Large Amplitude Hamiltonian of a Triatomic Molecule

R. Wallace and Ch. V. S. Ramachandra Rao
Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

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An expression for the Hamiltonian $H(\varrho_1, \varrho_2, \varrho_3)$ of a vibrating-rotating triatomic molecule is derived using three curvilinear coordinates $\varrho_1, \varrho_2, \varrho_3$ in such a way that the Hamiltonian obtained is applicable to any bent triatomic molecule and allows for large displacements in all the three modes of motion. A variational technique is then used to calculate the low lying vibrational energy levels (v_1, v_2, v_3) of the H_2O molecule in its $\tilde{X}^1A_1$ ground state. The kinetic energy of the Hamiltonian $T(\varrho_1, \varrho_2, \varrho_3)$ takes into account the large amplitude character of the three modes together with their interaction. But in order to minimize the formidable amount of computation, a simple quadratic potential $V(\varrho_1, \varrho_2, \varrho_3)$ is assumed for all the three modes which only serves to illustrate the method of calculation.

1. Introduction

Large amplitude motions in polyatomic molecules[1], particularly the bending motion in a triatomic molecule[2], has been of considerable interest in recent years. Brand and Rao[3] have obtained the Hamiltonian of a triatomic molecule allowing for two large amplitude stretching motions corresponding to the vibrations ν_1 and ν_3. The present paper is a sequel to and a generalization of their work and treats all the three modes of a triatomic molecule as large amplitude motions. The H_2O molecule is considered for illustration.

The notation of the present paper is similar to that used in [3]. Even though both the papers have many features in common, merely for the sake of completeness and continuity, we repeat the relevant formulae of the previous work[3].

Figure 1 illustrates the reference configuration of a bent triatomic molecule in the molecule-fixed coordinate system. Since we are now treating the complete motion of the molecule, there are neither small displacements $d_{\alpha i}$ nor constraints on them. We describe the three modes of motion of the molecule by the coordinates ϱ_1, ϱ_2 and ϱ_3 where ϱ_1 and ϱ_3, the coordinates representing the stretching motions, are defined by [3].

$$2\,\varrho_1 = r_1 + r_2\,, \quad \text{and} \quad 2\,\varrho_3 = r_1 - r_2\,. \qquad (1)$$

r_1 and r_2 are the instantaneous values of the bond lengths of the reference configuration. The bending angle is $\pi - \varrho_2$ where ϱ_2 is the supplement of the reference angle. The quantities $a_{\alpha i}(\varrho_1, \varrho_2, \varrho_3)$ denoting the reference positions 1, 2, 3 (see Fig. 1) are same as given in [3] but are now rewritten as:

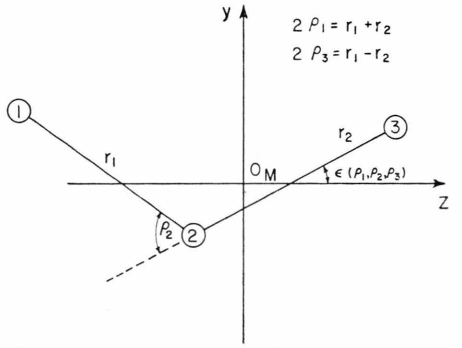

Fig. 1. The molecule-fixed coordinate system (xyz) with origin O_M and the reference configuration $(1, 2, 3)$ defined by the position vectors $a_{\alpha i}(\varrho_s)$, $(i = 1, 2, 3)$.

$$\begin{aligned}
&a_{x_1} = a_{x_2} = a_{x_3} = 0\,,\\
&M\,a_{y_1} = [(m_2 + m_3)\sin(\varrho_2 - \varepsilon) - m_3 \sin\varepsilon]\,\varrho_1\\
&\qquad + [(m_2 + m_3)\sin(\varrho_2 - \varepsilon) + m_3 \sin\varepsilon]\,\varrho_3\,,\\
&M\,a_{y_2} = -\,[m_1 \sin(\varrho_2 - \varepsilon) + m_3 \sin\varepsilon]\,\varrho_1\\
&\qquad - [m_1 \sin(\varrho_2 - \varepsilon) - m_3 \sin\varepsilon]\,\varrho_3\,,\\
&M\,a_{y_3} = -\,[m_1 \sin(\varrho_2 - \varepsilon) - (m_1 + m_2)\sin\varepsilon]\,\varrho_1\\
&\qquad - [m_1 \sin(\varrho_2 - \varepsilon) + (m_1 + m_2)\sin\varepsilon]\,\varrho_3\,,\\
&M\,a_{z_1} = -\,[(m_2 + m_3)\cos(\varrho_2 - \varepsilon) + m_3 \cos\varepsilon]\,\varrho_1\\
&\qquad - [(m_2 + m_3)\cos(\varrho_2 - \varepsilon) - m_3 \cos\varepsilon]\,\varrho_3\,,\\
&M\,a_{z_2} = [m_1 \cos(\varrho_2 - \varepsilon) - m_3 \cos\varepsilon]\,\varrho_1\\
&\qquad + [m_1 \cos(\varrho_2 - \varepsilon) + \mathrm{m}_3 \cos\varepsilon]\,\varrho_3\,, \qquad (2)\\
&M\,a_{z_3} = [m_1 \cos(\varrho_2 - \varepsilon) + (m_1 + m_2)\cos\varepsilon]\,\varrho_1\\
&\qquad + [m_1 \cos(\varrho_2 - \varepsilon) - (m_1 + m_2)\cos\varepsilon]\,\varrho_3.
\end{aligned}$$

