CHEM20212
Computational Chemistry II:
Fundamentals of electronic structure theory

3 Matrix mechanics

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Course Overview

1 Electronic structure of atoms • Introduction • Hydrogenic atoms • Multi-electron atoms • Ground *vs.* excited states	**4 Hückel theory** • Constructing a Hückel matrix • Molecular orbitals • Benzene anion • Electrophilic and nucleophilic attack
2 Electronic structure of molecules • Molecular orbitals • Molecular electronic structure • Energy hierarchy	**5 Spin Hamiltonians** • A "how-to" guide • Matrix elements • Example: $S = 1/2$ • Example: $S = 1$
3 Matrix mechanics • Vector (Hilbert) spaces • Bra-ket notation • Operators and expectation values • Matrix diagonalisation	**6 Workshop**

Intended learning objectives

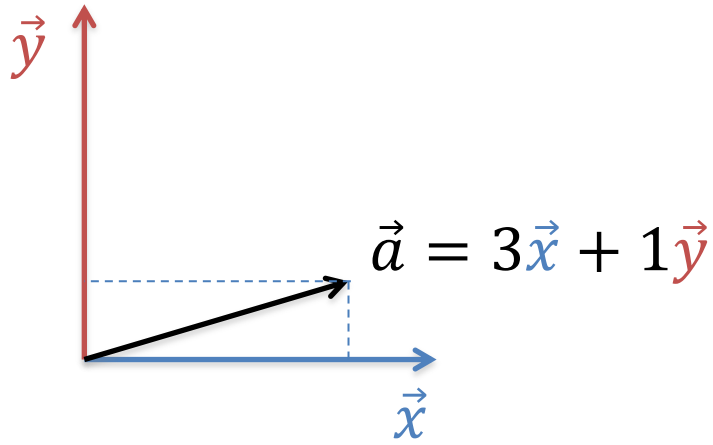
1. Construct approximate wave functions for single and multi-electron atoms
2. Explain the energy hierarchy of multi-electron atoms
3. Differentiate the concepts of ground and excited electronic states, including spin and orbital states
4. Mathematically expand and visualise the spatial wave functions of atoms and simple molecules as a linear combination of MOs and basis functions
5. Mathematically describe the connection between matrix diagonalisation and solution to the Schrödinger equation
6. Construct a Hückel Hamiltonian matrix
7. Employ Bra-Ket notation to evaluate the matrix elements of a simple spin Hamiltonian

Matrix mechanics

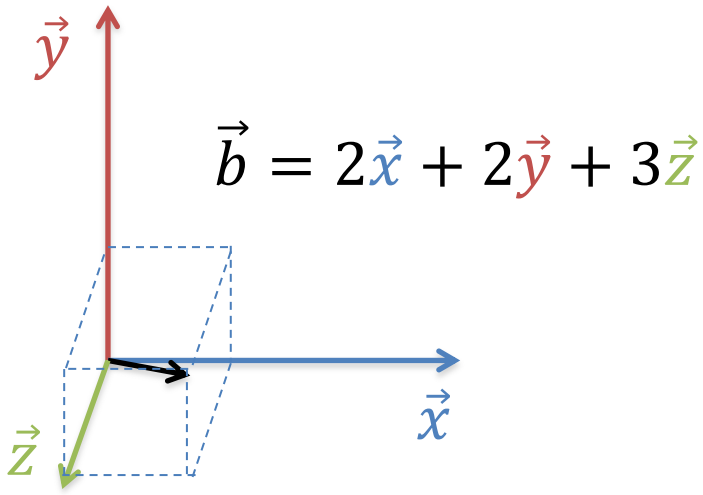
- Solving the Schrödinger equation is crucial to solve our problems…
- … but how do we actually do it when there's no analytic solution?
- We use the techniques of ***matrix mechanics***, developed by Werner Heisenberg

Vector spaces

- You know vectors in Euclidian space:
  - 2D:



  - 3D:



Vector spaces

- Can also express vectors in matrix notation:

$$\vec{x} \equiv \begin{bmatrix}1\\0\end{bmatrix}, \vec{y} \equiv \begin{bmatrix}0\\1\end{bmatrix} \qquad \vec{a} \equiv 3\begin{bmatrix}1\\0\end{bmatrix} + 1\begin{bmatrix}0\\1\end{bmatrix} = \begin{bmatrix}3\\1\end{bmatrix}$$

- Also works in the 3D basis:

$$\vec{x} \equiv \begin{bmatrix}1\\0\\0\end{bmatrix}, \vec{y} \equiv \begin{bmatrix}0\\1\\0\end{bmatrix}, \vec{z} \equiv \begin{bmatrix}0\\0\\1\end{bmatrix} \qquad \vec{a} \equiv 3\begin{bmatrix}1\\0\\0\end{bmatrix} + 1\begin{bmatrix}0\\1\\0\end{bmatrix} + 0\begin{bmatrix}0\\0\\1\end{bmatrix} = \begin{bmatrix}3\\1\\0\end{bmatrix}$$

$$\vec{b} \equiv 2\begin{bmatrix}1\\0\\0\end{bmatrix} + 2\begin{bmatrix}0\\1\\0\end{bmatrix} + 3\begin{bmatrix}0\\0\\1\end{bmatrix} = \begin{bmatrix}2\\2\\3\end{bmatrix}$$

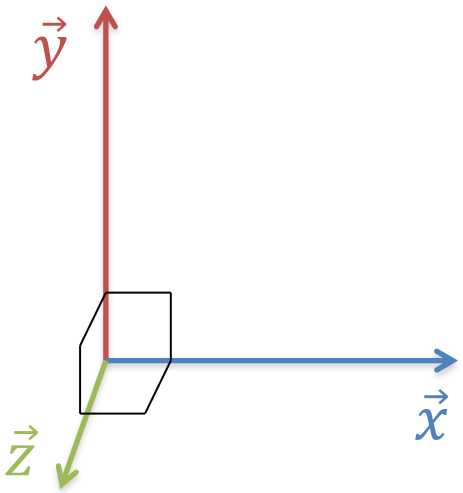
- General vector: $\begin{bmatrix}C_1\\C_2\\C_3\end{bmatrix}$

Vector spaces

- The x, y and z vectors are the ***basis vectors*** of 3D space
  - Any vector in 3D space can be expressed with x, y and z

- This is possible because they are three ***orthogonal*** vectors in a three dimensional space
  - Orthogonal is defined to mean the dot product is zero:

$$\vec{x} \cdot \vec{y} = \vec{y} \cdot \vec{z} = \vec{z} \cdot \vec{x} = 0$$



Dot product in matrix notation:

$$\vec{x} \cdot \vec{y} \equiv \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}^T \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = 0$$

Bra-ket notation

- Dirac got sick of using matrix/vector(/integral) notation all the time, so invented a new notation:

$$\vec{x} \equiv \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \equiv |x\rangle, \quad \vec{y} \equiv \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \equiv |y\rangle, \quad \vec{z} \equiv \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \equiv |z\rangle$$

'Ket'

- The dot product in ***bra-ket notation*** (*a.k.a.* inner product):

'Bra'

$$|x\rangle^T = \langle x|, \quad \vec{x} \cdot \vec{y} \equiv \langle x|y\rangle = 0$$

'Bra-ket'

Hilbert spaces

- This concept can be generalised to ***arbitrary*** dimension:

$$|q\rangle \equiv \begin{bmatrix} 1 \\ 0 \\ \vdots \\ 0 \\ 0 \end{bmatrix}, |w\rangle \equiv \begin{bmatrix} 0 \\ 1 \\ \vdots \\ 0 \\ 0 \end{bmatrix}, \cdots, |e\rangle \equiv \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 1 \\ 0 \end{bmatrix}, |r\rangle \equiv \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix}$$

- These basis vectors define the space; they are all orthogonal and normalised:

$$\langle q|q\rangle = 1, \langle q|w\rangle = 0$$

- These are known as ***Hilbert spaces***. Generally, vectors in these spaces can have complex coefficients, so the bra is actually the conjugate transpose:

$$\langle a| = |a\rangle^{\dagger} = \left(|a\rangle^{T}\right)^{*} = \overline{|a\rangle^{T}}$$

FEED FORWARD:
Make sure you can conjugate!

