

## On adiabatic separation of stretching and bending vibrations

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It is pointed out that current practice adiabatic treatment of bending motion in stretch-bend hamiltonians is flawed. It does not give the correct wavefunction in the limiting case of separable motion. This defect is remedied by introducing a variational parameter which is determined by minimizing the energy. Relative accuracy of various adiabatic approximations is examined for a model hamiltonian in two cases, first when the stretching frequency is higher, and second, when the bending frequency is higher.

### 1. Introduction

Even if we know the potential energy surface for a triatomic molecule, the calculation of its rovibrational spectrum remains a formidable task. There are six degrees of freedom, which, if the system is symmetric and separable, resolve into rotations, a symmetric stretch, an antisymmetric stretch, and bending vibrations. Elaborate variational calculations are required to achieve usefully accurate predictions of the energy of a state with even a modest number of quanta. Efficient approximations which focus on the essential physics and reduce the amount of calculation are therefore required.

In the spirit of the Born-Oppenheimer approximation, adiabatic separation of stretching from bending (and sometimes rotational) motions has been invoked for this purpose [1-8]. We illustrate the extant approximations for a model hamiltonian with one stretching and one bending mode [9]

$$H(r, \xi) = -\frac{1}{2m} \frac{\partial^2}{\partial r^2} + V_M(r) - \frac{1}{2mr^2} \frac{\partial}{\partial \xi} (1 - \xi^2) \frac{\partial}{\partial \xi} + V_A(\xi), \quad (1.1)$$

where  $0 \leq r < \infty$  is the stretching coordinate and  $-1 \leq \xi \leq 1$  is the bending coordinate. ( $\xi$  is the cosine of the bending angle.) The motion is subject to a Morse potential in the stretching coordinate,

$$V_M(r) = D\{1 - \exp[-a(r - r_0)]\}^2, \quad (1.2 a)$$

and an anharmonic angular potential in the bending coordinate,

$$V_A(\xi) = \frac{\lambda_1^2}{(1 - \xi)} + \frac{\lambda_2^2}{(1 + \xi)}. \quad (1.2 b)$$

The angular potential has a minimum at  $\xi = (\lambda_2 - \lambda_1)/(\lambda_2 + \lambda_1)$ . In the rest of this paper, we will extend the range of  $r$  to  $-\infty < r < \infty$  as is customary for the Morse potential, taking care that the parameters in the potential are such that the error incurred is negligible. (All wavefunctions of interest should have effectively decayed

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to zero at  $r = 0$ .) The centrifugal coupling between stretching and bending motions through the appearance of  $1/r^2$  in the 'kinetic energy' for bending is a characteristic feature of molecular vibrations. Note that the eigenfunctions of  $H(r, \xi)$  are separable when  $V_A(\xi) = 0$ .

Two different adiabatic approximations which have been used in the past are summarized in § 2 and § 3. In the adiabatic stretch (AS) approximation, stretching is presumed to occur in an effective potential which depends on the average over bending motion. Conversely, in the adiabatic bend (AB) approximation, the bending motion is influenced by stretching in an average sense only. One expects adiabatic stretch to be the better approximation when bending motion is faster, and conversely, adiabatic bend to be the better approximation when stretching motion is faster.

Johnson, Skodje and Reinhardt [1] have tested this assumption for a model hamiltonian with two degrees of freedom and Johnson and Reinhardt [2] have carried out a similar analysis of adiabatic approximations for vibrational spectrum of water molecule in states of zero angular momentum. (The model hamiltonian in the former paper is different from ours but has similar coupling between stretching and bending motion.) In both these papers it was found that adiabatic stretch was often the better approximation, even when the stretching frequency was a few times the bending frequency, and particularly when the bending mode was excited. We quote from the abstract of [2]:

'The conventional adiabatic approach, in which the slower bending motion experiences an effective force due to averaging over the faster stretching modes, is reaffirmed to be accurate for excited stretching states. For states with any appreciable bending excitation, however, it turns out that the adiabatic calculations quickly erode in reliability. In answer to this problem, the reverse adiabatic procedure (with the bend treated first) is also implemented here. While counterintuitive, this latter method is found to yield a significant improvement for calculating bending overtones, as well as many of the combination bands.'

