Programming Project 1: Vibrational Frequencies and Normal Modes

Description

The aim of this programming project is compute harmonic vibrational frequencies using second derivatives of the potential energy surface. See section 3 for details on the theory.

In essence, the task of this project is boils down to two steps:

1. formation of the mass-weighted Hessian matrix, which has elements

$$(\tilde{\mathbf{H}}_0)_{AB} = \left(\frac{\partial^2 E_e}{\partial \tilde{X}_A \partial \tilde{X}_B}\right)_0 = \frac{1}{\sqrt{M_A}}\left(\frac{\partial^2 E_e}{\partial X_A \partial X_B}\right)_0 \frac{1}{\sqrt{M_B}} \tag{1}$$

where $M_{3A-2} = M_{3A-1} = M_{3A}$ and $X_{3A-2}, X_{3A-1}, X_{3A}$ are the mass and X, Y, Z coordinates of the Ath nucleus, and $\tilde{X}_A = \sqrt{M_A}X_A$ represents a mass-weighted coordinate.

2. diagonalization of the mass-weighted Hessian matrix

$$\tilde{\mathbf{H}}_0 = \mathbf{L}\mathbf{\Lambda}\mathbf{L}^T \qquad \mathbf{\Lambda} = \begin{pmatrix} \lambda_1 & 0 & \dots & 0 \\ 0 & \lambda_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \lambda_{3N} \end{pmatrix} \tag{2}$$

where column vectors of the $\mathbf{L}$ matrix are orthonormal eigenvectors $\boldsymbol{l}_1, \dots, \boldsymbol{l}_{3N}$ of the mass-weighted Hessian matrix, and $\lambda_1, \dots, \lambda_{3N}$ are the corresponding eigenvalues.

In matrix notation, the mass-weighting can be written as

$$\tilde{\mathbf{H}}_0 = \mathbf{M}^{-\frac{1}{2}}\mathbf{H}_0\mathbf{M}^{-\frac{1}{2}} \qquad \mathbf{M} \equiv \begin{pmatrix} M_1 & 0 & \dots & 0 \\ 0 & M_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & M_{3N} \end{pmatrix} \tag{3}$$

where $\mathbf{H}_0$ is the Hessian matrix in ordinary Cartesian coordinates. For eigenvalues $\lambda_A > 0$, λ_A corresponds to the square of the frequency of molecular vibration $\lambda_A = \omega_A^2$ along the direction of motion represented by the corresponding eigenvector, which is $\mathbf{M}^{-\frac{1}{2}}\boldsymbol{l}_A$. This direction of motion corresponds to a *vibrational normal coordinate*, typically represented by Q_A, and motion along this coordinate corresponds to a displacement of

$$\Delta\mathbf{X}(Q_A) = Q_A\mathbf{M}^{-\frac{1}{2}}\boldsymbol{l}_A \tag{4}$$

relative to the reference configuration $\mathbf{X}_0$. In addition to the vibrational modes, there will be three *translational normal coordinates* for which $\lambda_A = 0$ and three *rotational normal coordinates* (two for linear systems) for which $\lambda_A = 0$ holds at an equilibrium geometry.

In order to complete this project you will need a hessian, molecule, code you wrote to extract information from an xyz file, and a file called `masses.py` containing masses for the most stable isotope of every element will also be provided. The files are available in the aptly named folder `extra-files/`.

1 Procedure

Make a file called `proj1.py` with the following code, which will tell Python where the necessary files are (obviously change the name to yours).

```
#!/usr/bin/env python3

import sys
sys.path.insert(0, '../extra-files')
sys.path.insert(0, '../../0/jevandezande')
```

1.1 Read in the molecule

Import your script, read in the file `molecule.xyz` and convert to Angstroms.

1.2 Read in the Hessian matrix

Read in each of the elements of the hessian matrix (`hessian.dat`) and save as a numpy matrix.

1.3 Generate $\mathbf{M}^{-\frac{1}{2}}$

Use the molecule that you read in to get the atoms of the molecule. You can then use the function get_mass from the file `masses.py` to find the mass of each of your atoms. Use these masses to generate $\mathbf{M}^{-\frac{1}{2}}$.

$$\mathbf{m} = \left[\frac{1}{\sqrt{M_1}}, \frac{1}{\sqrt{M_2}}, \frac{1}{\sqrt{M_3}}, \ldots, \frac{1}{\sqrt{M_{3N}}}\right] \quad \text{where } M_{3A-2} = M_{3A-1} = M_{3A} \text{ is the mass of the } A^{\text{th}} \text{ atom} \qquad (5)$$

using the `get_mass()` function in `masses.py`, which can be called as follows.

```
>>> import masses
>>> masses.get_mass("C")
12
>>> masses.get_mass("H")
1.00782503207
>>> masses.get_mass("O")
15.99491461956
>>> masses.get_mass("N")
14.00307400478
>>> masses.get_mass("P")
30.973761629
```

The square root of a number can be determined either by using the exponential operator in Python $\mathtt{a**b} = a^b$ or by using the square root function [1] provided by the NumPy package.

