On the variational solution of the coupled breathing rotation-vibration of a spherical top molecule

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Abstract On the basis of the solutions of the isotropic 3-D harmonic oscillator, we show how to evaluate the matrix elements for the coupled rotation-vibration of the totally symmetric breathing mode of a rotating spherical top molecule, whereby the anharmonic potential energy is expanded in a power series of r. It is shown also how to obtain the ro-vibrational spectrum when used in conjunction with the variational method to obtain eigenvalues.

Keywords Spherical top · Ro-vibration · Breathing motion

1 Introduction

The Schrödinger equation of the isotropic, i.e. spherically symmetric, three dimensional rotating oscillator

$$\left\{ -\frac{\hbar^2}{2M}\nabla^2 + V(r) + \frac{\hbar^2 J(J+1)}{2I} \right\} \Psi(r,\theta,\phi) = E\ \Psi(r,\theta,\phi) \qquad (1)$$

can be solved explicitly when the potential energy function $V(r)$ is the spherically symmetric harmonic function [1,2] and it has been the subject of any introductory text in Quantum Mechanics. Nevertheless, the real potential function is generally a

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Morse-like functional whose solution is of much more difficulty. A variety of algebraic methods can be used and are found in the literature, to solve exactly the one-dimensional Morse oscillator, radial Coulomb and radial oscillator problems [3–5]; analytic formulae for perturbation corrections to the eigenvalues of a perturbed Morse oscillator, applied to the calculation of the ro-vibrational energy levels of a diatomic molecule have been given [6] and the problem of vibration-rotation coupling within the model of the Morse oscillator [7] have been also addressed. Nevertheless the vibrational potential function is generally more complex and is sometimes poorly described by the Morse function. It is usually expressed as a power series in r and, in turn, one must resort to variational procedures to find approximate solutions to Eq. 1 in these cases.

We are interested in the theoretical calculation of ro-vibrational transitions in molecules within the variational method and it is the subject of this work to describe a simple approach to determine the ro-vibrational states and the ro-vibrational transitions, of the coupled rotation-vibration motion, for the particular vibrational motion that does not destroy the symmetry, in a molecule of spherical symmetry such as fullerene.

2 Model

The breathing, totally symmetric, vibrational motion of a rotating spherical molecule, such as the one in Fig. 1a, or a rotating spherical top molecule such as methane, can be modeled as a rotating spherical shell whose mass is $M = \sum_i m_i$. Here the m_i's are the masses of the atoms on the surface and furthermore we assume, by symmetry reasons, that the mass M is uniformly distributed.

The breathing vibrational motion is a uniform expansion of the whole molecule and it means that each atom on the surface is either, receding from or approaching to, each other in a manner proportional to r^2 i.e. the rate of change of the sphere surface
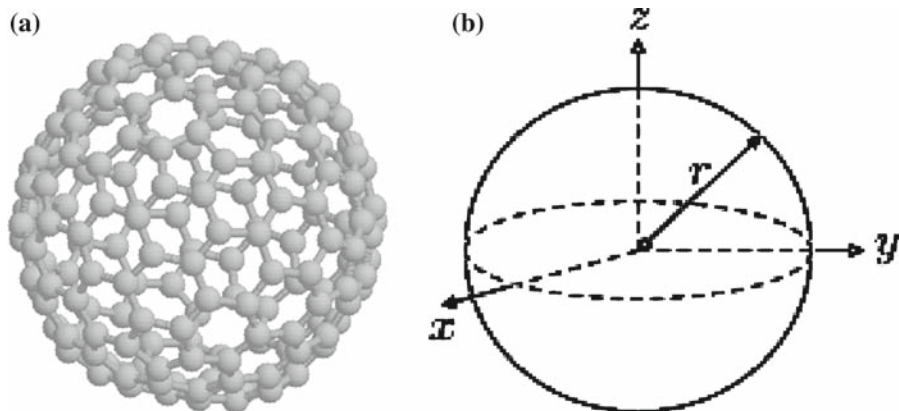

Fig. 1 (**a**) A spherical molecule that concentrates the mass on its surface. (**b**) Thin spherical shell model whose moment of inertia is $I = \frac{2}{3}Mr^2$

with r. Therefore in principle, it is possible to express the potential energy for this motion in terms of the single variable r.

If R_0 is the equilibrium radius, the potential energy for this breathing motion can be expressed in a power series in r

$$V(r) = A_2(r - R_0)^2 + A_3(r - R_0)^3 + A_4(r - R_0)^4 + A_5(r - R_0)^5 + \cdots \quad (2)$$

Upon expansion of Eq. 2 and collecting all terms that do not contain r^2 we obtain $V'(r)$, the anharmonic correction to the potential

$$V'(r) = \left[\sum_{k=n \neq 2}^{m>n} \left\{ \begin{matrix} (-1)^k \ n = \text{even} \\ (-1)^{k-1} \ n = \text{odd} \end{matrix} \right\} \frac{k!}{n!(k-n)!} A_k R_0^{k-n} \right] r^n \quad (3)$$

