  ( $m = 1$ ,  $\alpha = 0.314$ ).

$P_{i \rightarrow f}$	0-1	0-2	0-3	1-2	1-3	2-3	2-4	3-4
$m = 0.006268$ $\alpha = 0.1278$	1.26-1	8.27-3	3.46-4	1.96-1	1.72-2	2.31-1	2.25-2	2.40-1
$m = 1/3$ $\alpha = 0.314$	1.36-1	3.16-1	3.41-1	8.48-2	7.36-2	1.01-1	1.07-1	7.13-3
$m = 1$ $\alpha = 0.314$	4.59-1	2.32-1	4.11-2	3.05-1	2.09-1	3.25-1	1.32-1	3.42-1

TABLE III. Converged transition probabilities for the system  $\text{He} + \text{H}_2$  ( $m = 2/3$ ,  $\alpha = 0.314$ ) at four different total energies. The energy is in units of  $\hbar\omega$ .

$E$	$P_{i \rightarrow f}$	0-1	0-2	0-3	1-2	1-3	2-3	2-4	3-4
4		1.84-1	4.18-3	...	7.82-2	...	...	...	...
6		4.87-1	1.59-1	1.24-2	3.85-1	9.27-2	3.20-1	1.89-2	1.33-1
8		2.97-1	4.10-1	1.98-1	2.00-2	2.86-1	5.01-2	2.65-1	1.96-1
10		5.49-2	2.27-1	3.70-1	2.33-1	4.51-6	1.83-1	1.62-3	1.19-1

TABLE IV. Converged transition probabilities for the system  $\text{Ne} + \text{HBr}$  (collision on H side) ( $m = 15.9642$ ,  $\alpha = 0.5584$ ) at six different total energies. The energy is in units of  $\hbar\omega$ .

$E$	$P_{i \rightarrow f}$	0-1	0-2	0-3	1-2	1-3	2-3	2-4	3-4
4		1.60-7	1.80-16	...	4.20-9	...	...	...	...
6		8.58-6	7.45-12	...	3.47-6	4.10-13	4.68-7	...	...
10		2.03-4	1.22-8	2.14-13	2.40-4	1.12-8	1.85-4	4.87-9	1.05-4
14		1.60-3	4.75-7	9.79-11	1.13-3	3.59-7	1.25-3	3.76-7	1.19-3
20		3.47-1	7.35-2	6.61-3	3.65-1	9.20-2	3.55-1	7.18-2	3.24-1
26		3.13-1	3.09-1	1.71-1	1.55-2	2.01-1	9.67-3	1.19-1	3.15-1

otic approach for most cases studied so far. In fact only for small  $m$  values in the sudden limit of short collision times (compared to the vibrational period) the adiabatic approach offers no definite advantage in convergence. However, for other reduced masses  $m \geq \frac{1}{3}$  the adiabatic approach converges much faster. On the average less than half of the number of states is needed. Whereas in the asymptotic representation closed channels are required especially for large values of  $m$ , the adiabatic approach requires a basis set with only two more than the minimal number of states. The adiabatic approach is especially advantageous for  $m \geq 1$  and low energies. This is in accord with our expectations since here the vibrational period is much shorter than the collision time and under these conditions we expect the vibrational wave functions to be able to adjust themselves adiabatically—in the sense of the Born-Oppenheimer approximation—as the collision progresses. This analogy might suggest that the adiabatic approach is only valid for small transition probabilities, but as illustrated in the previous section the improvement in the rate of convergence is independent of the size of the transition probability.

At the present stage in the development of our new

approach we have made no effort to produce a computationally fast method. Our experience based on the calculations presented here is that the computing time in this new representation, for one energy, is comparable to that of the usual asymptotic representation. The saving in time due to the faster convergence is compensated by the additional transformations necessary to obtain the diabatic representation. However such a transformation need not be repeated for further calculations with the same system at different energies or, in a three-dimensional calculation, for different partial waves. Consequently we are quite confident that the new procedure is considerably faster than the usual asymptotic approach and is expected to reduce the computing time by about one order of magnitude.