The above expressions together with the constraint conditions[3]

$$e_{\alpha\beta\gamma} \sum_i m_i\, a_{\beta i}(\varrho_s)\,(\partial a_{\gamma i}/\partial \varrho_s) = 0 \quad (s = 1, 2, 3) \qquad (3)$$

Reprint requests to Ch. V. S. Rao, Computer Section, Inco, *Thompson, Manitoba*, R8N 1P3, Canada.

give the following partial derivatives for ε (see Fig. 1)

$$\varepsilon_1 = \frac{\partial\varepsilon}{\partial\varrho_1} = \left(-\frac{2\,M_{13}\,\varrho_3\sin\varrho_2}{M^2\,I_{xx}}\right),$$

$$\varepsilon_2 = \frac{\partial\varepsilon}{\partial\varrho_2} = \frac{1}{2} + \frac{2\,M_1\,\varrho_1\,\varrho_3}{M^2\,I_{xx}} \tag{4}$$

and

$$\varepsilon_3 = \frac{\partial\varepsilon}{\partial\varrho_3} = \frac{2\,M_{13}\,\varrho_1\sin\varrho_2}{M^2\,I_{xx}}$$

where

$$M\,I_{xx} = (M_1 + 2\,M_{13}\cos\varrho_2 + M_3)\,\varrho_1^2 \tag{5}$$
$$+\,2(M_1 - M_3)\,\varrho_1\,\varrho_3 + (M_1 - 2\,M_{13}\cos\varrho_2 + M_3)\,\varrho_3^2$$

and

$$M_1 = m_1(m_2 + m_3)\,M\,, \qquad M_3 = m_3(m_1 + m_2)\,M\,,$$
$$M_{13} = m_1\,m_3\,M\,, \qquad M = m_1 + m_2 + m_3\,. \tag{6}$$

ε_1, ε_2 and ε_3 satisfy the relations

$$\varepsilon_1\,\varrho_1 + \varepsilon_3\,\varrho_3 = 0 \tag{7}$$

and

$$(2\,M_{13}\sin\varrho_2)\,\varepsilon_2 = (\varrho_1 + \varrho_3)\,[M_1(\varepsilon_3 - \varepsilon_1) + M_{13}\cos\varrho_2(\varepsilon_3 + \varepsilon_1)]\,. \tag{8}$$

The expression for the angle ε is obtained as

$$\varepsilon(\varrho_1, \varrho_2, \varrho_3) = \tfrac{1}{2}\,(\varrho_2 - \varrho_2^e) + \frac{u_1 - u_3}{\sqrt{(u_1 + u_3)^2 - 4\,u_{13}^2}}\, \tan^{-1}\cdot\left[\sqrt{\frac{u_1 + u_3 - 2\,u_{13}}{u_1 + u_3 + 2\,u_{13}}}\tan(\varrho_2/2)\right], \tag{9}$$

where the constant of integration, unlike in [2, 3] is determined in such a way that $\varepsilon = 0$ when $\varrho_i = \varrho_i^e$ ($i = 1, 2, 3$). This is because we intend to use a simple quadratic potential even for ϱ_2. ϱ_i^e is the equilibrium value ϱ_i. u_1, u_3 and u_{13} are given by

$$u_1 = M_1(\varrho_1 + \varrho_3)^2/M\,, \quad u_3 = M_3(\varrho_1 - \varrho_3)^2/M$$

and

$$u_{13} = M_{13}(\varrho_1^2 - \varrho_3^2)/M\,. \tag{10}$$

The expression (9) for $\varepsilon(\varrho_1, \varrho_2, \varrho_3)$ obtained from ε_2 of (4) is not completely compatible with ε_1 and ε_3 unless it is supplemented by the relations (7) and (8). Thus for the sake of consistency, we obtain all the needed partial derivatives of (12) from (9).

2. The Hamiltonian

Corresponding to the volume element

$$\mathrm{d}\tau = \mathrm{d}\varrho_1\,\mathrm{d}\varrho_2\,\mathrm{d}\varrho_3\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\,\mathrm{d}\chi\,, \tag{11}$$

the classical kinetic energy expression

$$2\,T = I_{\alpha\beta}\,\omega_\alpha\,\omega_\beta \quad (\alpha, \beta = x, y, z; 1, 2, 3) \tag{12A}$$

takes the quantum-mechanical operator form

$$2\,T = \mu^{1/4}\,\Pi_\alpha\,\mu_{\alpha\beta}\,\mu^{-1/2}\,\Pi_\beta\,\mu^{1/4}\,. \tag{12B}$$

In the above, we note absence of terms involving vibrational co-ordinates Q_k, "vibrational angular momenta" π_α and the Coriolis coupling constants ζ_{kl}^α. This is the result of treating all three modes of motion as large amplitude motions.