1.4 Form $\mathbf{H}_0$ and $\mathbf{M}^{-\frac{1}{2}}$ as NumPy matrices

This can be achieved using the Numpy functions `numpy.matrix()` [2] and `numpy.diag()`. [3]

1.5 Form the mass-weighted Hessian $\tilde{\mathbf{H}}_0 = \mathbf{M}^{-\frac{1}{2}}\mathbf{H}_0\mathbf{M}^{-\frac{1}{2}}$

For NumPy matrices `A` and `B`, `A*B` returns the matrix product.

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[1] http://docs.scipy.org/doc/numpy/reference/generated/numpy.sqrt.html
[2] http://docs.scipy.org/doc/numpy/reference/generated/numpy.matrix.html
[3] http://docs.scipy.org/doc/numpy/reference/generated/numpy.diag.html

1.6 Determine the eigenvalues and eigenvectors of $\tilde{\mathbf{H}}_0$

This can be achieved using the `eigh()` function [4] in the `numpy.linalg` module.

1.7 Determine the vibrational frequencies

The eigenvalues that we extracted correspond to frequencies. However, wavenumbers are not a true unit of frequency, which physically corresponds to inverse time rather than inverse length. The "conversion factor" between frequencies in wavenumbers (denoted $\tilde{\nu}$) and true frequencies ν is the speed of light in a vacuum c.

$$\tilde{\nu} = \frac{\nu}{c}$$

Be sure that you are aware of the difference between angular frequency (radians/time) and true temporal frequency (cycles/time) before attempting this.

1.8 Generate an `.xyz` file containing the normal modes

Note that the Cartesian displacements represented by normal modes correspond to $\mathbf{M}^{-\frac{1}{2}}\boldsymbol{l}_A$ rather than the eigenvectors $\boldsymbol{l}_A$ themselves. All distance units for this file must be in Ångströms, so you will have to apply a unit conversion to both the reference configuration and the mode displacements before printing. The format of this extended `.xyz` file used for mode visualization is described below.

1.9 Visualize in Jmol

Obviously, you should visualize the modes after completing step 1.8. If you have Jmol installed, the file generated in that step (call it `modes.xyz`) can be opened at the command line with the command `jmol modes.xyz`. In Jmol, select `Vibrate...` under `Tools` and click on `Start vibration`. The comment line corresponding to each mode will appear in the lower left corner, and you can cycle through the various modes with the left and right arrow icons.

You should also check your vibrational modes by running a frequency computation in Psi4 with the same method and level of theory. The simplest way to do this is to copy the input file for your reference geometry computation in the previous project and replace `energy('scf')` with `frequencies('scf')`. You may be surprised at first to find that your rotational normal modes are significantly different from zero. The reason for this is that the geometry you were given is not an equilibrium structure for H_2O at the RHF/cc-pVDZ level, and the eigenvalues corresponding to rotational modes are, in general, nonzero away from equilibrium. The motivation for starting with a non-equilibrium geometry is that the lifting the degeneracy between rotational and translational motion reduces the numerical error in the diagonalization procedure for determining the corresponding eigenvectors. As a final step to this project, you should determine the equilibrium geometry for water at the RHF/cc-pVDZ level and compute new frequencies by first running your scripts for determining the Hessian numerically and then running your frequency computation. You should notice two things:

1. you should now have six frequencies near zero (within 50 cm^{-1} real or imaginary)

2. your rotational and translational modes will now be barely recognizable when you visualize them in Jmol

After this is done, congratulate yourself and take a break.

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[4] `http://docs.scipy.org/doc/numpy/reference/generated/numpy.linalg.eigh.html#numpy.linalg.eigh`

2 Extra Files and File Formats

2.1 `masses.py`

This file provides an easy way to retrieve the mass (in atomic mass units) of the most stable isotope of an element by atomic symbol. You should look at this file and be sure you understand what it does. It contains a dictionary [5] to convert from atomic symbol to atomic number as well as a list of isotopic masses (corresponding to the most stable isotope) indexed by atomic number. The `get_mass()` function assumes a string argument, converts the string to uppercase, grabs the corresponding atomic number, and then returns the corresponding mass in the list.

2.2 `.xyz` files for visualizing vibrational modes

The file format for visualizing a single normal mode in Jmol is

```
N
COMMENT LINE 1
A1 x1 y1 z1    dx1 dy1 dz1
A2 x2 y2 z2    dx2 dy2 dz2
...
AN xN yN zN    dxN dyN dzN
```

which amounts to a standard `.xyz` geometry file (described in the previous handout) with the Cartesian displacement vector for each atom printed next to its Cartesian coordinates. For visualizing multiple motions, this format is simply repeated with an intervening empty line.

```
N
COMMENT LINE 1
A1 x1 y1 z1    dx11 dy11 dz11
A2 x2 y2 z2    dx12 dy12 dz12
...
AN xN yN zN    dx1N dy1N dz1N

N
COMMENT LINE 2
A1 x1 y1 z1    dx21 dy21 dz21
A2 x2 y2 z2    dx22 dy22 dz22
...
AN xN yN zN    dx2N dy2N dz2N


...


N
COMMENT LINE N
A1 x1 y1 z1    dxN1 dyN1 dzN1
A2 x2 y2 z2    dxN2 dyN2 dzN2
...
AN xN yN zN    dxNN dyNN dzNN
```

Note that, in order to use this file for visualization, the length units must be Ångströms.

