

# CHEM3023: Spins, Atoms and Molecules

## Lecture 10

### Normal modes and molecular structure optimisation

C.-K. Skylaris

#### Learning outcomes

- Be able to describe molecular vibrations and chemical reactions using the potential energy surface
- Be able to perform molecular structure optimisation using Hartree-Fock calculations

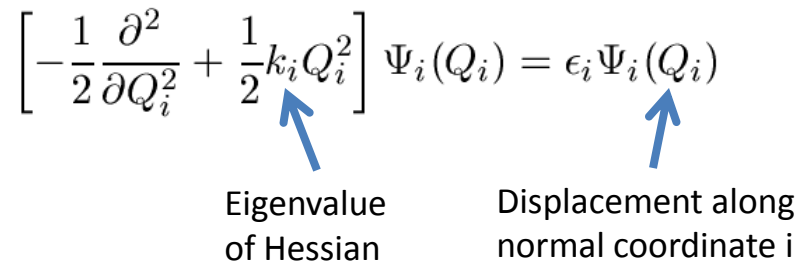
# Polyatomic molecules: Normal coordinates

- Molecules with more than two atoms can also be treated with the harmonic approximation
- Their  $3N_{\text{at}}$  atomic coordinates can be transformed to **normal coordinates**
- In normal coordinates the nuclear Schrödinger equation decomposes into  $3N_{\text{at}}$  **independent harmonic oscillator equations** (see OPTIONAL notes, at the end)
- The vibrational frequencies that result can be used to predict IR spectra
- The **zero point vibrational energy** of a molecule can be computed by adding to  $E_{\text{pES}}$  the zero point energy of each normal mode
- Thermodynamic properties (e.g. vibrational entropy and free energy) can also be computed by taking into account the contribution from each normal mode using the laws of statistical mechanics

# Normal modes

$3N_{\text{at}}$  harmonic oscillator Schrödinger equations

$$\left[ -\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} k_i Q_i^2 \right] \Psi_i(Q_i) = \epsilon_i \Psi_i(Q_i)$$



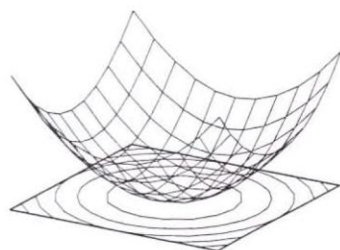
Eigenvalue of Hessian                  Displacement along normal coordinate i

$$E = \epsilon_1 + \epsilon_2 + \dots + \epsilon_{3N_{\text{at}}} \quad \Psi_{\text{nuc}}(\mathbf{Q}) = \Psi_1(Q_1) \Psi_2(Q_2) \dots \Psi_{3N_{\text{at}}}(Q_{3N_{\text{at}}})$$

- Each normal mode describes one collective motion that the atoms can do, independently of the other normal modes
- The total motion (within the harmonic approximation) is the superposition of the normal modes
- Many useful properties can be derived from the above. First we will examine how we can use the Hessian eigenvalues to characterise stationary points

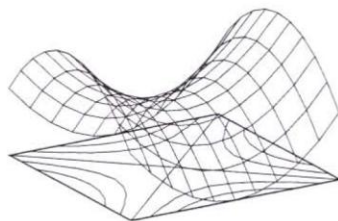
# Characterisation of stationary points

- For nonlinear molecules 6 normal mode frequencies are zero because they describe the translation and rotation of the entire molecule
- If all the remaining frequencies are positive, the molecular geometry is a minimum point on the PES



Reactant/Product  
(minimum)

- If one of the remaining frequencies is imaginary (square root of negative second derivative w.r.t. normal coordinate) and all the rest are positive, the molecular geometry is a saddle point on the PES (maximum along one normal mode direction and minimum along all others)



Transition state  
(saddle point)

## Zero-point vibrational energy

Under the harmonic approximation, the nuclear motion at a stationary point on the PES can be split into independent vibrations along the normal coordinates

$$\left[ -\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} k_i Q_i^2 \right] \Psi_i(Q_i) = \epsilon_i \Psi_i(Q_i)$$

The solution of the Schrödinger equation for a harmonic oscillator is well known, with energy levels (not in atomic units):

