

# Molecular Vibrations

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# Why Estimate Molecular Vibrations?

- ▶ Simulation of vibrational spectrum (identification of molecules)
- ▶ Vibrational corrections to enthalpy
- ▶ (Small) vibrational corrections to polarizability and other properties
- ▶ Understanding of vibrational motion could assist dynamics experiments and “mode-selective” chemistry

## Small Vibrations in Classical Mechanics

The classic reference is Wilson, Decius, and Cross, *Molecular Vibrations* (Dover, New York, 1980). Cheap book, makes a good reference.

Let us focus on purely classical systems at first; all the results carry over to quantum mechanics.

For small vibrations, the motion of atom  $\alpha$  away from its equilibrium value may be described by  $\Delta x_\alpha, \Delta y_\alpha, \Delta z_\alpha$ , with kinetic energy

$$T = \frac{1}{2} \sum_{\alpha=1}^N M_\alpha \left[ \left( \frac{d\Delta x_\alpha}{dt} \right)^2 + \left( \frac{d\Delta y_\alpha}{dt} \right)^2 + \left( \frac{d\Delta z_\alpha}{dt} \right)^2 \right]$$

If we switch to mass-weighted coordinates, such as  $q_1 = \sqrt{M_1}\Delta x_1$ ,  $q_2 = \sqrt{M_1}\Delta y_1$ ,  $q_3 = \sqrt{M_1}\Delta z_1$ ,  $q_4 = \sqrt{M_2}\Delta x_2$ , etc., then the kinetic energy operator becomes simpler since the mass factors are now absorbed

$$T = \frac{1}{2} \sum_{i=1}^{3N} \dot{q}_i^2$$
$$V = V_0 + \sum_{i=1}^{3N} \left( \frac{\partial V}{\partial q_i} \right)_0 q_i + \frac{1}{2} \sum_{i=1}^{3N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \dots$$

(1)

Remember that at equilibrium,  $(\partial V / \partial q_i)_0 = 0$ ; we can also set  $V_0 = 0$ . Also abbreviate  $(\partial^2 V / \partial q_i \partial q_j)_0$  as just  $f_{ij}$ .

## Newton's Equations of Motion

We can rewrite Newton's equations of motion as

$$\frac{d}{dt} \frac{\partial T}{\partial \dot{q}_j} + \frac{\partial V}{\partial q_j} = 0 \quad j = 1, 2, \dots, 3N$$

or

$$\ddot{q}_j + \sum_{i=1}^{3N} f_{ij} q_i = 0$$

A possible solution to this equation is

$$q_i = a_i \cos(\sqrt{\lambda} t + \phi)$$

where the angular frequency is  $\sqrt{\lambda}$ ; this is just  $\sqrt{k/m}$  in harmonic oscillator — the  $m$  has been absorbed by the mass-weighted coordinate system used here!

Substitute the last expression into the differential equations to get

$$\sum_{i=1}^{3N} (f_{ij} - \delta_{ij}\lambda) a_i = 0 \quad j = 1, 2, \dots, 3N$$

or in matrix notation, just  $\underline{\underline{\mathbf{F}}} \underline{\mathbf{a}} = \lambda \underline{\mathbf{a}}$ . *This is an eigenvalue equation!* We have a solution to this system of  $3N$  linear equations only if  $\lambda$  has special values obtainable from the secular determinant

$$\begin{vmatrix} f_{11} - \lambda & f_{12} & f_{13} & \cdots & f_{1,3N} \\ f_{21} & f_{22} - \lambda & f_{23} & \cdots & f_{2,3N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ f_{3N,1} & f_{3N,2} & f_{3N,3} & \cdots & f_{3N,3N} - \lambda \end{vmatrix} = 0$$

## Normal Modes of Vibration

The matrix eigenvalue equation is equivalent to matrix diagonalization which is equivalent to solving the secular determinant for each  $\lambda$  ( $N$  of them). Once we have the eigenvalues  $\lambda_k$  we can get the corresponding eigenvectors  $\underline{\mathbf{a}}_k$ , giving the motion of each atom for the given eigenvalue  $\lambda_k$ :

$$q_{ik} = a_{ik} \cos \left( \sqrt{\lambda_k} t + \phi_k \right).$$

The eigenvectors  $\underline{\mathbf{a}}_k$  are the *normal modes* of vibration. *For each normal mode, all the atoms move with the same frequency and phase, but with different amplitudes.*

## Normal Coordinates

We can define a new set of coordinates using the normal modes. This gives us the “normal coordinates”

$$Q_k = \sum_{i=1}^{3N} a_{ik} q_i \quad k = 1, 2, \dots, 3N$$

Since the eigenvectors of a real, symmetric matrix ( $\underline{\mathbf{F}}$ ) are orthogonal,  $T$  and  $V$  become diagonal (no cross terms):

$$T = \frac{1}{2} \sum_{k=1}^{3N} \dot{Q}_k^2$$
$$V = \frac{1}{2} \sum_{k=1}^{3N} \lambda_k Q_k^2$$

The Hamiltonian is separable in this representation!