While this conclusion is not necessarily wrong, the assumption underlying it is flawed. A sensible adiabatic approximation which replaces a nonseparable wavefunction by a separable or quasi-separable wavefunction should, in the limit of separability, give the exact wavefunction. It is seen that the AS approximation (§ 2) satisfies this criterion but the AB approximation (§ 3) does not. (Recall that the eigenfunctions of  $H(r, \xi)$  are separable when  $V_A(\xi) = 0$ .) In any comparison, the AB approximation is inherently at a disadvantage.

This defect is remedied in § 4 by introducing a variational parameter in the wavefunction and minimizing the expectation value of energy. Thus modified, the adiabatic bend (or MAB) approximation is on the same footing as the AS approximation provided that diagonal nonadiabatic corrections are added to AS energies (AS + NAC approximation). This is because the diagonal nonadiabatic corrections to the MAB energies are strictly zero (i.e.  $E^{\text{MAB}} = E^{\text{MAB} + \text{NAC}}$ ). Stated differently, MAB energy is the expectation value of the hamiltonian in an approximate wavefunction, and should be compared with a similar expectation value. It is our contention that a truly meaningful comparison can be made only between MAB and AS + NAC approximations.

This is done in § 5 for two cases, first when the stretching frequency is higher than the bending frequency, and second, when the bending frequency is higher than the stretching frequency. In the first case, while the comparison between AS and AB

approximations is erratic, in accordance with the observations made in [1] and [2], the MAB approximation is systematically superior to the AS + NAC approximation. In the second case, the AS approximation is found to be superior to the AB approximation, and the AS + NAC approximation superior to the MAB approximation. This is just as expected. The point here is that when there is stronger coupling between stretching and bending motions, the MAB approximation, by virtue of its correct limiting behaviour, is a considerable improvement over the AB approximation.

Our conclusion is that as far as possible, one should diagonalize the hamiltonian matrix in the basis of adiabatic states. This assures that a tractable calculation gives upper bounds to true energies. If that is not possible, one should certainly prefer the modified adiabatic bend approximation to the adiabatic bend approximation.

## 2. Adiabatic stretch

In the adiabatic stretch (AS) approximation, the bending equation is first solved for a fixed value of the stretching coordinate. Averaging over bending motion then gives an effective potential for stretching and the solution of the corresponding Schrödinger equation gives a quasi-separable approximation to the wavefunction. Thus,

$$\left[ -\frac{1}{2mr^2} \frac{d}{d\xi} (1 - \xi^2) \frac{d}{d\xi} + V_A(\xi) - U_\mu(r) \right] \chi_\mu(r; \xi) = 0, \quad (2.1 a)$$

$$\left[ -\frac{1}{2m} \frac{d^2}{dr^2} + V_M(r) + U_\mu(r) - E_{\nu\mu}^{\text{AS}} \right] \phi_{\nu\mu}(r) = 0, \quad (2.1 b)$$

with

$$\psi(r, \xi) = \phi_{\nu\mu}(r) \chi_\mu(r; \xi). \quad (2.1 c)$$

By assumption, the dependence of  $\chi_\mu(r; \xi)$  on  $r$  is weak and the adiabatic energy  $E_{\nu\mu}^{\text{AS}}$  amounts to the expectation value of  $H(r, \xi)$  in the state defined by (2.1 c) disregarding the dependence of  $\chi_\mu(r; \xi)$  on  $r$ . For our choice of the angular potential,

$$\chi_\mu(r, \xi) = N_\mu^{\alpha, \beta} (1 - \xi)^{\alpha/2} (1 + \xi)^{\beta/2} P_\mu^{\alpha, \beta}(\xi), \quad (2.2 a)$$

where  $P_\mu^{\alpha, \beta}(\xi)$  is the Jacobi polynomial [10] of degree  $\mu$ , its indices  $\alpha$  and  $\beta$  depend on  $r$ ,

$$\alpha = 2r\lambda_1\sqrt{m}, \quad \beta = 2r\lambda_2\sqrt{m}, \quad (2.2 b)$$

and  $N_\mu^{\alpha, \beta}$  is the normalization constant,

$$N_\mu^{\alpha, \beta} = \left[ \frac{(2\mu + \alpha + \beta + 1) \Gamma(\mu + 1) \Gamma(\mu + \alpha + \beta + 1)}{2^{\alpha + \beta + 1} \Gamma(\mu + \alpha + 1) \Gamma(\mu + \beta + 1)} \right]^{1/2}. \quad (2.2 c)$$

The corresponding effective potential in the stretching coordinate is

$$U_\mu(r) = \frac{1}{2mr^2} (\mu + \frac{1}{2}(\alpha + \beta))(\mu + \frac{1}{2}(\alpha + \beta) + 1). \quad (2.2 d)$$

