RECURSIVE COMPUTATION OF HAMILTONIAN MATRIX ELEMENTS USING HARMONIC OSCILLATOR EIGENFUNCTIONS: APPLICATION TO THE INVERSION OF AMMONIA AND TO THE METHYL TORSION + ALDEHYDIC HYDROGEN WAGGING OF ACETALDEHYDE

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Abstract—A program able to use hybrid free rotor plus harmonic oscillator basis functions for the variational study of large and small amplitude vibrations is developed. The Hamiltonian matrix elements between harmonic oscillator eigenfunctions and polynomial terms are calculated using a recursive algorithm. This technique permits use of only one basic algorithm to compute the kinetic and potential parts of the Hamiltonian. In addition, the program can handle potential functions perturbed with Gaussian barriers and obtain the quantum mechanical average of a magnitude. The program is used to test the efficiency of Taylor series vs polynomial + Gaussian potential functions for the description of the ammonia inversion mode. The data for the construction of the potential functions are obtained by *ab initio* methodology at the QCISD/6-311G+ +(3 *df*, 3 *dp*) level. The quantum mechanical average values for the structural parameters of ammonia are computed and compared to the fully optimized *ab initio* results. The simultaneous methyl torsion + aldehydic hydrogen wagging motions in the S_0 state of acetaldehyde are used to illustrate the efficiency of mixed free rotor + harmonic oscillator basis functions.

INTRODUCTION

The harmonic approximation is the classical approach to the study of molecular vibrations. This approximation is applied within the normal coordinates system with all the vibrational modes being small amplitude and uncoupled to each other. In these conditions, the kinetic terms can be considered constant with the motion, and the potential function shows a simple quadratic variation on the normal mode (Wilson *et al.*, 1980). When the vibrations exhibit some anharmonicity the potential function can be described using higher order polynomials and the kinetic terms can be expanded in a Taylor series on the vibrational coordinate. These anharmonic cases can be solved variationally or perturbationally on the basis of the harmonic oscillator (Harthcock & Laane, 1985). A different approach can be applied to the periodic motions found in organic molecules. These vibrations are usually expressed as angular displacements. Thus, the wavefunction can be expanded in the free rotor basis and the kinetic and potential terms can be described by Fourier expansions. The use of free rotor basis functions and Fourier series for an arbitrary number of vibrations has been previously considered (Muñoz-Caro *et al.*, 1994). An extension of this technique would be the simultaneous use of different types of basis functions, in particular free rotor plus harmonic oscillator hybrid basis functions. This hybrid basis would permit the simultaneous treatment of large and small amplitude vibrational motions. Thus, stretching, bending and torsion could be considered together as well as their interactions.

In this paper we present a tool for the variational calculation of vibrational energy levels using free rotor plus harmonic oscillator hybrid basis functions. The program is specially useful for the treatment of several large amplitude vibrations. The computation of the Hamiltonian matrix elements between harmonic oscillator eigenfunctions is implemented recursively. In this form, only one algorithm is needed to describe the potential function as a Taylor series of an arbitrary order. In addition, two algorithms are only necessary to compute the kinetic part when the kinetic elements depend on the vibrational coordinate. The evaluation of matrix elements for potentials with Gaussian perturbations is implemented as well as the computation of quantum mechanical averages in the different vibrational states. The ability of Taylor series and polynomial + Gaussian forms to incorporate the information obtained from *ab initio* calculations is analyzed through the inversion motion of ammonia. The quantum-mechanical averaged and the equilibrium structural parameters of ammonia are compared. In addition, the use of a mixed free

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rotor + harmonic oscillator basis functions is compared with a double free rotor basis set for the methyl torsion + aldehydic hydrogen wagging in the S_0 state of acetaldehyde.

THEORY

A variational treatment for an arbitrary number of simultaneous, coupled vibrations was previously developed (Muñoz-Caro et al., 1994) and a program for the application of this methodology using free rotor eigenfunctions was presented (Muñoz-Caro & Niño, 1994; Niño & Muñoz-Caro, 1994). In this methodology, the Hamiltonian matrix elements are derived from the general expression of the pure vibrational Hamiltonian (Pickett, 1972; Harthcock & Laane, 1985):

$$\hat{H} = \sum_i^n \sum_j^n \left(-B_{ij} \frac{\partial^2}{\partial q_i \partial q_j} - \frac{\partial B_{ij}}{\partial q_i} \frac{\partial}{\partial q_j} \right) + \hat{V}, \quad (1)$$

