

QUASI-BOUND STATES OF COUPLED MORSE OSCILLATORS

I. BENJAMIN, R.H. BISSELING, R. KOSLOFF, R.D. LEVINE

The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University, Jerusalem 91904, Israel

J. MANZ

Lehrstuhl für Theoretische Chemie, Technische Universität München, D-8046 Garching, West Germany

and

H.H.R. SCHOR

Departamento de Química, ICEX, Universidade Federal de Minas Gerais, 30 000 Belo Horizonte, Brazil

Received 2 January 1985; in final form 26 February 1985

Quasi-bound (resonance) states are present in the continuous spectrum of the Hamiltonian of two coupled Morse oscillators. Two different methods for approximating these as localized states are compared. The algebraic approach is shown to be in very good accord with the other method which is formulated in coordinate space and hence is differential in character. For these highly excited states an intermultiplet mixing term is included in the algebraic Hamiltonian.

1. Introduction

Bound states of two coupled Morse oscillators have been the subject of much recent discussion [1–8]. Such a Hamiltonian has however also a continuous spectrum. It corresponds to an atom interacting with an oscillator via a potential which has an attractive part. Embedded in this continuum we expect to find quasi-bound states [9–11] where the atom is (temporarily) bound to an excited state of the oscillator. The purpose of this Letter is to compare two different ways of approximating these as localized states. One method is based on wavefunctions in coordinate space and the second is algebraic.

The primary conclusion is the agreement between the two approximation methods and the exact scattering computation [11]. The reason why such an agreement is required is that one is approximating a quasi-bound state by a bound one. This is achieved by “decoupling” a manifold of bound states from the continuum to which they are in fact coupled [12]. Hence all such procedures are inherently approximate.

Such a comparison is particularly important for the algebraic approach, where the geometrical significance of the procedure is less obvious. What is done in that approach is to express the Hamiltonian using the generators of a compact * Lie group. The resulting spectrum of the Hamiltonian is then necessarily discrete. It is then found that the bound state spectrum extends beyond the nominal dissociation energy [14,15]. The total number of bound levels is however finite, and the density of such states declines past the dissociation energy and ultimately vanishes. For diatomic molecules [14] the bound states past the nominal dissociation threshold can be unambiguously identified as the states quasi-bound by the centrifugal barrier (“rotational predissociation” [16]). Quasi-bound states are however also found in the algebraic treatment of non-rotating triatomic molecules [15]. There is considerable indirect evidence that these are the states corresponding to “vibrational predissociation”. The

* For the technical definition of “compact” and other group theoretic terms, see ref. [13].

present study is the first direct demonstration of this interpretation.

The agreement between the algebraic and the coordinate space ("differential") approach is found not only for the energy levels but also for the wavefunctions.

2. Coordinate space Hamiltonian

In coordinate space the Hamiltonian used is that employed in the scattering computations [11,17]: Two equivalent Morse oscillators coupled by a cross kinetic energy term

$$H = H_{AB} + H_{BA} + (\hbar^2/m_B)\partial^2/\partial r_{AB}\partial r_{BA} + D_e \quad (1)$$

Here H_{AB} (and H_{BA}) are Hamiltonians of a Morse oscillator corresponding to the two bond modes, AB and BA of ABA.

$$H_{AB} = -(\hbar^2/2\mu_{AB})\partial^2/\partial r_{AB}^2 + D_e\{\exp[-2a(r_{AB} - r_0)] - 2\exp[-a(r_{AB} - r_0)]\} \quad (2)$$

and similarly for H_{BA} . The reduced mass is as usual $\mu_{AB} = m_A m_B / (m_A + m_B)$. The mass of the central atom is taken here (as in several other corresponding studies [11,18,19]) to be low $m_B = 6m_A$. The two Morse oscillators are thus strongly coupled. The second parameter which deserves special mention is the value of the anharmonicity parameter x_e , where [16]

$$x_e = \omega_0 x_0 / \omega_e, \quad \omega_e x_e = \hbar^2 a^2 / 2\mu_{AB}, \\ D_e = \omega_e^2 / 4\omega_e x_e, \quad (3)$$

$x_e = 1/19.85$ in the present model. This is an atypically high value implying a very anharmonic oscillator. Note that the number, $(N+1)/2$, of bound states of the Morse oscillator is related to x_e as the highest integer value below $2D_e/\omega_e + 1/2$.