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[5] https://docs.python.org/2/tutorial/datastructures.html#dictionaries

3 Background

3.1 The Born-Oppenheimer Approximation

Under the Born-Oppenheimer approximation the stationary-states [6] of nuclear motion Ψ_{Nu} arise as solutions of the nuclear motion equation.

$$\hat{H}_{\text{Nu}}\Psi_{\text{Nu}}(\mathbf{X}) = E\Psi_{\text{Nu}}(\mathbf{X}) \qquad \hat{H}_{\text{Nu}} \equiv \hat{T}_{\text{Nu}} + E_e(\mathbf{X}) \tag{6}$$

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

$$\hat{H}_e(\mathbf{X})\Psi_e(\mathbf{r}_1, \ldots, \mathbf{r}_n; \mathbf{X}) = E_e(\mathbf{X})\Psi_e(\mathbf{r}_1, \ldots, \mathbf{r}_n; \mathbf{X}) \tag{7}$$

Equation (7) can be solved approximately at any point $\mathbf{X} = (\mathbf{R}_1, \ldots, \mathbf{R}_N)$ using your favorite electronic structure software package (PSI4, CFOUR, Molpro, Gaussian, etc.) and electronic structure method (MP2, CCSD, CISD, etc.).

3.2 Normal Coordinates and the Vibrational Schrödinger Equation

One of the major barriers to solving the nuclear motion equation (6) 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.

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

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

$$E_e(\mathbf{X}) \approx E_e(\mathbf{X}_0) + \frac{1}{2} \sum_{AB}^{3N} \left(\frac{\partial^2 E_e}{\partial X_A \partial X_B} \right)_0 \Delta X_A \Delta X_B \tag{8}$$

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. [7]

$$\hat{T}_{\text{Nu}} = -\frac{1}{2} \sum_A^{3N} \frac{\partial^2}{\partial \tilde{X}_A^2} \tag{9}$$

The nuclear motion equation (6) then becomes

$$\left(-\frac{1}{2} \sum_A^{3N} \frac{\partial^2}{\partial \tilde{X}_A^2} + \frac{1}{2} \sum_{AB}^{3N} \left(\frac{\partial^2 E_e}{\partial \tilde{X}_A \partial \tilde{X}_B} \right)_0 \tilde{X}_A \tilde{X}_B \right) \Psi_{\text{Nu}}(\tilde{\mathbf{X}}) = E_{\text{Nu}}\Psi_{\text{Nu}}(\tilde{\mathbf{X}}) \qquad E_{\text{Nu}} \equiv E - E_e(\mathbf{X}_0) \tag{10}$$

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

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[6] http://en.wikipedia.org/wiki/Stationary_state

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

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

$$(\tilde{\mathbf{H}}_0)_{AB} = \left(\frac{\partial^2 E_e}{\partial \tilde{X}_A \partial \tilde{X}_B}\right)_0 \tag{11}$$

were diagonal, we would have a sum of harmonic oscillator Hamiltonians [8] in equation (10). This dream of a simple Hamiltonian can be realized by choosing a new set of 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 $\mathbf{L}$ [9]

$$\tilde{\mathbf{H}}_0 = \mathbf{L}\boldsymbol{\Lambda}\mathbf{L}^T \qquad \boldsymbol{\Lambda} = \begin{pmatrix} \lambda_1 & 0 & \dots & 0 \\ 0 & \lambda_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \lambda_{3N} \end{pmatrix} \qquad \mathbf{L}\mathbf{L}^T = \mathbf{L}^T\mathbf{L} = \mathbf{1} \tag{12}$$

where the columns of $\mathbf{L}$ are eigenvectors $\boldsymbol{l}_1, \dots, \boldsymbol{l}_{3N}$ of $\tilde{\mathbf{H}}_0$. The mass-weighted Hessian can be put into this form by expressing our coordinates in the basis of its eigenvectors. These new coordinates are called *normal coordinates*, and the coordinate vector is traditionally referred to as $\mathbf{Q}$. The relationship between normal coordinates and mass-weighted Cartesian displacement coordinates is $\mathbf{Q} = \mathbf{L}^T\tilde{\mathbf{X}}$, so that the relationship to Cartesian displacements is

$$\mathbf{Q} = \mathbf{L}^T\mathbf{M}^{\frac{1}{2}}\Delta\mathbf{X} \qquad \mathbf{M}^{\frac{1}{2}} \equiv \begin{pmatrix} \sqrt{M_1} & 0 & \dots & 0 \\ 0 & \sqrt{M_2} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \sqrt{M_{3N}} \end{pmatrix} \tag{13}$$

Cartesian displacements therefore depend on the normal coordinates by the following relationship.

$$\Delta\mathbf{X} = (\mathbf{L}^T\mathbf{M}^{\frac{1}{2}})^{-1}\mathbf{Q} = \mathbf{M}^{-\frac{1}{2}}\mathbf{L}\mathbf{Q}$$

