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Semiclassical study of the vibrational excitation of H₂ in collision with He

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Abstract. The vibrational excitation and dissociation probabilities of H₂ in a collinear collision with He are calculated, using the semi-classical time-dependent method along with the accurate H₂ molecular potential of Kołos and Wolniewicz. The complete set of bound and continuum eigenfunctions are represented in terms of a truncated basis set of harmonic oscillator functions. The results differ significantly from the Morse potential quantum mechanical calculations of Clark and Dickinson. In addition, a state-dependent interaction potential is suggested to allow for the different average sizes of the H₂ molecule in its initial and final states. The state dependent potential greatly enhances the transition probabilities to highly excited states and the continuum.

1. Introduction

In much of the early work on the vibrational excitation of diatomic molecules in collision with atoms (see Takayanagi 1963, 1965 and Rapp and Kassal 1969 for reviews), the internal motion of the molecule is approximated by a harmonic oscillator. Following the work of Mies (1964), Hunding (1970), and Morse and LaBrecque (1971), Clark and Dickinson (1973) have performed exact quantum mechanical calculations based on a Morse potential model which show that the harmonic oscillator results are often in error by an order of magnitude or more.

Even the Morse oscillator approximation is questionable for excited vibrational levels since the Morse potential does not have the correct asymptotic form. For example, the H₂ potential used by Clark and Dickinson (1973) possesses eighteen bound states instead of the correct number fifteen. In a previous paper (Lin and Drake 1972) we suggested a procedure in which the hamiltonian is diagonalized in a truncated basis set of harmonic oscillator wavefunctions in order to represent accurately the complete set of bound and continuum anharmonic vibrational eigenfunctions in a convenient analytical form. The best available vibrational potential can be used, and if the harmonic oscillator basis set is sufficiently large, all the bound states are accurately represented, and the higher-lying states provide a discrete variational representation for the dissociation continuum. Closed-channel continuum states are then easily included in a close-coupling calculation and transition probabilities into the continuum can be obtained.

In this paper, the method is applied in the time-dependent formalism to the collinear collision of a hydrogen molecule with a helium atom. The hydrogen molecule is chosen because it has only 15 bound vibrational levels and the effects of anharmonicity became

apparent at low vibrational quantum number. Also excitation to vibrational levels near the dissociation limit can be studied in a basis set of modest size. In addition, we test a suggested state dependent interaction potential which allows for the different sizes of the anharmonic molecule in its initial and final states.

2. Theory

The semiclassical time-dependent method outlined in this section is basically that of Rapp and Sharp (1965), but the details are repeated to make clear the modifications that have been made. Consider a diatomic molecule BC in collision with a structureless atom A as shown in figure 1. In the time-dependent formalism, the solution to the Schrödinger equation

$$[H_0 + V(y, t)]\psi(y, t) = \frac{i\hbar\partial\psi(y, t)}{\partial t} \quad (1)$$

is expanded in the form

$$\psi(y, t) = \sum_n a_n(t)\psi_n(y) e^{-i\epsilon_n t} \quad (2)$$

where

$$H_0\psi_n(y) = \epsilon_n\psi_n(y) \quad (3)$$

and y is the internal vibrational coordinate. The time-dependent potential $V(y, t)$ is obtained from the interaction potential $V(y, x)$ between the collision partners as discussed below. Substituting expansion (2) into (1), one obtains the set of coupled differential equations

$$\dot{a}_j(t) = (i\hbar)^{-1} \sum_n a_n(t)V_{jn}(t) \exp(i\epsilon_{jn}t) \quad (4)$$

where

$$V_{jn}(t) = \int \psi_j^*(y)V(y, t)\psi_n(y) dy \quad (5)$$

and

$$\epsilon_{jn} = \epsilon_j - \epsilon_n. \quad (6)$$

The set of coupled equations is solved numerically for the time-dependent coefficients $a_j(t)$ subject to the initial conditions

$$\begin{aligned} |a_k(-\infty)|^2 &= 1 \\ |a_j(-\infty)|^2 &= 0 \quad \text{if } j \neq k. \end{aligned} \quad (7)$$

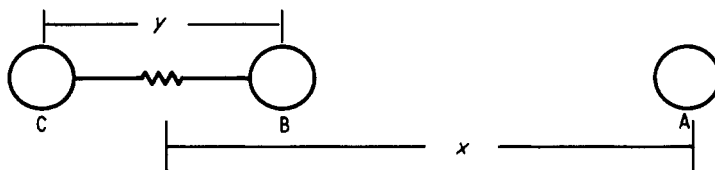


Figure 1.