3. The algebraic Hamiltonian

A simple algebraic Hamiltonian for two coupled, equivalent, Morse oscillators has been discussed recently [8]. This Hamiltonian is simpler than that given by (1). (It is closely related to the 1-1 resonance approximation to the Hamiltonian (1), which was in-

troduced in ref. [6].) The primary simplifying feature of the algebraic Hamiltonian as used in ref. [8] is that it has a good constant of the motion. This is P , the sum of the vibrational quantum numbers of the two local modes. For many ABA triatomics, the multiplets of levels corresponding to different values of P hardly overlap in energy. Hence terms which couple levels of different values of P are likely to have only a small effect. Neglecting such terms is therefore a realistic approximation, and the aforementioned algebraic Hamiltonian provides an accurate description of the overtones of the stretching modes of many ABA [8] (and ABC [20]) triatomics. Other model Hamiltonians (e.g., refs. [3,6]) for which P is a good quantum number are known.

Explicitly, the algebraic Hamiltonian used in ref. [8] is given by

$$H = A[C_2(O^{(1)}_2) + C_2(O^{(2)}_2)] + BC_2(O_2) + \lambda C_2(U_2). \quad (4)$$

Here $-4A = \omega_e x_e$ and the first term is the two uncoupled Morse oscillators. The magnitude of B affects only the distance between multiplets, and not the spacings of levels within a multiplet (cf. (5) below), and λ is the coupling amongst the local modes. The first two terms in (4) are diagonal. Using $|n, m\rangle$ to designate a local state with n quanta in one mode and m in the other,

$$\langle m, n | H | n, m \rangle = 4A[n(n-N) + m(m-N)] + 4BP(P-2N) + \lambda[n(N-m) + m(N-n)], \quad (5)$$

$$\langle m+1, n-1 | H | n, m \rangle = -\lambda[n(m+1)(N-m)(N-n+1)]^{1/2}. \quad (6)$$

As can be seen from (6), $P = n + m$ is a good quantum number. The numerical value of λ used in the algebraic approach is one that ensures that the Hamiltonian (1), will, to order $1/N$, have off-diagonal elements (6) of the same numerical value as the algebraic Hamiltonian (4).

4. Intermultiplet mixing

As a measure of the importance of the interaction between adjacent multiplets one can compare the en-

ergy gap (denoted by W in the figures) between the highest energy level of a given multiplet and the level just below it (in the same multiplet) and the energy gap (denoted by D in the figures) between the same highest level and the lowest level of the next higher multiplet. Once D becomes comparable to W , energy gap considerations no longer restrict intermultiplet mixing.

Fig. 1 contrasts the situation for water (parameters in the Hamiltonian (4) from ref. [8]) and for the parameters in (4) for the present problem. Since the highest observed overtones in water are in the $P = 5$ multiplet, intermultiplet coupling can be safely neglected. Not so in the present problem (and in all problems for the quasi-bound states where P is comparable to N). To see this analytically consider first the sim-

