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Coding tips

Google frequently
Ask for help
You are not your code
Frustration isn't failure
Try a variety of tutorials/books/resources
Comment generously
Debugging is learning
Feeling clueless is ok
Coding is thinking, give it time
Celebrate your own wins

Have fun!

1:11 PM - 13 Nov 2019

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CH40208: TOPICS IN COMPUTATIONAL CHEMISTRY

EIGENVALUES AND EIGENVECTORS (IN PYTHON)

HOUSEKEEPING → EXAMS

- 4/12/19 (next week): Class test 1 → Programming exam
  You will have a structured piece of code to build
  (similar to, but not as big as the Data Analysis exercise)
  2.5 hours → 10:20 start

- 11/12/19 (two weeks time): Class test 2 → test-driven development exam
  You will be given a series of tests and tasked with writing code that passes these.
  (very similar to the week 5 exercise).
  2 hours → 10:20 start

- Open book exam!

- NO INTERNET!!

HOUSEKEEPING → FEEDBACK FORMS

- Super helpful for us! Please complete one of these if you have not already done so!
- From last week's feedback:
  - Live coding examples

FIRST: HOUSEKEEPING

- Drew's "office hours" 2:00–5:00*.

THIS WEEK: EIGENVECTORS AND EIGENVALUES

- Vectors & Matrices recap
- A geometric explanation of eigenvalues and eigenvectors.
- Applications:
  - more molecular rotations!
    → finding principal rotation axes and moments of inertia (theory & Python)
  - solving the Schrödinger equation
    → molecular orbitals and orbital energies (theory & a little bit of Python)

VECTORS AND MATRICES — REVIEW FROM LAST WEEK

DEMO

EIGENVALUES AND EIGENVECTORS

DEMO

EIGENVALUES AND EIGENVECTORS

$$\lambda \mathbf{v} = \mathbf{M} \cdot \mathbf{v}$$

λ = eigenvalue of $\mathbf{M}$

$\mathbf{v}$ = eigenvector of $\mathbf{M}$

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Applications in chemistry:

- molecular rotations: principal rotation axes & moments of inertia.

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Applications in chemistry:

- molecular rotations: principal rotation axes & moments of inertia.
- molecular vibrations: normal modes & vibrational frequencies.

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Applications in chemistry:

- molecular rotations: principal rotation axes & moments of inertia.
- molecular vibrations: normal modes & vibrational frequencies.
- $\mathbf{H\Psi} = E\mathbf{\Psi}$: molecular orbitals & their energies.

PRINCIPAL ROTATION AXES AND MOMENTS OF INERTIA

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- Molecular rotational energy levels depend on the molecule's moments of inertia.
- Used for
  - interpreting rotational spectra.
  - calculating the rotational partition function:

$$q_{\mathrm{rot}} = \frac{\pi^{\frac{1}{2}}}{\sigma}\left(\frac{k_{\mathrm{B}}T}{hcA}\right)^{\frac{1}{2}}\left(\frac{k_{\mathrm{B}}T}{hcB}\right)^{\frac{1}{2}}\left(\frac{k_{\mathrm{B}}T}{hcC}\right)^{\frac{1}{2}}$$

  - *A*, *B*, and *C* are the principal moments of inertia of a non-linear molecule.

MOMENTS OF INERTIA ARE ANALOGOUS TO INERTIAL MASS

linear motion

$$\mathbf{F} = m\,\mathbf{a} \qquad \mathbf{p} = m\,\mathbf{v}$$

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linear motion

$$\mathbf{F} = m\,\mathbf{a} \qquad \mathbf{p} = m\,\mathbf{v}$$

angular motion

$$\boldsymbol{\tau} = \mathbf{I}\,\boldsymbol{\alpha} \qquad \mathbf{L} = \mathbf{I}\,\boldsymbol{\omega}$$

ANGULAR MOMENTUM

- Diatomic molecule (rigid rotor)
  - $L = I\,\omega$
  - $I = \sum_i m_i r_i^2$
  - $I = \mu r^2$

ANGULAR MOMENTUM

- Diatomic molecule (rigid rotor)
  - $L = I\,\omega$
  - $I = \sum_i m_i r_i^2$
  - $I = \mu r^2$
- Polyatomic molecule
  - $\mathbf{L} = \mathbf{I}\,\boldsymbol{\omega}$
  - $$\begin{bmatrix} L_x \\ L_y \\ L_z \end{bmatrix} = \begin{bmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{yx} & I_{yy} & -I_{yz} \\ -I_{zx} & -I_{zy} & I_{zz} \end{bmatrix} \cdot \begin{bmatrix} \omega_x \\ \omega_y \\ \omega_z \end{bmatrix}$$