The Hamiltonian representing the pure vibrational levels ($J = 0$) is given by

$$H(\varrho_1, \varrho_2, \varrho_3) = \frac{-\hbar^2}{2\,h\,c}\left[\mu_{rr}\frac{\partial^2}{\partial\varrho_r^2} + \sum_{s(\neq r)}\mu_{rs}\frac{\partial^2}{\partial\varrho_r\,\partial\varrho_s} + \sum_s\frac{\partial\mu_{rs}}{\partial\varrho_s}\frac{\partial}{\partial\varrho_r} + \mu^{1/4}\frac{\partial}{\partial\varrho_r}\left\{\mu_{rr}\,\mu^{-1/2}\frac{\partial}{\partial\varrho_r}\,\mu^{1/4}\right\} + \frac{1}{4}\,\mu^{1/4}\sum_{s(\neq r)}\frac{\partial}{\partial\varrho_r}\left\{\mu_{rs}\,\mu^{-5/4}\frac{\partial\mu}{\partial\varrho_s}\right\}\right] + V(\varrho_1, \varrho_2, \varrho_3)\,. \tag{12}$$

In the above, summation over r is assumed. The fourth and fifth terms of the above expression within the brackets, when expanded, take the form

$$\frac{1}{4}\,\mu^{-1}\frac{\partial\mu_{rr}}{\partial\varrho_r}\frac{\partial\mu}{\partial\varrho_r} - \frac{5}{16}\,\mu^{-2}\,\mu_{rr}\left(\frac{\partial\mu}{\partial\varrho_r}\right)^2 + \frac{1}{4}\,\mu^{-1}\,\mu_{rr}\frac{\partial^2\mu}{\partial\varrho_r^2}$$

and

$$\frac{1}{4}\mu^{-1}\sum_{s(\neq r)}\mu_{rs}\frac{\partial^2\mu}{\partial\varrho_r\,\partial\varrho_s} + \frac{1}{4}\,\mu^{-1}\sum_{s(\neq r)}\frac{\partial\mu}{\partial\varrho_r}\frac{\partial\mu_{rs}}{\partial\varrho_s} - \frac{5}{16}\,\mu^{-2}\sum_{s(\neq r)}\mu_{rs}\frac{\partial\mu}{\partial\varrho_r}\frac{\partial\mu}{\partial\varrho_s}\,.$$

The complete set of elements of $I_{\alpha\beta}$ and I_{st} ($\alpha, \beta = x, y, z$; $s, t = 1, 2, 3$), evaluated explicitly from [3]

$$I_{\alpha\beta} = e_{\alpha\gamma\varepsilon}\,e_{\beta\delta\varepsilon}\sum_i m_i\,a_{\gamma i}\,a_{\delta i} \tag{13}$$

and

$$I_{st} = \sum_i m_i\frac{\partial a_{\alpha i}}{\partial\varrho_s}\frac{\partial a_{\alpha i}}{\partial\varrho_t}$$

are given by

$$I_{xx} = [M_1(\varrho_1 + \varrho_3)^2 + M_3(\varrho_1 - \varrho_3)^2 + 2\,M_{13}(\varrho_1^2 - \varrho_3^2)\cos\varrho_2]/M^2\,,$$

$$I_{yy} = [M_1\cos^2(\varrho_2 - \varepsilon)\,(\varrho_1 + \varrho_3)^2 + M_3\cos^2\varepsilon\,(\varrho_1 - \varrho_3)^2 + 2\,M_{13}\cos\varepsilon\cos(\varrho_2 - \varepsilon)\,(\varrho_1^2 - \varrho_3^2)]/M^2\,,$$

$$
\begin{aligned}
I_{zz} = [&M_1 \sin^2(\varrho_2 - \varepsilon)\,(\varrho_1 + \varrho_3)^2 \\
&+ M_3 \sin^2 \varepsilon\,(\varrho_1 - \varrho_3)^2 \\
&- 2\,M_{13} \sin \varepsilon \sin(\varrho_2 - \varepsilon)\,(\varrho_1{}^2 - \varrho_3{}^2)]/M^2\,,
\end{aligned}
\tag{14}
$$

$$
\begin{aligned}
I_{yz} = [&M_1 \sin 2\,(\varrho_2 - \varepsilon)\,(\varrho_1 + \varrho_3)^2 \\
&- M_3 \sin 2\,\varepsilon\,(\varrho_1 - \varrho_3)^2 \\
&+ 2\,M_{13} \sin(\varrho_2 - 2\,\varepsilon)\,(\varrho_1{}^2 - \varrho_3{}^2)]/2\,M^2\,,
\end{aligned}
$$

$$I_{11} = -\,I_{xx}\,\varepsilon_1{}^2 + (M_1 + M_3 + 2\,M_{13} \cos \varrho_2)/M^2, \tag{14 A}$$

$$I_{22} = -\,I_{xx}\,\varepsilon_2{}^2 + M_1(\varrho_1 + \varrho_3)^2/M^2\,, \tag{14 B}$$