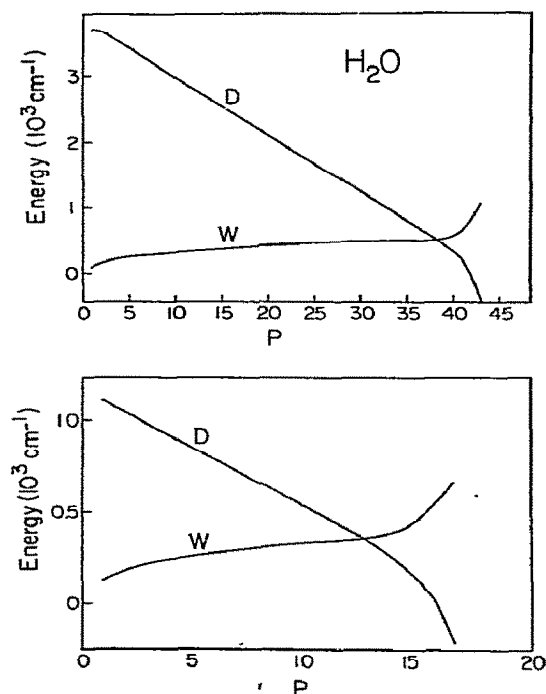


Fig. 1. Inter (D) and intra (W) multiplet energy gaps versus $P = n + m$. Energy in 10^3 cm^{-1} . (a) Water ($A = -18.96 \text{ cm}^{-1}$, $B = -1.14 \text{ cm}^{-1}$, $\lambda = 1.03 \text{ cm}^{-1}$, $N = 44$). (b) The same Hamiltonian, (4), as used for water but with parameters conforming to the present problem ($A = -15.92 \text{ cm}^{-1}$, $B = 0.70 \text{ cm}^{-1}$, $\lambda = 3.38 \text{ cm}^{-1}$, $N = 19$). Note the far higher value of λ/A as compared to water. The result is that the energy scale in (b) is expanded as compared to (a).

pler case when $\lambda \ll A$ (weak coupling between the local modes). Within a multiplet, the range of energy levels is determined by the anharmonicity A and equals AP . The energy separation between the centers of two consecutive multiplets is determined by the frequency and equals $\approx -4(A + 2B)(N - P)$. ($-4AN$ is the frequency, ω_e , at the bottom of the well.) Hence for small λ values intermultiplet mixing is important only as P approaches N . However, a larger than typical value of λ (as is true here because of the low m_B/m_A ratio) will cause a further broadening of the range of energies in a multiplet. Fig. 2 is similar to fig. 1 except that the energy and the Hamiltonian parameters are in reduced units [8], and the only difference between the two panels in fig. 2 is the value of λ . (Fig. 2 is for $N = 19$ corresponding to $x_e = 1/19.85$, which is the value used here.)

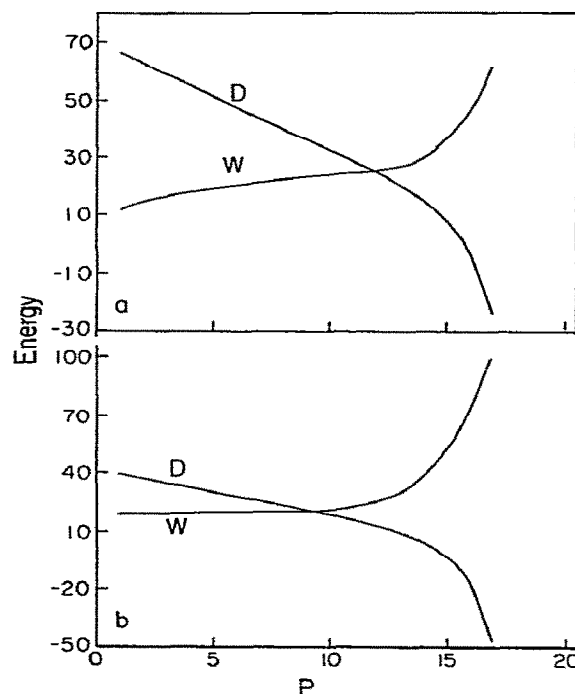


Fig. 2. Energy gaps (in units of $-A/\cos \chi$) versus P , as in fig. 1, for the Hamiltonian (4) with the same N as the present problem and with the parameters $B = 0$, $A = -\cos \chi$ and $\lambda = 10 \sin \chi/N$ (dimensionless). χ is the reduced coupling parameter between the local modes, $\tan \chi = -N\lambda/10A$ [8]. The two plots differ in the magnitude of the coupling: (a) $\chi = 0.2\pi$, (b) $\chi = 0.4\pi$.

The evidence then is that one must break the $O(2)$ symmetry of the Hamiltonian (4) and allow inter-multiplet mixing.

