

Stretching vibrations of a H₂S molecule

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Abstract

Stretching vibration of a molecule can be calculated with Morse oscillator, and a complex system of it can be solved with perturbation theory. As perturbation of Morse oscillator is difficult to calculate, Harmonic Coupled Anharmonic Oscillators model is applied to solve the vibration of H₂S molecule.

Keywords: Morse oscillator, H₂S, HCAO model

Introduction

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 isⁱ

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

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 ,

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

$$\omega_x = \alpha^2 \frac{\hbar}{2\mu}$$

$$k = \frac{\omega}{\omega_x}$$

The n-th eigenvalue of a Morse oscillator is:

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

In the local mode model for a XY₂ type molecule like H₂S, as a good approximation, the two H-S stretching vibration modes can be considered as two degenerated Morse oscillators with additional coupling terms:

$$H = H^{(0)} + H^{(1)}$$

$$H^{(0)} = \frac{p_1^2 + p_2^2}{2\mu} + D_e[(1 - e^{-\alpha r_1})^2 + (1 - e^{-\alpha r_2})^2]$$

$$H^{(1)} = g_{rr} p_1 p_2 + f_{rr} r_1 r_2$$

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

The energy of $H^{(0)}$ part is its eigenvalue, and the energy of $H^{(1)}$ part is its exception on $|n\rangle$, while

$$|n\rangle = A_n e^{-\frac{\alpha^2 x^2}{2}} H_n(\alpha x)$$

$$E_n = (n + \frac{1}{2})\hbar\omega$$

Parameters and unit conversions used for calculations

$$D_e = 38667.2857 \text{ cm}^{-1}$$

$$\alpha = 1.6627 \text{ \AA}^{-1}$$

$$f_{rr} = -987.05 \text{ cm}^{-1} \text{ \AA}^{-2}$$

$$\beta = 92.11^\circ$$

$$m_S = 31.97207073 \text{ amu}^{\text{ii}}$$

$$m_H = 1.0078250319 \text{ amu}$$

$$\hbar = 1.054571800 \times 10^{-34} \text{ J} \cdot \text{s}^{\text{iii}}$$

$$1 \text{ eV} = 1.6021766208 \times 10^{-19} \text{ J}$$

$$1 \text{ eV} = 8065.5409 \text{ cm}^{-1}$$

$$1 \text{ amu} = 1.660539040 \times 10^{-27} \text{ kg}$$

Algorithms

As $H^{(0)} = \frac{p_1^2 + p_2^2}{2\mu} + D_e[(1 - e^{-\alpha r_1})^2 + (1 - e^{-\alpha r_2})^2]$, the “basic” energy of $|m, n\rangle$ is $E_m + E_n$.

For perturbation part $H^{(1)} = g_{rr'} p_1 p_2 + f_{rr'} r_1 r_2$ (which uses the harmonic oscillator), we know:^{iv}

$$x_{n',n} = \frac{1}{\sqrt{2}} (\sqrt{n+1} \delta_{n',n+1} + \sqrt{n} \delta_{n',n-1}) \sqrt{\frac{\hbar}{\mu\omega}}$$

$$p_{n',n} = \frac{i}{\sqrt{2}} (\sqrt{n+1} \delta_{n',n+1} - \sqrt{n} \delta_{n',n-1}) \sqrt{\mu\omega\hbar}$$

Let $P_{m,k} = p_{1,m,k} p_{2,m,k}$ and $x_{m,k} = x_{1,m,k} x_{2,m,k}$.

Then $H^{(1)} = g_{rr} (P_{m,k}) + f_{rr} (x_{m,k})$

As we only need the 1st-order correction, the result is $H = H^{(0)} + H^{(1)}$.

