Stretching vibrations of a XY_2 molecule as a training project for "Quantum Physics"

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You should write a formal paper either in English or in Chinese, following the Instruction to Authors provided by the APS journal *Physical Review A*. The document (xxx.pdf) together with all the supplementary files (programs etc) must be enclosed in one zip file named "your-ID.zip" (like PBXXAAAYYY.zip) and sent to hushuiming@gmail.com. The deadline for submission is 24:00 of JAN 31, 2018.

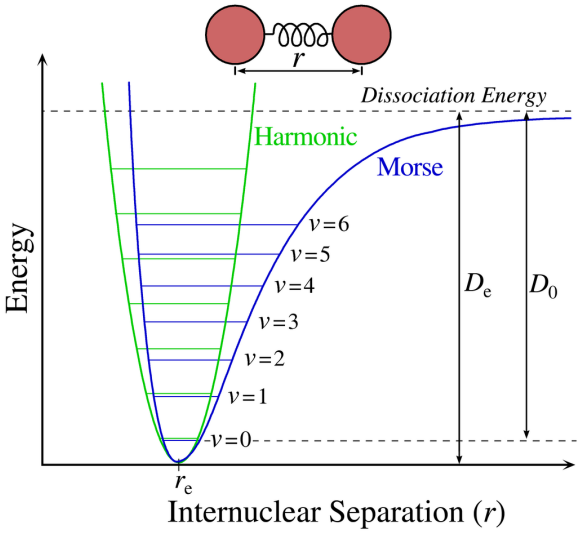

FIG. 1. Morse potential and its harmonic approximation. (https://en.wikipedia.org/wiki/Morse_potential)

To describe the stretching vibrations in a molecule, it is better to use the Morse oscillator model than the simple harmonic oscillator model. The Hamiltonian for a Morse oscillator is [1]

$$H = \frac{p^2}{2\mu} + D_e(1 - e^{-\alpha r})^2 \tag{1}$$

Where r is the deviation of the bond length from its equilibrium value, μ is the reduced mass, D_e and α are the Morse dissociation energy and exponent, respectively. Alternatively D_e and α can be replaced by the Morse frequency ω and anharmonicity ω_x,

$$\omega = \alpha\sqrt{\frac{2D_e}{\mu}} \tag{2}$$

$$\omega_x = \alpha^2\hbar/2\mu \tag{3}$$

$$k = \frac{\omega}{\omega_x} = \frac{2}{\alpha\hbar}\sqrt{2D_e\mu} \tag{4}$$

The n-th eigenvalue and eigenfunction of a Morse oscillator are:

$$|n\rangle = N_n e^{-y/2} y^{(k-2n-1)/2} L_n^{k-2n-1}(y) \tag{5}$$

$$E_n = \hbar\omega(n + \frac{1}{2}) - \hbar\omega_x(n + \frac{1}{2})^2 \tag{6}$$

where

$$y = ke^{-\alpha r}$$

$$N_n = [\frac{\alpha n!(k-2n-1)}{\Gamma(k-n)}]^{1/2} \tag{7}$$

$\Gamma(z)$ and L_n^{k-2n-1} are the gamma function and the associated Laguerre function, respectively.

In the local mode model for a XY_2 type molecule like H_2S, as a good approximation, the two H-S stretching vibration modes can be considered as two degenerated Morse oscillators with additional coupling terms:

$$H = H_0 + H_1$$

$$H_0 = \frac{p_1^2 + p_2^2}{2\mu} + D_e[(1 - e^{-\alpha r_1})^2 + (1 - e^{-\alpha r_2})^2]$$

$$H_1 = g_{rr'}p_1p_2 + f_{rr'}r_1r_2 \tag{8}$$

where $\mu = \frac{m_S m_H}{m_S + m_H}$ and $g_{rr'} = \frac{\cos\beta}{m_S}$. m_H, m_S are the values of the atomic mass of Hydrogen and Sulfur, respectively. $\beta = 92.11°$ is the equilibrium H-S-H angle.

You are supposed to determine the energy levels of the main isotopologue of the hydrogen sulfide molecule ($H_2^{32}S$). Our suggestions are as following: Try to give the matrix presentation of the Hamiltonian. Use the Morse oscillator model when calculating the H_0 terms, and use the harmonic oscillator basis functions as approximate Morse oscillator functions when calculating the contribution from the H_1 term (Harmonic Coupled Anharmonic Oscillators, HCAO model). Use parameters D_e = 38667.2857

cm^{-1}, $\alpha = 1.6627$ $Å^{-1}$, $f_{rr'} = -987.05$ $cm^{-1}Å^{-2}$, to calculate the energy levels below 20000 cm^{-1} (1 eV=8065.5409 cm^{-1}): energies (in cm^{-1}) and wavefunctions (4 largest components). Compare your results with the experimental values given in Table. I (Ref. [2] and references there in). Note that the zero point energy has been removed therefore the ground state energy is zero.

You may get additional BONUS if you can refine the parameters (D_e, α, and $f_{rr'}$) according to the experimental values based on a least-squares fitting procedure.

TABLE I. Observed vibrational energy levels of $H_2^{32}S$. (in cm^{-1})

n	m		E_v	n	m		E_v
0	0		0.0000	4	0	+	9911.023
1	0	+	2614.4079	4	0	-	9911.023
1	0	-	2628.4552	3	1	+	10188.301
2	0	+	5144.9862	3	1	-	10194.448
2	0	-	5147.2205	5	0	±	12149.458
1	1	+	5243.1014	4	1	+	12524.628
3	0	+	7576.3833	4	1	-	12525.202
3	0	-	7576.5466	6	0	±	14291.122
2	1	+	7752.2638	7	0	±	16334.162
2	1	-	7779.3208				

[1] P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).
[2] O.N. Ulenikov, A.-W. Liu, E.S. Bekhtereva, O.V. Gromova, L.-Y. Hao, and S.-M. Hu, *J. Mol. Spectrosc.*, **226**, 57-70 (2004).