In principle one can construct an algebraic Hamiltonian which is strictly equivalent to the coordinate space Hamiltonian (1). Here we adopt a simpler procedure, namely including only the lowest-order terms which fail to conserve P . To understand the route to such a term it is easiest to begin with the classical limit of the Hamiltonian (4). This was computed in refs. [8,21] and to order $1/N$ is

$$\begin{aligned} H &= H_0(I_1, I_2) + V(I_1, I_2, \theta_1, \theta_2), \\ H_0(I_1, I_2) &= -4ANI_1 + 4AI_1^2 - 4ANI_2 + 4AI_2^2 \\ &\quad + 4B(P - N)^2 + 2AN^2 \\ &\quad + \lambda[I_1(N - I_2) + I_2(N - I_1)], \\ V(I_1, I_2, \theta_1, \theta_2) &= -2\lambda N(I_1 I_2)^{1/2} \cos(\theta_1 - \theta_2). \end{aligned} \quad (7)$$

I_i and θ_i are the action and angle variables for the i th bond and $P = I_1 + I_2$. As is evident the classical limit is that of two anharmonic oscillators with a 1 : 1 resonance term of the same type discussed in ref. [6].

The conservation of $P = I_1 + I_2$ follows from the fact that the Hamiltonian (7) is cyclic in the conjugate angle variable, $\theta_1 + \theta_2$. To break the $O(2)$ symmetry we therefore add the next higher resonance, which is a 1 : 2 term. The Fourier analysis [6] of the Hamiltonian (1) shows that the coupling coefficients of the 1 : 1 ($V_{11} \cos(\theta_1 - \theta_2)$) and 1 : 2 ($V_{21} \cos(2\theta_1 - \theta_2)$) terms must be in the ratio [6]

$$V_{21}/V_{11} = -[(1 - \omega_1/\omega_0)/(1 + \omega_1/\omega_0)]^{1/2}, \quad (8)$$

where $\omega_1 = \omega_e - 2\omega_e x_e I_1$. Hence to order $1/N$,

$$V_{21}/V_{11} = -(I_1/N)^{1/2}. \quad (9)$$

In the classical limit, the lowest non-linear resonance term that will induce intermultiplet coupling is therefore, using (7) for V_{11}

$$V_{21} = -V_{11}(I_1/N)^{1/2} = 2(\lambda/N)NI_1(NI_2)^{1/2}. \quad (10)$$

Due to conservation of parity there is also a V_{12} term. Hence the 1 : 2 resonance terms to be added to (7) are

$$\begin{aligned} S(I_1, I_2, \theta_1, \theta_2) &= 2\eta NI_1(NI_2)^{1/2} \cos(\theta_2 - 2\theta_1) \\ &\quad + 2\eta NI_2(NI_1)^{1/2} \cos(\theta_1 - 2\theta_2), \end{aligned} \quad (11)$$

with $\eta = \lambda/N$.

The algebraic operator whose classical limit to order $1/N$ (determined by the method of ref. [21]) is (11) is given by

$$S = \eta[Q_{1+}Q_{2-}(Q_{1+} + Q_{2-}) + Q_{1-}Q_{2+}(Q_{1-} + Q_{2+})] \quad (12)$$

The matrix elements of S are implied by

$$\begin{aligned} S|n, m\rangle &= s_1^+ |n+1, m-2\rangle + s_1^- |n-1, m+2\rangle \\ &\quad + s_2^+ |n+2, m-1\rangle + s_2^- |n-2, m+1\rangle, \end{aligned} \quad (13)$$

$$\begin{aligned} s_1^+ &= \eta[(N-n)(n+1)(N-m+1) \\ &\quad \times m(m-1)(N-m+2)]^{1/2}, \end{aligned}$$

$$\begin{aligned} s_1^- &= \eta[(N-n+1)n(N-m) \\ &\quad \times (m+1)(m+2)(N-m-1)]^{1/2}, \end{aligned}$$

$$\begin{aligned} s_2^+ &= \eta[(N-m)(m+1)(N-n+1) \\ &\quad \times n(n-1)(N-n+2)]^{1/2}, \end{aligned}$$

$$\begin{aligned} s_2^- &= \eta[(N-m+1)m(N-n) \\ &\quad \times (n+1)(n+2)(N-n-1)]^{1/2}. \end{aligned} \quad (14)$$

These matrix elements have been computed from the definition [22] of the Q operators

$$Q_+|n\rangle = [(N-n)(n+1)]^{1/2}|n+1\rangle,$$

$$Q_-|n\rangle = [(N-n+1)n]^{1/2}|n-1\rangle. \quad (15)$$

The implication of (13) is that S couples states of the multiplet P only to the neighbouring, $P \pm 1$, multiplets. As a consequence, the (multiplet P) block-diagonal representation (5), (6) of the Hamiltonian H (4) is blown up to a tri-block-diagonal representation (5), (6), (13) of the Hamiltonian $H + S$, (4), (11). Needless to say it is numerically simpler to diagonalize this algebraic tri-block-diagonal matrix than the non-sparse coordinate representation matrix of the Hamiltonian (1).