$$I_{33} = -\,I_{xx}\,\varepsilon_3{}^2 + (M_1 + M_3 - 2\,M_{13} \cos \varrho_2)/M^2, \tag{14 C}$$

$$I_{12} = -\,I_{xx}\,\varepsilon_1\,\varepsilon_2 + I_{xx}(\varepsilon_1 - \varepsilon_3)/2\,, \tag{14 D}$$

$$I_{23} = -\,I_{xx}\,\varepsilon_2\,\varepsilon_3 + I_{xx}(\varepsilon_3 - \varepsilon_1)/2\,, \tag{14 E}$$

$$I_{31} = -\,I_{xx}\,\varepsilon_3\,\varepsilon_1 + m_2(m_1 - m_3)/M\,. \tag{14 F}$$

$I_{\alpha\beta}$, which is now a 6×6 matrix, incorporates the rotations and all the vibrations and has the following form

$$
I_{\alpha\beta} = \begin{vmatrix}
I_{xx} & 0 & 0 & 0 & 0 & 0 \\
0 & I_{yy} & I_{yz} & 0 & 0 & 0 \\
0 & I_{yz} & I_{zz} & 0 & 0 & 0 \\
0 & 0 & 0 & I_{11} & I_{12} & I_{13} \\
0 & 0 & 0 & I_{12} & I_{22} & I_{23} \\
0 & 0 & 0 & I_{13} & I_{23} & I_{33}
\end{vmatrix}\,. \tag{15}
$$

The six quantities I_{st} ($s, t = 1, 2, 3$) being functions of $\varrho_1, \varrho_2, \varrho_3$ are not independent and there exist three relations among them. These relations are obtained in Appendix A.

The three dimensional Schrödinger's equation

$$
\begin{aligned}
[T(\varrho_1, \varrho_2, \varrho_3) + V(\varrho_1, \varrho_2, \varrho_3)]\,\psi\,\varrho_1, \varrho_2, \varrho_3) \\
= E_{v_1 v_2 v_3}\,\psi(\varrho_1, \varrho_2, \varrho_3)
\end{aligned}
\tag{16}
$$

corresponding to the Hamiltonian (12) takes the form

$$
\begin{aligned}
A\,\frac{\partial^2\psi}{\partial\varrho_1{}^2} &+ B\,\frac{\partial^2\psi}{\partial\varrho_2{}^2} + C\,\frac{\partial^2\psi}{\partial\varrho_3{}^2} + 2\,D\,\frac{\partial^2\psi}{\partial\varrho_1\,\partial\varrho_2} \\
&+ 2\,E\,\frac{\partial^2\psi}{\partial\varrho_2\,\partial\varrho_3} + 2\,F\,\frac{\partial^2\psi}{\partial\varrho_3\,\partial\varrho_1} + 2\,P\,\frac{\partial\psi}{\partial\varrho_1} \\
&+ 2\,Q\,\frac{\partial\psi}{\partial\varrho_2} + 2\,R\,\frac{\partial\psi}{\partial\varrho_3} + (S + V - E)\,\psi = 0\,.
\end{aligned}
\tag{17}
$$

The geometrical nature of this equation which turns out to be elliptic[4] analogous to the two dimensional case[3] is discussed in Appendix B.

For small amplitude vibrations, I is a constant matrix. For a non-linear symmetric triatomic molecule like H_2O ($m_1 = m_3$, $r_1{}^e = r_2{}^e$), we have $\varepsilon_1 = 0$, $I_{13}{}^e = 0$ and $I_{23}{}^e = 0$. Choosing the symmetry coordinates as[5]

$$S_1 = \sqrt{2}\,(\varrho_1 - \varrho_1{}^e)\,, \qquad S_2 = (\varrho_2 - \varrho_2{}^e)\,, \tag{18}$$

and

$$S_3 = \sqrt{2}\,\varrho_3\,,$$

we see that the above Hamiltonian reduces to

$$
\begin{aligned}
H(S_1, S_2, S_3) = \tfrac{1}{2}\,(G^{-1}_{A_1})_{11}\,\dot{S}_1{}^2 + (G^{-1}_{A_1})_{12}\,\dot{S}_1\,\dot{S}_2 \\
+ \tfrac{1}{2}\,(G^{-1}_{A_1})_{22}\,\dot{S}_2{}^2 + \tfrac{1}{2}\,G^{-1}_{33}\,\dot{S}_3{}^2 + V(S_1, S_2, S_3)\,.
\end{aligned}
\tag{19}
$$

The notation in the above is standard[5].