In § 5 we also consider diagonal nonadiabatic corrections (NAC) to AS energies [11],

$$\Delta E_{\nu\mu}^{\text{NAC}} = -\frac{1}{2m} \int dr d\xi \phi_{\nu\mu}^*(r) \chi_{\mu}^*(r; \xi) \times \left[ \frac{d}{dr} \phi_{\nu\mu}(r) \frac{d}{dr} \chi_{\mu}(r; \xi) + \phi_{\nu\mu}(r) \frac{d^2}{dr^2} \chi_{\mu}(r; \xi) \right].$$

The first term is zero on integration over  $\xi$  because

$$\int d\xi \chi_{\mu}^*(r; \xi) \frac{d}{dr} \chi_{\mu}(r; \xi) = \frac{1}{2} \frac{d}{dr} \int d\xi |\chi_{\mu}(r; \xi)|^2 = 0,$$

where the last equality follows from the fact that  $\chi_{\mu}(r; \xi)$  is normalized. For the purpose of computing the remaining integral, it is convenient to invoke the expansion

$$\frac{d}{dr} \chi_{\mu}(r; \xi) = \sum_{\mu' \neq \mu} a_{\mu\mu'}(r) \chi_{\mu'}(r; \xi),$$

so that

$$\Delta E_{\nu\mu}^{\text{NAC}} = \frac{1}{2m} \int dr \phi_{\nu\mu}^*(r) \left[ \sum_{\mu' \neq \mu} a_{\mu\mu'}^2(r) \right] \phi_{\nu\mu}(r). \quad (2.3 a)$$

By differentiating (2.1 a) with respect to  $r$  and projecting onto  $\chi_{\mu}(r; \xi)$ , it can be shown that

$$a_{\mu\mu'}(r) = \frac{2}{r} \frac{1}{(U_{\mu'}(r) - U_{\mu}(r))} \int d\xi \chi_{\mu'}^*(r; \xi) V_A(\xi) \chi_{\mu}(r; \xi). \quad (2.3 b)$$

Remaining integrals in (2.3 a) and (2.3 b) are calculated easily by quadrature.

### 3. Adiabatic bend

In the alternative adiabatic bend (AB) approximation, one averages over the stretching mode and solves an effective bending equation. Thus [12]

$$\left[ -\frac{1}{2m} \frac{d^2}{dr^2} + V_M(r) - \varepsilon_v^s \right] \phi_v(r) = 0, \quad (3.1 a)$$

followed by

$$\left[ -\frac{1}{2m} \langle 1/r^2 \rangle_v \frac{d}{d\xi} (1 - \xi^2) \frac{d}{d\xi} + V_A(\xi) - \varepsilon_{\nu\mu}^b \right] \chi_{\nu\mu}(\xi) = 0, \quad (3.1 b)$$

gives a separable approximation to the wavefunction,

$$\psi_{\nu\mu}(r, \xi) = \phi_v(r) \chi_{\nu\mu}(\xi), \quad (3.1 c)$$

and the adiabatic approximation to energy,

$$E_{\nu\mu}^{\text{AB}} = \varepsilon_v^s + \varepsilon_{\nu\mu}^b. \quad (3.1 d)$$

The adiabatic energy is the expectation value of  $H(r, \xi)$  in the state defined by (3.1 c).

For our choice of  $V_M(r)$  and  $V_A(\xi)$ , eigenproblems (3.1 a) and (3.1 b) can be solved analytically but the integral which defines the effective value of the stretching coor-

dinate during bending motion,

$$(1/r_{\text{eff}}^2) \equiv \langle 1/r^2 \rangle_v = \int dr \phi_v^*(r) \frac{1}{r^2} \phi_v(r),$$

must be calculated numerically [13]. The function  $\phi_v(r)$  is the standard wavefunction of the one-dimensional Morse oscillator,

$$\phi_v(r) = \left[ \frac{a(\eta - 2v - 1)\Gamma(v + 1)}{\Gamma(\eta - v)} \right]^{1/2} \exp(-x/2) x^{\eta-1-2v/2} L_v^{\eta-2v-1}(x), \quad (3.2)$$

where  $\eta = \sqrt{(8mD)/a}$  and  $x = \eta \exp(-a(r - r_0))$ . The angular function  $\chi_{v\mu}(\xi)$  is the one given in (2.2 a) with  $r$  replaced by its effective value  $r_{\text{eff}}$ . The stretching and bending contributions to adiabatic energy are respectively,

$$\varepsilon_v^s = \left( \frac{2D}{m} \right)^{1/2} a(v + 1/2) - \frac{a^2}{2m} (v + 1/2)^2, \quad (3.3 a)$$

and

$$\varepsilon_{v\mu}^b = \frac{1}{2m} \langle 1/r^2 \rangle_v (\mu + (\lambda_1 + \lambda_2)r_{\text{eff}}\sqrt{m})(\mu + 1 + (\lambda_1 + \lambda_2)r_{\text{eff}}\sqrt{m}). \quad (3.3 b)$$