ANGULAR MOMENTUM

$$\mathbf{I} = \begin{bmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{yx} & I_{yy} & -I_{yz} \\ -I_{zx} & -I_{zy} & I_{zz} \end{bmatrix}$$

moments of inertia

$$I_{xx} = \sum_i m_i(y_i^2 + z_i^2)$$

$$I_{yy} = \sum_i m_i(x_i^2 + z_i^2)$$

$$I_{zz} = \sum_i m_i(x_i^2 + y_i^2)$$

products of inertia

$$I_{xy} = \sum_i m_i x_i y_i$$

$$I_{xz} = \sum_i m_i x_i z_i$$

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complex / non-intuitive

$$\mathbf{I} = \begin{bmatrix} I_{xx} & 0 & 0 \\ 0 & I_{yy} & 0 \\ 0 & 0 & I_{zz} \end{bmatrix}$$

simple / intuitive

ANGULAR MOMENTUM

elements of inertia matrix depend on positions in $\{x, y, z\}$ coordinate system

moments of inertia

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can we choose a “better” set of {*x*, *y*, *z*} basis vectors?

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can we choose a “better” set of {*x*, *y*, *z*} basis vectors?

YES! (if we use the eigenvectors of $\mathbf{I}$ as basis vectors)

ANGULAR MOMENTUM

the goal:

$$\mathbf{L} = \begin{bmatrix} I_{xx} & 0 & 0 \\ 0 & I_{yy} & 0 \\ 0 & 0 & I_{zz} \end{bmatrix} \cdot \omega$$

ANGULAR MOMENTUM

$$\lambda_1 \mathbf{v}_1 = \mathbf{I}\,\mathbf{v}_1$$
$$\lambda_2 \mathbf{v}_2 = \mathbf{I}\,\mathbf{v}_2$$
$$\lambda_3 \mathbf{v}_3 = \mathbf{I}\,\mathbf{v}_3$$

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ANGULAR MOMENTUM

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ANGULAR MOMENTUM

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eigenvectors define a “natural” coordinate system → principal axes of rotation

eigenvalues give the principal moments of inertia.

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eigenvectors define a “natural” coordinate system → principal axes of rotation

eigenvalues give the principal moments of inertia.

QUESTIONS?

ALIGNING A MOLECULE WITH THE PRINCIPAL AXES OF ROTATION

$$\lambda_1 \mathbf{v}_1 = \mathbf{I}\,\mathbf{v}_1 \qquad \mathbf{i} \rightarrow \mathbf{v}_1$$
$$\lambda_2 \mathbf{v}_2 = \mathbf{I}\,\mathbf{v}_2 \qquad \mathbf{j} \rightarrow \mathbf{v}_2 \qquad \mathbf{R} = \begin{bmatrix} \mathbf{v}_1 & \mathbf{v}_2 & \mathbf{v}_3 \\ & & \end{bmatrix}$$
$$\lambda_3 \mathbf{v}_3 = \mathbf{I}\,\mathbf{v}_3 \qquad \mathbf{k} \rightarrow \mathbf{v}_3$$

To rotate $\{x, y, z\}$ so that they align with the principal axes we would use the rotation matrix where the eigenvectors of $\mathbf{I}$ are the columns.

ALIGNING A MOLECULE WITH THE PRINCIPAL AXES OF ROTATION

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$$\lambda_3 \mathbf{v}_3 = \mathbf{I}\,\mathbf{v}_3 \qquad \mathbf{k} \rightarrow \mathbf{v}_3$$

$$\mathbf{R} = \begin{bmatrix} \mathbf{v}_1 & \mathbf{v}_2 & \mathbf{v}_3 \\ & & \end{bmatrix}$$

To rotate $\{x, y, z\}$ so that they align with the principal axes we would use the rotation matrix where the eigenvectors of $\mathbf{I}$ are the columns.

BUT we want to rotate our molecule so that the principal axes are aligned with $\{x, y, z\}$. This is the inverse operation, so we invert the matrix $\mathbf{R}$.

EXAMPLE WITH A LINEAR DIATOMIC

DEMO

MOLECULAR ORBITALS AND ENERGIES EIGENFUNCTIONS AND EIGENVALUES

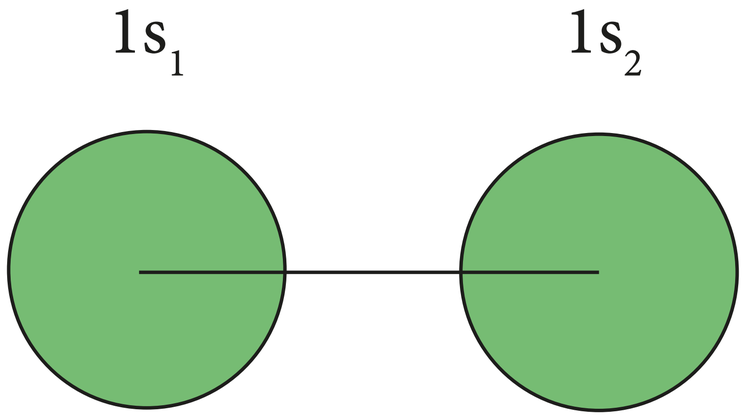
The TISE is an eigenvalue equation: $\mathbf{H}\Psi = E\Psi$

