

Lecture: Vibrational analysis in quantum chemical calculations

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1 Introduction

1.1 Motivation

- atoms in molecules are not fixed
- they oscillate (vibrate) around an equilibrium geometry
- these vibrations can be excited by absorption of electromagnetic radiation of the corresponding wavelength (resonant frequency)

→ infrared radiation

- this effect is used for the identification and analysis of substances (IR, Raman spectroscopy)

But:

- in most cases, chemical intuition or reference data is necessary for the identification substances
- information about the type of the vibration (e.g. the normal modes) requires additional experimental effort
- detailed insight can be obtained from theoretical calculations

1.2 Phenomenological picture

Vibrational spectra are related to motions of nuclei around their equilibrium positions in a molecule. In order to calculate vibrational spectroscopic properties, we need to evaluate certain quantities (energy, dipole moment and polarizability) as a function of the nuclear coordinates. Considering the potential energy as an example this results in a high-dimensional graph, the potential energy surface (PES). The coordinates in which the PES is constructed do not necessarily need to be Cartesian nuclear coordinates, in

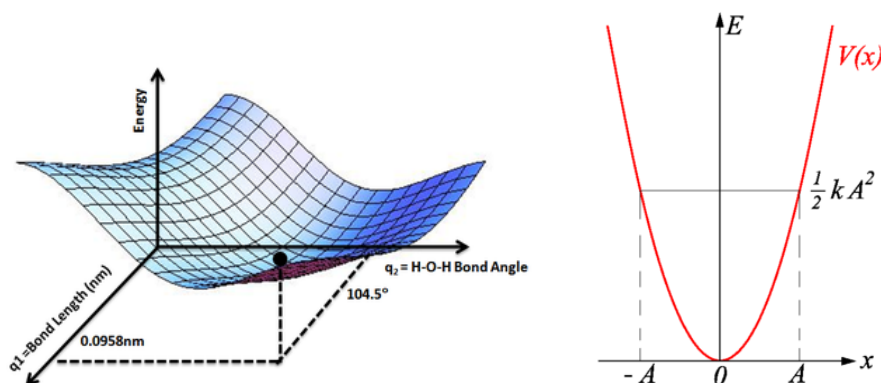


Figure 1: Potential energy function. Left: as a function of two coordinates in the case of a water molecule, right: as a function of one coordinate in the harmonic potential.¹

most cases, different choices are more convenient. This is demonstrated in Fig. 1, where a simplified PES for a water molecule is shown dependent on the bond lengths and the bond angle. For comparison, the potential energy of a harmonic oscillator is also given. The task of computational chemistry is now the characterization of molecular vibrations, i.e., the evaluation of vibrational frequencies and energies as well as intensities. The key step lies in the determination of the PES, or at least of a sufficiently large part of it. Therefore, two main approaches are available:

1. Molecular dynamics

In the molecular dynamics framework, the coordinates of atoms are changed along a timescale according to equations of motion. The energy is evaluated along that trajectory and from that the PES may be constructed for certain regions of the coordination phase space.

2. Static quantum chemistry

Quantum chemical methods are used to characterize the potential energy surface in a small region around the minimum structure. This method will be discussed in the following.

2 Theoretical background of vibrational analysis

2.1 The Born–Oppenheimer approximation

We first consider the Hamiltonian \hat{H}

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{eN} + \hat{V}_{ee} + \hat{V}_{NN} \quad (1)$$

¹Pictures from https://en.wikipedia.org/wiki/Potential_energy_surface and http://en.citizendium.org/wiki/Harmonic_oscillator_%28classical%29

where \hat{T} denotes kinetic terms, \hat{V} potential energy terms, N refers to nuclei and e to electrons. We now apply the Born–Oppenheimer approximation. That means that as long as electrons are considered, the nuclei may be considered to be stationary, because the nuclear masses are orders of magnitude larger than the electronic mass. The kinetic energy of nuclei \hat{T}_N now vanishes and the nuclear-nuclear repulsion \hat{V}_{NN} is a constant additive term to the electronic energy. The electronic Hamiltonian \hat{H}_{el} now reduces to