This shows that a motion along the various coordinates $Q_1, \dots, Q_{3N}$ corresponds to a Cartesian displacement by

$$\Delta\mathbf{X}(Q_1, \dots, Q_{3N}) = Q_1\left(\mathbf{M}^{-\frac{1}{2}}\boldsymbol{l}_1\right) + Q_2\left(\mathbf{M}^{-\frac{1}{2}}\boldsymbol{l}_2\right) + \dots + Q_{3N}\left(\mathbf{M}^{-\frac{1}{2}}\boldsymbol{l}_{3N}\right) \tag{14}$$

where the $\boldsymbol{l}_A$ represent column vectors of $\mathbf{L}$, i.e. $\mathbf{L} = \begin{pmatrix} \boldsymbol{l}_1 & \dots & \boldsymbol{l}_{3N} \end{pmatrix}$. We see that each Q_A corresponds to a collective displacement $\Delta\mathbf{X} = \mathbf{M}^{-\frac{1}{2}}\boldsymbol{l}_A$ of several nuclei. The noral coordinates for water are included in an appendix to this handout, and a more detailed interpretation of what these motions represent will be given in the next section. Note that the Hessian matrix $\mathbf{H}$ changes continuously across the potential energy surface, so that each point on the surface is associated with its own set of normal coordinates. Although the normal coordinates at every point span the full space $\mathbb{R}^{3N}$ of nuclear configurations, [10] the normal coordinates at a particular point on the potential surface are generally only physically appropriate for describing nuclear motion within a small region about that configuration.

Expressing equation (10) in terms of these newfangled coordinates, we are left with

$$\left(-\frac{1}{2}\sum_A^{3N}\frac{\partial^2}{\partial Q_A^2} + \frac{1}{2}\sum_A^{3N}\lambda_A Q_A^2\right)\Psi_{\text{Nu}}(\mathbf{Q}) = E_{\text{Nu}}\Psi_{\text{Nu}}(\mathbf{Q}) \tag{15}$$

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

[9]http://en.wikipedia.org/wiki/Symmetric_matrix#Decomposition

[10]i.e., any set of nuclear positions can be specified by a set of values for $Q_1, \dots, Q_{3N}$

(details of the coordinate transformation are shown in an appendix). The Hamiltonian in (15) has the marvelously simple form we were hoping for:

$$\hat{H}_{\text{Nu}} \approx \sum_{A=1}^{3N} \hat{\mathfrak{h}}_A \qquad \hat{\mathfrak{h}}_A \equiv -\frac{1}{2}\frac{\partial^2}{\partial Q_A^2} + \frac{1}{2}\lambda_A Q_A^2 \tag{16}$$

The only approximation for $\hat{H}_{\text{Nu}}$ here is the truncation of the potential energy surface Taylor expansion at second order. As long as λ_A is a positive real number, $\hat{\mathfrak{h}}_A$ is a harmonic oscillator Hamiltonian and we can make the identification $\lambda_A = \omega_A^2$ 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, $\hat{\mathfrak{h}}_A$ actually takes the form of a free-particle Hamiltonian [11]

$$\hat{\mathfrak{h}}_A = -\frac{1}{2}\frac{\partial^2}{\partial Q_A^2} \tag{17}$$

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.

3.2.1 Classical Interpretation of Normal Coordinate Motions

Let $\Delta\mathbf{X}$ represent a displacement from the equilibrium geometry $\mathbf{X}_0$ to some new geometry $\mathbf{X}$:

$$\Delta\mathbf{X} \equiv \mathbf{X} - \mathbf{X}_0 \tag{18}$$

Then note that $\mathbf{H}_0\cdot\Delta\mathbf{X}$ represents the change in the potential energy surface gradient between those two points

$$\mathbf{H}_0 \cdot \Delta\mathbf{X} = \nabla E_e - (\nabla E_e)_0$$

which can be seen by expanding the gradient at $\mathbf{X}$ relative to the gradient at $\mathbf{X}_0$:

$$\frac{\partial E_e}{\partial X_A} \approx \left(\frac{\partial E_e}{\partial X_A}\right)_0 + \sum_B \left(\frac{\partial}{\partial X_B}\frac{\partial E_e}{\partial X_A}\right)_0 \Delta X_B \tag{19}$$

Since $\mathbf{X}_0$ is an equilibrium geometry, the gradient $(\nabla E_e)_0$ vanishes at that point, and we have simply

$$\mathbf{H}_0 \cdot \Delta\mathbf{X} = \nabla E_e$$

Mass-weighting our coordinate axes leaves the same form of expression.

$$\tilde{\mathbf{H}}_0 \cdot \Delta\tilde{\mathbf{X}} = \tilde{\nabla} E_e$$

Now, consider what it means for our displacement to be an eigenvector of $\tilde{\mathbf{H}}$.

$$\tilde{\mathbf{H}}_0 \cdot \Delta\tilde{\mathbf{X}} = \lambda\Delta\tilde{\mathbf{X}} \tag{20}$$

This means that $\Delta\tilde{\mathbf{X}}$ is proportional to the potential energy surface gradient at the displaced geometry

$$\lambda\Delta\tilde{\mathbf{X}} = \tilde{\nabla} E_e$$

Explicitly, this can be written as

$$\lambda\sqrt{M_A}(X_A - (\mathbf{X}_0)_A) = \frac{\partial E_e}{\partial\sqrt{M_A}X_A}$$

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[11]http://en.wikipedia.org/wiki/Free_particle#Non-Relativistic_Quantum_Free_Particle

If we multiply both sides of the equation by $\sqrt{M_A}$, we find that

$$\lambda M_A (X_A - (\mathbf{X}_0)_A) = \frac{\partial E_e}{\partial X_A} \tag{21}$$