where n represents the number of vibrations and the qs are the vibrational coordinates. The kinetic terms B_{ij} are obtained from the elements of the ro-vibrational G matrix (Muñoz-Caro & Niño, 1993; Niño & Muñoz-Caro, 1994). The kinetic and potential parts of equation (1) are expressed as Fourier series on the vibrational coordinates. Thus,

$$B_{ij} = \sum_k B_{ijk}^0 \prod_l^n f_{ijkl} \quad (2)$$

and

$$V = \sum_k V_k^0 \prod_j^n f_{kj}. \quad (3)$$

The f functions of equations (2) and (3) represent the trigonometric terms. The Hamiltonian, equation (1), is solved variationally and the basis functions are expressed as a product of the free rotor solutions, one for each vibration:

$$\varphi_m = \prod_k^n g_{mk}. \quad (4)$$

After application of the variational technique we obtain for the kinetic elements when $i \neq j$,

$$\langle \varphi_m | \hat{T} | \varphi_n \rangle = \sum_i^n \sum_j^n \sum_k^{N_B} B_{ijk}^0$$

$$\times [\langle g_{mi} | f_{ijki} | g_{ni}' \rangle \langle g_{mj} | f_{ijkj} | g_{nj}' \rangle$$

$$+ \langle g_{mi} | f_{ijki}' | g_{ni} \rangle \langle g_{mj} | f_{ijkj} g_{nj}' \rangle]$$

$$\times \prod_{p \neq ij}^n \langle g_{mp} | f_{ijkp} | g_{np} \rangle \quad (5)$$

whereas for $i = j$,

$$\langle \varphi_m | \hat{T} | \varphi_n \rangle = \sum_i^n \sum_k^{N_B} (B_{iik}^0 [\langle g_{mi} | f_{iiki} | g_{ni}'' \rangle$$

$$+ \langle g_{mi} | f_{iiki}' | g_{ni}' \rangle] \prod_{p \neq i}^n \langle g_{mp} | f_{iikp} | g_{np} \rangle \quad (6)$$

The potential part is obtained as:

$$\langle \varphi_m | \hat{V} | \varphi_n \rangle = \sum_i^{N_V} V_i^0 \prod_p^n \langle g_{mp} | f_{ip} | g_{np} \rangle. \quad (7)$$

The original implementation of this method uses equation (5) directly. However, the computational efficiency can be enhanced by defining:

$$A = \langle g_{mi} | f_{ijki} | g_{ni}' \rangle,$$

$$B = \langle g_{mi} | f_{ijkj}' | g_{ni} \rangle,$$

$$C = \langle g_{mj} | f_{ijkj} | g_{nj}' \rangle,$$

$$D = \langle g_{mj} | f_{ijkj}' | g_{nj} \rangle. \quad (8)$$

Thus, equation (5) becomes:

$$\langle \varphi_m | \hat{T} | \varphi_n \rangle = \sum_i^n \sum_j^i \sum_k^{N_B} B_{ijk}^0 [A \cdot (2C + D)$$

$$+ B \cdot C)] \prod_{p \neq ij}^n \langle g_{mp} | f_{ijkp} | g_{np} \rangle, \quad (9)$$

where the second summation runs from j to i. In this form, the number of terms to evaluate is reduced in $(n^2 - n)/2$ elements.

Equations (5–7) are derived using the orthonormalization property of the basis. Thus, we will obtain the same equations for any orthonormal basis set. In particular, they can be used with harmonic oscillator eigenfunctions, introducing in the potential and kinetic terms a Taylor series for the corresponding vibrational coordinates. Thus, in addition to trigonometric terms, some of the f functions in equations (2) and (3) can adopt the form q^i where q is one of the vibrational coordinates. These kinetic and potential terms must belong to the totally symmetric representation of the non-rigid group of the molecule. The appropriate symmetry for the kinetic and potential functions can be obtained by applying the projection operator to the corresponding Taylor series.