$$\hat{H}_{\text{el}} = \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee} \quad (2)$$

which we now use to formulate the electronic Schrödinger equation

$$\hat{H}_{\text{el}}(\mathbf{r}|\mathbf{R})|\psi_{\text{el}}(\mathbf{r}|\mathbf{R})\rangle = E_{\text{el}}(\mathbf{R})|\psi_{\text{el}}(\mathbf{r}|\mathbf{R})\rangle \quad (3)$$

with explicit dependence on electronic coordinates \mathbf{r} and parametric dependence on nuclear coordinates \mathbf{R} . For this problem, many well-known methods are available to obtain approximate solutions to obtain wavefunctions and energy for given nuclear coordinates.

This could now be repeated to obtain energies for different choices of \mathbf{R} so that one would obtain points of the PES in a discretized phase space. Assuming that the step size $\Delta\mathbf{R}$ would be chosen small, this would satisfy the adiabatic condition so that the displacement would be an adiabatic process. The PES which is modeled in such a way is therefore called an *adiabatic surface*.

2.2 The Schrödinger equation of nuclear motion

As a second step of the Born–Oppenheimer approximation, the kinetic energy of the nuclei is reinserted again by adding it to the adiabatic PES to obtain the Schrödinger equation of nuclear motion:

$$(\hat{T}_N + E_{\text{el}})\Psi = E\Psi \quad (4)$$

The calculation of the complete adiabatic energy surface and the solution of this Schrödinger equation would be far too expensive. Instead, it is recalled that vibrational spectra are related to vibrations around the equilibrium geometry. Consequently, it is sufficient to calculate E_{el} only *once* for the equilibrium geometry and approximate it in its immediate vicinity. This is done by a Taylor series expansion of E_{el} around the minimum positions \mathbf{R}_0 which is truncated after the second order term:

$$V(\mathbf{R}) = E_{\text{el}}(\mathbf{R}_0) + \left(\frac{dE_{\text{el}}}{d\mathbf{R}}\right)^T (\mathbf{R} - \mathbf{R}_0) + \frac{1}{2}(\mathbf{R} - \mathbf{R}_0)^T \left(\frac{d^2E_{\text{el}}}{d\mathbf{R}^2}\right) (\mathbf{R} - \mathbf{R}_0) \quad (5)$$

At this point, one is free to choose the reference energy to be the electronic energy $E_{\text{el}}(\mathbf{R}_0)$. Furthermore the energy gradient $\left(\frac{dE_{\text{el}}}{d\mathbf{R}}\right)$ vanishes since \mathbf{R}_0 is a stationary point (the minimum). If $\Delta\mathbf{R}$ is introduced for the displacement vector $\mathbf{R} - \mathbf{R}_0$ and the matrix \mathbf{F} denotes the $3N \times 3N$ force matrix of second derivatives, the nuclear Schrödinger equation reads as

$$\left(-\sum_{i=1}^{3N} \frac{1}{2M_i} \frac{\partial^2}{\partial R_i^2} + \frac{1}{2}\Delta\mathbf{R}^T \mathbf{F} \Delta\mathbf{R}\right) \Psi = E\Psi \quad (6)$$

Next, mass weighted coordinates are inserted:

$$y_i = \sqrt{M_i} \Delta R_i \quad (7)$$

$$\frac{\partial^2}{\partial y_i^2} = \frac{1}{M_i} \frac{\partial^2}{\partial R_i^2} \quad (8)$$

It is realized that the force matrix elements now need to be weighted by the masses, as well:

$$F'_{ij} = \frac{F_{ij}}{\sqrt{M_i M_j}} \quad (9)$$

which yields for the Schrödinger equation in mass-weighted coordinates \mathbf{y}

$$\left(- \sum_{i=1}^{3N} \frac{1}{2} \frac{\partial^2}{\partial y_i^2} + \frac{1}{2} \mathbf{y}^T \mathbf{F}' \mathbf{y} \right) \Psi = E \Psi . \quad (10)$$