3. Computational Details

A variational method similar to that used previously[3,6] was employed here to obtain the low lying vibrational energy levels of H_2O molecule. The matrix elements of the Hamiltonian are obtained by numerical integration and the resulting matrix is diagonalized. There is a factorization of the final matrix into two blocks because of the vanishing matrix elements between $|v_1 v_2 v_3^{\text{even}}\rangle$ and $|v_1 v_2 v_3{}^{\text{odd}}\rangle$ basis functions. For computational convenience, the Hamiltonian (12) is transformed into dimensionless coordinates q_i given by

$$q_i = (\gamma_i{}^0\,I_{ii})^{1/2}\,(\varrho_i - \varrho_i{}^e) \quad (i = 1, 2, 3) \tag{20}$$

where $\gamma_i{}^0 = 4\,\pi^2\,c\,\nu_i{}^0/h$ (ergs^{-1} sec^{-2}) are the scaling factors and the "reduced masses" I_{ii} are functions of $\varrho_1, \varrho_2, \varrho_3$.

Strictly speaking, the potential for the bending mode should be taken as a double minimum potential and that is what the large amplitude problem in triatomic molecules is mostly about[2]. But since our aim here is merely to illustrate the method of calculation for the complete problem and consequently to reduce the formidable amount of computation, we assume a simple quadratic form of the potential for all the three modes. Thus

$$
\begin{aligned}
V(\varrho_1, \varrho_2, \varrho_3) = \tfrac{1}{2}\,K_1(\varrho_1 - \varrho_1{}^e)^2 \\
+ \tfrac{1}{2}\,K_2(\varrho_2 - \varrho_2{}^e)^2 + \tfrac{1}{2}\,K_3(\varrho_3 - \varrho_3{}^e)^2\,.
\end{aligned}
\tag{21}
$$

In the case of H_2O, $\varrho_3{}^e = 0$. For the basis functions $|v_1 v_2 v_3\rangle$, we use a "triangular selection" with n_1 functions in q_1, n_2 functions in q_2 and n_3 functions in q_3 and set a maximum value, $v_{\max}$, on the sum of the quantum numbers $v_1 + v_2 + v_3 \leqq v_{\max}$.

Since the calculated frequencies are merely for illustration, we choose a small basis set, take $v_{\max} = 3$ and obtain the lowest four frequencies corresponding to ν_1, ν_2, $2\nu_2$ and ν_3. Were we to choose a double minimum potential for the ν_2 mode, as we normally should, the number of basis functions, particularly for $|v_2\rangle$ woudl be very high for a rigorous calculation with consequent increase in the amount of computation.

In transforming the partial derivatives of H in (12), it is necessary to take into account the variation of I_{ii} $(i = 1, 2, 3)$ with respect to ϱ_1, ϱ_2, ϱ_3. The resulting Hamiltonian then takes the form

$$H(\varrho_1, \varrho_2, \varrho_3) = f_1 p_1^2 + f_2 p_2^2 + f_3 p_3^2 + f_4 p_1 p_2 + f_5 p_2 p_3 + f_6 (i p_1) + f_7 (i p_2) + f_8 (i p_3) (f_9 + V) \quad (22)$$

in which the f_i are functions of ϱ_1, ϱ_2, ϱ_3 and H is in units of cm^{-1}. In the above, we note the absence of a term $p_1 p_3$ with coefficient μ_{13} which turns out to be exactly zero (see Appendix A). In the two large-amplitude Hamiltonian[3] representing the stretching motions in ν_1 and ν_3 μ_{13} is small but non-zero.

We now need to obtain the matrix elements $\langle v_1' v_2' v_3' | H | v_1 v_2 v_3\rangle$ of H. The matrix elements of $p_i = -i(\partial/\partial q_i)$ and the products of p_i are well known[5], but those of f_i and V must be evaluated numerically. The latter require the evaluation of integrals of the form

$$I_k = \langle v_1' v_2' v_3' | f_k | v_1'' v_2'' v_3''\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \cdot \exp[-(q_1^2 + q_2^2 + q_3^2)]\, F_k \, dq_1 \, dq_2 \, dq_3 \,. \quad (23)$$

F_k is given by

$$F_k = [\varphi_{v_1'}(q_1)\, \varphi_{v_2'}(q_2)\, \varphi_{v_3'}(q_3)\, \varphi_{v_1''}(q_1)\, \varphi_{v_2''}(q_2) \cdot \varphi_{v_3''}(q_3)] \times f_k(\varrho_1, \varrho_2, \varrho_3) \quad (24)$$

where

$$\varphi_v = (2^v v! \sqrt{\pi})^{-1/2} H_v(q) \,,$$

and $H_v(q)$ is a Hermite polynomial in the dimensionless coordinates q. The integrals are evaluated numerically using the Gauss-Hermite quadrature formula[7]

$$I_n = \sum_{i=1}^{M} \sum_{j=1}^{M} \sum_{k=1}^{M} W_i W_j W_k F_n(a_i, a_j, a_k) \,. \quad (25)$$

The a_i $(i = 1, 2, \ldots, M)$ are the M roots of the M-th degree Hermite equation $H_M(q) = 0$ and W_i are the weights[7].

