

Molecular vibrations

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Let us assume that we minimized the energy of a given electronic state of a molecule containing M atoms $[E_n(\{\mathbf{R}_A\})]$ with respect to the position of all the atoms $\{\mathbf{R}_A\}$. In other words, we found a geometry $\{\mathbf{R}_{A,0}\}$ such that the gradient of the energy for the state Ψ_n is null:

$$\nabla_A E_n(\{\mathbf{R}_A\})|_{\{\mathbf{R}_{A,0}\}} = \mathbf{0}, \quad (1)$$

for all atoms A . To simplify our notation we will replace the nuclear coordinates of individual atoms with the vector \mathbf{R} defined as:

$$\mathbf{R} = (X_1, Y_1, Z_1, X_2, Y_2, Z_2, \dots, X_M, Y_M, Z_M), \quad (2)$$

which has $3M$ elements in total, three coordinates times the number of atoms M . Using this notation we can express the stationary condition as

$$\left. \frac{\partial E_n(\mathbf{R})}{\partial R_\alpha} \right|_{\mathbf{R}_0} = 0, \text{ for } \alpha = 1, \dots, 3M. \quad (3)$$

Neglecting the nonadiabatic couplings (Born–Oppenheimer approximation) we can compute the vibrational states at the geometry \mathbf{R}_0 by solving the nuclear Schrödinger equation:

$$\left[\hat{T}_N + E_n(\mathbf{R}) \right] \chi_{nv} = \mathcal{E}_{nv} \chi_{nv}. \quad (4)$$

To avoid computing the potential energy surface $E_n(\mathbf{R})$ at points other than \mathbf{R}_0 , we expand the electronic energy $E(\mathbf{R})$ in a Taylor series around \mathbf{R}_0 (N.B., for convenience we got rid of the electronic state label n):

$$E(\mathbf{R}) = E(\mathbf{R}_0) + \sum_{\alpha} \left. \frac{\partial E(\mathbf{R})}{\partial R_\alpha} \right|_{\mathbf{R}_0} \delta R_\alpha + \frac{1}{2} \sum_{\alpha, \beta} \left. \frac{\partial^2 E(\mathbf{R})}{\partial R_\alpha \partial R_\beta} \right|_{\mathbf{R}_0} \delta R_\alpha \delta R_\beta + \dots, \quad (5)$$

The harmonic approximation to the potential energy surface

where we introduced the quantity $\delta R_\alpha = R_\alpha - R_{\alpha,0}$, the displacement of the coordinate α with respect to the equilibrium value $R_{\alpha,0}$. Since we are at a stationary point, the linear term is null. The harmonic approximation consists in truncating the Taylor expansion of $E(\mathbf{R})$ after the quadratic term. Thus, the nuclear Hamiltonian in the harmonic approximation is given by:

$$\hat{H}_N = - \sum_{\alpha}^{3M} \frac{1}{2M_\alpha} \frac{\partial^2}{\partial R_\alpha^2} + E(\mathbf{R}_0) + \frac{1}{2} \sum_{\alpha,\beta}^{3M} H_{\alpha\beta} \delta R_\alpha \delta R_\beta, \quad (6)$$

where we introduced a compact notation for the *Hessian* matrix: $H_{\alpha\beta} = \left. \frac{\partial^2 E(\mathbf{R})}{\partial R_\alpha \partial R_\beta} \right|_{\mathbf{R}_0}$ and indicated the mass of the atom corresponding to the coordinate R_α with M_α . This Hamiltonian is quadratic with respect to the displacement of the atom coordinates (δR_α) but its form is not identical to that of the harmonic oscillator. Our next task is perform a series of coordinate transformations that will allow us to rewrite \hat{H}_N as a *sum* of harmonic oscillator Hamiltonians.

The first step is to introduce *mass-weighted displacements*, \mathbf{q} :

$$q_\alpha = \sqrt{M_\alpha} \delta R_\alpha. \quad (7)$$

In this system of coordinates the derivative with respect to R_α becomes:

$$\frac{\partial}{\partial R_\alpha} = \sum_{\beta} \frac{\partial q_\beta}{\partial R_\alpha} \frac{\partial}{\partial q_\beta} = \sqrt{M_\alpha} \frac{\partial}{\partial q_\alpha}, \quad (8)$$

so that the nuclear Hamiltonian operator simplifies to

$$\hat{H}_N = - \sum_{\alpha}^{3M} \frac{1}{2} \frac{\partial^2}{\partial q_\alpha^2} + \frac{1}{2} \sum_{\alpha,\beta}^{3M} \tilde{H}_{\alpha\beta} q_\alpha q_\beta, \quad (9)$$

$$\frac{\partial q_\beta}{\partial R_\alpha} = \frac{\partial R_\beta - R_{\beta,0}}{\partial R_\alpha} = \sqrt{M_\beta} \delta_{\alpha\beta}$$

where $\tilde{H}_{\alpha\beta}$ is the *mass-weighted Hessian*:

$$\tilde{H}_{\alpha\beta} = \left. \frac{\partial^2 E(\mathbf{R})}{\partial q_\alpha \partial q_\beta} \right|_{\mathbf{R}_0} = \frac{H_{\alpha\beta}}{\sqrt{M_\alpha M_\beta}}. \quad (10)$$