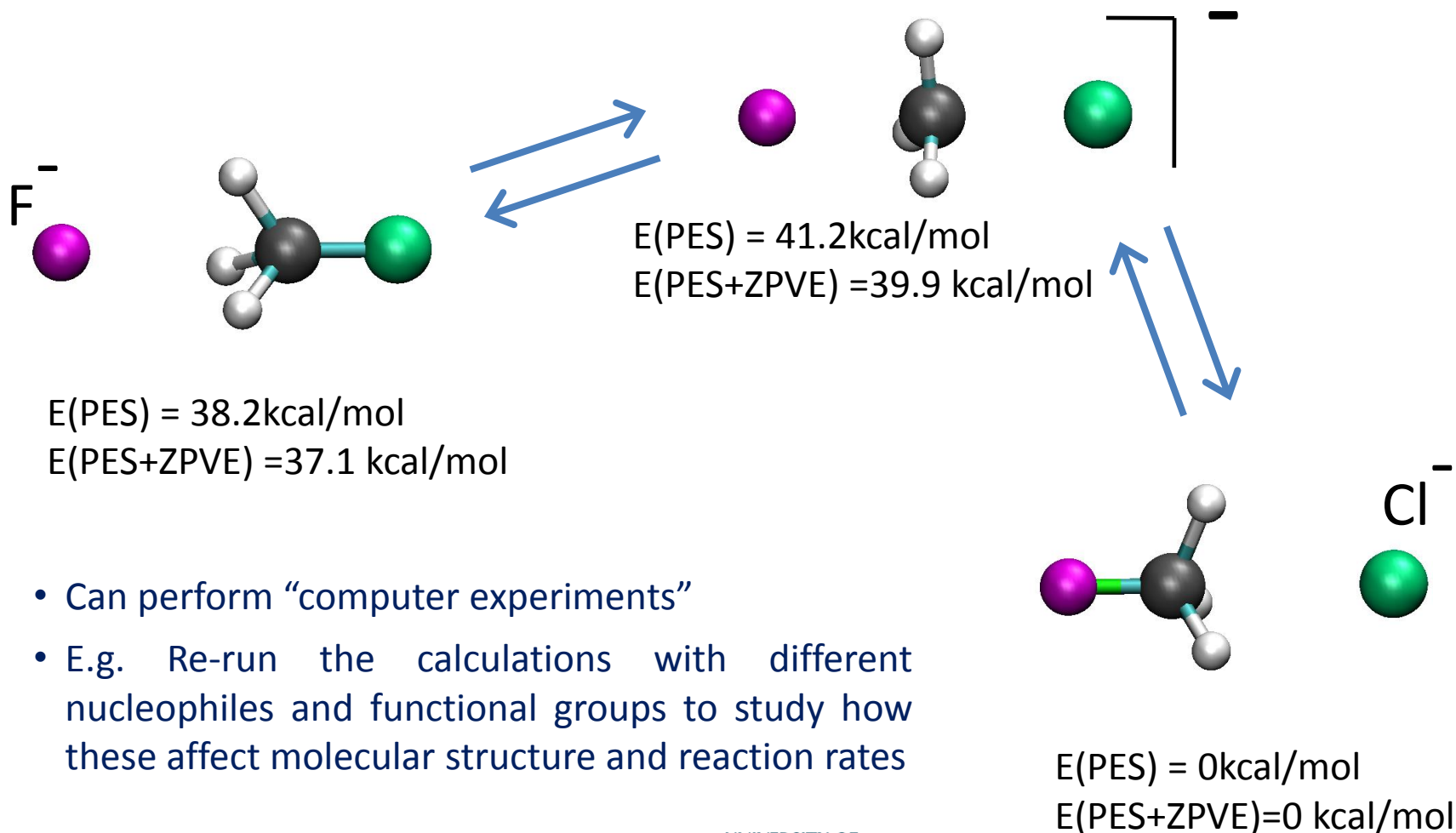
$$\epsilon_i = \left( n_i + \frac{1}{2} \right) h\nu_i \quad n_i = 0, 1, 2, \dots \quad \nu_i = \frac{\sqrt{k_i}}{2\pi}$$

Therefore the energy of a molecule (at 0K) should include the sum of all its vibrational levels and is called the zero-point vibrational energy

$$U_0 = E_{PES} + \sum_{i=1}^{3N_{at}-6} \frac{1}{2} h\nu_i$$

## Example: Nucleophilic attack reaction

Hartree-Fock calculations with 6-31+G\* basis set



- Can perform “computer experiments”
- E.g. Re-run the calculations with different nucleophiles and functional groups to study how these affect molecular structure and reaction rates