From a classical perspective, the gradient of the potential energy $\dfrac{\partial E_e}{\partial X_A}$ is simply a Cartesian component of (minus) the force [12] acting on one of the nuclei. Using Newton's second law, this gives

$$\lambda M_A (X_A - (\mathbf{X}_0)_A) = -M_A (\ddot{\mathbf{X}})_A$$

where $\ddot{\mathbf{X}} \equiv \dfrac{d^2 \mathbf{X}}{dt^2}$. Dividing both sides by M_A, we see that the displacement corresponds to a motion parallel to the acceleration

$$-\lambda(\mathbf{X} - \mathbf{X}_0) = \ddot{\mathbf{X}} \tag{22}$$

Compare this to Hooke's law for a 1D oscillator, which is $m\ddot{x} = -m\omega^2(x - x_0)$. We see, then, that normal coordinates with positive eigenvalues $\lambda > 0$ correspond to directions of motion along which the potential is "spring-like", inducing a force that accelerates the nuclei back to their equilibrium position along the direction of displacement. It is useful to consider the cases $\lambda = 0$ and $\lambda < 0$ as well. When $\lambda = 0$, as for translational and rotational modes at equilibrium, there is no force to constrain the motion along these coordinates. When λ is negative, as will be true of one or more modes at non-equilibrium points, equation (22) shows that displacement induces an acceleration of the nuclei *away* from the reference geometry.

3.2.2 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 (15).

$$\left(\sum_{A=1}^{3N} \hat{\mathfrak{h}}_A \right) \Psi_{\text{Nu}}(\mathbf{Q}) = E_{\text{Nu}} \Psi_{\text{Nu}}(\mathbf{Q}) \qquad \hat{\mathfrak{h}}_A = -\frac{1}{2} \frac{\partial^2}{\partial Q_A^2} + \frac{1}{2} \lambda_A Q_A^2$$

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

$$\Psi_{\text{Nu}}(Q_1, \ldots, Q_{3N}) = \psi_1(Q_1)\psi_2(Q_2) \cdots \psi_{3N}(Q_{3N}) \tag{23}$$

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

$$\hat{\mathfrak{h}}_A \psi_A(Q_A) = \varepsilon \psi_A(Q_A) \tag{24}$$

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.[13]

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

$$-\frac{1}{2} \frac{\partial^2 \psi(Q_A)}{\partial Q_A^2} = \varepsilon \psi(Q_A) \tag{25}$$

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[12] http://en.wikipedia.org/wiki/Classical_mechanics#Work_and_energy

[13] e.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.

Solutions to this differential equation are given by

$$\psi_{P_A}(Q_A) = e^{iP_A(Q_A - \theta_A)} \tag{26}$$

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

Although $\lambda = 0$ also holds for rotational modes at equilibrium, normal coordinates are only appropriate for parametrizing infinitesimal rotations and quickly break down for larger rotational motions (see the images in section 3.3.2). 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 (section 3.3.2) with vibrational ones (section 3.3.3), 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. [14]

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

$$-\frac{1}{2}\frac{\partial^2 \psi(Q_A)}{\partial Q_A^2} + \frac{1}{2}\lambda_A Q_A^2 = \varepsilon \psi(Q_A) \tag{27}$$

are given by

$$\psi_{n_A}(Q_A) = \frac{1}{\sqrt{2^n n!}}\left(\frac{\omega_A}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\omega_A Q_A^2}\,\mathrm{He}_n(\sqrt{\omega_A}Q_A) \qquad \omega_A^2 = \lambda_A \tag{28}$$

with energies $\varepsilon_{n_A} = \omega_A(n_A + \frac{1}{2})$, where $\mathrm{He}_n(x)$ is the nth Hermite polynomial.

$$\mathrm{He}_n(x) = (-1)^n e^{x^2}\left(\frac{d^n}{dx^n}e^{-x^2}\right) \tag{29}$$

Hence, the solution to the *vibrational Schrödinger equation* [15]

$$\sum_{A=1}^{3N-6}\left(-\frac{1}{2}\frac{\partial^2}{\partial Q_A^2} + \omega_A^2 Q_A^2\right)\Psi_{\text{vib}} = E_{\text{vib}}\Psi_{\text{vib}} \tag{30}$$

is given by

$$\Psi_{n_1,\ldots,n_{3N-6}}(Q_1,\ldots,Q_{3N-6}) = \prod_{A=1}^{3N-6}\psi_{n_A}(Q_A) \tag{31}$$

with vibrational energy

$$E_{n_1,\ldots,n_{3N-6}} = \sum_{A=1}^{3N-6}\omega_A\left(n_A + \frac{1}{2}\right) \tag{32}$$