We have also shown that the adiabatic approach provides new insight into the dynamics of vibrationally inelastic collisions. We can see this best by referring to Fig. 2. For the simple two-state case we find that there are two diabatic potential curves which show an oscillatory behavior with respect to  $F_{v_0}$ . This behavior is not unexpected since we are actually describing the coupled oscillator problem in a stationary state formalism. The two curves are out of phase by  $180^\circ$  and

therefore cross each other at several values of  $F_{r_0}$ . This takes account of the fact that the energy flows from one oscillator to the other. The strength of the coupling is given by  $W_{01}$ . The extension to more oscillators is described in Fig. 3 and in Fig. 5. Figures 2, 3 and 5 also suggest that one might expect transitions from one diabatic potential to the other to occur predominantly at the crossing points. To see if this is the case we have approximated the transition probabilities using the Landau-Zener approximation. The results were found to be in poor agreement with the exact results. This indicates that transitions also occur at regions outside the immediate vicinity of the crossing points. It is possible that incorporating the Demkov<sup>21</sup> procedure to account for transitions where crossing points are energetically inaccessible would make such an elegant approximate treatment feasible.

Another approximation suggested by the rapid convergence of the adiabatic approach is to use the distorted wave approximation. Eno and Balint-Kurti<sup>13a</sup> have used this approximation with good success. However, they did not employ the Smith transformation to shift the nonadiabatic coupling terms into the diabatic potential matrix. Thus a more efficient distorted wave approximation would be based on Eq. (19). These examples illustrate how the new adiabatic diabatic approach opens up the possibility of developing new efficient approximations to the problem of vibrational excitation.

## ACKNOWLEDGMENTS

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## APPENDIX A: THE ALGEBRA OF ANTISYMMETRIC MATRICES

**Definition:** An antisymmetric matrix  $\mathbf{B}$  is defined as the real matrix having the following feature

$$\tilde{\mathbf{B}} = -\mathbf{B}, \quad (\text{A1})$$

where  $\tilde{\mathbf{B}}$  is obtained from  $\mathbf{B}$  by interchanging the rows and column.

**Theorem I:** An antisymmetric matrix has only imaginary (or zero) eigenvalues and the transformation matrix is unitary.

**Proof:** Let us define a matrix  $\mathbf{D}$  such that

$$\mathbf{D} = i\mathbf{B}. \quad (\text{A2})$$

Since  $\mathbf{B}$  is antisymmetric  $\mathbf{D}$  is Hermitian and therefore has only real eigenvalues  $\lambda'$  and the corresponding transformation matrix is unitary. Thus

$$\mathbf{D}\mathbf{S} = \mathbf{S}\lambda'. \quad (\text{A3})$$

Dividing both sides by  $i$  leads to

$$\mathbf{B}\mathbf{S} = \mathbf{S}(-i\lambda'), \quad (\text{A4})$$

where now  $\lambda = -i\lambda'$  is the eigenvalue matrix of  $\mathbf{B}$ . From (A4) we notice that the eigenvalues are pure imaginary

(or zero) and the matrix  $\mathbf{S}$  which was shown to be unitary is the transformation matrix of  $\mathbf{B}$ , i. e.,

$$\mathbf{S}\mathbf{S}^* = \mathbf{S}^*\mathbf{S} = \mathbf{I}, \quad (\text{A5})$$

where  $\mathbf{S}^* \equiv \tilde{\mathbf{S}}^*$  and  $*$  denotes the complex conjugate.

**Theorem II:** If  $\lambda$  and  $\mathbf{s}$  are an eigenvalue and the corresponding eigenvector of  $\mathbf{B}$  so are  $\lambda^*$  and  $\mathbf{s}^*$ .

