Normal Mode Coordinates

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

$$\hat{H}(x) = \sum_i -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial x_i^2} + V_0 + \sum_i \frac{\partial V}{\partial x_i}(x_i - x_{0i})$$

$$+ \sum_{i,j} \frac{1}{2} \frac{\partial^2 V}{\partial x_i \partial x_j}(x_i - x_{0i})(x_j - x_{0j}) + \ldots$$

\hspace{1cm} (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

$$\frac{\partial V}{\partial x_i} = 0 \quad \forall i.$$ \hspace{1cm} (2)

Now use mass-scaled coordinates relative to $x_0$

$$x_i - x_{0i} \rightarrow \frac{1}{\sqrt{m_i}} \tilde{x}_i \quad \Rightarrow \quad \frac{\partial}{\partial x_i} \rightarrow \sqrt{m_i} \frac{\partial}{\partial \tilde{x}_i}$$ \hspace{1cm} (3)

so that the Hamiltonian is

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

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

$$\mathcal{H}_{ij} = \frac{1}{\sqrt{m_i \sqrt{m_j}}} \frac{\partial^2 V}{\partial x_i \partial x_j}. \hspace{1cm} (5)$$

Normal coordinates, $q$, are defined by an orthonormal transformation

$$\tilde{x}_i = \sum_{\alpha} D_{\alpha i} q_\alpha \hspace{1cm} (6)$$

$$D^T D = 1 \hspace{1cm} (7)$$

where the matrix $D$ contains the eigenvectors of the Hessian,

$$D \mathcal{H} D^T = w. \hspace{1cm} (8)$$

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

$$w_{ij} = \omega_i^2 \delta_{ij}. \hspace{1cm} (9)$$

As the eigenvectors are orthonormal,

$$\sum_i \frac{\partial^2}{\partial \tilde{x}_i^2} = \sum_{\alpha} \frac{\partial^2}{\partial q_\alpha^2}. \hspace{1cm} (10)$$
and so
\[
\hat{H}(q) = V_0 + \sum_{\alpha} \frac{\hbar^2}{2} \frac{\partial^2}{\partial q_{\alpha}^2} + \sum_{\alpha} \frac{1}{2} \omega_{\alpha}^2 q_{\alpha}^2 + \ldots \tag{11}
\]
Comparing this to the Hamiltonian for a harmonic oscillator,
\[
\hat{H}(q) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2} + \frac{1}{2} m \omega^2 q^2, \tag{12}
\]
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
\[
q_{\alpha} \to \sqrt{\frac{\hbar}{\omega_{\alpha}}} Q_{\alpha} \implies \frac{\partial}{\partial q_{\alpha}} \to \sqrt{\frac{\omega_{\alpha}}{\hbar}} \frac{\partial}{\partial Q_{\alpha}} \tag{13}
\]
\[
\hat{H}(Q) = V_0 + \frac{\hbar \omega_{\alpha}}{2} \left( \sum_{\alpha} -\frac{\partial^2}{\partial Q_{\alpha}^2} + Q_{\alpha}^2 \right) + \ldots \tag{14}
\]

Notes
1. If atomic units are used in which \( \hbar = 1 \) this can be written
\[
\hat{H}(Q) = V_0 + \frac{\omega_{\alpha}}{2} \left( \sum_{\alpha} -\frac{\partial^2}{\partial Q_{\alpha}^2} + Q_{\alpha}^2 \right) + \ldots \tag{15}
\]
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 \( D \). To transform between cartesian and dimensionless coordinates,
\[
Q = \tilde{D}(x - x_0) \tag{16}
\]
\[
x = x_0 + \tilde{D}'Q \tag{17}
\]
where the transformation matrices are no longer orthonormal, but related to the Hessian eigenvectors by
\[
\tilde{D}_{\alpha i} = D_{\alpha i} \sqrt{\frac{m_i \omega_{\alpha}}{\hbar}} \tag{18}
\]
\[
\tilde{D}'_{\alpha i} = D_{\alpha i} \sqrt{\frac{\hbar}{m_i \omega_{\alpha}}} \tag{19}
\]
Inserting constants, if \( x \) is in Å,
\[
\sqrt{m_i \hbar \omega_{\alpha}} \quad = \quad 15.4644 \sqrt{\frac{m_i \hbar \omega_{\alpha}}{[\text{amu}] [\text{eV}]}} = 0.172 \sqrt{\frac{m_i \hbar \omega_{\alpha}}{[\text{amu}] [\text{cm}^{-1}]}} \tag{20}
\]

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