## Finding the equilibrium geometry

- The Potential Energy Surface (PES),  $E_{PES}(\mathbf{X})$ , is a function of the  $3 \times N_{at}$  nuclear coordinates:

$$X_1, X_2, \dots, X_{3N_{at}} = R_{1x}, R_{1y}, R_{1z}, R_{2x}, R_{2y}, R_{2z}, \dots, R_{N_{at}x}, R_{N_{at}y}, R_{N_{at}z}$$

- At each point on the PES an atom “feels” a force, according to

$$F_i = -\frac{E_{PES}}{\partial X_i}$$

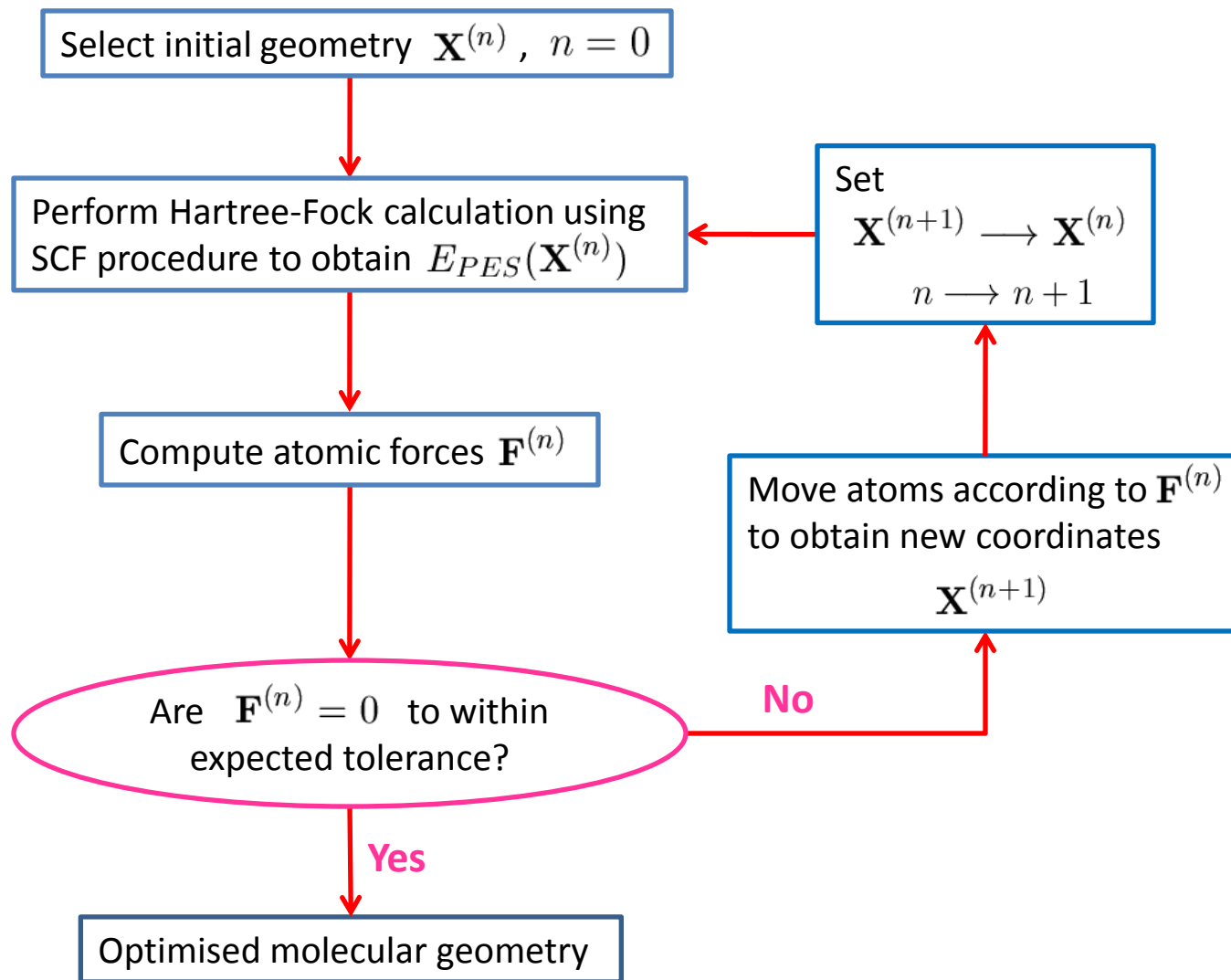
which points to the direction of lowest energy