Wavefunctions constructed using LCAO are vectors: $\Psi = \sum c_i \phi_i$

Using this atomic orbital basis, the Hamiltonian operator is a matrix:

$$\mathbf{H} = \begin{bmatrix} h_{11} & h_{12} & h_{13} & h_{14} \\ h_{21} & h_{22} & h_{23} & h_{24} \\ h_{31} & h_{32} & h_{33} & h_{34} \\ h_{41} & h_{42} & h_{43} & h_{44} \end{bmatrix}$$

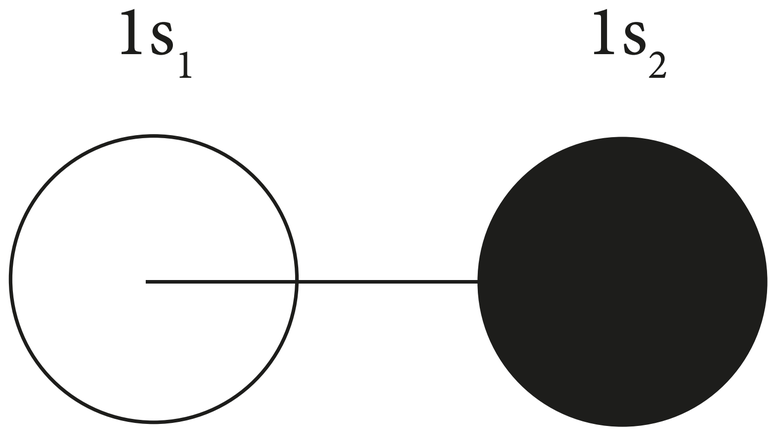
EXAMPLE: H_2



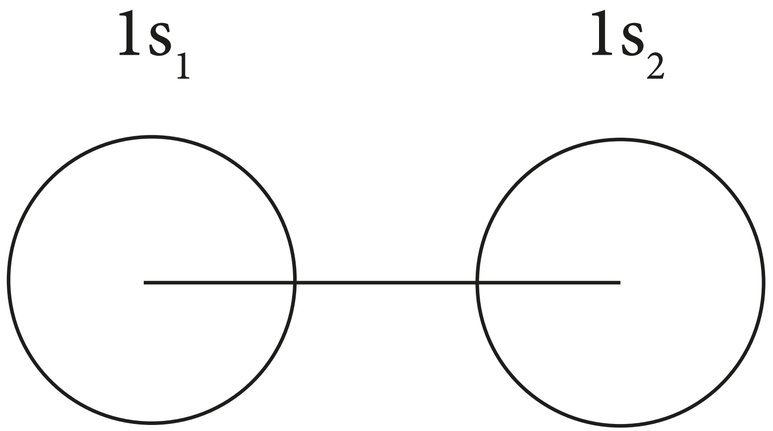
$$\mathbf{\Psi} = c_1\boldsymbol{\phi}_1 + c_2\boldsymbol{\phi}_2$$

$$\mathbf{H} = \begin{bmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{bmatrix} = \begin{bmatrix} \epsilon & S_{12} \\ S_{12} & \epsilon \end{bmatrix}$$

FIND THE EIGENVALUES AND EIGENVECTORS OF THE HAMILTONIAN MATRIX



$$\Psi_2 = \frac{1}{\sqrt{2}}(c_1\phi_1 - c_2\phi_2) \qquad E_2 = \epsilon + S_{12}$$



$$\Psi_1 = \frac{1}{\sqrt{2}}(c_1\phi_1 + c_2\phi_2) \qquad E_1 = \epsilon - S_{12}$$

CHECK THIS WORKS WITH NUMPY.LINALG.EIG

DEMO

EXERCISE

Exercise

Today's exercise is to calculate principal moments of inertia and principal rotation axes of a series of molecules, and then to rotate these molecules so that the principal axes are aligned with $\{x, y, z\}$.
The coordinates of each molecule can be downloaded from Moodle, where you will also find a `visualisation2.py` module that contains some code for visualising your molecules and their orientations.
In terms of planning your code, you want to be able to perform the following sequence of steps:

1. Each file contains data in the format $\{x, y, z, m\}$ for each atom, where m is the atomic mass of that atom. You will first want to read this in, and extract the atomic coordinates and masses.
2. Construct the inertia matrix $\mathbf{I}$.
3. Calculate the eigenvalues and eigenvectors of $\mathbf{I}$.
4. Operate on your atomic coordinates to generate new coordinates, with the molecular principal axes aligned with $\{x, y, z\}$.
5. Use the `visualisation.show()` function to look at your rotated molecules. Do these look how you would expect from what you know about molecular symmetry?

* centre the molecule on the COM