Hilbert spaces

- Example:

$$|a\rangle = (2+3i)|q\rangle + -6|r\rangle \equiv \begin{bmatrix} 2+3i \\ 0 \\ \vdots \\ 0 \\ -6 \end{bmatrix}$$

FEED FORWARD: Practice normalising and checking orthogonality

Note conjugation!

$$|b\rangle = 4|w\rangle + (1-i)|r\rangle \equiv \begin{bmatrix} 0 \\ 4 \\ \vdots \\ 0 \\ 1-i \end{bmatrix}$$

– Are $|a\rangle$ and $|b\rangle$ orthogonal?

$$\langle a|b\rangle = \big((2-3i)\langle q| - 6\langle r|\big)(4|w\rangle + (1-i)|r\rangle)$$

$$= (8-12i)\langle q|w\rangle + (2-3i)(1-i)\langle q|r\rangle - 24\langle r|w\rangle - (6+6i)\langle r|r\rangle$$

$$= -6(1+i)$$

No!

Operators and expectation values

- ***Operators*** in quantum mechanics ***represent measurements***

- $\Psi[\vec{x}]$ is delocalised; probability density given by $\Psi[\vec{x}]^*\Psi[\vec{x}]$ (Born interpretation)
- To compare with experiment we must integrate over all spatial and spin coordinates coordinates:

$$\langle \hat{A} \rangle = \int_x \overline{\Psi[\vec{x}]} \hat{A} \Psi[\vec{x}] d\vec{x}$$

  - $\langle \hat{A} \rangle$ is called the ***expectation value*** of operator $\hat{A}$

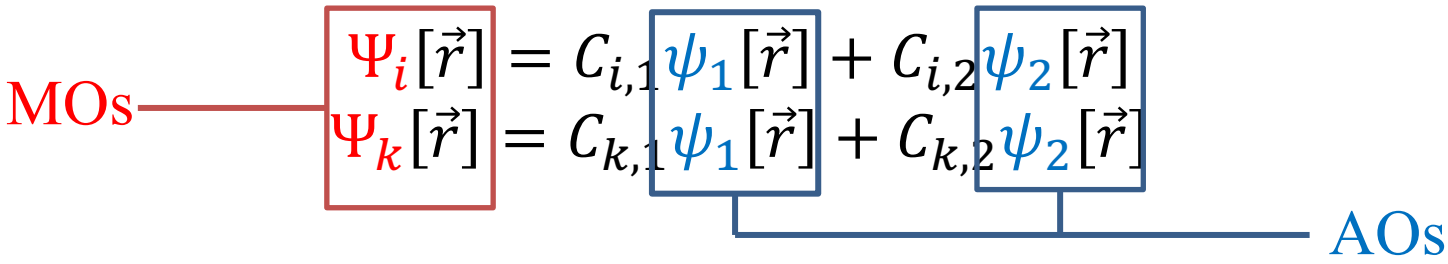
- The Hamiltonian is an operator that measures the total energy

$$\langle E \rangle \equiv \langle \hat{H} \rangle = \int_r \overline{\Psi[\vec{x}]} \hat{H} \Psi[\vec{x}] d\vec{x}$$

Operators and expectation values

- So, we need to do a lot of integrals with our wavefunctions; can Bra-Ket notation make things simpler?