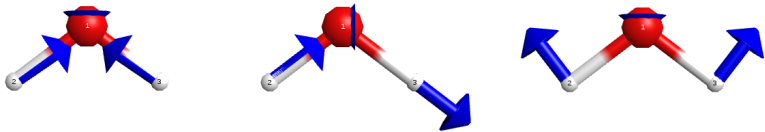


Figure 1: Normal modes of vibration for the H<sub>2</sub>O molecule. From left to right: the  $a_1$  symmetric stretch, the  $b_2$  antisymmetric stretch, and the  $a_1$  bend.

## Transition to Quantum Mechanical Models

What happens for quantum mechanics, and for polyatomic molecules? Use Harmonic Oscillator model.

- ▶  $3N-6$  frequencies ( $3N-5$  for linear molecules); the rest are translations and rotations with zero frequency
- ▶ In normal mode coordinates, Hamiltonian is separable: wavefunction is a product and energy is a sum. Total vibrational energy is  $\sum_i \omega_i \hbar (v_i + 1/2)$
- ▶ Minimum energy (due to uncertainty principle) is “zero point vibrational energy” (ZPVE or ZPE), where  $v_i = 0$  for all  $i$ .  
$$\text{ZPVE} = \frac{1}{2} \hbar \sum_i \omega_i$$

## How Would We Get Harmonic Frequencies for a Molecule?

- ▶ Easy — just diagonalize the second derivative matrix  $\underline{\underline{\mathbf{F}}}$ , called the *Hessian*. The frequencies  $\omega_i$  are the square roots of the eigenvalues,  $\sqrt{\lambda_i}$ . Recall  $f_{ij} = (\partial^2 V / \partial q_i \partial q_j)$ .
- ▶ Potential energy  $V$  is just  $E_e$  (B.O. approximation!): Need  $\partial E_e^2 / \partial q_i \partial q_j$ .
- ▶ Compute second derivative of  $E_e$  in terms of Cartesian displacements ( $x_\alpha, y_\alpha, z_\alpha$ , call them  $\tilde{q}_i$ ) and it's easy to transform to mass-weighted coordinates, using  $\underline{\underline{\mathbf{F}}} = \underline{\underline{\mathbf{M}}}^{-1/2} \underline{\underline{\tilde{\mathbf{F}}}} \underline{\underline{\mathbf{M}}}^{-1/2}$ .
- ▶ How do we get  $\partial^2 E_e / \partial x_\alpha \partial y_\beta$ , etc? Need second derivative of electronic energy vs nuclear coordinates. Compute *analytically* (using formula) or *numerically* from finite differences of energies or gradients:

$$\frac{\partial^2 E_e}{\partial x_\alpha \partial y_\beta} \approx \left[ \left( \frac{\partial E_e}{\partial y_\beta} \right) \Big|_{x_\alpha = x_{\alpha 0} + \Delta x_\alpha} - \left( \frac{\partial E_e}{\partial y_\beta} \right) \Big|_{x_\alpha = x_{\alpha 0} - \Delta x_\alpha} \right] / 2\Delta x_\alpha.$$

## Analytic Hessian Better than Numerical

- ▶ In principle, time required is similar for analytic vs numerical (note: for benzene HF/6-31G\*, energy takes < 1 second, gradient takes 2 s, freq takes 57 s on my desktop computer)
- ▶ Can need gradients from many displaced geometries — up to  $6N$  (+ and - for each of  $3N$  coordinates) — unless reduced by point group symmetry
- ▶ Numerical Hessian contains numerical errors (divide small number by small number)
- ▶ (Can land on wrong solution if displacement drops symmetry)

## Availability of Analytic Derivatives

Method	Gradient	Hessian
HF, DFT	Y	Y
CI	Y	N
CCSD, CCSD(T)	Y	S
MP2	Y	S
CASSCF	Y	S
CIS	Y	Y
EOM-CCSD	S	N
TD-DFT	S	N

S = available in some packages; Y = widely available

## Approximate Average Errors in Harmonic Frequencies

(Using polarized double and triple zeta basis sets)

Method	Error
HF	11%
CISD	4-6%
CCSD	1-4%
CCSD(T)	1-3%

Anharmonicity accounts for another  $\sim 2-3\%$  difference from experimental fundamental frequencies. Many workers employ *scaling factors* for each level of theory to better predict fundamental frequencies.