The quantity $P_{k \rightarrow j} = |a_j(\infty)|^2$ is then the probability for a transition from state k to state j .

Following our previous suggestion (Lin and Drake 1972), the vibrational functions ψ_n are expanded in terms of a truncated set of harmonic oscillator functions

$$\psi_n(y) = \sum_k c_{nk} \phi_k(y) \quad (8)$$

where

$$\phi_k(y) = \left[\left(\frac{\alpha}{\pi} \right)^{1/2} \frac{1}{2\pi} \right]^{1/2} H_k(\xi) \exp(-\xi^2/2) \quad (9)$$

and $\xi = \alpha^{1/2}(y - y_0)$. The parameters y_0 and α are not determined *a priori*, but can be chosen to give a good overall representation of the anharmonic oscillator spectrum. The coefficients c_{nk} in (8) are determined by the conditions

$$\langle \psi_n | \psi_m \rangle = \delta_{nm} \quad (10)$$

$$\langle \psi_n | H_0 | \psi_m \rangle = \epsilon_n \delta_{nm}. \quad (11)$$

The ϵ_n are then variational upper bounds to the exact eigenvalues of H_0 .

In this work, a 60-term harmonic expansion is used, together with the theoretical H_2 vibrational potential of Kołos and Wolniewicz (1965, 1968). Since our aim is to study transitions to all bound states and the low-lying continuum, the parameters y_0 and α are chosen to give good overall agreement with the exact eigenvalues of Kołos and Wolniewicz. The values used are $y_0 = 1.4011$ and $\alpha = 9.765$ in atomic units. Table 1 gives the eigenvalues relative to the dissociation limit, together with the expectation values $y_n = \langle \psi_n | y | \psi_n \rangle$ of the internuclear separation. The accuracy of the eigenvalues is much better than can be attained with a Morse potential.

Table 1. Energies and expectation values of y for H_2

v	$E(v)^a$ (cm^{-1})	$E(v)^b$ (cm^{-1})	$\langle \psi_v y \psi_v \rangle^b$ (au)
0	-36118.09	-36111.90	1.4748
1	-31956.03	-31948.08	1.5722
2	-28029.39	-28020.21	1.6742
3	-24333.25	-24322.39	1.7819
4	-20864.57	-20851.89	1.8964
5	-17622.33	-17609.89	2.0211
6	-14607.84	-14595.90	2.1634
7	-11825.02	-11813.91	2.3313
8	-9281.13	-9270.74	2.5020
9	-6987.48	-6978.34	2.5975
10	-4960.67	-4952.61	2.7090
11	-3223.54	-3216.97	3.0674
12	-1808.00	-1803.03	3.4257
13	-759.02	-755.97	4.0113
14	-138.86	-113.86	4.8817

^a Kołos and Wolniewicz (1965, 1968).

^b Present work.

The He-H₂ interaction potential is chosen to have the purely repulsive nearest neighbour form

$$V(y, x) = V_0 \exp[-(x - \gamma y)/L] \quad (12)$$

where $\gamma = m_C/(m_B + m_C)$ and L is a parameter determining the range of the interaction. In order to compare our results with other calculations, we make the usual choice $L = 0.2 \text{ \AA}$.

In the semiclassical approach, the time-dependent potential $V(y, t)$ experienced by the quantum oscillator is obtained from $V(y, x)$ by integrating the classical equation of motion for the x coordinate (Rapp and Kassal 1968). If the molecule is held fixed at a particular internuclear separation \bar{y} during the generation of the classical trajectory for x , then the potential (12) yields the time-dependent form

$$V(y, t) = V_0 \operatorname{sech}^2\left(\frac{v_0 t}{2L}\right) \exp(\gamma Y/L) \quad (13)$$

where $Y = y - \bar{y}$ and v_0 is the initial relative velocity. The value of V_0 depends on assumptions made about the nature of the collisions of atom A with the molecule BC. If BC is treated as a rigid unit (infinite binding energy) then

$$V_0 = \frac{1}{2} m v_0^2 \quad (14)$$

with

$$m = \frac{m_A(m_B + m_C)}{m_A + m_B + m_C} \quad (15)$$

In the opposite extreme suggested by Mahan (1970), the binding energy of BC is neglected and V_0 is determined by allowing A to collide elastically with B alone. In this case

$$V_0 = \frac{1}{2} \mu v_0^2 \quad (16)$$

with

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad (17)$$

The latter choice is the one made by Heidrich, Wilson and Rapp (1971) in their approximate semiclassical ITFITS procedure. Results obtained with the two extreme choices are compared in the following section.

