

Programming Project 1 Theory

The harmonic approximation to the nuclear Schrödinger equation

The Born-Oppenheimer Approximation

Under the Born-Oppenheimer approximation the stationary-states ¹ of nuclear motion Ψ_{Nu} arise as solutions of the nuclear motion equation.

$$\hat{H}_{\text{Nu}}\Psi_{\text{Nu}}(\mathbf{X}) = E\Psi_{\text{Nu}}(\mathbf{X}) \quad \hat{H}_{\text{Nu}} \equiv \hat{T}_{\text{Nu}} + E_e(\mathbf{X}) \quad (1)$$

The potential energy term $E_e(\mathbf{X})$ in the nuclear motion Hamiltonian is defined through the clamped-nuclei Schrödinger equation.

$$\hat{H}_e(\mathbf{X})\Psi_e(\mathbf{r}_1, \dots, \mathbf{r}_n; \mathbf{X}) = E_e(\mathbf{X})\Psi_e(\mathbf{r}_1, \dots, \mathbf{r}_n; \mathbf{X}) \quad (2)$$

Equation (2) can be solved approximately at any point $\mathbf{X} = (\mathbf{R}_1, \dots, \mathbf{R}_N)$ using your favorite electronic structure software package (Psi4, CFOUR, Molpro, Gaussian, etc.) and electronic structure method (MP2, CCSD, CISD, etc.).

Normal Coordinates and the Vibrational Schrödinger Equation

One of the major barriers to solving the nuclear motion equation (1) is the difficulty of determining the potential energy surface $E_e(\mathbf{X})$ at a sufficiently large number of points. Since the nuclei generally remain relatively localized about an equilibrium configuration \mathbf{X}_0 , a good first approach is to approximate the potential surface by a Taylor expansion.

$$E_e(\mathbf{X}) \approx E_e(\mathbf{X}_0) + \sum_A^{3N} \left(\frac{\partial E_e}{\partial X_A} \right)_0 \Delta X_A + \frac{1}{2} \sum_{AB}^{3N} \left(\frac{\partial^2 E_e}{\partial X_A \partial X_B} \right)_0 \Delta X_A \Delta X_B \quad \Delta \mathbf{X} = \mathbf{X} - \mathbf{X}_0$$

Equilibrium structures occur at minima on the potential energy surface, so that the second term is zero and only the quadratic term remains.

$$E_e(\mathbf{X}) \approx E_e(\mathbf{X}_0) + \frac{1}{2} \sum_{AB}^{3N} \left(\frac{\partial^2 E_e}{\partial X_A \partial X_B} \right)_0 \Delta X_A \Delta X_B \quad (3)$$

For convenience, we use mass-weighted coordinates $\tilde{X}_A \equiv \sqrt{M_A} \Delta X_A$ in order to remove the explicit dependence of the kinetic energy operator on nuclear masses. ²

$$\hat{T}_{\text{Nu}} = -\frac{1}{2} \sum_A^{3N} \frac{\partial^2}{\partial \tilde{X}_A^2} \quad (4)$$

The nuclear motion equation (1) then becomes

$$\left(-\frac{1}{2} \sum_A^{3N} \frac{\partial^2}{\partial \tilde{X}_A^2} + \frac{1}{2} \sum_{AB}^{3N} \left(\frac{\partial^2 E_e}{\partial \tilde{X}_A \partial \tilde{X}_B} \right)_0 \tilde{X}_A \tilde{X}_B \right) \Psi_{\text{Nu}}(\tilde{\mathbf{X}}) = E_{\text{Nu}} \Psi_{\text{Nu}}(\tilde{\mathbf{X}}) \quad E_{\text{Nu}} \equiv E - E_e(\mathbf{X}_0) \quad (5)$$

which brings us to the crucial step that motivates this project.

¹http://en.wikipedia.org/wiki/Stationary_state

²Explicitly, we can write $\frac{\mathbf{\hat{P}}_A^2}{2M_A} = -\frac{1}{2M_A} \frac{\partial^2}{\partial X_A^2} = -\frac{1}{2} \frac{\partial^2}{\partial (\sqrt{M_A} \Delta X_A)^2} = -\frac{1}{2} \frac{\partial^2}{\partial \tilde{X}_A^2}$. ($\hbar = 1$ since we are working in atomic units)

the crucial step that motivates this project: Note that, if the mass-weighted Hessian matrix

$$(\tilde{\mathbf{H}}_0)_{AB} = \left(\frac{\partial^2 E_e}{\partial \tilde{X}_A \partial \tilde{X}_B} \right)_0 \quad (6)$$