The total molecular energy at equilibrium is the sum of translational, rotational, vibrational, and electronic contributions.
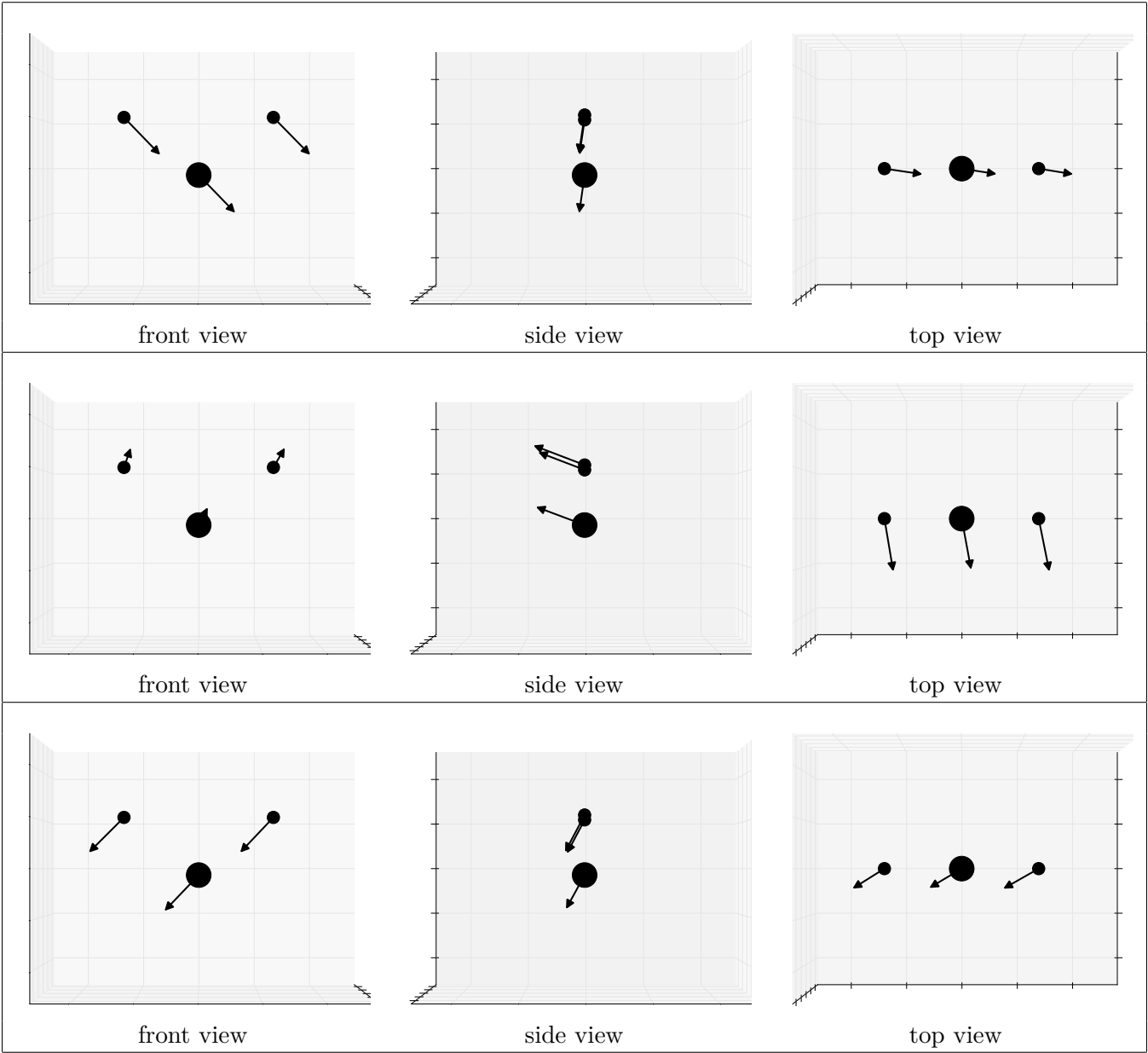
$$E = \frac{\mathbf{P}_{\text{CM}}^2}{2M_{\text{tot}}} + E_{\text{vib}} + E_{\text{rot}} + E_e(\mathbf{X}_0) \tag{33}$$