5. Results

The eigenvalues (and eigenfunctions) of the algebraic Hamiltonian H (given by (4)) and the algebraic Hamiltonian $H + S$ (S given by (12)) were computed.

The number ** of bound and quasi-bound states were found to be the same for both computations, namely 100, the number of Morse oscillator states squared. The eigenvalues of these two algebraic Hamiltonians were different by rms deviation of 6×10^{-3} eV, and even more of a prominent difference was found for the wavefunctions (see below). The reason is, of course, that the Hamiltonian H precludes intermulti-

plet mixing. Such eigenvalues that did change were, as expected, near the boundaries of the multiplets where the coupling induced by S is particularly important.

The eigenvalues for the Hamiltonian $H + S$ are given, for all 100 states, in table 1. The parameters used in table 1 were optimized for a best fit to the first 55 states computed by coordinate space methods. (With the result that, say, η does not quite have the classical value of λ/N , and A differs slightly from $-\omega_e x_e/4$.) The rms deviation of the fit is 2.3×10^{-3} eV. The reason for the existing deviation is, in part, that only the lowest two resonances in the Fourier expansion of the momentum coupling were taken into account.

** This number (100) is determined by N . Since $x_e = (N + 1)^{-1}$, the value of N and hence the number of states is immediately given in terms of the parameters in the coordinate space Hamiltonian (1).

Table 1
Energy levels of two coupled Morse oscillators (eV)

Symmetric states				Asymmetric states			
algeb. a)	coord. b)	algeb. a)	coord. b)	algeb. a)	coord. b)	algeb. a)	coord. b)
-0.61100	-0.61100	0.30609	0.31436			0.39118	0.39364
-0.48174	-0.48313	0.32557	0.32083	-0.46584	-0.46443	0.41232	0.40325
-0.36140	-0.36347	0.33251	0.33115	-0.35161	-0.35096	0.42076	0.42494
-0.32716	-0.32579	0.33940	0.34445	-0.24804	-0.24794	0.42979	0.43955
-0.25214	-0.25402	0.37533	0.37280	-0.19665	-0.19636	0.46269	0.45274
-0.22251	-0.22173	0.38927	0.39650	-0.15669	-0.15685	0.49264	0.49180
-0.15762	-0.15856	0.40868	0.41538	-0.10451	-0.10376	0.50791	0.51913
-0.12333	-0.12369	0.42495	0.43556	-0.07882	-0.07884	0.51660	0.53143
-0.07987	-0.08011	0.43732	0.44366	-0.02486	-0.02532	0.55677	0.53448
-0.07322	-0.07497	0.46335	0.46768	-0.01183	-0.01082	0.58445	0.57138
-0.03183	-0.03313	0.48503	0.48118	0.02720	0.02633	0.58785	0.59830
-0.01544	-0.01508	0.49468	0.50565	0.04049	0.03603	0.60770	0.61044
0.00924	0.00945	0.51528	0.52447	0.05834	0.05446	0.64627	0.63389
0.02742	0.02624	0.53312	0.53025	0.06000	0.06294	0.66390	0.66017
0.05483	0.05228	0.55119	0.55793	0.07730	0.07314	0.69879	0.67260
0.05996	0.06137	0.55766	0.58298	0.10883	0.10847	0.70790	0.70456
0.07730	0.07312	0.58324	0.59267	0.12404	0.12502	0.76824	0.71691
0.08626	0.08713	0.60765	0.60509	0.16040	0.16174	0.79260	0.74438
0.11970	0.12178	0.62386	0.62565	0.18499	0.18475		
0.14639	0.13955	0.63534	0.64954	0.19310	0.19700		
0.15658	0.15669	0.65581	0.66594	0.20944	0.21043		
0.17319	0.17542	0.67058	0.67565	0.23746	0.23296		
0.19231	0.19627	0.69235	0.69840	0.24957	0.24598		
0.20925	0.20746	0.70851	0.71231	0.28147	0.28369		
0.21135	0.21055	0.73790	0.73060	0.30458	0.30206		
0.23565	0.24090	0.76082	0.74281	0.31223	0.31758		
0.26543	0.26708	0.78982	0.75742	0.32629	0.33245		
0.29015	0.29384			0.35440	0.35525		