#### 4. Modified adiabatic bend

The principal defect of the AB approximation is that it does not give the correct wavefunction in the separable limit,  $V_A(\xi) = 0$ . This is remedied by continuing to regard  $\psi(r, \xi)$  as separable but requiring it to depend on a parameter  $\tau$ . This parameter is introduced in the stretching and bending functions by temporarily adding a centrifugal term  $\tau/2mr^2$  (to be subtracted eventually) and averaging over stretching motion [14]. The stretching part then satisfies a modified equation,

$$\left[ -\frac{1}{2m} \frac{d^2}{dr^2} + V_M(r) + \frac{\tau}{2mr^2} - \varepsilon_v^s(\tau) \right] \phi_v(\tau; r) = 0. \quad (4.1 a)$$

The bending equation is the same as (3.1 b) except for an additional dependence on  $\tau$

$$\left[ -\frac{1}{2m} \langle 1/r^2 \rangle_{\tau, v} \frac{d}{d\xi} (1 - \xi^2) \frac{d}{d\xi} + V_A(\xi) - \varepsilon_{v\mu}^b(\tau) \right] \chi_{v\mu}(\tau; \xi) = 0. \quad (4.1 b)$$

The wavefunction is the product of its stretching and bending parts,

$$\psi_{v\mu}(\tau; r, \xi) = \phi_v(\tau; r) \chi_{v\mu}(\tau; \xi), \quad (4.1 c)$$

and the MAB approximation to energy is the expectation value of  $H(r, \xi)$  in this state

$$E_{v\mu}^{\text{MAB}}(\tau) = \varepsilon_v^s(\tau) + \varepsilon_{v\mu}^b(\tau) - \frac{\tau}{2m} \langle 1/r^2 \rangle_{\tau, v}. \quad (4.1 d)$$

(Note the subtraction of the expectation value of the centrifugal potential in the last term of equation (4.1 d). The parameter  $\tau$  is determined variationally by minimizing the energy. It is clear that the wavefunction (4.1 c) reduces to the exact separable wavefunction in the limit  $V_A(\xi) = 0$ , and that in this case  $\tau$  depends on the bending quantum number  $\mu$  but not on the stretching quantum number  $v$ .

In order to calculate the value of  $\tau$  at which  $E_{v\mu}^{\text{MAB}}(\tau)$  is stationary, differentiate equation (4.1 *a*) with respect to  $\tau$  and project onto  $\phi_v(\tau; r)$ . This gives,

$$\frac{d}{d\tau} \varepsilon_v^s(\tau) = \frac{1}{2m} \langle 1/r^2 \rangle_{\tau, v}.$$

Similarly differentiate the bending equation (4.1 *b*) with respect to  $\tau$  and project onto  $\chi_{v, \mu}(\tau; \xi)$ . This gives

$$\frac{d}{d\tau} \varepsilon_{v\mu}^b(\tau) = [\varepsilon_{v\mu}^b(\tau) - \langle \chi_{v\mu}(\tau; \xi) | V_A(\xi) | \chi_{v\mu}(\tau; \xi) \rangle] \frac{d}{d\tau} (\ln \langle 1/r^2 \rangle_{\tau, v}).$$

Using these equations in (4.1 *d*), one can show that stationarity of adiabatic energy requires  $\tau$  to satisfy the following equation:

$$\frac{\tau}{2m} \langle 1/r^2 \rangle_{\tau, v} = \varepsilon_{v\mu}^b(\tau) - \langle \chi_{v\mu}(\tau; \xi) | V_A(\xi) | \chi_{v\mu}(\tau; \xi) \rangle. \quad (4.2)$$

We have used this relation to calculate successive approximations to  $\tau$  beginning with the AB approximation ( $\tau = 0$ ). This iterative sequence is found to converge very rapidly. We have further assumed that even in the nonseparable case, there is a common optimal value of  $\tau$  for all states with the same bending quantum number  $\mu$ . The adiabatic functions of equation (4.1 *c*) are not orthogonal when  $\mu_1 \neq \mu_2$ , but this is a small price one must pay for ensuring correct limiting behaviour in the separable case.