One small point concerns the evaluation of ϱ_1, ϱ_2, ϱ_3 for each a_j in order to calculate $f_i(\varrho_1, \varrho_2, \varrho_3)$ in (22). In the relations

$$a_j = (\gamma_i^0 I_{ii})^{1/2} (\varrho_i - \varrho_i^e) \,, \quad (i = 1, 2, 3;\; j = 1, 2, \ldots, M) \,, \quad (26)$$

since I_{ii} are functions of ϱ_1, ϱ_2, ϱ_3, the calculation is not nearly straight forward. We obtain the initial set of ϱ_1, ϱ_2, ϱ_3 values for a given a_j assuming the values of I_{ii} at $\varrho_i = \varrho_i^e$ $(i = 1, 2, 3)$. Then a least-squares calculation is made to fit each value of a_j and the best set of ϱ_1, ϱ_2, ϱ_3 values is obtained. If M values of a_j are chosen for numerical integration, then the $M \times M \times M$ sets of ϱ_1, ϱ_2, ϱ_3 values form a three-dimensional grid. We then evaluate the basis functions $|v_1 v_2 v_3\rangle$ which are functions of q_1, q_2, q_3 as well as the coefficients $f_i(\varrho_1, \varrho_2, \varrho_3)$ of (22) at $M \times M \times M$ grid points to be used in numerical evaluation of matrix elements.

4. Application to the H_2O Molecule

We illustrate the method of calculation for H_2O molecule using a simple quadiatic form for the potential function. As was already mentioned, we choose to do so merely to avoid the large amount of computation one has to undertake if the ν_2 mode is correctly represented by a double minimum potential.

The Hamiltonian matrix $\langle v_1' v_2' v_3' | H | v_1 v_2 v_3\rangle$ factors into two symmetry blocks because there should be no mixing of $|v_1 v_2 v_3^{\text{even/odd}}\rangle$ basis functions with $|v_1 v_2 v_3^{\text{odd/even}}\rangle$. However, as was the case with the two-dimensional calculation[3], because of the terms linear in p_i, both types of functions must be employed to compute the energy levels with either v_3^{even} or v_3^{odd}.

The size of the basis set employed is 20 with $v_1 + v_2 + v_3 \leqq 3$. The scaling factors ν_1^0, ν_2^0 and ν_3^0 are chosen as 3657, 1595 and 3756 cm^{-1} respectively. The structural parameters and a simple set of force constants used in the calculation are given in Table I. This table also gives the observed frequencies for the lowest four vibrational levels as well as the frequencies calculated on the basis of small amplitude (19) and large amplitude (22) Hamiltonians. No attempt was made to refine the force constants. In view of the many limitations involved in obtaining the final numbers, any discussion of their significance is not quite meaningful. In spite of this, the fact that the overtone of ν_2 coming from

Table 1. Observed and calculated frequencies (in cm^{-1}) for the ground electronic $\tilde{X}\,^1A_1$ state of H_2O molecule[a].

		Calculated $G(v_1, v_2, v_3)$[b]		
(v_1, v_2, v_3)	obs	small amplitude Hamiltonian (19)	large amplitude Hamiltonian (22)	Force constants[c]
(0, 1, 0)	1594.8	1594.38	1594.47	$K_1 = 15.21513$ mdyn/Å
(0, 2, 0)	3151.5	3191.51	3182.77	$K_2 = 0.64331$ mdyn · Å/rad^2
(1, 0, 0)	3656.7	3664.45	3677.86	$K_3 = 15.52931$ mdyn/Å
(0, 0, 1)	3755.8	3756.0	3762.18	

[a] Geometry is taken as $\varrho_1^e = 0.957$ Å, $\varrho_2^e = 75.7°$, $\varrho_3^e = 0.0$Å.

[b] Frequencies are calculated using a simple potential

$$V = \tfrac{1}{2} K_1 (\varrho_1 - \varrho_1^e)^2 + \tfrac{1}{2} K_2 (\varrho_2 - \varrho_2^e)^2 + \tfrac{1}{2} K_3\, \varrho_3^2 .$$

[c] Force constants K_i are obtained from $K_i = 10^{-9} \cdot 4\,\pi^2 c^2 (\nu_i^\circ)^2 (I_{ii})^e$ and are not refined.

the large amplitude Hamiltonian is closer to the observed value does indicate the trend of the calculation.

5. Conclusions

On the basis of a three-dimensional Schrödinger's equation describing the large amplitude motions in the three modes of a triatomic molecule, we have calculated the lowest four vibrational frequencies of H_2O in its $\tilde{X}\,^1A_1$ ground electronic state. Since our aim here is to present the complete mathematical formalism and demonstrate the method of calculation, we have not attempted to obtain the best set of numbers either for the frequencies or for the realistic potential field of the molecule. We have thus used only 20 basis functions with $v_1 + v_2 + v_3 \leqq 3$ to obtain the Hamiltonian matrix and a $6 \times 6 \times 6$ grid for numerical integration to obtain the matrix elements of $f_k(\varrho_1, \varrho_2, \varrho_3)$.

Two avenues are now open if one intends to use the Hamiltonian (22) to obtain a good set of numbers using a double minimum potential for ν_2. Either one can employ the present method and expend a large amount of computer time, which may not be prohibitive, or look for a rigorous straight forward numerical technique of solving the three-dimensional Schrödinger's equation obviating the necessity of having to evaluate numerically the matrix elements of a Hamiltonian with a large basis set.