- The stationary points (equilibrium geometries and transition states) are defined by:

$$\frac{E_{PES}}{\partial X_1} = \frac{E_{PES}}{\partial X_2} = \dots = \frac{E_{PES}}{\partial X_{3N_{at}}} = 0$$

- To optimise the geometry we need to allow the atoms to move according to the forces that act on them, until these forces become zero. This is also called “geometry relaxation”

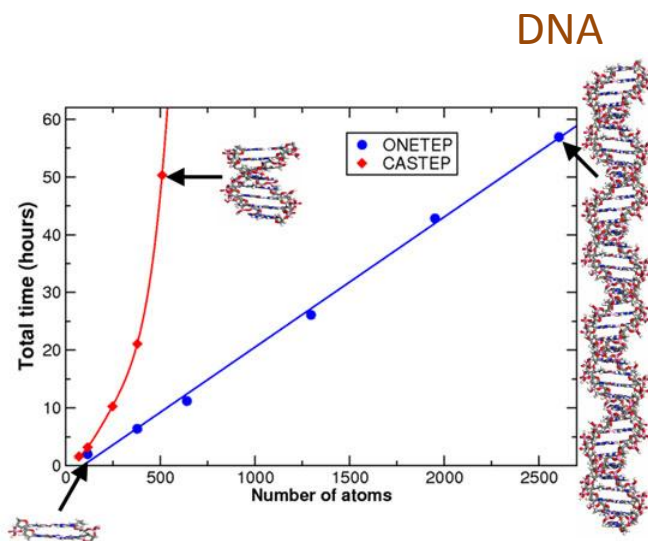
# Geometry optimisation procedure





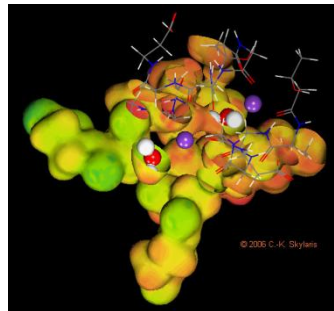
# Recent developments in quantum chemistry

- Density Functional Theory (DFT) includes electronic correlation at a level of complexity similar to that of Hartree-Fock theory
- Linear-scaling DFT: Quantum simulations are being extended to thousands of atoms. Possible to study entire biomolecules and nanostructures

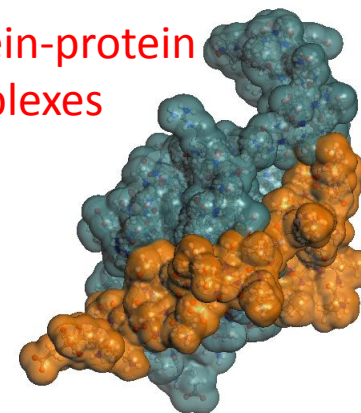


[www.onetep.soton.ac.uk](http://www.onetep.soton.ac.uk)

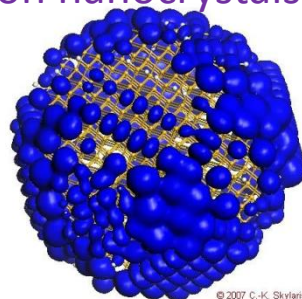
Ion channels



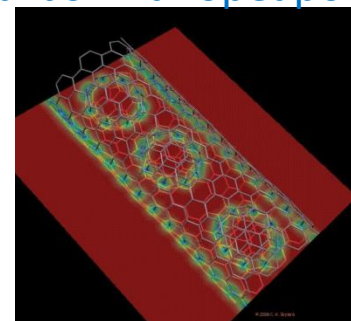
Protein-protein complexes



Silicon nanocrystals



Carbon nanopeapods



## We have come a long way...




*The Villa Hertzog, where wave mechanics was discovered during the Christmas holidays, 1925–26.*



The underlying laws necessary for the mathematical theory of ... the whole of **chemistry** are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble...