### 5. Numerical practice, results and discussion

In order to evaluate the accuracy of various adiabatic approximations, we need to establish a standard for comparison. This is done by diagonalizing the matrix representation of (1.1) in a large basis set. We have used product functions of the form

$$\psi_{v\mu}(r, \xi) = \phi_v(r) \chi_\mu(\xi). \quad (5.1)$$

The stretching basis functions are

$$\phi_v(r) = \left[ \frac{a\Gamma(v+1)}{\Gamma(v+\rho+1)} \right]^{1/2} \exp(-x/2) x^{(\rho+1)/2} L_v^\rho(x), \quad (5.2 a)$$

where  $L_v^\rho(x)$  is an associated Laguerre polynomial in the variable  $x = \eta \exp(-a(r-r_0))$  with  $\eta = \sqrt{(8mD)/a}$ . The index  $\rho$  is in principle arbitrary but the choice  $\rho = \eta - 2N$ , where  $N$  is the largest integer smaller than  $\frac{1}{2}(\eta + 1)$ , is particularly convenient. The first  $N$  stretching functions  $\{\phi_i(r), i = 0, 1, 2, \dots, N-1\}$  then span the bound states of the Morse oscillator and higher functions bring in coupling to the continuous spectrum [15]. The angular basis functions,

$$\chi_\mu(\xi) = N_v^{\alpha, \beta} (1 - \xi)^{\alpha/2} (1 + \xi)^{\beta/2} P_\mu^{\alpha, \beta}(\xi), \quad (5.2 b)$$

were defined previously in equation (2.2 *a*) but the indices  $\alpha$  and  $\beta$  now do not depend on  $r$ . The choice we have made,

$$\alpha = 2\lambda_1 r_0 \sqrt{m}, \quad \beta = 2\lambda_2 r_0 \sqrt{m}, \quad (5.2 c)$$

is natural for our model potential. It should be noted that all energies quoted as being variational have been checked for convergence with respect to changes in the

size of the basis set and the parameters  $\rho$ ,  $\alpha$  and  $\beta$ . The coupling to the continuum states of the Morse potential is very weak and we have not found it necessary to include more than  $N + 1$  stretching functions.

The matrix elements of  $f(x)$  between stretching basis functions are calculated in one fell swoop as follows. The basis set is first augmented by  $M$  functions and the matrix representation of  $x$  (which happens to be tridiagonal) in the  $(N + M)$  basis functions is diagonalized by an orthogonal transformation:

$$\tilde{O}^T \tilde{x} \tilde{O} = \tilde{x}^{\text{diag}}.$$

A diagonal matrix of  $f(x)$  evaluated at the eigenvalues of  $\tilde{x}$  is then constructed and one reverts to the original basis by making the inverse orthogonal transformation,

$$\tilde{f} = \tilde{O} \tilde{f}^{\text{diag}} \tilde{O}^T.$$

The  $(N \times N)$  submatrix of  $\tilde{f}$  is the matrix of desired integrals [16]. The number of extra basis functions required naturally depends on the rate of convergence of the Taylor series expansion of  $f(x)$ . We have found  $M = 15$  to be quite satisfactory in all our calculations. All angular integrals are also calculated in this way.

In table 1 we compare errors incurred in various adiabatic approximations when the stretching frequency ( $\omega_s \approx 3870 \text{ cm}^{-1}$ ) is a few times the bending frequency ( $\omega_b \approx 1200 \text{ cm}^{-1}$ ). The minimum of the Morse potential was chosen to coincide with the  $\text{H}_2\text{O}$  bond length in Radau coordinates [17] and the dissociation energy chosen was that for breakup into  $\text{H} + \text{OH}$ . The scaling parameter matched the shape of the Morse potential near its minimum to the potential energy surface for water at its minimum. Similarly, the angular parameters  $\lambda_1$  and  $\lambda_2$  were such that the minimum in the angular potential and its shape near it also corresponded closely to the water molecule. The stretching and bending frequencies quoted above are therefore close to those for water.