**Proof:** It is given

$$\mathbf{s}_i \mathbf{B} \mathbf{s}_i = \lambda_i. \quad (\text{A6})$$

Taking the transpose of both sides yields

$$\mathbf{s}_i \tilde{\mathbf{B}} \mathbf{s}_i^* = \lambda_i, \quad (\text{A7})$$

now since  $\tilde{\mathbf{B}} = -\mathbf{B}$  we get that

$$\tilde{\mathbf{s}}_i \mathbf{B} \mathbf{s}_i^* = -\lambda_i = \lambda_i^* \quad (\text{A8})$$

namely  $\lambda_i^*$  and  $\mathbf{s}_i^*$  are eigenvalue and eigenvector of  $\mathbf{B}$ .

**Theorem III:** Each antisymmetric matrix of an odd order has at least one zero eigenvalue.

**Proof:** From the previous theorem we have found that both  $\lambda_i$  and  $\lambda_i^*$  are eigenvalues of  $\mathbf{B}$ . Since an odd ordered matrix has an odd number of eigenvalues at least one has to be zero.

## APPENDIX B

The transformation matrix  $\mathbf{A}$  is chosen to satisfy

$$\frac{d\mathbf{A}}{dR} + \boldsymbol{\tau}^1 \mathbf{A} = 0, \quad (\text{B1})$$

where  $\boldsymbol{\tau}^1$  is an antisymmetric matrix defined by

$$\tau_{nm}^1(R) = \left\langle \phi_n \left| \frac{d}{dR} \right| \phi_m \right\rangle. \quad (\text{B2})$$

Differentiating Eq. (B1) with respect to  $R$  leads to

$$\frac{d^2\mathbf{A}}{dR^2} + \boldsymbol{\tau}^1 \frac{d\mathbf{A}}{dR} + \frac{d\boldsymbol{\tau}^1}{dR} \mathbf{A} = 0. \quad (\text{B3})$$

The term  $d\boldsymbol{\tau}^1/dR$  can be reexpressed as

$$\begin{aligned} \frac{d\boldsymbol{\tau}^1}{dR} &= \left\langle \frac{d\phi_n}{dR} \left| \frac{d\phi_m}{dR} \right\rangle + \left\langle \phi_n \left| \frac{d^2\phi_m}{dR^2} \right\rangle \right. \\ &= \sum_k \left\langle \frac{d\phi_n}{dR} \left| \phi_k \right\rangle \left\langle \phi_k \left| \frac{d\phi_m}{dR} \right\rangle + \left\langle \phi_n \left| \frac{d^2\phi_m}{dR^2} \right\rangle \right. \\ &= \tilde{\boldsymbol{\tau}}^1 \boldsymbol{\tau}^1 + \boldsymbol{\tau}^2. \end{aligned} \quad (\text{B4})$$

Inserting this into Eq. (B3) and since  $\tilde{\boldsymbol{\tau}}^1 = -\boldsymbol{\tau}^1$  we obtain

$$\frac{d^2\mathbf{A}}{dR^2} + \boldsymbol{\tau}^1 \frac{d\mathbf{A}}{dR} - \boldsymbol{\tau}^1 \boldsymbol{\tau}^1 \mathbf{A} + \boldsymbol{\tau}^2 \mathbf{A} = 0. \quad (\text{B5})$$

Making once more use of (B1) we finally get the desired result

$$\frac{d^2\mathbf{A}}{dR^2} + 2\boldsymbol{\tau}^1 \frac{d\mathbf{A}}{dR} + \boldsymbol{\tau}^2 \mathbf{A} = 0. \quad (\text{B6})$$

<sup>1(a)</sup> J. D. Lambert, *Vibrational and Rotational Relaxation in Gases* (Clarendon, Oxford, 1977); (b) J. P. Toennies, *Ann. Rev. Phys. Chem.* **27**, 225 (1976).

