Normal modes and coordinates

Liu ruoxi

April 23, 2024

In cartesian coordinates, expanding the potential operator around a point x_0, the Hamiltonian can be written as

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

where V_0 is $V_{x(0)}$ and the derivatives are evaluated at x_0. If x_0 is at a minimum energy point, then

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

Now use mass-scaled coordinates relative to x_0

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

so that the Hamiltonian is

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

where H_{ij} is the mass-weighted Hessian

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

$$V(\tilde{\mathbf{x}}_\mathbf{i}) = V_0 + \frac{1}{2}\sum_{ij} H_{ij}\tilde{x}_i\tilde{x}_j + \dots \tag{6}$$

Diagonalize the Hessian matrix

$$H_{ij} = U_{i\alpha}D_{\alpha\alpha}U^\dagger_{\alpha j} \tag{7}$$

For the potential operator, we have

$$V(\tilde{\mathbf{x}}_\mathbf{i}) = V_0 + \frac{1}{2}\sum_{ij\alpha} U_{i\alpha}D_{\alpha\alpha}U^\dagger_{\alpha j}\tilde{x}_i\tilde{x}_j = V_0 + \frac{1}{2}\sum_\alpha \left(\sum_i U_{i\alpha}\tilde{x}_i\right)\left(\sum_j U^\dagger_{\alpha j}\tilde{x}_j\right)D_{\alpha\alpha} + \dots \tag{8}$$

A transformation of coordinates from the original mass-scaled coordinates $\tilde{x}_i$ to a new set of coordinates Q_α

$$Q_\alpha = \sum_i U_{i\alpha}\tilde{x}_i \tag{9}$$

Substitute formula 9 into formula 8, we have a new representation of the potential operator that

$$V(\mathbf{Q}) = V_0 + \frac{1}{2}\sum_\alpha D_{\alpha\alpha}Q_\alpha^2 + \dots \tag{10}$$

For the kinetic energy operator, we have

$$T(\tilde{\mathbf{x}}_\mathbf{i}) = \sum_i \left(-\frac{\hbar^2}{2} \frac{\partial^2}{\partial \tilde{x}_i^2} \right) \tag{11}$$

$$\frac{\partial}{\partial \tilde{x}_i} = \sum_\alpha \frac{\partial Q_\alpha}{\partial \tilde{x}_i} \frac{\partial}{\partial Q_\alpha} = \sum_\alpha U_{i\alpha} \frac{\partial}{\partial Q_\alpha} \tag{12}$$

Substitute formula 12 into formula 11, we have a new representation of the kinetic energy operator that

$$\begin{aligned} T(\mathbf{Q}) &= -\frac{1}{2} \sum_i \left(\sum_\alpha U_{i\alpha} \frac{\partial}{\partial Q_\alpha} \right) \left(\sum_i U_{i\beta} \frac{\partial}{\partial Q_\beta} \right) \\ &= -\frac{1}{2} \sum_{i\alpha\beta} U_{i\alpha} U_{i\beta} \frac{\partial^2}{\partial^2 Q_\alpha Q_\beta} \\ &= -\frac{1}{2} \sum_{\alpha\beta} \left(\sum_i U_{i\alpha} U_{i\beta} \frac{\partial^2}{\partial^2 Q_\alpha Q_\beta} \right) \end{aligned} \tag{13}$$

For the orthogonality of U, we have

$$\sum_i U_{i\alpha} U_{i\beta} = \delta_{\alpha\beta} \tag{14}$$

Substitute formula 14 into formula 13, simplify that

$$T(\mathbf{Q}) = -\frac{1}{2} \sum_{\alpha\beta} \delta_{\alpha\beta} \frac{\partial^2}{\partial^2 Q_\alpha Q_\beta} = -\frac{1}{2} \sum_\alpha \frac{\partial^2}{\partial^2 Q_\alpha} \tag{15}$$

The total Hamiltonian is

$$\hat{H}(\mathbf{Q}) = T + V = V_0 - \frac{1}{2} \sum_\alpha \left(\frac{\partial^2}{\partial Q_\alpha^2} + Q_\alpha^2 D_{\alpha\alpha} \right) + \dots \tag{16}$$

Define Q'_α as

$$Q'_\alpha = \sqrt{\omega_\alpha} Q_\alpha \tag{17}$$

where ω_α is the frequency of the normal mode α. The Hamiltonian can be written as

$$\hat{H}(\mathbf{Q}') = V_0 - \frac{1}{2} \hbar \omega_\alpha \left(\sum_\alpha \frac{\partial^2}{\partial Q'^2_\alpha} + Q'^2_\alpha \right) + \dots \tag{18}$$