### Computational Quantum:

- **Chemistry**
- **Materials Science**
- **Molecular Biology**
- **Solid State Physics**

 HECToR - UK National Supercomputing Service

...comprises 1416 compute blades, each of which has 4 dual-core processor sockets. This amounts to a total of 11,328 cores, each of which acts as a single CPU.  
... peak performance of the system is 59 Tflops.

## Summary / Reading assignment

- Normal coordinates (Cramer, pages 336-338)
- Zero-point vibrational energy (Cramer, pages 355-357)
- Molecular geometry optimisation and transition state search on potential energy surface (Cramer, pages 40-46)

## OPTIONAL: The nuclear Schrödinger equation

We will work with the Taylor expansion of the PES up to second order

$$E_{PES}(\mathbf{X}) \simeq E_{PES}(\mathbf{X}_0) + (\mathbf{X} - \mathbf{X}_0)^\dagger \mathbf{g}(\mathbf{X}_0) + \frac{1}{2}(\mathbf{X} - \mathbf{X}_0)^\dagger \mathbf{H}(\mathbf{X}_0)(\mathbf{X} - \mathbf{X}_0)$$

where we have  $3N_{at}$  nuclear coordinates:

$$X_1, X_2, \dots, X_{3N_{at}} = R_{1x}, R_{1y}, R_{1z}, R_{2x}, R_{2y}, R_{2z}, \dots, R_{N_{at}x}, R_{N_{at}y}, R_{N_{at}z}$$

If  $\mathbf{X}_0$  is a stationary point (lets call it point  $\mathbf{X}_s$ ), the gradient is zero by definition  $\mathbf{g}(\mathbf{X}_s) = 0$  and the PES simplifies to:

$$E_{PES}(\mathbf{X}) \simeq E_{PES}(\mathbf{X}_s) + \frac{1}{2}(\mathbf{X} - \mathbf{X}_s)^\dagger \mathbf{H}(\mathbf{X}_s)(\mathbf{X} - \mathbf{X}_s)$$

- A stationary point on the PES can be either an equilibrium geometry (reactant, product) or a transition state

# The nuclear Schrödinger equation

We will use the second order PES (**harmonic approximation**), expanded around a stationary point, as the potential in the nuclear Schrödinger equation

$$E_{PES}(\mathbf{X}) \simeq E_{PES}(\mathbf{X}_s) + \frac{1}{2}(\mathbf{X} - \mathbf{X}_s)^\dagger \mathbf{H}(\mathbf{X}_s)(\mathbf{X} - \mathbf{X}_s) = E_{PES}(\mathbf{X}_s) + \frac{1}{2}\Delta\mathbf{X}^\dagger \mathbf{H}(\mathbf{X}_s)\Delta\mathbf{X}$$

$$\left[ \sum_{i=1}^{3N_{at}} -\frac{1}{2m_i} \frac{\partial^2}{\partial X_i^2} + E_{PES}(\mathbf{X}) \right] \Psi_{nuc}(\mathbf{X}) = E' \Psi_{nuc}(\mathbf{X})$$

 Kinetic energy  
of nuclei

 Potential energy  
of nuclei

 Nuclear  
wavefunction

where  $m_1 = M_1, m_2 = M_1, m_3 = M_1$  and  $m_4 = M_2, m_5 = M_2, m_6 = M_2$  etc.

We can re-arrange to incorporate the (constant) energy of the stationary point to the right hand side

$$\left[ \sum_{i=1}^{3N_{at}} -\frac{1}{2m_i} \frac{\partial^2}{\partial X_i^2} + E_{PES}(\mathbf{X}_s) + \frac{1}{2}\Delta\mathbf{X}^\dagger \mathbf{H}(\mathbf{X}_s)\Delta\mathbf{X} \right] \Psi_{nuc}(\mathbf{X}) = E' \Psi_{nuc}(\mathbf{X})$$

$$\left[ \sum_{i=1}^{3N_{at}} -\frac{1}{2m_i} \frac{\partial^2}{\partial X_i^2} + \frac{1}{2}\Delta\mathbf{X}^\dagger \mathbf{H}(\mathbf{X}_s)\Delta\mathbf{X} \right] \Psi_{nuc}(\mathbf{X}) = (E' - E_{PES}(\mathbf{X}_s)) \Psi_{nuc}(\mathbf{X})$$

$$\left[ \sum_{i=1}^{3N_{at}} -\frac{1}{2m_i} \frac{\partial^2}{\partial X_i^2} + \frac{1}{2}\Delta\mathbf{X}^\dagger \mathbf{H}(\mathbf{X}_s)\Delta\mathbf{X} \right] \Psi_{nuc}(\mathbf{X}) = E \Psi_{nuc}(\mathbf{X})$$