The use of a Taylor series in the potential function implies the evaluation of matrix elements of the form:

$$\langle \Psi_m | q^i | \Psi_n \rangle \quad (10)$$

where the Ψs represent the harmonic oscillator eigenfunctions, that correspond to the g functions of equation (4):

$$\Psi_n = \left[\left(\frac{\gamma}{\pi} \right)^{1/2} \cdot \frac{1}{2^n n!} \right]^{1/2} H_n(\xi) \exp[-\xi^2/2],$$

$$n = 0, 1, 2, \ldots \quad (11)$$

Here, $H_n(\xi)$ is the Hermite polynomial of order n and $\xi = \gamma^{1/2} q$. The parameter γ is obtained as $(V_0 B_0)^{1/2}$ with V_0 and B_0 corresponding to the pure harmonic case:

$$\hat{H} = -B_0 \frac{d^2}{dq^2} + V_0 q^2 \quad (12)$$

The matrix elements, equation (10), can be obtained using the recurrence relation between

harmonic oscillator eigenfunctions (Powell & Crasemann, 1961):

$$q \cdot \Psi_n = (n/2\gamma)^{1/2}\Psi_{n-1} + [(n+1)/2\gamma]^{1/2}\Psi_{n+1}. \quad (13)$$

Thus,

$$q^i\Psi_n = (n/2\gamma)^{1/2}q^{i-1}\Psi_{n-1} + [(n+1)/2\gamma]^{1/2}q^{i-1}\Psi_{n+1} \quad (14)$$

and the matrix elements are obtained as:

$$\langle \Psi_m|q^i|\Psi_n \rangle = (n/2\gamma)^{1/2}\langle \Psi_m|q^{i-1}|\Psi_{n-1} \rangle$$
$$+ [(n+1)/2\gamma]^{1/2}\langle \Psi_m|q^{i-1}|\Psi_{n+1} \rangle. \quad (15)$$

This equation can be used to implement recursively the evaluation of matrix elements between harmonic oscillator wavefunctions and polynomial terms. Thus, equation (15) represents the inductive clause (Smith, 1987) for the recursion procedure whereas the basis clause corresponds to the orthonormalization relation between harmonic oscillator eigenfunctions:

$$\langle \Psi_m|\Psi_n \rangle = \delta_{mn} \quad (16)$$

with δ being the Kronecker delta. The pseudocode for the recursive computation of Hamiltonian elements is shown in Fig. 1.

The matrix elements involving the first derivative of harmonic oscillator wavefunctions are necessary to

account for the dependence of the kinetic terms on the vibrational coordinate. The expression is readily obtained from the recurrence relations (Powell & Crasemann, 1961):

$$\xi\Psi_n + \Psi_n' = \sqrt{2n}\Psi_{n-1},$$
$$\xi\Psi_n - \Psi_n' = \sqrt{2(n+1)}\Psi_{n-1}. \quad (17)$$

Thus,

$$\Psi_n' = \sqrt{n/2}\Psi_{n-1} - \sqrt{(n+1)/2}\Psi_{n+1} \quad (18)$$

and the matrix elements become

$$\langle \Psi_m|q^i|\Psi_n' \rangle = \sqrt{n/2}\langle \Psi_m|q^i|\Psi_{n-1}' \rangle$$
$$- \sqrt{(n+1)/2}\langle \Psi_m|q^i|\Psi_{n+1} \rangle. \quad (19)$$

The elements involving second derivatives of the harmonic oscillator wavefunctions are obtained from equation (11) and the recurrence relations between Hermite polynomials (Powell & Crasemann, 1961):

$$H_n' = 2nH_{n-1},$$
$$\xi H_n = nH_{n-1} + (1/2)H_{n+1}. \quad (20)$$

Thus,

$$\Psi_n'' = \sqrt{n(n-1)/2} \cdot \Psi_{n-2} - (n+1/2)\Psi_n$$
$$+ \sqrt{(n+1)\cdot(n+2)/2} \cdot \Psi_{n+2} \quad (21)$$

Begin Recursive Function Osci (m,i,n,γ)

m is the quantum number of the first harmonic oscillator eigenfunction
i is the power of the monomial term
n is the quantum number of the second harmonic oscillator eigenfunction
γ is the parameter used for the definition of the vibrational coordinate

If i=0 then   /* Base Clause of the recursive function */

    If m=n then
      Osci ← 1
    else
      Osci ← 0
    end_if

else   /* Inductive Clause */
    If n≥0 then
      Factor1 ← $(n/2\gamma)^{1/2}$ * Osci(m,i-1,n-1,γ)
      Factor2 ← $((n+1)/2\gamma)^{1/2}$ * Osci(m,i-1,n+1,γ)
    else
      Factor1 ← 0
      Factor2 ← 0
    end_if

    Osci ← Factor1+Factor2
end_if

end_function

Fig. 1. Recursive implementation for the computation of integrals between harmonic oscillator eigenfunctions and polynomial terms.

and the matrix elements become:

$$\langle \Psi_m | q^i | \Psi_n'' \rangle = \sqrt{n(n-1)}/2 \cdot \langle \Psi_m | q^i | \Psi_{n-2} \rangle$$
$$- (n+1/2) \cdot \langle \Psi_m | q^i | \Psi_n \rangle$$
$$+ \sqrt{(n+1) \cdot (n+2)}/2$$
$$\times \langle \Psi_m | q^i | \Psi_{n+2} \rangle. \qquad (22)$$

Equations (19) and (22) can be evaluated through equation (15). Thus, only equation (15) is necessary for the computation of all the Hamiltonian elements.