The value of \bar{y} in (13) is not well defined because the molecule is oscillating throughout the collision. In a completely coupled semiclassical calculation, the molecule is allowed to oscillate during the generation of the classical trajectories, with the transition probabilities depending on the initial phase of the oscillator (Locker and Wilson 1970). Since the results must then be phase-averaged, this considerably increases the complexity of the calculation. We therefore approximate \bar{y} by its expectation value $y_n = \langle \psi_n | y | \psi_n \rangle$ in the calculation of the diagonal matrix elements $V_{nn}(t)$, and by $(y_n + y_m)/2$ in the calculation of the off-diagonal matrix elements $V_{nm}(t)$. For an anharmonic oscillator, y_n becomes progressively larger with increasing vibrational quantum number and remains well-defined for continuum states in our finite basis set representation. This procedure may approximate the phase averaged results of a completely coupled semiclassical calculation. Physically, one expects the anharmonic oscillator to spend a greater percentage of its time at large internuclear separations with increasing vibrational quantum number, and

our choice for \bar{y} ensures that the principle of detailed balance is satisfied if the initial state is an excited state. Explicitly, the potential energy matrix elements are

$$V_{nm}(t) = V_0 \operatorname{sech}^2\left(\frac{v_0 t}{2L}\right) U_{nm} \quad (18)$$

where

$$U_{nm} = \langle \psi_n | \exp[\gamma(y - y_{nm})/L] | \psi_m \rangle \quad (19)$$

and

$$y_{nm} = (y_n + y_m)/2. \quad (20)$$

U_{nm} can be evaluated analytically using formulae given by Rapp and Sharp (1963). Results obtained from the above procedure are compared with those obtained from the conventional choice $y_{nm} = y_e$, where y_e is the equilibrium internuclear separation, in the following section.

3. Results and discussion

Calculations were performed for three distinct cases. In the first (case I), we make the traditional choices $\bar{y} = r_e$ and $V_0 = mv_0^2/2$, with m given by equation (15). In the second (case II), V_0 is changed to $V_0 = \mu v_0^2/2$, with μ given by equation (17). In the third (case III), $V_0 = mv_0^2/2$ and $\bar{y} = y_{nm}$ as given by equation (20). As a check on the numerical procedures, we first reproduced the 4-state time-dependent harmonic oscillator calculations of Rapp and Sharp (1963) using their approximation to the interaction matrix elements.

The results for case I are given in table 2 for several total energies (including the ground state vibrational energy) in units of $\hbar\omega_e/2$. Although 60 eigenfunctions are

Table 2. Transition probabilities $P_{0 \rightarrow v}$ for case I (see text)^a

E^b	4	6	8	10
v				
0	0.9978	0.9802	0.9343	0.8588
1	0.0022	0.0196	0.0632	0.1300
2		0.0002	0.0025	0.0103
3			0.0001	0.0008
4				0.0001
E	12	16	18	21
v				
0	0.7614	0.5518	0.4669	0.3921
1	0.2101	0.3719	0.4328	0.4664
2	0.0247	0.0568	0.0717	0.1063
3	0.0034	0.0145	0.0188	0.0210
4	0.0004	0.0040	0.0071	0.0088
5		0.0009	0.0022	0.0038
6		0.0002	0.0005	0.0013
7			0.0001	0.0003
8				0.0001

^a Results obtained with the first 10 eigenfunctions listed in table 1.

^b E is the total energy (including the ground state vibrational energy) in units of $\hbar\omega_e/2$.

obtained from the harmonic oscillator basis set, we retained only as many as needed for convergence in the solution of the time-dependent equations. Except for transitions to high vibrational levels, the results tend to fall between the Morse oscillator and harmonic oscillator results of Clark and Dickinson (1973), but differ significantly from either. The total energy required to dissociate H_2 is about $17.4\hbar\omega_e/2$. At $E = 20$, the probability of transitions to the continuum is extremely small. As a check on the numerical accuracy, the transition probabilities sum to unity to at least the number of figures quoted in all cases, and detailed balance is satisfied to the same accuracy.

The results of case II are given for one energy in table 3. Evidently, the replacement of m by μ in the calculation of V_0 changes the larger transition probabilities by only a few percent.