As noted in [1] and [2], the comparison between AS and AB approximations is indeed erratic. Although AB approximation is superior for all states with 2 or more stretching quanta, it is clearly inferior for  $v = 0$  and  $v = 1$  states when the bending mode is excited. Note, however, the more meaningful comparison between AS + NAC and MAB approximations. The MAB approximation is superior in all cases except ( $v = 1, \mu = 2$ ) and ( $v = 1, \mu = 3$ ) when it is marginally inferior. This is caused by a near degeneracy of zeroth-order states and consequent strong interaction between them.

In table 2, we make a similar comparison in another case where the bending frequency ( $\omega_b \approx 2150 \text{ cm}^{-1}$ ) is slightly more than twice the stretching frequency ( $\omega_s \approx 930 \text{ cm}^{-1}$ ). The parameters here were obtained from the previous case by first halving the scale parameter  $a$  in the Morse potential and reducing the dissociation energy to a quarter of its previous value. This conserves the number of bound states supported by the potential and reduces the stretching frequency to nearly a quarter of its previous value. The angular parameters  $\lambda_1$  and  $\lambda_2$  were then doubled, leaving the position of the minimum in the potential intact but stiffening it and nearly doubling the bending frequency. The coupling between stretching and bending motions is now stronger.

As expected, the AS approximation is now superior to the AB approximation and the AS + NAC approximation is also superior to the MAB approximation. We do not attach any significance to the spurt in the AS error for  $\mu = 3$  and  $\mu = 4$  states. At these energies there is appreciable nonadiabatic coupling between several

Table 1. A comparison of the errors incurred in adiabatic stretch (AS), adiabatic bend (AB), adiabatic stretch with diagonal nonadiabatic corrections (AS + NAC) and modified adiabatic bend (MAB) approximations. Variational energies (measured on an absolute scale) are from diagonalization of a  $200 \times 200$  matrix and have been checked for convergence with respect to variations in the size of the basis set and its parameters. The model potential parameters,  $D = 39593.22 \text{ cm}^{-1}$ ,  $a = 2.510 \text{ \AA}^{-1}$ ,  $r_0 = 0.937 \text{ \AA}$ ,  $\lambda_1^2 = 15203.94 \text{ cm}^{-1}$ , and  $\lambda_2^2 = 4301.70 \text{ cm}^{-1}$ , were chosen to mimic the stretching and bending vibrations of water molecule. The minimum value of the potential is  $17840.02 \text{ cm}^{-1}$ . Typical stretching and bending frequencies are  $\approx 3870 \text{ cm}^{-1}$  and  $\approx 1200 \text{ cm}^{-1}$  respectively. The stretching and bending quantum numbers are  $\nu$  and  $\mu$  respectively.

$\nu$	$\mu$	$E_{\text{var}}$	$E_{\text{AS}} - E_{\text{var}}$	$E_{\text{AB}} - E_{\text{var}}$	$E_{\text{AS+NAC}} - E_{\text{var}}$	$E_{\text{MAB}} - E_{\text{var}}$
0	0	20433.79	-0.83	0.92	1.38	0.50
	1	21621.98	-2.48	5.46	4.06	1.58
	2	22840.72	-1.32	16.90	13.61	5.27
	3	24088.43	3.29	36.87	30.73	12.73
	4	25362.70	13.17	67.38	56.62	25.24
1	0	24300.01	-5.27	-0.88	-3.07	-1.32
	1	25468.93	-17.34	-1.32	-11.19	-5.49
	2	26644.87	-4.83	27.21	9.66	15.14
	3	27881.18	-21.73	31.17	4.61	6.15
	4	29143.81	-34.68	44.99	7.02	1.10
2	0	27956.02	-10.75	-3.73	-8.78	-4.17
	1	29093.55	-21.95	2.19	-15.80	-2.19
	2	30271.47	-43.24	1.98	-29.41	-10.53
	3	31476.17	-62.33	9.66	-37.09	-16.46
	4	32706.10	-78.13	26.56	-38.19	-19.31
3	0	31397.38	-12.95	-3.29	-10.97	-3.73
	1	32522.62	-42.80	-11.19	-37.09	-15.58
	2	33676.18	-72.87	-14.27	-59.48	-27.43
	3	34857.83	-103.37	-12.51	-79.23	-40.16
	4	36066.26	-133.88	-4.83	-95.69	-52.67
4	0	34631.78	-19.31	-7.46	-17.56	-7.90
	1	35737.71	-61.89	-22.83	-56.40	-27.43
	2	36871.95	-106.23	-35.12	-93.72	-48.94
	3	38034.51	-153.19	-44.33	-130.15	-73.09
	4	39223.84	-201.92	-48.72	-165.70	-99.20

states. We wish to draw the reader's attention to the considerable improvement the MAB approximation now affords over the AB approximation. This is entirely in keeping with stronger stretch-bend coupling.

