Molecular Vibrations

Consider a molecule with N atoms and suppose we know how the energy varies as we move the atoms. Then the total electronic energy may be thought of as a function of the coordinates of each atom. So $E = E(x_1, x_2, \cdots x_{3N})$ where $x_1, x_2,$ and x_3 are the coordinates of atom 1, $x_4, x_5,$ and x_6 of atom 2, and so on. Now expand this function about the *equilibrium* position $x_1^0, x_2^0, x_3^0, x_4^0, \cdots x_{3\mathrm{N}}^0$.

$$E = E(\text{equilibrium}) + \sum_{i=1}^{3N} \left(\frac{\partial E}{\partial x_i}\right)_{x_i^0} (x_i - x_i^0) +$$
$$\sum_{i,j}^{3N} \left(\frac{\partial^2 E}{\partial x_i \partial x_j}\right)_{x_i^0 x_j^0} (x_i - x_i^0)(x_j - x_j^0)/2 + \cdots$$

Since the equilibrium position is a minimum in *E*, all of the first derivatives vanish.

$$\left(\frac{\partial E}{\partial x_i}\right)_{x_i^0} \equiv 0$$

Now, represent the second derivative matrix at equilibrium by f_{ij}

$$f_{ij} = \left(\frac{\partial^2 E}{\partial x_i \partial x_j}\right)_{eq.}$$

and let $x_i - x_i^0 = q_i$.

Then, keeping terms up to quadratic (the harmonic approximation), we have

$$E = E_{eq} + \frac{1}{2}\sum_{i,j}^{3N} f_{ij} q_i q_j.$$

Keep in mind that this energy represents the change in the electronic energy as the nuclei move. This is also the potential energy function for nuclear motion.

To keep our notation consistent with convention, we are going to replace *E* by *V* and E_{eq} by V^0. A trivial but potentially confusing change. So,

$$V = V^0 + \frac{1}{2}\sum_{ij} f_{ij} q_i q_j.$$

The kinetic energy for the nuclei is $T = \frac{1}{2}\sum_{i=1}^{3N} m_i \dot{x}_i^2$ where $\dot{x}_i = \frac{dx_i}{dt}$ and m_i is the mass of the ith coordinate; i. e., m_1, m_2, and m_3 are the same and are the mass of atom 1, etc.

Note, since $x_i - x_i^0 = q_i$, we have $\dot{x}_i = q_i$

$\therefore T = \frac{1}{2}\sum m_i \dot{q}_i^2$.

Let's define a set of coordinates $\{a_i\}$ called mass-weighted coordinates

$$a_i = \sqrt{m_i} q_i$$

Then,

$$V = V^0 + \frac{1}{2}\sum_{i,j} \frac{f_{ij}}{\sqrt{m_i m_j}} a_i a_j$$

or

$$V = V^0 + \frac{1}{2}\sum_{i,j} F_{ij} a_i a_j$$

where $F_{ij} = \frac{f_{ij}}{\sqrt{m_i m_j}}$

also $T = \frac{1}{2}\sum_{i=1}^{3N} m_i \dot{q}_i^2 = \frac{1}{2}\sum_{i=1}^{3N} \dot{a}_i^2$.

The equations of motion of the atoms are given by Lagrange's equations.

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{a}_i}\right) + \left(\frac{\partial V}{\partial a_i}\right) = 0 \qquad i = 1, 2, \ldots 3N$$

So, $\frac{\partial T}{\partial \dot{a}_i} = \dot{a}_i$ and $\therefore \frac{d}{dt}\left(\frac{\partial T}{\partial \dot{a}_i}\right) = \ddot{a}_i$

also $\frac{\partial V}{\partial a_i} = \sum_{j=1}^{3N} F_{ij} a_j$

So, $\ddot{a}_i + \sum_{j=1}^{3N} F_{ij} a_j = 0$.

A particular solution to these equations may be found by the ansatz

$$a_i = A_i \cos(\omega t + \varepsilon)$$

where ε is an arbitrary phase.

Aside:

$$\ddot{a}_i = -\omega^2 A_i \cos(\omega t + \varepsilon)$$

or

$$\ddot{a}_i = -\omega^2 a_i$$

$$\therefore\ -\omega^2 a_i + \sum_{j=1}^{3N} F_{ij} a_j = 0$$

Define the matrix **F**

$$(\mathbf{F})_{ij} = F_{ij} = \frac{f_{ij}}{\sqrt{m_i m_j}}$$

and the vector $\vec{a} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_{3N} \end{pmatrix}$.

Then the equations of motion become

$$\mathbf{F}\,\vec{a} = \omega^2\,\vec{a}.$$

ω^2 is the eigenvalue and $\vec{a}$ is an eigenvector of **F**. Since **F** is 3N × 3N, it has 3N eigenvalues and 3N eigenvectors. Let's label them

$$\mathbf{F}\,\vec{a}_i = \omega_i^2\,\vec{a}_i \qquad i = 1;\cdot\cdot 3N$$

For every vector $\vec{a}_i$, we have a ω_i^2. The $\vec{a}_i$ define what are called normal modes, and ω_i is the frequency of the ith normal mode.