were diagonal, we would have a sum of harmonic oscillator Hamiltonians³ in equation (5). This dream of a simple Hamiltonian can be realized by choosing a new set of coordinates $\{q_1, \dots, q_{3N}\}$, called *normal coordinates*, in terms of which the Hessian is diagonal. Since the mass-weighted Hessian $\tilde{\mathbf{H}}_0$ is real and symmetric, it can be diagonalized by a real orthogonal matrix $\tilde{\mathbf{Q}}$ ⁴

$$\tilde{\mathbf{H}}_0 = \tilde{\mathbf{Q}} \mathbf{K} \tilde{\mathbf{Q}}^T \quad \mathbf{K} = \begin{pmatrix} k_1 & 0 & \dots & 0 \\ 0 & k_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & k_{3N} \end{pmatrix} \quad \tilde{\mathbf{Q}} \tilde{\mathbf{Q}}^T = \tilde{\mathbf{Q}}^T \tilde{\mathbf{Q}} = \mathbf{1} \quad (7)$$

where the columns of $\tilde{\mathbf{Q}}$ are eigenvectors $\tilde{\mathbf{q}}_1, \dots, \tilde{\mathbf{q}}_{3N}$ of $\tilde{\mathbf{H}}_0$. Back-transforming to un-mass-weighted Cartesian space gives the *normal modes* of the system.

$$\mathbf{q}_1 = \mathbf{M}^{-1/2} \tilde{\mathbf{q}}_1 \quad \mathbf{q}_2 = \mathbf{M}^{-1/2} \tilde{\mathbf{q}}_2 \quad \dots \quad \mathbf{q}_{3N} = \mathbf{M}^{-1/2} \tilde{\mathbf{q}}_{3N} \quad \text{where } \mathbf{M} \equiv \begin{pmatrix} m_1 & 0 & 0 & 0 & \dots \\ 0 & m_1 & 0 & 0 & \dots \\ 0 & 0 & m_1 & 0 & \dots \\ 0 & 0 & 0 & m_2 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (8)$$

Each *normal coordinate* q represents a motion along the *normal mode* \mathbf{q}_A .

Expressing equation (5) in terms of these newfangled coordinates, we are left with

$$\left(-\frac{1}{2} \sum_A^{3N} \frac{\partial^2}{\partial q^2} + \frac{1}{2} \sum_A^{3N} k_A q^2 \right) \Psi_{\text{Nu}}(\mathbf{q}) = E_{\text{Nu}} \Psi_{\text{Nu}}(\mathbf{q}) \quad (9)$$

(details of the coordinate transformation are shown in an appendix). The Hamiltonian in (9) has the marvelously simple form we were hoping for:

$$\hat{H}_{\text{Nu}} \approx \sum_{A=1}^{3N} \hat{\mathbf{h}}_A \quad \hat{\mathbf{h}}_A \equiv -\frac{1}{2} \frac{\partial^2}{\partial q^2} + \frac{1}{2} k_A q^2 \quad (10)$$

The only approximation for \hat{H}_{Nu} here is the truncation of the potential energy surface Taylor expansion at second order. As long as k_A is a positive real number, $\hat{\mathbf{h}}_A$ is a harmonic oscillator Hamiltonian and we can make the identification $k_A = \omega_A^2$ where ω_A is the oscillator frequency in a.u. It will turn out that, at an equilibrium geometry, $\tilde{\mathbf{H}}_0$ has several zero eigenvalues – one for each translational and rotational degree of freedom for the entire nuclear framework with respect to its center of mass. For these motions, $\hat{\mathbf{h}}_A$ actually takes the form of a free-particle Hamiltonian⁵

$$\hat{\mathbf{h}}_A = -\frac{1}{2} \frac{\partial^2}{\partial q^2} \quad (11)$$

although this form is somewhat misleading for rotational motion. In order to get a clearer picture of what a normal coordinate physically represents, it helps to shift to a classical picture for a moment.

³The Hamiltonian of a single harmonic oscillator is $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 \hat{x}^2}{2}$, or $\hat{H} = -\frac{1}{2} \frac{\partial^2}{\partial q^2} + \frac{\omega^2}{2} q^2$ in mass-weighted coordinates with atomic units. The frequency of oscillation is ω .