So far, this is a $3N$ dimensional Schrödinger equation, because all differential equations are coupled. This is now transformed to a system of $3N$ uncoupled differential equations by diagonalization of the matrix \mathbf{F}' using a unitary transformation. A unitary transformation corresponds to a rotation of the coordinate systems which is performed by a unitary matrix \mathbf{U} which has certain properties. The coordinates are thus transformed to

$$\mathbf{q} = \mathbf{U} \mathbf{y} \quad (11)$$

which is inserted into the Schrödinger equation

$$\left(- \sum_{i=1}^{3N} \frac{1}{2} \frac{\partial^2}{\partial \mathbf{q}_i^2} + \frac{1}{2} \mathbf{q}^T (\mathbf{U} \mathbf{F}' \mathbf{U}^T) \mathbf{q} \right) \Psi = E \Psi \quad (12)$$

where the matrix $\mathbf{U} \mathbf{F}' \mathbf{U}^T$ is now diagonal and abbreviated with \mathbf{H} (not to be confused with the Hamilton operator \hat{H}). Finally, the Schrödinger equation of nuclear motion simplifies to

$$\left(- \sum_{i=1}^{3N} \frac{1}{2} \frac{\partial^2}{\partial \mathbf{q}_i^2} + \frac{1}{2} \mathbf{q}^T \mathbf{H} \mathbf{q} \right) \Psi = E \Psi . \quad (13)$$

Since furthermore, \mathbf{H} is diagonal in the system of \mathbf{q} -coordinates, the vectors \mathbf{q}_i are eigenvectors of \mathbf{H} with eigenvalues ε_i so that the eigenvalue equations

$$\mathbf{H} \mathbf{q}_i = \varepsilon_i \mathbf{q}_i \quad (14)$$

so that one finally arrives at

$$\sum_{i=1}^{3N} \left(- \frac{1}{2} \frac{\partial^2}{\partial \mathbf{q}_i^2} + \frac{1}{2} \varepsilon_i \mathbf{q}_i^2 \right) \Psi = E \Psi . \quad (15)$$

Recalling that the Hamiltonian for a one-dimensional harmonic oscillator is given by

$$-\frac{1}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \quad (16)$$

it is easily identified that the $3N$ -dimensional Schrödinger equation of nuclear motion has been reduced to $3N$ uncoupled equations, each of which are of the form of a harmonic oscillator.

2.3 Vibrational frequencies

The eigenvectors \mathbf{q}_i are the mass-weighted vibrational normal coordinates and the eigenvalues ε_i can be transformed to the vibrational frequencies

$$\nu_i = \frac{1}{2\pi}\sqrt{\varepsilon_i} \quad (17)$$

in analogy to the vibrational frequency of the harmonic oscillator

$$\nu_i^{\text{ho}} = \frac{1}{2\pi}\sqrt{\frac{k}{\nu}}. \quad (18)$$

If vibrational frequencies need to be evaluated, these mathematical operations are not necessary, because it is finally recognized that the evaluation of the hessian and subsequent diagonalization is sufficient. If this is done in practice, six of the eigenvalues (five for linear molecules) are zero. These correspond to translational and rotational degrees of freedom. If the stationary point is a true minimum, the remaining eigenvalues of the hessian are positive and the vibrational frequencies are real. The occurrence of imaginary frequencies indicates that the stationary point is a saddle point, in particular exactly one imaginary frequency characterizes transition states. The eigenvector corresponding to this imaginary frequency is the direction, in which the energy decreases towards products or educts.

2.4 Intensities of vibrational modes

The evaluation of the intensity of each vibrational mode is also possible from quantum chemical calculations, but the derivation won't be covered here. In order to calculate vibrational intensities, the transition dipole moment is required for infrared spectra. Fermi's golden rule is applied to evaluate the transition rate for a transition from an initial to a final state in the presence of an external perturbation. The expectation value of the molecular dipole moment is again expanded in a Taylor series around the minimum geometry, where again normal coordinates are applied. This finally results in a formula for the IR intensity:

$$\mathcal{A}_\nu = \frac{1}{4\pi\epsilon_0} \frac{N_A\pi}{3c} \left(\frac{\partial \bar{\mu}}{\partial \mathbf{q}_i} \right)_0^2, \quad (19)$$

which involves the derivative of the dipole moment.