a) Using the algebraic Hamiltonian $H + S$ (eqs. (4), (12)) with parameters $A = -1.97336 \times 10^{-3}$ eV, $B = 0.086286 \times 10^{-3}$ eV, $\lambda = 0.418533 \times 10^{-3}$ eV, $\eta = 0.019779 \times 10^{-3}$ eV, $N = 19$.

b) Using the coordinate space Hamiltonian H (eq. (1)) with parameters $D_e = 0.76$ eV, $a = 1$ au $^{-1}$, $m_A = 35/31$ amu, $m_B = 210/31$ amu (adapted from ref. [11]). The algebraic and coordinate space results differ by rms = 0.00228 eV.

Higher terms will give higher order in the generators and will improve the fit.

Table 1 also shows the best results obtained by diagonalizing the coordinate space Hamiltonian in the basis of 100 products of Morse functions $|n_{AB}\rangle|n_{BA}\rangle$, where $0 \leq n_{AB}, n_{BA} \leq 9$ denote the vibrational quanta in the AB, BA bonds [11]. The convergence has been tested by comparison with alternative (hyperspherical DIVAH) basis functions, and with exact scattering results [11]. It is believed that (at least) the lowest 55 states are well converged. For some of the lower quasi-bound states the coordinate space computation has also been checked by using these states as initial states for time propagation [19]. To the best numerical accuracy, such states did exhibit a pure exponential decay.

It should be stressed that the use of a unitary representation of the compact algebras to describe the system precludes the pure algebraic calculation of the width ‡ , but we can use the double Morse coefficients to build a geometric representation of the wavefunctions and to propagate it in time in the geometric representation of the potential [19]. Such a calculation was done on the state (16^+) . It was found that the lifetime of this resonance was $\tau = 0.163$ ps which is very close to the lifetime $\tau = 0.168$ ps in the purely coordinate space approach. As a result, the width of this resonance state was 4.0×10^{-3} eV, which is one order of magnitude smaller than the average separation between the resonances.

It is not always realized that the algebraic approach does provide wavefunctions (i.e. eigenvectors; see, for example ref. [15]). In the present problem these are the expansion coefficients of the wavefunction in products of Morse eigenfunctions of both bonds. Such coefficients were found to be in good agreement with the coordinate space computations. As expected, many states (in particular the "local modes" [3,11,19]) have dominant coefficients for states $|n, m\rangle$ in a single multiplet $P = n + m$, but there are also others (in particular the "delocalized" and the "hyperspherical modes" [11,18,19]) with dominant coefficients from neighbouring multiplets $P, P \pm 1$. The intermultiplet mixing, section 4, is essential for accurate accounts of such non-local modes.

As examples for the changes in the wavefunctions caused by the intermultiplet mixing consider the following cases:

(1) The wavefunction for the symmetric state with energy -0.07987 eV is approximately given by

$$\psi_{E=-0.07987 \text{ eV}} = 0.92|50^+\rangle + 0.3|22^+\rangle + 0.2|41^+\rangle.$$

This is a local mode state in the multiplet $P = 5$, but the next dominant contribution is from the state with a different P .

(2) The resonance state with energy 0.17319 eV (symmetric) has its dominant contributions (more than 80%) from the states $|43^+\rangle$ (34%) and $|71^+\rangle$ (46%) which belongs to two different multiplets.

6. Summary

In the algebraic approach to bound-state problems the Hamiltonian is expressed in terms of generators of a compact group. The resulting spectrum is then purely discrete. Yet realistic algebraic Hamiltonians predict states higher in energy than the nominal dissociation threshold. By comparison with more conventional (coordinate space based) methods and with scattering computations, these higher energy states are identified as the quasi-bound ("resonance") states of the Hamiltonian.