<sup>2</sup> M. Faubel and J. P. Toennies, *Adv. At. Mol. Phys.* **13**, 229 (1977).

- <sup>3</sup>(a) P. McGuire, J. Chem. Phys. **62**, 525 (1975); (b) C. S. Lin and D. Secrest, J. Chem. Phys. **70**, 199 (1979); (c) J. Schaefer and W. A. Lester, J. Chem. Phys. **62**, 1913 (1975); (d) B. H. Choi, R. T. Poe, and K. T. Tang, Chem. Phys. Lett. **48**, 237 (1977).
- <sup>4</sup>(a) F. A. Gianturco, *The Transfer of Molecular Energies by Collisions* (Springer-Verlag, Heidelberg, 1979); (b) H. Rabitz in *Dynamics of Molecular Collisions* Part A, edited by W. H. Miller (Plenum, New York, 1976).
- <sup>5</sup>(a) D. Secrest and B. R. Johnson, J. Chem. Phys. **45**, 4556 (1966); (b) A. P. Clark and A. S. Dickinson, J. Phys. B **6**, 164 (1973).
- <sup>6</sup>J. M. Bowman, G. Drolshagen, and J. P. Toennies, J. Chem. Phys. **71**, 2270 (1979).
- <sup>7</sup>M. Born and J. R. Oppenheimer, Ann. Phys. (Leipzig) **84**, 457 (1927).
- <sup>8</sup>F. T. Smith, Phys. Rev. **179**, 111 (1969).
- <sup>9</sup>(a) M. Baer, Chem. Phys. Lett. **35**, 112 (1975); Chem. Phys. **15**, 49 (1976); (b) Z. H. Top and M. Baer, J. Chem. Phys. **66**, 1363 (1977).
- <sup>10</sup>(a) Z. H. Top and M. Baer, Chem. Phys. **25**, 1 (1977); (b) M. Baer and J. A. Beswick, Phys. Rev. A **19**, 1599 (1979).
- <sup>11</sup>R. D. Levine, B. R. Johnson, and R. B. Bernstein, J. Chem. Phys. **50**, 1694 (1969).
- <sup>12</sup>N. A. Mullaney and D. G. Truhlar, Chem. Phys. **39**, 91 (1979).
- <sup>13</sup>(a) L. Eno and G. G. Balint-Kurti, J. Chem. Phys. **71**, 1447 (1979); (b) R. J. Cross, Jr., J. Chem. Phys. **71**, 1426, 1433 (1979).
- <sup>14</sup>L. M. Delves, Nucl. Phys. **9**, 391 (1959); **20**, 275 (1960).
- <sup>15</sup>Note added in proof: The solution given by Eq. (21) is only exact if  $\tau^1(R)$  commutes with  $\int_{R_0}^R \tau^1(R) dR$ . In general Eq. (21) is only an approximate solution of Eq. (17) analogous to the exponential approximation in time dependent theory. For our special potential model however  $\tau^1(R)$  does commute with  $\int_{R_0}^R \tau^1(R) dR$  and therefore  $A(R)$  is exactly given by Eq. (21). We are grateful to A. Askar for calling this to our attention.
- <sup>16</sup>(a) L. D. Landau, Phys. Z. Sowjetunion **2**, 46 (1932); (b) C. Zener, Proc. R. Soc. (London) Ser. A **137**, 696 (1932).
- <sup>17</sup>J. M. Jackson and N. F. Mott, Proc. Roy. Soc. (London) Ser. A **137**, 703 (1932).
- <sup>18</sup>W. E. Baylis (private communication).
- <sup>19</sup>R. G. Gordon in *Methods in Computational Physics*, Vol. 10 (Academic, New York, 1971), p. 81ff.
- <sup>20</sup>D. Secrest, J. Chem. Phys. **51**, 421 (1969).
- <sup>21</sup>Yu. N. Demkov, Sov. Phys. JETP **18**, 138 (1964).