

Harmonic vibrational analysis at non-stationary points – some comments

Most of what follows below is from Wilson, Decius, and Cross, Molecular Vibrations (Dover, 1955).
Special thanks to Dr. Greg Schenter (PNNL) for many helpful discussions.

All of the logic valid for the classical treatment also applies to the quantum oscillator, so I'll stick to the classical picture.

Classically, the kinetic energy in cartesian coordinates is:

$$T = \frac{1}{2} \sum_{\alpha=1}^N m_{\alpha} \left[\left(\frac{d\Delta x_{\alpha}}{dt} \right)^2 + \left(\frac{d\Delta y_{\alpha}}{dt} \right)^2 + \left(\frac{d\Delta z_{\alpha}}{dt} \right)^2 \right]$$

to simplify, change to mass-weighted cartesians, i.e.,

$$q_1 = \sqrt{m_1} \Delta x_1 \quad ; \quad q_2 = \sqrt{m_1} \Delta y_1 \quad ; \quad q_3 = \sqrt{m_1} \Delta z_1 \quad ; \quad q_4 = \sqrt{m_2} \Delta x_2 \quad ; \quad \dots$$

The kinetic energy in these coordinates is then:
$$T = \frac{1}{2} \sum_{i=1}^{3N} \left(\frac{dq_i}{dt} \right)^2 = \frac{1}{2} \sum_{i=1}^{3N} \dot{q}_i^2$$

The potential energy can be written as:

$$V = V_0 + \sum_{i=1}^{3N} \left(\frac{\partial V}{\partial q_i} \right)_0 q_i + \frac{1}{2} \sum_{ij}^{3N} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \text{higher order terms}$$

or by shifting the zero of energy so that $V_0 = 0$, simply:

$$V = \sum_{i=1}^{3N} g_i q_i + \frac{1}{2} \sum_{ij}^{3N} F_{ij} q_i q_j + \text{higher order terms}$$

Newton's equation of motion is:
$$\frac{d}{dt} \frac{\partial T}{\partial \dot{q}_j} + \frac{\partial V}{\partial q_j} = 0 \quad \text{for } j = 1, 2, 3, \dots, 3N$$

Substituting:
$$\ddot{q}_j + g_j + \sum_i^{3N} F_{ij} q_i = 0 \quad \text{for } j = 1, 2, 3, \dots, 3N \quad (1)$$

IF the gradient is zero ($g_j = 0$), we are at a stationary point and our differential eqn. is:

$$\ddot{q}_j + \sum_i^{3N} F_{ij} q_i = 0 \quad \text{This leads to the usual secular determinant for eigenvalues } \lambda$$

In that case, 6 eigenvalues will be identically zero (to numerical precision)

3 = translations

3 = rotations

IF the gradient is not zero, then we must solve Eq. (1)

This part is easy, however. We just need to change to the following coordinates:

$$q'_i = q_i - g_j \quad \text{i.e., shift the original ones by the non-zero gradient components}$$

Since neither coordinate depends on time, the kinetic energy is unchanged. In the case of the potential energy,

$$\frac{\partial V}{\partial q} = \frac{\partial V}{\partial q'} \frac{\partial q'}{\partial q} = \frac{\partial V}{\partial q'} \quad \text{and} \quad \frac{\partial^2 V}{\partial q \partial q_j} = \frac{\partial^2 V}{\partial q' \partial q'_j}$$

So neither the gradients nor hessian change with this coordinate transformation

The differential equation then becomes:

$$\ddot{q}'_j + \sum_i^{3N} F_{ij} q'_i = 0 \quad \text{which has exactly the same form as before !}$$

The difference now, of course, is that some of the previously zero frequencies are now non-zero

The key seems to be the separation of translations and rotations from the vibrations. For a complete separation, the 2 sets of Eckart conditions must be satisfied:

$$\sum_{\alpha=1}^N m_{\alpha} \Delta x_{\alpha} = 0 \quad ; \quad \sum_{\alpha=1}^N m_{\alpha} \Delta y_{\alpha} = 0 \quad ; \quad \sum_{\alpha=1}^N m_{\alpha} \Delta z_{\alpha} = 0 \quad \begin{array}{l} \text{Eckart condition \#1} \\ \text{fix origin to equilibrium position} \\ \text{(translations)} \end{array}$$

$$\sum_{\alpha=1}^N m_{\alpha} \left(y_{\alpha}^e \Delta z_{\alpha} - z_{\alpha}^e \Delta y_{\alpha} \right) = 0$$

$$\sum_{\alpha=1}^N m_{\alpha} \left(z_{\alpha}^e \Delta x_{\alpha} - x_{\alpha}^e \Delta z_{\alpha} \right) = 0$$

$$\sum_{\alpha=1}^N m_{\alpha} \left(x_{\alpha}^e \Delta y_{\alpha} - y_{\alpha}^e \Delta x_{\alpha} \right) = 0$$

Eckart condition #2
axes must rotate with molecule frame
(rotations)

One can show that our coordinate change from $q \rightarrow q'$ does not affect the translational modes (e.g., our coordinate change is in itself just a translation)

However, this change in coordinates does seem to prevent the 2nd Eckart conditions from being fulfilled [proof left to the reader :^)]. Hence we have lost our exact separation of rotations and vibrations !

Of course, one way out of this dilemma would appear to be to work in internal coordinates rather than cartesians, since the secular equation built from the former do not include these translations and rotations by definition.

Unfortunately, now the resulting frequencies depend on your choice of internal coordinates !!

To see this, denote the cartesians by q and a particular choice of internal coordinates by s . The force constant matrix in internals is related to the one in cartesians by:

$$\mathbf{F} = \frac{\partial^2 V}{\partial s \partial s} = \frac{\partial q}{\partial s} \frac{\partial^2 V}{\partial q \partial q} \frac{\partial q}{\partial s} + \frac{\partial V}{\partial q} \frac{\partial^2 q}{\partial s \partial s}$$

The last term, which is directly proportional to the non-zero gradient, reflects these differences and is obviously also affected by the choice of internals (the 2nd deriv. of q with respect to s).

Note that projecting out the rotational modes before diagonalization of the secular determinant just corresponds to changing to one set of internal coordinates and will also yield eigenvalues contaminated to some degree by rotations. As noted in the Gaussian white paper on this subject, one can compare the frequencies obtained both with and without projection to assess the degree of contamination.

One additional note, if the only non-zero gradient component is orthogonal to all the other vibrations, it is possible to completely separate the translations and rotations from the vibrations, yielding $3N-7$ real frequencies and 1 imaginary frequency corresponding to the reaction coordinate.