Table 3. Transition probabilities $P_{0 \rightarrow v}$ for case II at $E = 10\hbar\omega_e/2$

v	$P_{0 \rightarrow v}$
0	0.8486
1	0.1357
2	0.0143
3	0.0013
4	0.0001

The results for case III given in table 4 show much more drastic changes. The transition probabilities to highly excited states are greatly enhanced and the dissociation probability becomes significant. The latter quantity is obtained by summing the

Table 4. Transition probabilities $P_{0 \rightarrow v}$ for case III (see text)

E	8	10	12	14	16	21	26
v							
0	0.5644	0.3229	0.1612	0.0731	0.0311	0.0031	0.0002
1	0.3022	0.3291	0.2560	0.1610	0.0881	0.0137	0.0021
2	0.0989	0.1972	0.2332	0.2010	0.1415	0.0374	0.0087
3	0.0262	0.0917	0.1601	0.1840	0.1617	0.0590	0.0108
4	0.0063	0.0370	0.0926	0.1388	0.1493	0.0771	0.0229
5	0.0015 ^a	0.0140	0.0490	0.0947	0.1248	0.0970	0.0429
6	0.0003 ^a	0.0052 ^a	0.0251	0.0617	0.0981	0.1018	0.0420
7	0.0001 ^a	0.0020 ^a	0.0127	0.0391	0.0743	0.1024	0.0452
8		0.0007 ^a	0.0060 ^a	0.0232	0.0537	0.1150	0.0887
9		0.0002 ^a	0.0024 ^a	0.0119 ^a	0.0336	0.1102	0.1228
10		0.0001 ^a	0.0010 ^a	0.0058 ^a	0.0192	0.0837	0.1104
11			0.0004 ^a	0.0026 ^a	0.0097	0.0504	0.0718
12			0.0001 ^a	0.0012 ^a	0.0047 ^a	0.0281	0.0430
13				0.0006 ^a	0.0027 ^a	0.0199	0.0355
14				0.0005 ^a	0.0026 ^a	0.0240	0.0512
P_{dis}^b				0.0008 ^a	0.0048 ^a	0.0772	0.3020
no. of states	20	25	30	30	30	30	30

^a Transitions to these states are energetically forbidden.

^b P_{dis} is the sum of all transition probabilities to states above the dissociation limit.

transition probabilities into all the discrete variational states lying above the dissociation threshold. Larger numbers of states were required for case III, but numerical overflow problems encountered in cases I and II with the same numbers of states were no longer present.

For purposes of comparison, we repeated the semiclassical (case I) calculation with a Morse potential approximation to the exact molecular potential. The results shown in table 5 establish a connection with the quantum mechanical results of Clark and Dickinson (1973) obtained with the same Morse potential. It is clear that the semiclassical method seriously overestimates the small transition probabilities, but the larger transition probabilities agree quite well. However the semiclassical values for $P_{0 \rightarrow 1}$ obtained with the exact potential are uniformly larger than the Morse potential results for $E \gtrsim 8$. For example at $E = 16$, the exact potential yields a $P_{0 \rightarrow 1}$ about 50% larger than the Morse potential value calculated either semiclassically or quantum mechanically.

Table 5. Comparison of semiclassical (case I) and quantum mechanical transition probabilities $P_{0 \rightarrow v}$ for the exact and morse potentials

E	6	8	10	12	16
v					
1	0.0196 ^a 0.0269 0.0073	0.0632 0.0591 0.0315	0.1300 0.1123 0.0739	0.2101 0.1698 0.129	0.3719 0.2663 0.245
2	0.0002 0.0004 2×10^{-6}	0.0025 0.0027 0.0002	0.0103 0.0099 0.0017	0.0247 0.0241 0.0066	0.0568 0.0712 0.0338

^a The first entry is the semiclassical result with the exact potential. The second entry is the semiclassical result with the Morse potential. The third entry is the quantum mechanical result of Clark and Dickinson (1973) with the Morse potential.

4. Discussion

The results of case I indicate that transition probabilities obtained from an accurate intermolecular potential differ significantly from the Morse oscillator results of Clark and Dickinson (1973). This is to be expected if the Morse potential does not contain the correct number of bound states. While the semiclassical and quantum methods of calculation agree for the larger transition probabilities, the Morse oscillator values appear to underestimate $P_{0 \rightarrow 1}$ in the energy range 12 to 16 by about as much as the harmonic oscillator results tabulated by Clark and Dickinson overestimate $P_{0 \rightarrow 1}$. A full quantum calculation using the exact potential is in progress.

As shown by case III the choice $\bar{y} = y_{nm}$ leads to much larger transition probabilities to highly excited states and the continuum. In addition, the distribution of probability over the vibrational levels is much flatter. The method involves, in effect, a state-dependent potential which allows for the larger average size of the anharmonic molecule in excited states, while maintaining the principle of detailed balance. The state-dependent potential partially compensates for the different interactions of the colliding particle with the molecule in its initial and final states.

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