An interesting case of study is represented by the inversion motion of a molecular moiety. This motion is described by a double minima potential, usually expressed by two different functional forms; a quadratic + quartic or a quadratic + Gaussian potential function. In the first case, equation (15), (19) and (22) permit us to obtain the Hamiltonian matrix. For the quadratic + Gaussian case, it is necessary to evaluate some integrals of the form:

$$\langle \Psi_m | \exp[-\beta \zeta^2] | \Psi_n \rangle \qquad (23)$$

Equation (23) can be calculated by means of a closed formula or by a recurrence relation, i.e. the diamond rule (Chan & Stelman, 1963). The recurrence relation needs the evaluation of equation (23) for increasing values of the m and n quantum numbers. This form of computation is easy to implement when the Hamiltonian matrix is not symmetry factorized. However, for several symmetry representations the application of the diamond rule implies the simultaneous evaluation and storage of the Hamiltonian matrices for each representation. Thus, we select the closed form for the evaluation of equation (23). Therefore, for $m < n$ and both even the closed formula yields (Chan & Stelman, 1963):

$$\langle \Psi_m | \exp[-\beta \zeta^2] | \psi_n \rangle = [1/(1+\beta)]^{1/2} (n!m!/2^n 2^m)^{1/2}$$
$$\times \sum_{l=0,2,\dots}^{m} \frac{(-\theta)^{(n+m)/2-l} \kappa^l}{l![(m-l)/2]![(n-l)/2]!}, \qquad (24)$$

with, $\kappa = 2/(1+\beta)$ and $\theta = \beta/(1+\beta)$. For the odd terms we have a similar expression with $l = 1, 3 \dots$ The elements mixing even and odd m and n values vanish by symmetry.

Since equation (24) uses exponential and factorial forms, the estimation of the roundoff error obtained using this expression is a matter of importance. Thus, high quantum numbers, 98 and 100, were used for m and n to increase the roundoff error in the summation of equation (24). The integral was evaluated using arbitrary precision arithmetic (Wolfram, 1991). Thus, 6, 10 and 20 significant digits were used in the calculations. All the cases yield the same value for the integral. In addition, a FORTRAN routine in double precision on a 32 bit machine reproduces the same result.

An important use of the eigenfunctions obtained for anharmonic vibrations is the computation of the quantum mechanical average of a magnitude in different vibrational states. To compute an average value we must express the desired magnitude as a function of the vibrational coordinates. Thus, if A represents the magnitude we have:

$$A(q_1, \dots q_n) = \sum_{i=1}^{\infty} a_i \cdot \prod_{j=1}^{n} f_{ij} \qquad (25)$$

where the fs are the Fourier or Taylor series expansion terms.

For a vibrational state described by its eigenfunction Ψ_k, the quantum mechanical average $\langle A \rangle_k$ is obtained as:

$$\langle A \rangle_k = \langle \Psi_k(q_1, \dots q_n) | A(q_1, \dots q_n) | \Psi_k(q_1, \dots q_n) \rangle. \qquad (26)$$

Using our previously calculated eigenfunction, equation (26) becomes:

$$\langle A \rangle_k = \sum_{l}^{N_f} \sum_{m}^{N_f} C_l^k C_m^k \left[\sum_{i=1}^{\infty} a_i \prod_{j}^{n} \langle g_{lj} | f_{ip} | g_{mj} \rangle \right], \qquad (27)$$

where N_f represents the number of basis functions and the Cs are the coefficients in the expansion of the eigenfunction in the g_{lj} basis. From a computational point of view, equation (27) can be implemented more efficiently as:

$$\langle A \rangle_k = \sum_{l}^{N_f} \left[\sum_{m=l+1}^{N_f} 2 \cdot C_l^k C_m^k \sum_{i=1}^{\infty} a_i \prod_{j}^{n} \langle g_{lj} | f_{ip} | g_{mj} \rangle \right.$$
$$\left. + (C_l^k)^2 \sum_{i=1}^{\infty} a_i \prod_{j}^{n} \langle g_{lj} | f_{ip} | g_{lj} \rangle \right]. \qquad (28)$$

This equation allows to compute the average value of geometric parameters or inertia moments for each vibrational state using the eigenfunctions obtained from equations (6), (7) and (9).