# Example Application

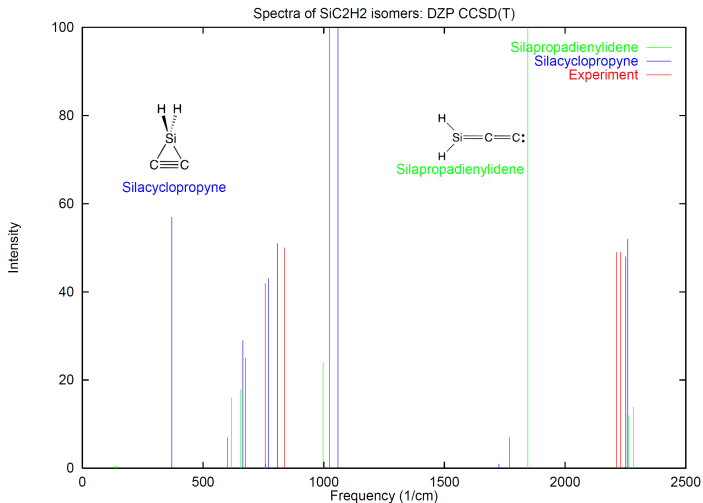


Figure 2: Computed spectra of 2 isomers of SiC<sub>2</sub>H<sub>2</sub> compared to experimental data. Intensities of peaks help with assignment.

## Scaling ZPVE's

In an enlightening paper, Grev, Janssen, and Schaefer [*J. Chem. Phys.* **95**, 5128 (1991)] showed that using scaled fundamental frequencies to estimate the ZPVE is *not* necessarily better than using unscaled frequencies. The reason is anharmonicity. If ZPVE's use scaling, they should have a *different* scaling factor than the individual frequencies.

$$G(v) = \sum_r \omega_r \left( v_r + \frac{1}{2} \right) + \sum_{r \geq s} \chi_{rs} \left( v_r + \frac{1}{2} \right) \left( v_s + \frac{1}{2} \right) + \dots,$$

$$\Delta^{harm} = G(0) - ZPVE^{harm} = \frac{1}{4} \sum_r \chi_{rr} + \frac{1}{4} \sum_{r > s} \chi_{rs}.$$

$$\Delta^{fund} = G(0) - ZPVE^{fund} = -\frac{3}{4} \sum_r \chi_{rr} - \frac{1}{4} \sum_{r > s} \chi_{rs}.$$



# Characterization of Stationary Points

- ▶ A *stationary point* is a geometry  $\tilde{\mathbf{q}}$  for which the gradient  $\partial E_e(\tilde{\mathbf{q}})/\partial \tilde{q}_i$  for all coordinates  $\tilde{q}_i$ : can be a (global or local) PES minimum, transition state, or higher order saddle point
- ▶ The *Hessian Index* is the number of negative force constants (corresponding to imaginary vibrational frequencies, often printed as negative frequencies)
- ▶ For a minimum, verify that there are no imaginary frequencies
- ▶ For a transition state, verify there is exactly one unique imaginary frequency

## Example Frequency Computation on H<sub>2</sub>O Using Psi4

```
memory 1 gb

molecule h2o {
  O
  H 1 0.946
  H 1 0.946 2 104.66
}

set basis 6-31G(d)
optimize('scf')
frequencies('scf')
```

==> Optimization Summary <==

Measures of convergence in internal coordinates in au.

Step	Total Energy	Delta E	MAX Force	RMS Force	MAX Disp	RMS Disp
1	-76.010694015	-76.010694015	0.002980	0.002333	0.018621	0.011082
2	-76.010718609	-0.000024594	0.000793	0.000674	0.003884	0.002338
3	-76.010720657	-0.000002047	0.000005	0.000005	0.000025	0.000015

Guess geometry was good, so optimization completes rapidly (3 steps).