We do not claim that the MAB approximation will always give more accurate energies than the AB approximation. This depends very much on the details of the interaction. If the AB energy is lower than the accurate energy (as it is in many entries in table 1), the MAB approximation must give still lower and hence less accurate energy.

A major drawback of all the adiabatic approximations is that they do not give a bound to the true energy. The surest way around this difficulty is to compute all nonadiabatic couplings and diagonalize the resulting matrix. Hylleras-Undheim theorem then assures that each eigenvalue is an upper bound to the exact energy of the corresponding state. This calculation is simplest in the basis of AB states and



Table 2. Relative accuracy of various adiabatic approximations when the bending frequency ( $\omega_b \approx 2150 \text{ cm}^{-1}$ ) is greater than the stretching frequency ( $\omega_s \approx 930 \text{ cm}^{-1}$ ). The model potential parameters are  $D = 9878.56 \text{ cm}^{-1}$ ,  $a = 1.255 \text{ \AA}^{-1}$ ,  $r_0 = 0.937 \text{ \AA}$ ,  $\lambda_1^2 = 60815.74 \text{ cm}^{-1}$  and  $\lambda_2^2 = 17206.81 \text{ cm}^{-1}$ . The minimum value of the potential is  $71360.08 \text{ cm}^{-1}$ .

$v$	$\mu$	$E_{\text{var}}$	$E_{\text{AS}} - E_{\text{var}}$	$E_{\text{AB}} - E_{\text{var}}$	$E_{\text{AS+NAC}} - E_{\text{var}}$	$E_{\text{MAB}} - E_{\text{var}}$
0	0	72990.67	-1.76	34.02	0.44	8.34
	1	75139.98	-4.39	244.49	0.88	20.41
	2	77151.91	-9.66	630.11	1.10	25.68
	3	79035.44	-16.46	1181.87	0.44	26.34
	4	80803.96	-34.02	1886.38	-10.75	14.92
1	0	73922.78	-0.88	56.62	1.32	28.09
	1	75995.71	-2.19	315.82	3.07	69.35
	2	77927.31	-6.36	753.46	3.73	94.81
	3	79730.29	-16.46	1356.35	-0.66	106.66
	4	81434.95	-59.48	2094.67	-37.97	81.43
2	0	74800.89	0.00	78.57	1.98	46.75
	1	76795.48	-0.22	384.30	4.83	114.79
	2	78644.77	-3.73	871.31	5.71	158.46
	3	80368.96	-21.95	1519.42	7.24	176.02
	4	82015.46	-100.96	2281.00	-81.43	126.86
3	0	75625.24	0.66	98.98	2.41	64.09
	1	77539.28	1.54	229.79	6.15	156.71
	2	79304.29	-2.41	983.25	6.58	216.40
	3	80951.67	-34.24	1669.54	-20.85	233.08
	4	82544.62	-159.56	2445.17	-142.22	151.00
4	0	76395.60	1.10	118.74	3.07	80.33
	1	78227.11	2.41	510.28	6.80	194.89
	2	79905.87	-2.63	1088.16	5.71	268.20
	3	81478.63	-54.87	1805.62	-42.58	277.42
	4	83019.78	-237.03	2588.48	-221.89	153.85

somewhat more difficult with MAB states because of their nonorthogonality. Non-adiabatic coupling between AS states is most difficult to calculate because one must calculate derivatives of functions which depend parametrically on the stretching coordinate.

If one chooses to ignore nonadiabatic couplings altogether, then the modified adiabatic bend approximation should certainly be preferred over the adiabatic bend approximation because of its sensible reduction in the limiting case of separable motion.