APPLICATION

The total energy results obtained from *ab initio* computations can be used to derive potential energy functions for the nuclei motion within the adiabatic approximation. Thus, it is necessary to express the energy results calculated for a suitable set of molecular geometries in a functional form. For torsional motions, such as the methyl torsion in the ground state of acetaldehyde, the use of Fourier series for the kinetic and potential functions and free rotor eigenfunctions for the basis set yields energy levels in good agreement with the experimental data (Niño et al., 1994b). For inversion motions expressed by an angular coordinate, such as the aldehydic wagging in the excited S_1 and T_1 states of acetaldehyde, the Fourier expansion and the free rotor basis are also able to reproduce the exponential results (Muñoz-Caro et al., 1994; Niño et al., 1994b). However, in this case, the technique lacks physical significance being necessary to use long Fourier series and basis sets. Two more realistic approaches to the inversion problem are represented by quadratic + quartic (Harthcock & Laane, 1985), and quadratic + Gaussian functional forms (Coon et al., 1966). These forms qualitatively
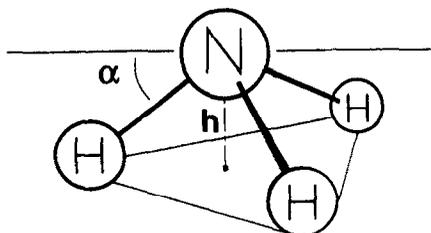
Fig. 2. Structural parameters for the ammonia molecule. The inversion coordinate is defined by h, the distance from the nitrogen to the plane of the three hydrogens. α represents the inversion angle.

Table 1. Character table for the G_2 inversion group of ammonia. E refers to the identity operation and E^* to the inversion of all the molecular coordinates

G_2	E	E^*
A_1	1	1
A_2	1	-1

reproduce the characteristics of the potential surfaces (Niño *et al.*, 1994a). However, very limited *ab initio* information can be introduced in these potential functions since they incorporate very few parameters. Thus, it is interesting to analyze the behaviour of pure quadratic + quartic or quadratic + Gaussian functions against more flexible functional forms. To this end, we select the inversion motion of ammonia.

Ammonia (NH_3) is the classical example of a molecular system bearing an inversion motion. In its ground electronic state the molecule is pyramidal belonging to the C_{3v} point group with the three hydrogens defining the base of the pyramid. The Q_2 bending mode produces an inversion of the pyramid by crossing a planar transition state of D_{3h} symmetry. The inversion coordinate for this motion is usually defined as the distance h, from the nitrogen to the plane of the hydrogens (Swalen & Ibers, 1962), see Fig. 2.

The potential and kinetic terms for the inversion motion of ammonia are derived from *ab initio* calculations. Thus, a grid of points on the inversion coordinate is defined and the *ab initio* results are fitted to functional forms adapted to the totally symmetric representation of the non-rigid group of the molecule. The non-rigid group for the inversion motion of ammonia is a G_2 group. Its elements are the identity, E, and the inversion of all the nuclei and electron coordinates, E^*. Therefore, we have two representations a_1 and a_2, symmetric and antisymmetric, respectively, with respect to the inversion motion (see Table 1).

Large and flexible basis sets are necessary for the *ab initio* description of the pyramidal structure of ammonia. In addition, diffuse functions are useful to

describe lone electron pairs and correlation energy is necessary to account for a correct barrier to inversion. Thus, calculations with correlation and triple split + polarization and diffuse functions were performed at the QCISD/6-311G+ +(3 df, 3 dp) level, including full molecular geometry optimization. The molecular structure is defined using the inversion coordinate h and the inversion angle α see Fig. 2. The fully optimized geometry is found for $\alpha = 20.19°$ and $h = 0.3495$ Å. The calculated barrier to inversion, 1893.38 cm^{-1}, is in good agreement with the 1884.7 cm^{-1} found by fitting the observed frequencies to the non-rigid invertor model (Špirko, 1983, 1989). This model accounts for the coupling of the inversion mode with the other vibrations. In addition to the $\alpha = 20.19°$ and to $\alpha = 0°$ (top of the barrier) points, computations of the total energy at $\alpha = 10$, 30 and 40° were performed to obtain an accurate description of the potential surface. Thus, a total of five points was considered and used to develop four different potential expressions of adapted symmetry:

$$V_a(h) = a + b \cdot h^2 + c \cdot h^4,$$

$$V_b(h) = a + b \cdot h^2 + c \cdot \exp[-d \cdot h^2],$$

$$V_c(h) = a + b \cdot h^2 + c \cdot h^4 + d \cdot h^6 + e \cdot h^8,$$

$$V_d(h) = a + b \cdot h^2 + c \cdot h^4 + d \cdot \exp[-e \cdot h^2]. \quad (29)$$

V_a is obtained solving a system of equations for $\alpha = 0$, 10 and 20.19°. For V_b the $\alpha = 0$, 10. 20.19 and 30° were used. V_c and V_d include the five points. The resulting potentials are shown in Table 2. The kinetic term B_h is computed for all the conformations and is found to be constant with a value of 6.778 cm^{-1} (2.487 amu^{-1}Å^{-2}). This is a consequence of the preservation, along the inversion motion of the symmetric top nature of ammonia.

The inversion energy levels obtained using equations (29) are compared in Table 3 with those derived from the non-rigid invertor model and with

Table 2. Potential functions, in cm^{-1}, for the inversion motion of ammonia. The a and c cases correspond to Taylor series and the b and d cases to polynomial + Gaussian forms on the inversion coordinate. The β parameters for the Gaussian forms of the b and d cases are 1.49818 and 1.34336 Å^{-2}, respectively. The e case shows the potential obtained by fitting to the experimental $v_2 - 1$, 2 and 3 levels within 0.1 cm^{-1}. The last column collects the Taylor expansion of the α-angle on the inversion coordinate h

Term	Case a	Case b	Case c	Case d	Case e	α
Constant	1893.38	$-91,417.20$	1893.38	$-125,536.00$	2019.74	—
h^2	$-27,364.10$	112,250.00	$-27,542.60$	143,640.00	$-28,916.03$	421.98
h^4	97,123.8	—	104,558.00	$-10,342.70$	120,282.20	-3331.91
h^6	—	—	$-50,579.60$	—	$-124,878.40$	11,683.20
h^8	—	—	13,751.40	—	65,705.32	$-13,156.90$
$\exp(-\beta h^2)$	—	93,310.50	—	127,429.00	—	—

Table 3. Calculated and observed energy levels, in cm^{-1}, for the inversion mode Q_2 of ammonia. The a, b, c and d cases correspond to the potential functions of Table 2. The kinetic term used was $B_h = 6.778$ cm^{-1}. Case e collects the results derived from the non-rigid invertor model (Špirko, 1983, 1989). Case f corresponds to the refined kinetic and potential terms (Case e of Table 2). The levels are classified by vibrational quantum number and inversion symmetry

v_2	Symmetry	Case a	Case b	Case c	Case d	Case e	Case f	Obs.[a]
0	a_1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	a_2	1.84	1.43	1.43	1.44	0.90	0.80	0.79
1	a_1	981.99	961.35	961.33	961.06	930.04	932.39	932.46
	a_2	1066.52	1025.91	1025.85	1025.74	967.34	968.16	968.12
2	a_1	1670.35	1632.17	1632.08	1631.72	1597.60	1597.48	1597.47
	a_2	2108.43	2015.62	2015.32	2015.30	1882.49	1882.17	1882.18
3	a_1	2700.60	2569.69	2569.17	2569.25	2384.02	2384.15	2384.17
	a_2	3344.51	3162.68	3161.85	3162.09	2890.81	2895.62	2895.61

[a] Data from Špirko (1983, 1989).

the experimental data. The differences between the observed and calculated inversion levels range from 3 to 16%. This is a consequence of our barrier value, that underestimates the effective value of about 2000 cm^{-1} found in previous studies (Swalen & Ibers, 1962). This effective value accounts for the coupling with the remaining vibrations. Thus, our pure inversion model cannot reproduce accurately the experimental results independently of the accuracy of the calculated potential surface. The quadratic + quartic form V_a gives the poorest description of the potential surface. This fact is reflected in the highest differences with the observed inversion levels, case a of Table 3. The b, c and d cases of Table 3 show equivalent results for the calculated energy levels, i.e the potential surfaces are very similar. In these cases the potential surface is described by a Taylor expansion V_c or a Gaussian form mixed with some polynomial terms, V_b and V_d. These results show that the accurate description of the potential surface by a Taylor series needs to extend the expansion beyond the quadratic term (compare V_a with V_c). Thus, if the same information is introduced in the V_b, V_c and V_d functional forms, the same description of the surface is obtained since it is always possible to describe an exponential function through a Taylor expansion.