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[14]This briefly discussed in N. V. Cohan and H. F. Hameka, *J. Chem. Phys.* 45, 4392 (1966).
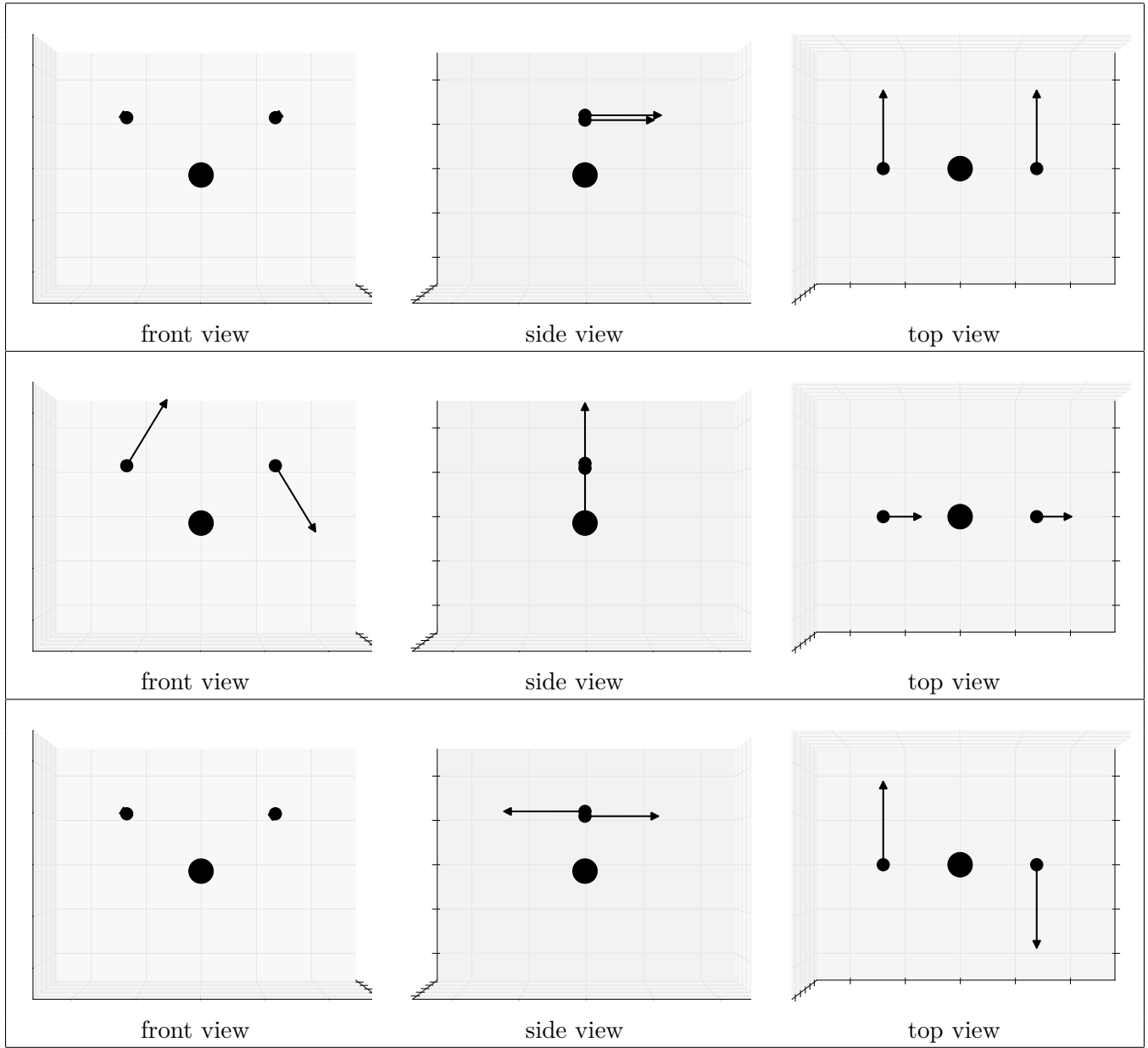
[15]This is simply equation (15) with translational and rotational modes omitted.

3.3 Appendix: Normal Coordinates for Water

3.3.1 Translational Modes

front view	side view	top view
front view	side view	top view
front view	side view	top view

3.3.2 Rotational Modes

front view	side view	top view
front view	side view	top view
front view	side view	top view

3.3.3 Vibrational Modes

| front view | side view | top view |

| front view | side view | top view |

| front view | side view | top view |
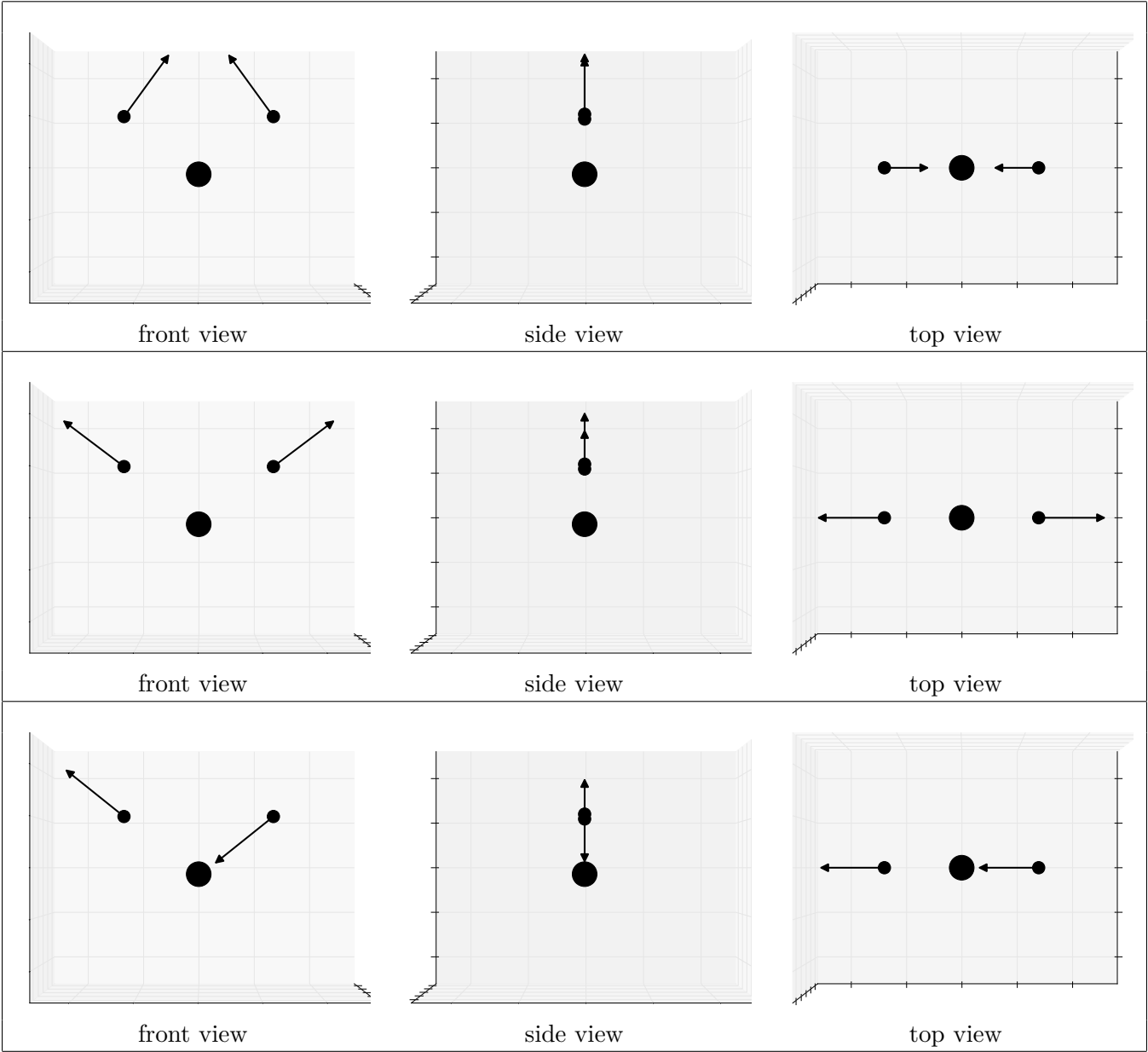
3.4 Appendix: Details of the Coordinate Transformation