While the harmonic part $V^0(r)$ is written:

$$V^0(r) = \left[\sum_{k=2}^{m>n} (-1)^k \frac{k!}{2(k-2)!} A_k R_0^{k-2} \right] r^2 = \frac{1}{2} M \omega^2 r^2 \quad (4)$$

Here, $M = \sum_i m_i$ is the mass of the spherical shell and the harmonic frequency ω is calculated directly from the squared bracket of Eq. 4. Taking only the harmonic part $V^0(r)$ of the potential energy, we solve next the Schrödinger equation for the breathing motion of a rotating spherical shell whose moment of inertia is $I = \frac{2}{3} M r^2$

$$\left\{ -\frac{\hbar^2}{2M} \nabla^2 + \frac{1}{2} M \omega^2 r^2 + \frac{3\hbar^2 J(J+1)}{4Mr^2} \right\} \Psi_{HO}(r, \theta, \phi) = E \Psi_{HO}(r, \theta, \phi) \quad (5)$$

After the definition $\gamma = \frac{M\omega}{\hbar}$, the well known solutions of Eq. 5 are found to be [1–3]

$$\psi_{HO}(r, \theta, \phi) = R(r) Y_{Jm}(\theta, \phi) \quad (6a)$$

and whose eigenvalues depend upon the quantum numbers k and J, such that:

$$E_{k,J} = \hbar\omega \left(2k + J + \frac{3}{2} \right) = \hbar\omega \left(N + \frac{3}{2} \right) \quad (6b)$$

where k is a non-negative integer; therefore, for each value of the single quantum number N we have:

$$J = N, N-2, N-4, \ldots, J_{Min} \quad \text{where} \quad J_{Min} = \begin{cases} 1 & \text{for } N \text{ odd} \\ 0 & \text{for } N \text{ even} \end{cases} \quad (7)$$

In Eq. 6a $Y_{lm}(\theta, \phi)$ is the usual spherical harmonics and the normalized radial function is:

$$R_{N,J}(r) = N_{N,J} \, r^J e^{-\frac{1}{2}\gamma r^2} L_{\frac{1}{2}(N-J)}^{(J+\frac{1}{2})}(\gamma r^2) \quad (8)$$

There, $L_{\frac{1}{2}(N-J)}^{(J+\frac{1}{2})}(\gamma r^2)$ is the generalized Laguerre's polynomial [8,9] of order $k = \frac{1}{2}(N-J)$ having γr^2 as variable and the normalization constant is:

$$N_{N,J} = \left[\frac{2^{N+J+2}\gamma^{J+\frac{3}{2}}}{\pi^{\frac{1}{2}}}\right]^{\frac{1}{2}}\left[\frac{[\frac{1}{2}(N-J)]![\frac{1}{2}(N+J)]!}{(N+J+1)!}\right]^{\frac{1}{2}}$$

$$= \sqrt{2}\left(\frac{\gamma}{\pi}\right)^{\frac{1}{4}}(2\gamma)^{\frac{J}{2}}\sqrt{\frac{2\gamma(N-J)!}{(N+J+1)!}} \tag{9}$$

The complete Schrödinger equation can now be written as

$$\left\{\hat{H}_{harmonic} + \left[\sum_{k=n\neq2}^{m>n}\left\{\begin{array}{l}(-1)^k\ n = \text{even}\\(-1)^{k-1}\ n = \text{odd}\end{array}\right\}\frac{k!}{n!(k-n)!}A_kR_0^{k-n}\right]r^n\right\}$$
$$\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi) \tag{10}$$

and solved variationally using as basis set the complete set of eigenfunctions given by (6a) and (8).

3 Matrix elements

Owing to the spherical symmetry of the problem, the relevant matrix elements, needed either for the variational solution of Eq. 10 or to compute corrections to the energy within a perturbation approach, are only those of the type $\langle r^\alpha\rangle_{v,m}, (\alpha=0, 1, 2, 3, 4, \ldots)$ and recalling that $x = \gamma r^2$, these matrix elements can be written as:

$$\langle r^\alpha\rangle_{v,m} = \frac{N_{v,J}N_{m,J}}{\gamma^{J+\frac{\alpha}{2}}}\int_0^\infty x^{(J+\frac{1}{2}+\frac{\alpha}{2})}e^{-x}\ L_{\frac{1}{2}(v-J)}^{(J+\frac{1}{2})}(x)\ L_{\frac{1}{2}(m-J)}^{(J+\frac{1}{2})}(x)dx \tag{11}$$

where, the space spanned by the variables $r = \frac{\sqrt{x}}{\sqrt{\gamma}}$ and x is the same. The integrals of the preceding equation may be numerically evaluated or algebraically expanded in power series; some of the first of these terms are given in Table 1 for illustrative purposes.

From Table 1, it is readily seen that the overlap integrals value $S_{vm} = \delta_{vm}$, follows immediately from $\langle r^\alpha\rangle_{v,m}$ when $\alpha = 0$ and also these terms allow the computation of the square of the normalization constant $(N_{vJ})^2$.

The matrix elements for $\alpha = 2$ are not listed because they are contained in the eigenvalues of Eq. 6b.

