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


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

\[
T = \frac{1}{2} \sum_{i=1}^{3N} \dot{q}_i^2
\]

\[
V = V_0 + \sum_{i=1}^{3N} \left( \frac{\partial V}{\partial q_i} \right)_0 q_i + \frac{1}{2} \sum_{i=1}^{3N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \cdots
\]

(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

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

or

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

A possible solution to this equation is

\[
q_i = a_i \cos \left( \sqrt{\lambda} t + \phi \right)
\]

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

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

or in matrix notation, just \( \mathbf{F} \mathbf{a} = \lambda \mathbf{a} \). 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

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

\[ Q_k = \sum_{i=1}^{3N} a_{ik} q_i \quad k = 1, 2, \ldots, 3N \]

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

\[ T = \frac{1}{2} \sum_{k=1}^{3N} \dot{Q}_k^2 \]

\[ V = \frac{1}{2} \lambda_k Q_k^2 \]

The Hamiltonian is separable — in normal mode coordinates, we can solve for the motion in each coordinate separately!
Degeneracy. From the discussion of the secular equation, it is seen that there are $3N - 6$ $\lambda$'s which are not zero and therefore $3N - 6$ modes of vibration and frequencies (for nonlinear molecules). However, the frequencies are not necessarily all distinct; some of the roots of the secular equation may occur more than once. Such frequencies are said to be degenerate. When a degenerate value of $\lambda$ is substituted in Eq. (10), Sec. 2-2, the resulting equations do not suffice to determine uniquely the quantities $l_{ik}$; instead there will be an infinite number of sets of values for

![Diagram of a water molecule with normal modes of vibration labeled $v_1$, $v_2$, and $v_3$.]

Fig. 2-1. Normal modes of vibration of the water molecule in mass-weighted coordinates. To represent actual relative motions in space, the arrows representing displacements of the oxygen atom should be only one-fourth as long as here shown.

![Diagram of an equilateral triangular molecule with normal modes of vibration labeled 1, 2, and 3.]

![Diagram of an alternative choice of the normal modes of vibration labeled 2' and 3'.]

Fig. 2-2. Normal modes of vibration for equilateral triangular type molecules. (a) One choice of the normal modes of vibration. (b) Alternative choice of the normal modes of motion for the degenerate frequencies. $2' = 3 + 2, 3' = 3 - 2$.

the $l_{ik}$'s which will satisfy the equations. These sets are, however, related. If $\lambda$ is doubly degenerate, i.e., occurs twice, then there will be only two independent sets of coefficients $l_{ik}$ and therefore two independent
Polyatomic Molecules

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 $\sum_i \omega_i \hbar (\nu_i + 1/2)$

- Minimum energy (due to uncertainty principle) is “zero point vibrational energy” (ZPVE or ZPE), where $\nu_i = 0$ 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 $F$, called the Hessian. The frequencies $\omega_i$ are the square roots of the eigenvalues, $\sqrt{\lambda_i}$.

- Where do we get $F$?

- 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 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
\( \mathbf{F} = \mathbf{M}^{-1/2} \tilde{\mathbf{F}} \mathbf{M}^{-1/2} \).

- How do we get \( \partial^2 E_e / \partial x_\alpha \partial y_\beta \), etc? Need second derivative of electronic energy vs nuclear coordinates. Can compute \textit{analytically} (using formula) or \textit{numerically} from finite differences of energies or gradients:

\[
\frac{\partial^2 E_e}{\partial x_\alpha \partial y_\beta} \approx \left[ \left. \left( \frac{\partial E_e}{\partial y_\beta} \right) \right|_{x_\alpha = x_\alpha + \Delta x_\alpha} - \left. \left( \frac{\partial E_e}{\partial y_\beta} \right) \right|_{x_\alpha = x_\alpha - \Delta x_\alpha} \right] / \Delta x_\alpha
\]
Analytic Hessian Better than Numerical

- Analytic Hessian might cost \( \sim 10-30x \) cost of energy; analytic gradient costs maybe \( \sim 1.5-2x \).

- 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

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<tr>
<th>Method</th>
<th>Gradient</th>
<th>Hessian</th>
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</thead>
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<tr>
<td>HF, DFT</td>
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<td>Y</td>
</tr>
<tr>
<td>CI</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>CCSD, CCSD(T)</td>
<td>Y</td>
<td>S</td>
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<td>MP2</td>
<td>Y</td>
<td>S</td>
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<tr>
<td>CIS</td>
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<td>Y</td>
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<tr>
<td>EOM-CCSD</td>
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<td>Y</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>N</td>
<td>N</td>
</tr>
</tbody>
</table>

*S = available in some packages; Y = widely available*
Approximate Average Errors in Harmonic Frequencies

(Using polarized double and triple zeta basis sets)

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<th>Method</th>
<th>Error</th>
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</tr>
<tr>
<td>CISD</td>
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<tr>
<td>CCSD</td>
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<tr>
<td>CCSD(T)</td>
<td>1-3%</td>
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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.
Spectra of SiC2H2 isomers: DZP CCSD(T)

- Silapropadienyldene
- Silacyclopropyne
- Experiment
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.