==> Coupled-Perturbed RHF Solver <==

Maxiter = 100  
Convergence = 1.000E-06  
Number of equations = 9

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Iter	Residual RMS	Max RMS	Remain	Time [s]
1	5.641e-01	7.913e-01	9	0
2	1.281e-01	1.617e-01	9	0
3	2.847e-02	4.582e-02	9	0
4	3.616e-03	5.984e-03	9	0
5	6.563e-04	9.567e-04	9	0
6	1.268e-04	1.936e-04	9	0
7	1.772e-05	3.157e-05	8	0
8	3.463e-06	7.071e-06	5	0
9	8.387e-07	1.536e-06	4	0
10	2.671e-07	1.862e-07	0	0

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Analytic 2nd derivative involves solving the Coupled-Perturbed Hartree-Fock (CPHF) Equations

Freq [cm <sup>-1</sup> ]	1826.6573	4070.3428	4188.6298
Irrep	A1	A1	B2
Reduced mass [u]	1.0823	1.0455	1.0829
Force const [mDyne/A]	2.1277	10.2057	11.1935
Turning point v=0 [a0]	0.2468	0.1682	0.1629
RMS dev v=0 [a0 u <sup>-1/2</sup> ]	0.1815	0.1216	0.1199
IR activ [km/mol]	107.2809	18.2191	58.1675
Char temp [K]	2628.1532	5856.3170	6026.5058
-----			
1	O	0.00 -0.00 -0.07	0.00 0.00 0.05
2	H	-0.00 0.43 0.56	0.00 0.58 -0.40
3	H	-0.00 -0.43 0.56	-0.00 -0.58 -0.40
			0.00 -0.07 0.00
			-0.00 0.56 -0.43
			-0.00 0.56 0.43

Summary of computed vibrational frequencies, their symmetries, IR intensities, and normal modes.

==> Thermochemistry Energy Analysis <==

Raw electronic energy, E0

Total E0, Electronic energy at well bottom at 0 [K] -76.01072066 [Eh]

Zero-point energy, ZPE\_vib = Sum\_i nu\_i / 2

Electronic ZPE	0.000 [kcal/mol]	0.000 [kJ/mol]	0.000000 [Eh]	
Translational ZPE	0.000 [kcal/mol]	0.000 [kJ/mol]	0.000000 [Eh]	
Rotational ZPE	0.000 [kcal/mol]	0.000 [kJ/mol]	0.000000 [Eh]	
Vibrational ZPE	14.418 [kcal/mol]	60.325 [kJ/mol]	0.022976 [Eh]	5042.815 [cm <sup>-1</sup> ]
Correction ZPE	14.418 [kcal/mol]	60.325 [kJ/mol]	0.022976 [Eh]	5042.815 [cm <sup>-1</sup> ]
Total ZPE, Electronic energy at 0 [K]			-75.987743 [Eh]	

Zero-point vibrational energy (ZPVE) is added to the electronic energy to get the energy at 0K.

Enthalpy,  $H_{trans} = E_{trans} + k_B * T$

Electronic H	0.000 [kcal/mol]	0.000 [kJ/mol]	0.00000000 [Eh]
Translational H	1.481 [kcal/mol]	6.197 [kJ/mol]	0.00236046 [Eh]
Rotational H	0.889 [kcal/mol]	3.718 [kJ/mol]	0.00141628 [Eh]
Vibrational H	14.419 [kcal/mol]	60.329 [kJ/mol]	0.02297799 [Eh]
Correction H	16.789 [kcal/mol]	70.245 [kJ/mol]	0.02675473 [Eh]
Total H, Enthalpy at 298.15 [K]			-75.98396593 [Eh]

Gibbs free energy,  $G = H - T * S$







Electronic G	0.000 [kcal/mol]	0.000 [kJ/mol]	0.00000000 [Eh]
Translational G	-8.837 [kcal/mol]	-36.975 [kJ/mol]	-0.01408304 [Eh]
Rotational G	-2.205 [kcal/mol]	-9.225 [kJ/mol]	-0.00351356 [Eh]
Vibrational G	14.418 [kcal/mol]	60.325 [kJ/mol]	0.02297662 [Eh]
Correction G	3.376 [kcal/mol]	14.125 [kJ/mol]	0.00538001 [Eh]
Total G, Free enthalpy at 298.15 [K]			-76.00534064 [Eh]

Summary of Enthalpy (H) and Gibbs free energy (G) at requested temperature.

# Visualization

Tools like WebMO can animate normal modes, and simulate the IR spectrum using a simple Gaussian broadening


Vibrational Modes

Mode	Symmetry	Frequency (cm <sup>-1</sup> )	IR (Raman) Intensity	Actions
1	A1	1826.2801	1	 
2	A1	4072.6366	1	 
3	B1	4190.9852	1	 

Frequency Scale Factor: 1.0

Normal Mode Amplitude: 1.0

Animation Speed: 50

IR Spectrum: 

Peak Width (cm<sup>-1</sup>): 40