Recall $\vec{a}_i = \begin{pmatrix} a_{1i} \\ a_{2i} \\ a_{3i} \\ \vdots \\ a_{3N,i} \end{pmatrix}$

and $a_{ki} = \sqrt{m_k}\, q_{ki} = A_{ki} \cos(\omega_i t + \varepsilon)$ or $q_{ki} = \dfrac{A_{ki}}{\sqrt{m_k}} \cos(\omega_i t + \varepsilon)$; $k = 1, \cdots 3N$

for a given normal mode (the ith) each coordinate hs the same frequency dependence. Indeed, we may write

$$\vec{a}_i = \begin{pmatrix} A_{1i}/\sqrt{m_1} \\ A_{2i}/\sqrt{m_2} \\ \vdots \\ A_{3N,i}/\sqrt{m_{3N}} \end{pmatrix} \cos(\omega_i t + \varepsilon)$$

Alternative (Matrix-Oriented) Formulations

Since **F** is symmetric and real, it may be diagonalized by a unitary matrix. Accordingly, let **U** diagonalize **F** where

$$\mathbf{U}^{+}\mathbf{U} = \mathbf{U}\mathbf{U}^{+} = \mathbf{1}.$$

Then, $\mathbf{U}^{+}\mathbf{F}\mathbf{U} = \boldsymbol{F} = \begin{pmatrix} \omega_1^2 & & & & \\ & \omega_2^2 & & \text{O} & \\ & & \omega_3^2 & & \\ & \text{O} & & \ddots & \\ & & & & \omega_{3N}^2 \end{pmatrix}$

The equation

$$V = V^0 + \frac{1}{2} \sum F_{ij} a_i a_j$$

may be rewritten as

$$V = V^0 + \frac{1}{2} \vec{a}^{+}\, \mathbf{F}\, \vec{a},$$

and, since $\mathbf{F} = \mathbf{U}\ \boldsymbol{F}\,\mathbf{U}^{+}$,

one has $\vec{a}^{+}\mathbf{F}\,\vec{a} = \vec{a}^{+}\mathbf{U}\ \boldsymbol{F}\,\mathbf{U}^{+}\vec{a}$ **.**

Let $\mathbf{U}^{+}\vec{a} = \vec{Q}$ then $\vec{a}^{+}\mathbf{U} = \vec{Q}^{+}$

So,

$$V = V^{0} + \frac{1}{2}\vec{Q}^{+}\ \boldsymbol{F}\ \vec{Q}$$
$$= V^{0} + \frac{1}{2}\sum_{k\ell} Q_k\,\omega_k^2\,\delta_{k\ell}\,Q_\ell$$

So,

$$V = V^{0} + \frac{1}{2}\sum_{k} Q_k^2\ \omega_k^2\,.$$

Now,

$$T = \frac{1}{2}\sum_{i=1}^{3N}\dot{a}_i^2 \equiv \frac{1}{2}\dot{\vec{a}}^{+}\dot{\vec{a}}$$

but $\vec{a} = \mathbf{U}\vec{Q}$.

So, $\dot{\vec{a}} = \mathbf{U}\dot{\vec{Q}}$

and $\therefore$

$$T = \frac{1}{2}\dot{\vec{Q}}^{+}\mathbf{U}^{+}\mathbf{U}\dot{\vec{Q}} = \frac{1}{2}\dot{\vec{Q}}^{+}\dot{\vec{Q}}$$
$$= \frac{1}{2}\sum_{k}\ \dot{Q}_k^2$$

$$\therefore \boldsymbol{\mathcal{E}} = T + V = \frac{1}{2}\sum_{k}\ \dot{Q}_k^2 + \frac{1}{2}\sum_{k}\ Q_k^2\,\omega_k^2$$

$$\boldsymbol{\mathcal{E}} = \sum_{k}\ \frac{1}{2}\left(\dot{Q}_k^2 + \omega_k^2 Q_k^2\right)$$

Using Lagrange's equations $\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{Q}_k}\right)+\frac{\partial V}{\partial Q_k}=0$, the equations of motion become

$$\ddot{Q}_k+\omega_k^2\,Q_k=0$$

and, therefore, the motion is harmonic with frequency ω_k.

In general,

$$Q_k=A\cos\omega_k t+B\sin\omega_k t$$

where

$$Q_k\left(0\right)=A$$

$$\dot{Q}_k\left(0\right)=-B\omega_k$$

or

$$Q_k=Q_k\left(0\right)\cos\omega_k t-\frac{\dot{Q}_k\left(0\right)}{\omega_k}\sin\omega_k t$$

Clearly, the time dependence of the normal coordinate depends on the initial conditions. This is equivalent to writing the solution as

$$Q_k=C_k\cos(\omega_k t+\varepsilon)$$