The model used to compute a series of energy levels is usually improved by fitting the results to a set of observed levels. This fit is performed through a least squares refinement of the potential function (Pariseau et al., 1965; Ueda & Shimanouchi, 1967; Hedberg & Mills, 1993). It is obtained an enhanced potential function and, in the harmonic case, the experimental force constants are derived. Recently, a different approach to this problem, applicable to several simultaneous harmonic or anharmonic vibrations, has been developed (Muñoz-Caro et al., 1995). This technique minimizes the difference between calculated and observed energy levels using a gradiental approach that involves the kinetic and potential terms. The results obtained for ammonia are refined using this procedure. Thus, the kinetic term B_h, the potential function shows as Case c of Table 2 and the observed $v_2 = 1$, 2 and 3 energy levels, see Table 3, are used. The refinement is applied until the difference between all the calculated and observed energy levels

falls below 0.1 cm^{-1}. The resulting energy levels are collected as Case f of Table 3. The resulting effective kinetic term is found to be $B_h = 6.504$ cm^{-1}. The refined potential is shown as Case e of Table 2. This potential yields an inversion barrier of 2019.74 cm^{-1} in agreement with the previous effective values.

To evidence the dependence of the geometric parameters on the vibrational state it is necessary to express the inversion angle α as a function of the inversion coordinate using the five points considered in the potential surface. The result is shown in the last column of Table 2. The averaged structural parameters, $\langle \alpha \rangle$ and $\langle h \rangle$, are obtained as:

$$\langle a \rangle = \langle \Psi_i(h) | \alpha(h) | \Psi_i(h) \rangle,$$

$$\langle h \rangle = \langle \Psi_i(h) | h^2 | \Psi_i(h) \rangle^{1/2}. \tag{30}$$

The results for the four first inversion levels are collected in Table 4. The α average values for the $v_2 = 0$ vibrational state [20.47° (a_1) and 20.54° (a_2)] are slightly different from the $\alpha = 20.19°$ calculated for the equilibrium position. The difference increases for higher vibrational states. For the inversion coordinate h the difference is more important: 0.3685 Å (a_1) and 0.3694 Å (a_2) obtained for $v_2 = 0$ against the 0.3495 Å ab initio equilibrium result. These differences are due to the deviation of the potential function from a quadratic symmetric form and to the existence of residual energy of vibration.

The utility of hybrid free rotor + harmonic oscillator basis sets can be illustrated in the study of the simultaneous methyl torsion + aldehydic hydrogen

Table 4. Average values of the inversion angle α and the inversion coordinate h for the first inversion levels (α in degees, h in Å)

v_2	Symmetry	$\langle \alpha \rangle$	$\langle h \rangle$
0	a_1	20.47	0.3685
	a_2	20.54	0.3694
1	a_1	15.39	0.3111
	a_2	18.11	0.3426
2	a_1	11.89	0.2862
	a_2	17.49	0.3473
3	a_1	17.99	0.3584
	a_2	19.82	0.3784

Table 5. Kinetic and potential terms, in cm^{-1}, for torsion and wagging in the S_0 state of acetaldehyde including correlation and standard deviation. The θ and α refer to the torsion and wagging angles, respectively

Term	B_θ	$B_{\theta\alpha}$	B_α	$V(\theta, \alpha)$
Cte	9.0231	-5.4845	21.7929	205.87
$\cos(3\theta)$	0.0738	-0.1034	0.1079	-207.62
$\cos(6\theta)$	0.0025	-0.0020	0.0022	1.75
α^2	-0.83×10^{-4}	0.38×10^{-3}	-0.0010	3.00
α^4	0.10×10^{-7}	-0.26×10^{-7}	0.62×10^{-7}	0.35×10^{-4}
$\alpha^2 \cos(3\theta)$	-0.60×10^{-4}	0.79×10^{-4}	-0.73×10^{-4}	0.24
$\alpha^4 \cos(6\theta)$	—	—		0.17×10^{-5}
$\alpha \sin(3\theta)$	0.0013	-0.0022	0.0020	12.94
$\alpha^3 \sin(3\theta)$	-0.53×10^{-6}	0.73×10^{-6}	-0.75×10^{-6}	—
$\alpha^2 \sin(3\theta)$	—	—	—	-0.22×10^{-5}
R	0.99913	0.99990	0.99998	1.00000
$\sigma(cm^{-1})$	2.57×10^{-3}	3.68×10^{-3}	4.96×10^{-3}	0.00