Similarly, Raman intensities are obtained applying Placzek's classical theory of polarizability. In this case, the expectation value of the induced dipole moment is obtained from the polarizability tensor. Again, a Taylor series expansion leads to the Raman intensity, which depends in this case on the geometry of the experimental setup. If for example, the incident beam propagates in y direction and is polarized in x direction, the detector is on the z axis. A polarization filter is now used to measure the intensity of scattered light with x polarization (I^{\parallel}) and y polarization (I^{\perp}). The intensities are given by

$$I_k^{\parallel} = \frac{\pi^2}{\epsilon_0^2} (\nu_{\text{in}} - \nu_k)^4 \frac{h}{8\pi^2 c \nu_k} \left(\frac{\partial \bar{\alpha}_{xx}}{\partial \mathbf{q}_k} \right)_0^2 \frac{1}{1 - \exp\left(-\frac{h c \nu_k}{k_B T}\right)} \quad (20)$$

and

$$I_k^{\perp} = \frac{\pi^2}{\epsilon_0^2} (\nu_{\text{in}} - \nu_k)^4 \frac{h}{8\pi^2 c \nu_k} \left(\frac{\partial \bar{\alpha}_{xy}}{\partial \mathbf{q}_k} \right)_0^2 \frac{1}{1 - \exp\left(-\frac{h c \nu_k}{k_B T}\right)} . \quad (21)$$

3 Applications

Vibrational analyses are not only used for comparison to experimental spectra. As vibrational frequencies are used to determine whether a stationary point is a true minimum, a transition state or a higher order saddle point, frequency calculations are also used when geometry optimizations or transition state searches are performed. Furthermore, the evaluation of vibrational modes is a necessary prerequisite for thermochemical calculations. In these approaches, the concepts of statistical thermodynamics are used to evaluate molecular partition functions and thereby study Free energies at finite temperatures. The target property to be evaluated is the system partition function Q , which can be decomposed into one particle partition functions q , e.g. for N identical particles according to

$$Q = \frac{q^N}{N!} . \quad (22)$$

The one-particle partition function is a sum over exponential terms, which runs over all quantum energy states:

$$q = \sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right) . \quad (23)$$

Assuming independent degrees of freedom, the total energy can be decomposed into electronic, translational, rotational and vibrational degrees of freedom, which means that q can be factorized into the corresponding contributions:

$$q_{\text{tot}} = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} . \quad (24)$$

The respective contributions are evaluated by insertion of the respective energy expressions which are obtained from the standard quantum chemical models: the particle in

a box for translational, the rigid rotor for rotational and the harmonic oscillator for vibrational contributions. The vibrational partition function can then be formulated as follows:

$$q_{\text{vib}} = \prod_i \frac{\exp\left(-\frac{h\nu_i}{k_{\text{B}}T}\right)}{1 - \exp\left(-\frac{h\nu_i}{k_{\text{B}}T}\right)} \quad (25)$$

where the product index runs over all vibrational modes of the molecule. The vibrational frequencies, which have been obtained from quantum chemical calculations as described above can now be inserted into eq. 25 to obtain the temperature dependent vibrational partition function. In a similar fashion, rotational and translational partition functions are obtained. The electronic partition function is calculated by insertion of the electronic energy into eq. 23 and the total partition function Q can be evaluated. Once Q is known, thermodynamic quantities can be calculated, the enthalpy for example equals

$$H = k_{\text{B}}T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V + k_{\text{B}}TV \left(\frac{\partial \ln Q}{\partial V} \right)_T . \quad (26)$$

This approach can now be applied to estimate gas phase properties at finite temperatures or even Free energies of simple reactions.

4 References

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