In this paper we have concentrated on the centrifugal coupling between stretching and bending motion and accordingly simplified the potential energy to a separable form  $V_1(r) + V_2(\xi)$ . The adiabatic stretch approximation is extended to the more realistic case of nonseparable potential  $V(r, \xi)$  with minimal modification. In the adiabatic bend approximation, one would first solve the radial equation

$$\left[ -\frac{1}{2m} \frac{d^2}{dr^2} + V(r, \xi) - U_v(\xi) \right] \phi_v(r; \xi) = 0. \quad (5.3 a)$$

In averaging over the radial motion, one must recognize that the averaged term

$$\langle 1/r^2 \rangle_v = \int dr \phi_v(r; \xi) (1/r^2) \phi_v(r; \xi)$$

depends on  $\xi$  and does not commute with the operator  $(d/d\xi)(1 - \xi^2)(d/d\xi)$ . The correct hermitian form for the effective bending hamiltonian must be used

$$\left[ -\frac{1}{4m} \left( \langle 1/r^2 \rangle_v \frac{d}{d\xi} (1 - \xi^2) \frac{d}{d\xi} + \frac{d}{d\xi} (1 - \xi^2) \frac{d}{d\xi} \langle 1/r^2 \rangle_v \right) + U_v(\xi) - E_{v\mu} \right] \chi_{v\mu}(\xi) = 0. \quad (5.3 b)$$

The adiabatic bend approximation once again suffers from the flaw that in the separable limit  $V(r, \xi) = V_1(r) + (1/r^2)V_2(\xi)$ , the approximate wavefunction  $\psi(r, \xi) = \phi_v(r; \xi)\chi_{v\mu}(\xi)$  does not reduce to the exact result. This flaw may be remedied by formulating a modified adiabatic bend approximation as before. Thus the modified stretching and bending equations would be

$$\left[ -\frac{1}{2m} \frac{d^2}{dr^2} + \frac{\tau}{2mr^2} + V(r, \xi) - U_v(\tau; \xi) \right] \phi_v(\tau; r; \xi) = 0, \quad (5.4 a)$$

and

$$\left[ -\frac{1}{4m} \langle 1/r^2 \rangle_{\tau, v} \frac{d}{d\xi} (1 - \xi^2) \frac{d}{d\xi} - \frac{1}{4m} \frac{d}{d\xi} (1 - \xi^2) \frac{d}{d\xi} \langle 1/r^2 \rangle_{\tau, v} + U_v(\tau; \xi) - E_{v, \mu}(\tau) \right] \chi_{v, \mu}(\tau; \xi) = 0. \quad (5.4 b)$$

The parameter  $\tau$  would then be determined by minimizing the MAB expectation value of energy,

$$E_{v\mu}^{\text{MAB}}(\tau) = E_{v\mu}(\tau) - \frac{\tau}{2m} \langle 1/r^2 \rangle_{\tau, v}. \quad (5.4 c)$$

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- [9] The kinetic energy operator in this hamiltonian may be interpreted as the kinetic energy of a three-particle system of zero angular momentum ( $J = 0$ ) in either Jacobi or Radau coordinates, with one of the radial variables frozen for simplicity. The centrifugal coupling between stretching and bending motions is a characteristic feature of molecular vibrations. In order to focus attention on this coupling, we have assumed that the potential is a separable function of the form  $V_1(r) + V_2(\xi)$ .
- [10] We follow the conventions of ABRAMOWITZ, M., and STEGUN, I., 1964, *Handbook of Mathematical Functions* (National Bureau of Standards, Washington D.C.), for special functions and orthogonal polynomials.
- [11] The calculation of these corrections is quite standard and the following formulae can be found in, for example: CHILD, M. S., 1974, *Molecular Collision Theory* (Academic Press), p. 89.
- [12] Here, assumption of a separable potential,  $V_M(r) + V_A(\xi)$ , yields the simplified,  $\xi$ -independent equation (3.1 a) with constant  $\epsilon_s^0$  instead of  $\epsilon_s^0(\xi)$ . Extension to the general case of nonseparable potential is outlined in § 5.
- [13] Strictly speaking, this integral diverges because of the singularity at  $r = 0$ . This happens because unlike true molecular potentials, Morse potential is not infinite at  $r = 0$  and the wavefunction, although exponentially small, is not zero. We evaluate the integral by quadrature, sampling the integrand at a number of preassigned points. The point  $r = 0$  is never sampled. The singularity is therefore effectively smoothed and the nature of smoothing depends on the degree of quadrature. We use the same number of quadrature points in an entire calculation to ensure uniform smoothing.
- [14] The analytical form of this term is suggested by a similar term  $l(l + 1)/2mr^2$  in the stretching equation in the separable limit  $V_A(\xi) = 0$ .
- [15] This property of the basis set is well known and we direct the reader to [2] for citations of previous work where it has been used.
- [16] This old trick underlies gaussian quadrature formulas where one is interested only in the (0, 0) element of the matrix. We have learned it from [2].
- [17] For water molecule, the values of Radau coordinates at equilibrium are only slightly different from the values of more commonly used bond coordinates.