To obtain an accurate description of the quasi-bound states where intermultiplet coupling is always important, and in view of the strong local mode coupling constant of the coordinate space Hamiltonian, a new term trilinear in the generators (breaking the $O(2)$ symmetry) was added to the algebraic Hamiltonian of ref. [8].

A system of two strongly coupled anharmonic oscillators is a well characterized example [17,24] of classically chaotic dynamics. Yet a compact Lie group provides a realistic description even of the quasi-bound states. Of course, quite a few of the eigenstates are linear combinations of many basis functions, with all expansion coefficients below 0.5 [25]. But the algebraic approach is fully able to account for such behaviour.

Acknowledgement

This work was partly supported by the Air Force

[†] Using non-unitary representation it was recently shown how a purely algebraic computation of the width can be performed [23].

Office of Scientific Research, Grant AFOSR 81-0030, the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The Fritz Haber Research Center is supported by the Minerva Gesellschaft für die Forschung, mbH, Munich, FRG.

References

- [1] R. Wallace, *Chem. Phys.* 11 (1975) 189.
- [2] O.S. Mortensen, B.R. Henry and M.A. Mohammadi, *J. Chem. Phys.* 75 (1981) 4800.
- [3] M.S. Child and R.T. Lawton, *Faraday Discussions* 71 (1981) 273.
- [4] M.S. Child and L. Halonen, *Advan. Chem. Phys.* 57 (1984) 1.
- [5] C. Jaffé and P. Brumer, *J. Chem. Phys.* 73 (1980) 5646.
- [6] E.L. Sibert III, W.P. Reinhardt and J.T. Hynes, *J. Chem. Phys.* 77 (1982) 3583, 3595.
- [7] M.L. Sage and J.A. Williams III, *J. Chem. Phys.* 78 (1983) 1348.
- [8] O.S. van Roosmalen, I. Benjamin and R.D. Levine, *J. Chem. Phys.* 81 (1984) 5986.
- [9] N. Rosen, *J. Chem. Phys.* 1 (1933) 319.
- [10] R.D. Levine, *Accounts Chem. Res.* 3 (1970) 273.
- [11] K.C. Kulander, *J. Chem. Phys.* 79 (1983) 1279; K.C. Kulander, J. Manz and H.H.R. Schor, *J. Chem. Phys.* 82 (1985), to be published.
- [12] R.D. Levine, *J. Chem. Phys.* 49 (1968) 51; R.D. Levine, R.B. Johanson, J.T. Muckerman and R.B. Bernstein, *J. Chem. Phys.* 49 (1968) 56.
- [13] B.G. Wybourne, *Classical groups for physicists* (Wiley, New York, 1974).
- [14] F. Iachello and R.D. Levine, *J. Chem. Phys.* 77 (1982) 3046.
- [15] O.S. van Roosmalen, F. Iachello, R.D. Levine and A.E.L. Dieperink, *J. Chem. Phys.* 79 (1983) 2515.
- [16] G. Herzberg, *Spectra of diatomic molecules* (Van Nostrand, Princeton, 1950).
- [17] R.M. Hedges Jr. and W.P. Reinhardt, *Chem. Phys. Letters* 91 (1982) 241; *J. Chem. Phys.* 78 (1983) 3964; E. Thiele and D.J. Wilson, *J. Chem. Phys.* 35 (1961) 1256.
- [18] J. Manz and H.H.R. Schor, *Chem. Phys. Letters* 107 (1984) 542.
- [19] R.H. Bisseling, R. Kosloff and J. Manz, to be published.
- [20] I. Benjamin, O.S. van Roosmalen and R.D. Levine, *J. Chem. Phys.* 81 (1984) 3352.
- [21] O.S. van Roosmalen, R.D. Levine and A.E.L. Dieperink, *Chem. Phys. Letters* 101 (1983) 512.
- [22] R.D. Levine, *Chem. Phys. Letters* 95 (1983) 87.
- [23] Y. Alhassid, F. Iachello and R.D. Levine, *Phys. Rev. Letters*, to be published.
- [24] T. Matsushita and T. Terasaka, *Chem. Phys. Letters* 105 (1984) 511.
- [25] G. Hose and H.S. Taylor, *J. Chem. Phys.* 76 (1982) 5356.