4 Ro-vibrational levels

We next solve variationally Eq. 10, for a fixed value of the rotational quantum number $J = 0, 1, 2, \ldots$, and a manifold of ro-vibrational energy levels $\{E_M\}_J$ (M being the

Table 1 Some of the first matrix elements of the operator r^α, $\alpha = 0, 1, 3, 4, \ldots$ computed on the basis of the isotropic 3-D harmonic oscillator eigenfunctions

$$\langle r^\alpha \rangle_{0,0} = \frac{N_{0,J} N_{0,J}}{\gamma^{J+\frac{\alpha}{2}}} \Gamma\left(J + \frac{3}{2} + \frac{\alpha}{2}\right)$$

$$\langle r^\alpha \rangle_{0,1} = \frac{N_{0,J} N_{1,J}}{\gamma^{J+\frac{\alpha}{2}}} \left(-\frac{\alpha}{2}\right) \Gamma\left(J + \frac{3}{2} + \frac{\alpha}{2}\right)$$

$$\langle r^\alpha \rangle_{0,2} = \frac{N_{0,J} N_{2,J}}{\gamma^{J+\frac{\alpha}{2}}} \left(\frac{\alpha}{8}\right)\left(-2 + \alpha^2\right) \Gamma\left(J + \frac{3}{2} + \frac{\alpha}{2}\right)$$

$$\langle r^\alpha \rangle_{0,3} = \frac{N_{0,J} N_{3,J}}{\gamma^{J+\frac{\alpha}{2}}} \left(\frac{-\alpha}{48}\right)\left(-6\alpha + \alpha^2 + 8\right) \Gamma\left(J + \frac{3}{2} + \frac{\alpha}{2}\right)$$

$$\langle r^\alpha \rangle_{1,1} = \frac{N_{1,J} N_{1,J}}{\gamma^{J+\frac{\alpha}{2}}} \left(\frac{1}{4}\right)\left(4J + 6 + 2\alpha + 4\alpha^2\right) \Gamma\left(J + \frac{3}{2} + \frac{\alpha}{2}\right)$$

$$\langle r^\alpha \rangle_{1,2} = \frac{N_{1,J} N_{2,J}}{\gamma^{J+\frac{\alpha}{2}}} \left(\frac{-\alpha}{16}\right)\left(2\alpha + \alpha^2 + 8J + 12\right) \Gamma\left(J + \frac{3}{2} + \frac{\alpha}{2}\right)$$

$$\langle r^\alpha \rangle_{1,3} = \frac{N_{1,J} N_{3,J}}{\gamma^{J+\frac{\alpha}{2}}} \left(\frac{\alpha}{96}\right)\left(12J\alpha + \alpha^3 - 24J + 4\alpha - 36\right) \Gamma\left(J + \frac{3}{2} + \frac{\alpha}{2}\right)$$

$$\langle r^\alpha \rangle_{2,2} = \frac{N_{2,J} N_{2,J}}{\gamma^{J+\frac{\alpha}{2}}} \left(\frac{1}{64}\right)\left(\begin{array}{l}\alpha^4 + \alpha^3 + 16J\alpha^2 + 36\alpha^2 + 64\alpha + 32J\alpha \\ + 128J + 32J^2 + 120\end{array}\right) \Gamma\left(J + \frac{3}{2} + \frac{\alpha}{2}\right)$$

$$\langle r^\alpha \rangle_{2,3} = \frac{N_{2,J} N_{3,J}}{\gamma^{J+\frac{\alpha}{2}}} \left(\frac{-\alpha}{384}\right)\left(\begin{array}{l}\alpha^4 + 4\alpha^3 + 24J\alpha^2 + 56\alpha^2 + 104\alpha + 48J\alpha \\ + 384J + 96J^2 + 360\end{array}\right) \Gamma\left(J + \frac{3}{2} + \frac{\alpha}{2}\right)$$

$$\langle r^\alpha \rangle_{3,3} = \frac{N_{3,J} N_{3,J}}{\gamma^{J+\frac{\alpha}{2}}} \left(\frac{1}{2304}\right)\left(\begin{array}{l}\alpha^6 + 6\alpha^5 + 106\alpha^4 + 384\alpha^3 + 2080\alpha^2 + 3408\alpha \\ + 6816J + 2880J\alpha + 1584J\alpha^2 + 576J^2\alpha + 288J^2\alpha^2 \\ + 144J\alpha^3 + 36J\alpha^4 + 3880J^2 + 383J^3 + 5040\end{array}\right) \Gamma\left(J + \frac{3}{2} + \frac{\alpha}{2}\right)$$

label of the corresponding energy level) is obtained. In doing so, it must be noted that in the harmonic part of the diagonal energy matrix elements

$$E_{kJ} = \hbar\omega\left(2k + J + \frac{3}{2}\right) = \hbar\omega\left(N_J + \frac{3}{2}\right),$$

as J increases the allowed values of N_J are restricted to start from $N_J = J$ since k must be a positive integer (the subscript J is used to differentiate the various sets of N values arising). Transitions energies can then be computed by subtracting the appropriate energy levels corresponding to $\Delta J = 0, \pm 1$

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