Tools for calculation

My own PC (Alienware 15 R2)

System: Ubuntu 16.04.3 LTS with kernel version 4.4.0-43-Microsoft

Compiler: g++ 5.4.0

Libraries: C++ standard libs, Armadillo^v

Results

The energies (in cm^{-1}) are shown as follows:

n	m		E_calculated	E_observed
0	0		0	0
1	0	+	2616.051	2614.4079
1	0	-	2625.5349	2628.4552
2	0	+	5146.1861	5144.9862
2	0	-	5146.1861	5147.2205
1	1	+	5241.5859	5243.1014
3	0	+	7576.1794	7576.3833
3	0	-	7576.1794	7576.5466
2	1	+	7757.4951	7752.2638
2	1	-	7776.463	7779.3208
4	0	+	9910.773	9911.023
4	0	-	9910.773	9911.023
3	1	+	10196.972	10188.301
3	1	-	10196.972	10194.448
5	0	\pm	12149.967	12149.458
4	1	+	12531.566	12524.628
4	1	-	12531.566	12525.202
6	0	\pm	14293.761	14291.122
7	0	\pm	16342.155	16334.162

As there is only 1st-order correction, there is some error to the observed data.

References

ⁱ Morse, P.M., 1929. Diatomic molecules according to the wave mechanics. II. Vibrational levels. *Physical Review*, 34(1), p.57.

ⁱⁱ de Laeter, J.R., Böhlke, J.K., De Bièvre, P., Hidaka, H., Peiser, H.S., Rosman, K.J.R. and Taylor, P.D.P., 2003. Atomic weights of the elements. Review 2000 (IUPAC Technical Report). *Pure and applied chemistry*, 75(6), pp.683-800.

ⁱⁱⁱ Mohr, P.J., Newell, D.B. and Taylor, B.N., 2016. CODATA recommended values of the fundamental physical constants: 2014. *Journal of Physical and Chemical Reference Data*, 45(4), p.043102.

^{iv} Zeng, J., 2008. Course on Quantum Mechanics (2nd edition).

^v Sanderson, C. and Curtin, R., 2016. Armadillo: a template-based C++ library for linear algebra. *Journal of Open Source Software*.

Appendix

Raw data

The matrix of energy is

2.69E+03	5.32E+03	7.84E+03	1.03E+04	1.26E+04	1.48E+04	1.70E+04	1.90E+04
5.31E+03	7.93E+03	1.05E+04	1.29E+04	1.52E+04	1.75E+04	1.96E+04	2.17E+04
7.84E+03	1.05E+04	1.30E+04	1.54E+04	1.77E+04	2.00E+04	2.21E+04	2.42E+04
1.03E+04	1.29E+04	1.54E+04	1.78E+04	2.02E+04	2.24E+04	2.46E+04	2.66E+04
1.26E+04	1.52E+04	1.77E+04	2.02E+04	2.25E+04	2.48E+04	2.69E+04	2.89E+04
1.48E+04	1.75E+04	2.00E+04	2.24E+04	2.47E+04	2.70E+04	2.92E+04	3.12E+04
1.70E+04	1.96E+04	2.21E+04	2.46E+04	2.69E+04	2.91E+04	3.13E+04	3.34E+04
1.90E+04	2.17E+04	2.42E+04	2.66E+04	2.89E+04	3.12E+04	3.33E+04	3.54E+04

The matrix of energy with ground state energy 0 is

0	2.63E+03	5.15E+03	7.58E+03	9.91E+03	1.22E+04	1.43E+04	1.63E+04
2.62E+03	5.24E+03	7.78E+03	1.02E+04	1.25E+04	1.48E+04	1.69E+04	1.90E+04
5.15E+03	7.76E+03	1.03E+04	1.27E+04	1.51E+04	1.73E+04	1.94E+04	2.15E+04
7.58E+03	1.02E+04	1.27E+04	1.52E+04	1.75E+04	1.97E+04	2.19E+04	2.39E+04
9.91E+03	1.25E+04	1.51E+04	1.75E+04	1.98E+04	2.21E+04	2.42E+04	2.63E+04
1.22E+04	1.48E+04	1.73E+04	1.97E+04	2.20E+04	2.43E+04	2.65E+04	2.85E+04
1.43E+04	1.69E+04	1.94E+04	2.19E+04	2.42E+04	2.64E+04	2.86E+04	3.07E+04
1.63E+04	1.90E+04	2.15E+04	2.39E+04	2.63E+04	2.85E+04	3.06E+04	3.27E+04

Credits

Ye Zuyang, the teaching assistant, who helped me a lot on this course and noticed me that the final matrix should not be diagonalized.

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