The second step in our derivation consists in transforming the coordinates so that the mass-weighted Hessian becomes diagonal. To this end we write $\tilde{H}_{\alpha\beta}$ as the matrix $\tilde{\mathbf{H}}$, with elements $(\tilde{\mathbf{H}})_{\alpha\beta} = \tilde{H}_{\alpha\beta}$. $\tilde{\mathbf{H}}$ is real and symmetric and therefore its eigenvectors form a real orthogonal matrix, that we indicate with the symbol \mathbf{L} :

Normal coordinates

$$\tilde{\mathbf{H}}\mathbf{L} = \mathbf{L}\boldsymbol{\lambda}. \quad (11)$$

The matrix $\boldsymbol{\lambda}$ is diagonal and contains the eigenvalues of $\tilde{\mathbf{H}}$. Taking advantage of the eigenvalue decomposition we can write: $\lambda_{\alpha\beta} = \delta_{\alpha\beta}\lambda_{\alpha\alpha}$

$$\frac{1}{2} \sum_{\alpha,\beta}^{3M} \tilde{H}_{\alpha\beta} q_{\alpha} q_{\beta} = \frac{1}{2} \mathbf{q}^T \tilde{\mathbf{H}} \mathbf{q} = \frac{1}{2} \mathbf{q}^T \mathbf{L} \boldsymbol{\lambda} \mathbf{L}^T \mathbf{q} = \frac{1}{2} \mathbf{Q}^T \boldsymbol{\lambda} \mathbf{Q}, \quad (12)$$

where we introduced the *normal coordinates* \mathbf{Q} , defined as:

$$\mathbf{Q} = \mathbf{L}^T \mathbf{q}. \quad (13)$$

$$Q_{\alpha} = \sum_{\beta} L_{\alpha\beta}^T q_{\beta} = \sum_{\beta} L_{\beta\alpha} q_{\beta}$$

It can be proven that the kinetic energy operator does not change form upon transformation from the mass-weighted to the normal coordinates, so that the nuclear Hamiltonian in normal coordinates is:

$$\hat{H}_N = \sum_{\alpha}^{3M} \left[-\frac{1}{2} \frac{\partial^2}{\partial Q_{\alpha}^2} + \frac{1}{2} \lambda_{\alpha} Q_{\alpha}^2 \right] = \sum_{\alpha} \hat{H}^{\text{HO}}(Q_{\alpha}, \lambda_{\alpha}). \quad (14)$$

We have therefore reduced the original quadratic Hamiltonian to a sum of *independent* harmonic oscillators [$\hat{H}^{\text{HO}}(Q_{\alpha}, \lambda_{\alpha})$].

Recall that for an harmonic oscillator with mass m and spring constant k , the Hamiltonian reads as:

$$\hat{H}^{\text{HO}} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} k x^2 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2, \quad (15)$$

since the angular frequency ω is defined as:

$$\omega = \sqrt{\frac{k}{m}}. \quad (16)$$

Moreover, the eigenvalues of the harmonic oscillator (E_v^{HO}) are given by

$$E_v^{\text{HO}} = \hbar \omega \left(v + \frac{1}{2} \right), \quad (17)$$

where v labels the vibrational level, with the ground vibrational level corresponding to $v = 0$.

Comparing Eq. (14) and Eq. (15) we deduce that the Hamiltonian of each normal mode α , $\hat{H}^{\text{HO}}(Q_{\alpha}, \lambda_{\alpha})$ is a special case of the harmonic oscillator with $m = 1$ and $\omega^2 = \lambda_{\alpha}$. Now can take advantage of a simple theorem which permits us to express the eigenvalues and the eigenfunctions of \hat{H}_N respectively as the *sum* of the eigenvalues

and the *product* of the eigenfunctions of each independent normal mode. If each mode Q_α is excited to the vibrational level v_α , then the total vibrational energy is (in atomic units):

$$\mathcal{E}_{n\mathbf{v}} = \sum_{\alpha} \sqrt{\lambda_{\alpha}} \left(v_{\alpha} + \frac{1}{2} \right). \quad (18)$$

Here we take advantage of the fact that the vibrational state can be uniquely represented via the occupation numbers of each mode, which are collected in the vector, \mathbf{v} .

For a molecule in its ground vibrational level, the zero-point vibrational energy (ZPVE) is

$$E_{\text{ZPVE}} = \frac{1}{2} \sum_{\alpha} \sqrt{\lambda_{\alpha}}. \quad (19)$$

Notice that for a molecule in vacuum this analysis also takes into account the *rotational and translational* degrees of freedom. For a non-linear molecule there are 6 rotational and translational degrees of freedom, while linear molecules have one less, 5. The normal modes corresponding to rotations and translations do not change the energy of a molecule and therefore are characterized by $\lambda_{\alpha} = 0$.