## Mass-weighted coordinates

The next step is to introduce mass-weighted coordinates:

$$Y_i = \sqrt{m_i} \Delta X_i$$

- These coordinates are defined in terms of displacements from the point  $\mathbf{X}_s$ , instead of absolute position
- Using the chain rule for differentiation show that the nuclear Schrödinger equation can be written in terms of the mass-weighted coordinates as follows:

$$\left[ \sum_{i=1}^{3N_{at}} -\frac{1}{2} \frac{\partial^2}{\partial Y_i^2} + \frac{1}{2} \mathbf{Y}^\dagger \mathbf{H} \mathbf{Y} \right] \Psi_{nuc}(\mathbf{Y}) = E \Psi_{nuc}(\mathbf{Y})$$

## Normal coordinates

Finally we need to work with the Hessian matrix. As it is a symmetric matrix, there exists a unitary matrix (of its eigenvectors) that can diagonalise it

$$\mathbf{H}\mathbf{U} = \mathbf{U}\mathbf{k} \Leftrightarrow \mathbf{U}^\dagger\mathbf{H}\mathbf{U} = \mathbf{k} \quad \mathbf{U}^\dagger\mathbf{U} = \mathbf{U}\mathbf{U}^\dagger = \mathbf{I}$$

The eigenvectors of the matrix can be used to transform the atomic displacement into **normal coordinates**

$$\mathbf{Q} = \mathbf{U}^\dagger\mathbf{Y} \Leftrightarrow Q_k = \sum_j U_{kj}^\dagger Y_j$$

Then, using the chain rule

$$\frac{\partial}{\partial Y_i} = \sum_k \frac{\partial}{\partial Q_k} \frac{\partial Q_k}{\partial Y_i} = \sum_k \frac{\partial}{\partial Q_k} U_{ki}^\dagger$$

and the following relation

$$\mathbf{Y}^\dagger\mathbf{H}\mathbf{Y} = \mathbf{Y}^\dagger\mathbf{U}\mathbf{U}^\dagger\mathbf{H}\mathbf{U}\mathbf{U}^\dagger\mathbf{Y} = \mathbf{Q}^\dagger\mathbf{k}\mathbf{Q}$$

Substituting all the normal coordinate terms into

$$\left[ \sum_{i=1}^{3N_{at}} -\frac{1}{2} \frac{\partial^2}{\partial Y_i^2} + \frac{1}{2} \mathbf{Y}^\dagger \mathbf{H} \mathbf{Y} \right] \Psi_{nuc}(\mathbf{Y}) = E \Psi_{nuc}(\mathbf{Y})$$

results in the following form

$$\sum_{i=1}^{3N_{at}} \left[ -\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} k_i Q_i^2 \right] \Psi_{nuc}(\mathbf{Q}) = E \Psi_{nuc}(\mathbf{Q})$$

which is very useful:

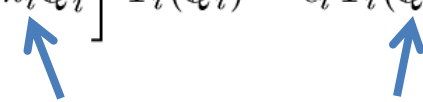
- The nuclear Hamiltonian has been split into a sum of  $3N_{at}$  independent Hamiltonians
- We can now split it into  $3N_{at}$  independent Schrödinger equations, and split the wavefunction into a product of wavefunctions, one for each coordinate



## Vibrational Hamiltonian

Each of the  $3N_{\text{at}}$  equations is actually a Schrödinger equation for a harmonic oscillator

$$\left[ -\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} k_i Q_i^2 \right] \Psi_i(Q_i) = \epsilon_i \Psi_i(Q_i)$$



Eigenvalue of Hessian                  Displacement along normal coordinate i

$$E = \epsilon_1 + \epsilon_2 + \dots + \epsilon_{3N_{\text{at}}} \qquad \Psi_{\text{nuc}}(\mathbf{Q}) = \Psi_1(Q_1) \Psi_2(Q_2) \dots \Psi_{3N_{\text{at}}}(Q_{3N_{\text{at}}})$$

- Each normal mode describes one collective motion that the atoms can do, independently of the other normal modes
- The total motion (within the harmonic approximation) is the superposition of the normal modes