wagging motions in the S_0 state of acetaldehyde. In the ground state the methyl torsion, Q_{15}, is the only large amplitude motion in acetaldehyde. In contrast, the wagging of the aldehydic hydrogen, Q_{14} mode, is an almost harmonic motion coupled to the torsion. In these conditions acetaldehyde can be classified under the G_6 non-rigid group, isomorphic to the C_{3v} point group. The study of the simultaneous torsion + wagging motions in the S_0 state of acetaldehyde has been performed using a double Fourier series to describe the kinetic and potential expansions and free rotor functions for the basis set (Niño et al., 1994b). However, the use of the Fourier series and free rotor functions for wagging is translated in large kinetic and potential developments and large basis size. This problem becomes more important when the number of vibrations increases.

To improve the efficiency of the variational method we use a Taylor series for describing the wagging in the kinetic and potential expansions. Harmonic oscillator functions are introduced in the basis set. The kinetic and potential functions are obtained by fitting to the Fourier + Taylor series the MP2(full)/6-311G(d, p) ab initio data used in the previous study of acetaldehyde (Niño et al., 1994b). The results are collected in Table 5. Introduction of harmonic oscillator functions reduces the size of the Hamiltonian

matrices. Thus, sizes of 83, 82 and 154 are used for the a_1, a_2 and e representations of the G_6 group. These data can be compared with the, 293 (a_1) 292 (a_2) and 630 (e) basis functions needed to obtain the same results with free rotor functions. The computed energy levels are collected in Table 6 and compared with the experimental and the previously calculated values. Table 6 shows that the free rotor + harmonic oscillator basis set reproduces both the free-rotor + free rotor basis and the experimental results using less computational resources.

CONCLUSIONS

A program for the variational study of anharmonic vibrations mixing free rotor plus harmonic oscillator basis functions is developed. The program can be used to describe several simultaneous vibrations of any kind: stretching, bending and torsion. The computation of integrals between kinetic or potential terms and harmonic oscillator eigenfunctions is developed in terms of a recursive algorithm. This procedure permits use polynomials of an arbitrary order for the kinetic and potential functions. In addition, the computation of matrix elements between harmonic oscillator eigenfunctions and Gaussian forms has been implemented. In this case, it is found that

Table 6. Torsional energy levels, in cm^{-1}, for the S_0 state of acetaldehyde

v_{14}	v_{15}	Symmetry	Calculation[a]	Calculation[b]	Observed
0	0	a_1	0.00	0.00	0.00
		e	0.07	0.10	0.0690
0	1	e	141.43	141.19	141.9935[c]
		a_2	143.37	144.41	143.7434[c]
0	2	a_1	252.96	252.57	255.2243[c]
		e	267.77	267.28	269.1121[c]
0	3	e	346.45	345.76	349.2337[d]
		a_2	407.80	408.60	408.2477[d]
0	4	a_1	423.45	422.42	425.5432[d]
		e	508.86	507.44	508.9440[d]

[a] Double free rotor basis set (Niño et al., 1994b)
[b] This work, harmonic oscillator + free rotor basis set.
[c] From Belov et al. (1993)
[d] Calculated by fitting the potential function to the observed $v_{15} = 0$, 1 and 2 levels (Ozkabak & Goodman, 1992)

the roundoff error obtained using a closed formula is negligible, even for high values of the vibrational quantum numbers. Finally, the evaluation of quantum mechanical averages is included in the program.

Application of these techniques to the Q_2 inversion mode of ammonia shows that the inversion potential is well described by a fourth-order polynomial + Gaussian form. An eight-order polynomial is necessary to obtain the same results using a Taylor series. The usual quadratic + quartic potential function gives the poorest description of the potential surface. Determination of the quantum mechanical average value for the inversion angle and inversion coordinate shows important differences from the equilibrium values.

The use of mixed free rotor + harmonic oscillator basis sets is applied to the methyl torsion + aldehydic hydrogen wagging in the S_0 state of acetaldehyde. The same results that in the case of a pure free rotor basis are obtained with a substantial saving in computational resources.

Program availability—The program is available as NIVELON from QCPE.

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