Acknowledgement

We are grateful to the National Research Council of Canada for financial assistance.

Appendix A

In [3], the following relation was obtained

$$I_{11} I_{33} - I_{13}^2 = 4 m_1 m_2 m_3 / M . \quad \text{(A1)}$$

In the present work, we notice initially that

$$\mu_{13} = I_{12} I_{23} - I_{22} I_{13} = 0 . \quad \text{(A2)}$$

We use the following notation for the constants

$$c_1 = (M_1 + M_3)/M , \quad c_2 = 2\, M_{13}/M , \quad \text{(A3)}$$

and

$$c_3 = M_1 M^2 / 4\, M_{13}^2 .$$

Dividing both sides of (14B), (14D) and (14E) by both sides of (14F), (note that $m_1 = m_3$ for H_2O), we have

$$\varepsilon_1 \varepsilon_3 I_{22} = I_{13} \left[\varepsilon_2^2 + \frac{c_3 I_{13}}{\sin^2 \varrho_2} \, \frac{(\varepsilon_3 - \varepsilon_1)^2}{\varepsilon_1 \varepsilon_3} \right] , \quad \text{(A4)}$$

$$\varepsilon_1 \varepsilon_3 I_{12} = I_{13} [\varepsilon_1 \varepsilon_2 + (\varepsilon_3 - \varepsilon_1)/2] , \quad \text{(A5)}$$

and

$$\varepsilon_1 \varepsilon_3 I_{23} = I_{13} [\varepsilon_2 \varepsilon_3 + (\varepsilon_1 - \varepsilon_3)/2] . \quad \text{(A6)}$$

(A5) and (A6) can be rewritten as

$$\varepsilon_1 (\varepsilon_3 I_{12} - I_{13} \varepsilon_2 + I_{13}/2) = I_{13} \varepsilon_3 / 2 , \quad \text{(A7)}$$

and

$$\varepsilon_1 (\varepsilon_3 I_{23} - I_{13}/2) = I_{13} \varepsilon_3 (\varepsilon_2 - 1/2) . \quad \text{(A8)}$$

Further, using the notation

$$\begin{aligned} x &= \varepsilon_2 - 1/2 , \\ x_1 &= (I_{12} x - I_{23}/2) , \\ x_2 &= (I_{23} x - I_{12}/2) , \end{aligned} \quad \text{(A9)}$$

and dividing (A7) by (A8), we have

$$(\varepsilon_3 I_{12} - I_{13} x)\, x = \tfrac{1}{2} (\varepsilon_3 I_{23} - I_{13}/2) . \qquad \text{(A10)}$$

From this follows

$$\varepsilon_3 = I_{13} (x^2 - 1/4)/x_1 . \qquad \text{(A11)}$$

Similarly

$$\varepsilon_1 = I_{13} (x^2 - \tfrac{1}{4})/x_2 . \qquad \text{(A12)}$$

From (A11) and (A12), we have

$$\varepsilon_1 \varepsilon_3 = I_{13}{}^2 (x^2 - \tfrac{1}{4})^2 / x_1 x_2 , \qquad \text{(A13)}$$

$$(\varepsilon_3 - \varepsilon_1)^2 = I_{13}{}^2 (x^2 - \tfrac{1}{4})^2 (x + \tfrac{1}{2})^2 \times (I_{23} - I_{12})^2 / x_1{}^2 x_2{}^2 , \qquad \text{(A14)}$$

and

$$\varepsilon_1 / \varepsilon_3 = x_1 / x_2 . \qquad \text{(A15)}$$

Substituting for $\varepsilon_1 \varepsilon_3$ and $(\varepsilon_3 - \varepsilon_1)^2$ from (A13) and (A14) in (A4), we have

$$\frac{I_{13}{}^2 I_{22} (x^2 - \tfrac{1}{4})^2}{x_1 x_2} = I_{13} \left[(x + \tfrac{1}{2})^2 + \frac{c_3 I_{13}}{\sin^2 \varrho_2} \, \frac{(I_{23} - I_{12})^2 (x + \tfrac{1}{2})^2}{x_1 x_2} \right] . \qquad \text{(A16)}$$

This may be simplified to

$$I_{22} I_{13} (x - \tfrac{1}{2})^2 = x_1 x_2 + \frac{c_3 I_{13}}{\sin^2 \varrho_2} (I_{23} - I_{12})^2 . \qquad \text{(A17)}$$

We also have, from (A9),

$$x_1 x_2 = x^2 I_{12} I_{23} - \frac{x}{2} (I_{12}{}^2 + I_{23}{}^2) + I_{12} I_{23}/4 , \qquad \text{(A18)}$$

Using (A2) and (A18), (A17) enables us to obtain x.