It is worth showing how this coordinate transformation works explicitly. In particular, we should show how the derivatives transform to arrive at equation (15). Since $\tilde{\mathbf{X}}^T \tilde{\mathbf{H}}_0 \tilde{\mathbf{X}} = (\mathbf{L}^T \tilde{\mathbf{X}})^T \mathbf{\Lambda} \mathbf{L}^T \tilde{\mathbf{X}}$, the normal coordinates are given in terms of mass-weighted Cartesian displacements as

$$\mathbf{Q} = \mathbf{L}^T \tilde{\mathbf{X}}$$

or

$$Q_A(\tilde{X}_1, \ldots, \tilde{X}_{3N}) = \sum_{B=1}^{3N} L_{BA} \tilde{X}_B \tag{34}$$

Then the derivative with respect to $\tilde{X}_A$ can be expressed in terms of derivatives with respect to normal coordinates $\{Q_A\}$ as

$$\frac{\partial}{\partial \tilde{X}_A} = \sum_B \frac{\partial Q_B}{\partial \tilde{X}_A} \frac{\partial}{\partial Q_B} = \sum_{BC} \frac{\partial L_{CB} \tilde{X}_C}{\partial \tilde{X}_A} \frac{\partial}{\partial Q_B} = \sum_B L_{AB} \frac{\partial}{\partial Q_B} \tag{35}$$

where we have used the fact that

$$\frac{\partial \tilde{X}_C}{\partial \tilde{X}_A} = \delta_{CA}$$

(δ_{CA} being the Kronecker delta [16]). Then we can see that the kinetic energy operator transforms as follows.

$$\sum_A \frac{\partial^2}{\partial \tilde{X}_A^2} = \sum_{ABC} \frac{\partial^2}{\partial Q_B \partial Q_C} L_{AB} L_{AC} = \sum_{BC} \frac{\partial^2}{\partial Q_B \partial Q_C} (\mathbf{L}^T \mathbf{L})_{BC}$$

Since $\mathbf{L}$ is an orthogonal matrix, $(\mathbf{L}^T \mathbf{L})_{BC} = (\mathbf{1})_{BC} = \delta_{BC}$, and so

$$\hat{T}_{\mathrm{Nu}} = -\frac{1}{2} \sum_A \frac{\partial^2}{\partial \tilde{X}_A^2} = -\frac{1}{2} \sum_B \frac{\partial^2}{\partial Q_B^2} \quad . \tag{36}$$

In a similar fashion, we can verify that the transformed Hessian matrix is in fact simply the Hessian with respect to normal coordinates by comparing

$$\left(\frac{\partial^2 E_e}{\partial \tilde{X}_A \partial \tilde{X}_B} \right)_0 = \sum_{CD} \left(\frac{\partial^2 E_e}{\partial Q_C \partial Q_D} \right)_0 L_{AC} L_{BD}$$

to

$$\left(\frac{\partial^2 E_e}{\partial \tilde{X}_A \partial \tilde{X}_B} \right)_0 = (\tilde{\mathbf{H}}_0)_{AB} = (\mathbf{L} \mathbf{\Lambda} \mathbf{L}^T)_{AB} = \sum_{CD} (\lambda_C \delta_{CD}) L_{AC} L_{BD}$$

which shows that

$$\left(\frac{\partial^2 E_e}{\partial Q_C \partial Q_D} \right)_0 = \lambda_C \delta_{CD} \tag{37}$$

That is, we have identified the diagonal elements $\{\lambda_A\}$ of $\mathbf{\Lambda}$ as corresponding to

$$\lambda_A \equiv \left(\frac{\partial^2 E_e}{\partial Q_A^2} \right)_0 \tag{38}$$

and shown that mixed derivatives are zero

$$\left(\frac{\partial^2 E_e}{\partial Q_A \partial Q_B} \right)_0 = 0 \qquad \text{if } A \neq B \; . \tag{39}$$

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[16] http://en.wikipedia.org/wiki/Kronecker_delta