⁴http://en.wikipedia.org/wiki/Symmetric_matrix#Decomposition

⁵http://en.wikipedia.org/wiki/Free_particle#Non-Relativistic_Quantum_Free_Particle

Solutions for Nuclear Motion in a Quadratic Well

Here I will simply report the quantum mechanical solution to the translational and vibrational components of equation (9).

$$\left(\sum_{A=1}^{3N} \hat{h}_A\right) \Psi_{\text{Nu}}(\mathbf{q}) = E_{\text{Nu}} \Psi_{\text{Nu}}(\mathbf{q}) \quad \hat{h}_A = -\frac{1}{2} \frac{\partial^2}{\partial q^2} + \frac{1}{2} k_A q^2$$

Since the Hamiltonian separates into a sum of independent Hamiltonians each involving only one coordinate, the form of the wavefunction is

$$\Psi_{\text{Nu}}(q_1, \dots, q_{3N}) = \psi_1(q_1) \psi_2(q_2) \cdots \psi_{3N}(q_{3N}) \quad (12)$$

where each one-coordinate wavefunction $\psi_A(q)$ is an eigenfunction (or, rather, *one of the* eigenfunctions) of the corresponding operator, \hat{h}_A .

$$\hat{h}_A \psi_A(q) = \varepsilon \psi_A(q) \quad (13)$$

We will only need solutions to the 1D free-particle and 1D harmonic oscillator Schrödinger equations for the present discussion, which can be found in any introductory quantum mechanics text worth reading.⁶

For the three normal coordinates that correspond to translations of the molecule as a whole, the potential term in \hat{h} vanishes (since $k = 0$) and we only need to solve a free-particle-like problem.

$$-\frac{1}{2} \frac{\partial^2 \psi(q)}{\partial q^2} = \varepsilon \psi(q) \quad (14)$$

Solutions to this differential equation are given by

$$\psi_P(q) = e^{iP(q-q_0)} \quad (15)$$

where q_0 is some undetermined phase shift. The distribution of eigenvalues is continuous in this case, $\varepsilon_P = \frac{P^2}{2}$, where P corresponds to a component of the linear momentum of the molecule as a whole.

Although $k = 0$ also holds for rotational modes at equilibrium, normal coordinates are only appropriate for parametrizing infinitesimal rotations and quickly break down for larger rotational motions. Furthermore, unlike translations, these modes are not truly “external” since they change the relative positions of the nuclei (and therefore change the energy for finite displacements). Proper parametrization of a full rotation about the center of mass in terms of fixed normal coordinates would actually require linear combinations of rotational modes with vibrational ones, and these motions are in general coupled to each other. For our purposes, we will simply note one can, to a good first approximation, ignore the interference of rotations when considering vibrational motion.

The remaining $3N - 6$ coordinates ($3N - 5$ for linear molecules) will always have $k > 0$ at an equilibrium geometry and so lead to true harmonic oscillator motion. The solutions to this problem

$$-\frac{1}{2} \frac{\partial^2 \psi(q)}{\partial q^2} + \frac{1}{2} k q^2 = \varepsilon \psi(q) \quad (16)$$

are given by

$$\psi_n(q) = \frac{1}{\sqrt{2^n n!}} \left(\frac{\omega}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\omega q^2} \text{He}_n(\sqrt{\omega}q) \quad \omega^2 = k \quad (17)$$

⁶e.g. R. Shankar *Principles of Quantum Mechanics*, which contains detailed discussions of both the free particle and harmonic oscillator. An electronic copy can be found [here](#).

with energies $\varepsilon_n = \omega(n + \frac{1}{2})$, where $\text{He}_n(x)$ is the n^{th} Hermite polynomial.

$$\text{He}_n(x) = (-1)^n e^{x^2} \left(\frac{d^n}{dx^n} e^{-x^2} \right) \quad (18)$$

Hence, the solution to the *vibrational Schrödinger equation* ⁷

$$\sum_{A=1}^{3N-6} \left(-\frac{1}{2} \frac{\partial^2}{\partial q_A^2} + \omega_A^2 q_A^2 \right) \Psi_{\text{vib}}(\mathbf{q}) = E_{\text{vib}} \Psi_{\text{vib}}(\mathbf{q}) \quad (19)$$

is given by

$$\Psi_{\mathbf{n}}(\mathbf{q}) = \prod_{A=1}^{3N-6} \psi_{n_A}(q_A) \quad (20)$$

with vibrational energy

$$E_{\mathbf{n}} = \sum_{A=1}^{3N-6} \omega_A \left(n_A + \frac{1}{2} \right) \quad (21)$$

The total molecular energy at equilibrium is the sum of translational, rotational, vibrational, and electronic contributions.

$$E = \frac{\mathbf{P}_{\text{CM}}^2}{2M_{\text{tot}}} + E_{\text{vib}} + E_{\text{rot}} + E_e(\mathbf{X}_0) \quad (22)$$

⁷This is simply equation (9) with translational and rotational modes omitted.