Normal Mode Coordinates

In cartesian coordinates, expanding the potential operator around a point $\mathbf{x}_0$, the Hamiltonian can be written

$$\begin{aligned}\hat{H}(\mathbf{x}) &= \sum_i -\frac{\hbar^2}{2m_i}\frac{\partial^2}{\partial x_i^2} + V_0 + \sum_i \frac{\partial V}{\partial x_i}(x_i - x_{0i}) \\ &\quad + \sum_{i,j}\frac{1}{2}\frac{\partial^2 V}{\partial x_i \partial x_j}(x_i - x_{0i})(x_j - x_{0j}) + \ldots \end{aligned} \tag{1}$$

where V_0 is $V(\mathbf{x}_0)$ and the derivatives are evaluated at $\mathbf{x}_0$. If $\mathbf{x}_0$ is at a minimum energy point, then

$$\frac{\partial V}{\partial x_i} = 0 \quad \forall i \quad . \tag{2}$$

Now use mass-scaled coordinates relative to $\mathbf{x}_0$

$$x_i - x_{0i} \rightarrow \frac{1}{\sqrt{m_i}}\tilde{x}_i \quad \Longrightarrow \quad \frac{\partial}{\partial x_i} \rightarrow \sqrt{m_i}\frac{\partial}{\partial \tilde{x}_i} \tag{3}$$

so that the Hamiltonian is

$$\hat{H}(\tilde{\mathbf{x}}) = \sum_i -\frac{\hbar^2}{2}\frac{\partial^2}{\partial \tilde{x}_i^2} + V_0 + \sum_{i,j}\frac{1}{2}\mathcal{H}_{ij}\tilde{x}_i\tilde{x}_j + \ldots \tag{4}$$

where $\mathcal{H}_{ij}$ is the mass-weighted Hessian

$$\mathcal{H}_{ij} = \frac{1}{\sqrt{m_i}\sqrt{m_j}}\frac{\partial^2 V}{\partial x_i \partial x_j} \quad . \tag{5}$$

Normal coordinates, $\mathbf{q}$ are defined by an orthonormal transformation

$$\tilde{x}_i = \sum_\alpha D_{\alpha i} q_\alpha \tag{6}$$

$$\mathbf{D}^T\mathbf{D} = \mathbf{1} \tag{7}$$

where the matrix $\mathbf{D}$ contains the eigenvectors of the Hessian,

$$\mathbf{D}\mathcal{H}\mathbf{D}^T = \mathbf{w} \quad . \tag{8}$$

For reasons that will be clear below, the diagonal eigenvalue matrix $\mathbf{w}$ can be written

$$w_{ij} = \omega_i^2 \delta_{ij} \quad . \tag{9}$$

As the eigenvectors are orthonormal,

$$\sum_i \frac{\partial^2}{\partial \tilde{x}_i^2} = \sum_\alpha \frac{\partial^2}{\partial q_\alpha^2} \tag{10}$$

and so

$$\hat{H}(\mathbf{q}) = V_0 + \sum_\alpha -\frac{\hbar^2}{2}\frac{\partial^2}{\partial q_\alpha^2} + \sum_\alpha \frac{1}{2}\omega_\alpha^2 q_\alpha^2 + \ldots \tag{11}$$

Comparing this to the Hamiltonian for a harmonic oscillator,

$$\hat{H}(q) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + \frac{1}{2}m\omega^2 q^2 \quad , \tag{12}$$

the second and third terms have the form of a set of harmonic oscillators of unit mass.

A neater expression for the normal mode Hamiltonian, Eq. (11), can be made by a final transformation to dimensionless coordinates

$$q_\alpha \to \sqrt{\frac{\hbar}{\omega_\alpha}} Q_\alpha \quad \Longrightarrow \quad \frac{\partial}{\partial q_\alpha} \to \sqrt{\frac{\omega_i}{\hbar}} \frac{\partial}{\partial Q_\alpha} \tag{13}$$

$$\hat{H}(\mathbf{Q}) = V_0 + \frac{\hbar\omega_\alpha}{2}\left(\sum_\alpha -\frac{\partial^2}{\partial Q_\alpha^2} + Q_\alpha^2\right) + \ldots \tag{14}$$

Notes

1. If atomic units are used in which $\hbar = 1$ this can be written

$$\hat{H}(\mathbf{Q}) = V_0 + \frac{\omega_\alpha}{2}\left(\sum_\alpha -\frac{\partial^2}{\partial Q_\alpha^2} + Q_\alpha^2\right) + \ldots \tag{15}$$

and the frequency has units of energy.

2. In the GAUSSIAN program, the normal modes are obtained as a set of orthonormal vectors. These are the columns of $\mathbf{D}$. To transform between cartesian and dimensionless coordinates,

$$\mathbf{Q} = \tilde{\mathbf{D}}(\mathbf{x} - \mathbf{x_0}) \tag{16}$$

$$\mathbf{x} = \mathbf{x}_0 + \tilde{\mathbf{D}}'\mathbf{Q} \tag{17}$$

where the transformation matrices are no longer orthonormal, but related to the Hessian eigenvectors by

$$\tilde{D}_{\alpha i} = D_{\alpha i}\sqrt{\frac{m_i\omega_\alpha}{\hbar}} \tag{18}$$

$$\tilde{D}'_{i\alpha} = D^T_{i\alpha}\sqrt{\frac{\hbar}{m_i\omega_\alpha}} \quad . \tag{19}$$

Inserting constants, if $\mathbf{x}$ is in Å,

$$\frac{\sqrt{m_i\hbar\omega_\alpha}}{\hbar} = 15.4644\sqrt{\frac{m_i}{[\mathrm{amu}]}\frac{\hbar\omega_\alpha}{[\mathrm{eV}]}} = 0.172\sqrt{\frac{m_i}{[\mathrm{amu}]}\frac{\hbar\omega_\alpha}{[\mathrm{cm}^{-1}]}} \tag{20}$$