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

\[
\Delta_{\text{fund}} = G(0) - ZPVE_{\text{fund}} = -\frac{3}{4} \sum_r \chi_{rr} - \frac{1}{4} \sum_{r > s} \chi_{rs},
\]

\[
\Delta_{\text{harm}} = G(0) - ZPVE_{\text{harm}} = \frac{1}{4} \sum_r \chi_{rr} + \frac{1}{4} \sum_{r > s} \chi_{rs}.
\]
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.
There are 5 alpha and 5 beta electrons
Requested basis set is STO-3G
There are 4 shells and 7 basis functions
A cutoff of 1.00-10 yielded 10 shell pairs
There are 4 function pairs

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Convergence criterion met

SF time: CPU 0.08 s wall 0.00 s
Final Alpha MO Eigenvalues

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<th>4</th>
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Final Alpha MO Coefficients

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</table>

Final Alpha density matrix.

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<td>-0.0112263</td>
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<td>0.2752409</td>
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</table>

Molecular Point Group: C2v 
Largest Abelian Subgroup: C2v 
Nuclear Repulsion Energy = 8.9077080996 hartrees
### Orbital Energies (e.u.) and Symmetries

**Alpha MOs, Restricted**
- Virtual
  - -20.252 -1.258 -0.594 -0.460 -0.393
  - 1 \( 1 \text{A1} \) 2 \( 1 \text{B1} \) 3 \( 3 \text{A1} \) 1 \( 1 \text{B2} \)

**Beta MOs, Restricted**
- Virtual
  - -20.252 -1.258 -0.594 -0.460 -0.393
  - 1 \( 1 \text{A1} \) 2 \( 1 \text{A1} \) 3 \( 3 \text{A1} \) 1 \( 1 \text{B2} \)

**Mulliken Net Atomic Charges**
- Atom
  - O: 0.165318
  - H: 0.165318

**Sum of atomic charges = 0.000000**

### Cartesian Multipole Moments

- Charge (ESU x 10^10)
  - 0.0000
- Dipole Moment (Debye)
  - X: 0.0000
  - Y: 0.0000
  - Z: -1.7094
- Quadrupole Moments (Debye-Ang)
  - XX: -4.4859
  - XY: 0.0000
  - XZ: 6.1256
- Octapole Moments (Debye-Ang^2)
  - XXX: 0.0000
  - YXX: 0.0000
  - ZXX: -5.3331
  - YYY: 0.0000
  - ZYY: 0.0000
  - ZZZ: -0.1747
- Hexadecapole Moments (Debye-Ang^3)
  - XXXX: -6.7321
  - XYY: 0.0000
  - XZYZ: -1.4596
  - XXYY: 0.0000
  - XXZZ: 0.0000
  - YXXZ: 0.0000
  - YZZ: 0.0000
  - ZXXX: 0.0000
  - ZYY: 0.0000
  - ZZ: -5.2191

**VIBRATIONAL ANALYSIS**

**VIBRATIONAL FREQUENCIES (CM^-1) AND NORMAL MODES**

**INFRARED INTENSITIES (RM/ML)**

**Frequencies:**
- 2169.95
- 4414.60
- 4392.63

**IR Intens:**
- 7.245
- 44.303
- 29.972

**Raman Active:**
- X: 0.000
- Y: 0.000
- Z: 0.000
- X: 0.000
- Y: 0.000
- Z: 0.000

**STANDARD THERMODYNAMIC QUANTITIES AT 298.18 K AND 1.00 ATM**

This Molecule has 0 Imaginary Frequencies
Zero point vibrational energy: 15.302 kcal/mol
Atom 1 Element O Has Mass 15.99491
Atom 2 Element H Has Mass 1.00783
Atom 3 Element H Has Mass 1.00783
Molecular Mass: 18.010570 amu
Principal axes and moments of inertia in atomic units:

<table>
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<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
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<td>0.00000</td>
</tr>
<tr>
<td>Y</td>
<td>0.00000</td>
<td>0.00000</td>
<td>1.00000</td>
</tr>
<tr>
<td>Z</td>
<td>0.00000</td>
<td>1.00000</td>
<td>0.00000</td>
</tr>
</tbody>
</table>

Rotational Symmetry Number is 2
The Molecule is an Asymmetric Top
Translational Enthalpy: 0.889 kcal/mol
Rotational Enthalpy: 0.889 kcal/mol
Vibrational Enthalpy: 15.303 kcal/mol
gas constant (RT): 0.593 kcal/mol
Translational Entropy: 34.609 cal/mol.K
Rotational Entropy: 10.672 cal/mol.K
Vibrational Entropy: 0.001 cal/mol.K
Total Enthalpy: 17.673 kcal/mol
Total Entropy: 45.281 cal/mol.K
Archival summary:

Thank you very much for using Q-Chem. Have a nice day.

Total job wall time: 3.00 s
Q-Chem finished
cicero.chemistry.gatech.edu on Fri Dec 15 14:51:32 EST 2000.

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