$$x = c_3 I_{13} / \sin^2 \varrho_2 . \qquad \text{(A19)}$$

We further use the following notation

$$\begin{aligned} d_1 &= (I_{33} - I_{11})/c_2 , \\ d_2 &= [I_{13}{}^2 - (I_{11} - c_1)(I_{33} - c_1)]/c_2{}^2 , \\ d_3 &= (c_1 I_{12} + I_{13} I_{23} - I_{11} I_{12})/(c_2 I_{12}) , \qquad \text{(A20)} \\ d_4 &= (2 c_2 c_3 I_{23} - c_2 I_{12})/(c_2 I_{12}) , \end{aligned}$$

and

$$d_5 = [2 c_3 (I_{13} I_{12} - I_{11} I_{23} + c_1 I_{23}) + (I_{11} I_{12} - I_{13} I_{23} - c_1 I_{12})]/(c_2 I_{12}) .$$

From expressions (14A), (14C) and (14F), we have

$$(I_{11} - c_1 - c_2 \cos \varrho_2)(I_{33} - c_1 + c_2 \cos \varrho_2) = I_{13}{}^2 \qquad \text{(A21)}$$

which leads to

$$\cos^2 \varrho_2 + d_1 \cos \varrho_2 + d_2 = 0 . \qquad \text{(A22)}$$

Substituting for ε_1 in (14A) from (14F) and then using (A15), we have

$$I_{11} = I_{13} \varepsilon_1 / \varepsilon_3 + c_1 + c_2 \cos \varrho_2 \qquad \text{(A23)}$$

and hence

$$I_{11} x_2 = I_{13} x_1 + (c_1 + c_2 \cos \varrho_2) x_2 . \qquad \text{(A24)}$$

Using (A19) in conjunction with (A9), the above reduces, upon simplification, to

$$\cos^3 \varrho_2 + d_3 \cos^2 \varrho_2 + d_4 \cos \varrho_2 + d_5 = 0 . \qquad \text{(A25)}$$

Substituting for $\cos^2 \varrho_2$ in the above from *(A22)* twice in succession, we obtain

$$\cos \varrho_2 = \frac{(d_2 d_3 - d_5 - d_1 d_2)}{(d_1{}^2 - d_2 - d_1 d_3 + d_4)} . \qquad \text{(A26)}$$

Now substituting for $\cos \varrho_2$ in (A22), we finally have

$$\begin{aligned} &(d_2 d_3 - d_5 - d_1 d_2)^2 \\ &\quad + d_1 (d_2 d_3 - d_5 - d_1 d_2)(d_1{}^2 - d_2 - d_1 d_3 + d_4) \\ &\quad + d_2 (d_1{}^2 - d_2 - d_1 d_3 + d_4)^2 = 0 . \qquad \text{(A27)} \end{aligned}$$

The d_i which are functions of ϱ_1, ϱ_2, ϱ_3 and the constants c_i are given by (A20) and (A3) respectively. Relations (A1), (A2) and (A27) which should exist among the six quantities I_{rs} $(r, s = 1, 2, 3)$ have been verified numerically for various sets of ϱ_1, ϱ_2, ϱ_3 values which form the $M \times M \times M$ grid as discussed in the text.

Appendix B

To classify the nature of the differential equation[4]

$$\left[\left(a \frac{\partial^2}{\partial q_1{}^2} + b \frac{\partial^2}{\partial q_2{}^2} + c \frac{\partial^2}{\partial q_3{}^2} + 2 d \frac{\partial^2}{\partial q_1 \partial q_2} + 2 e \frac{\partial^2}{\partial q_2 \partial q_3} + 2 f \frac{\partial}{\partial q_3 \partial q_1} \right) + \left(2 p \frac{\partial}{\partial q_1} + 2 q \frac{\partial}{\partial q_2} + 2 r \frac{\partial}{\partial q_3} + (S + V - E) \right) \right] \psi = 0 , \qquad \text{(B1)}$$

consider the quadratic form

$$Q(q_1, q_2, q_3) = a q_1{}^2 + b q_2{}^2 + c q_3{}^2 + + 2 d q_1 q_2 + 2 e q_2 q_3 + 2 f q_3 q_1 , \qquad \text{(B2)}$$

with

$$Q_u = \begin{vmatrix} a & d & f \\ d & b & e \\ f & e & c \end{vmatrix} . \qquad \text{(B3)}$$

Let r and t be the number of positive and negative eigenvalues of Q_u respectively. Then $s = |r - t|$ gives the absolute value of the *signature* of Q_u. The differential equation (B1) is characterized as elliptic if $s = 3$. In the present case, equation (17) representing the large-amplitude motions in a triatomic molecule turns out to be elliptic as was the case with the two-large amplitude equation[3]. It is too cumbersome to show this analytically. So for illustration, we give below the results for a typical set of ϱ_1, ϱ_2, ϱ_3 values even though it is found to be true for all the sets considered in the text.

For $\varrho_1 = 0.9872$ Å, $\varrho_2 = 80.88^0$ and $\varrho_3 = 0.0302$ Å, we have

$$Q_u = \begin{vmatrix} -1844.68 & -68.81 & 0.0 \\ -68.81 & -749.98 & -2.10 \\ 0.0 & -2.10 & -1867.93 \end{vmatrix} . \qquad \text{(B4)}$$

The eigenvalues of Q_u are -1848.99, -745.67 and -1867.93. Thus $r = 0$; $t = 3$ and hence $s = |r - t| = 3$.

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