- Let's take a pair of spatial MOs, constructed from two AOs:



- A simple integral might be:

$$\int_r \Psi_i[\vec{r}]^* \Psi_k[\vec{r}] d\vec{r} = \int_r \overline{\{C_{i,1}\psi_1[\vec{r}] + C_{i,2}\psi_2[\vec{r}]\}}\{C_{k,1}\psi_1[\vec{r}] + C_{k,2}\psi_2[\vec{r}]\} d\vec{r}$$

Operators and expectation values

- Expanding:

$$\int_r \overline{\{C_{i,1}\psi_1[\vec{r}] + C_{i,2}\psi_2[\vec{r}]\}}\{C_{k,1}\psi_1[\vec{r}] + C_{k,2}\psi_2[\vec{r}]\}d\vec{r}$$

$$= \int_r \begin{bmatrix} \overline{C_{i,1}\psi_1[\vec{r}]}C_{k,1}\psi_1[\vec{r}] + \overline{C_{i,1}\psi_1[\vec{r}]}C_{k,2}\psi_2[\vec{r}] \\ +\overline{C_{i,2}\psi_2[\vec{r}]}C_{k,1}\psi_1[\vec{r}] + \overline{C_{i,2}\psi_2[\vec{r}]}C_{k,2}\psi_2[\vec{r}] \end{bmatrix} d\vec{r}$$

$$= \int_r \overline{C_{i,1}\psi_1[\vec{r}]}C_{k,1}\psi_1[\vec{r}]d\vec{r} + \int_r \overline{C_{i,1}\psi_1[\vec{r}]}C_{k,2}\psi_2[\vec{r}]d\vec{r}$$

$$+ \int_r \overline{C_{i,2}\psi_2[\vec{r}]}C_{k,1}\psi_1[\vec{r}]d\vec{r} + \int_r \overline{C_{i,2}\psi_2[\vec{r}]}C_{k,2}\psi_2[\vec{r}]d\vec{r}$$

Operators and expectation values

- Assuming that our basis functions (AOs) are ***orthonormal***: $\int_r \overline{\psi_1[\vec{r}]}\psi_1[\vec{r}]d\vec{r} = 1 \qquad \int_r \overline{\psi_1[\vec{r}]}\psi_2[\vec{r}]d\vec{r} = 0$

$$= C_{i,1}{}^* C_{k,1} \int_r \overline{\psi_1[\vec{r}]}\psi_1[\vec{r}]d\vec{r} + C_{i,1}{}^* C_{k,2} \int_r \overline{\psi_1[\vec{r}]}\psi_2[\vec{r}]d\vec{r}$$

$$+ C_{i,2}{}^* C_{k,1} \int_r \overline{\psi_2[\vec{r}]}\psi_1[\vec{r}]d\vec{r} + C_{i,2}{}^* C_{k,2} \int_r \overline{\psi_2[\vec{r}]}\psi_2[\vec{r}]d\vec{r}$$

$$= \overline{C_{i,1}}C_{k,1} + \overline{C_{i,2}}C_{k,2} \equiv \begin{bmatrix}\overline{C_{i,1}} & \overline{C_{i,2}}\end{bmatrix}\begin{bmatrix}C_{k,1}\\ C_{k,2}\end{bmatrix} \equiv \langle\psi_i|\psi_k\rangle$$

- Generally, the combination of a bra and ket implies an integral over all space (and spin)!

Solving the Schrödinger equation

- So, wavefunctions can be expressed as vectors in a finite basis:

$$\begin{bmatrix} C_{i,1} \\ C_{i,2} \\ \vdots \\ C_{i,N} \end{bmatrix} \equiv |\Psi_i\rangle$$

- The Schrödinger equation in this notation:

$$\hat{\bar{\bar{H}}}|\Psi_i\rangle = E_i|\Psi_i\rangle$$

- This looks just like a matrix-vector equation:

$$\begin{bmatrix} A_{1,1} & A_{1,2} & \cdots & A_{1,N} \\ A_{2,1} & A_{2,2} & \cdots & A_{2,N} \\ \vdots & \vdots & \ddots & \vdots \\ A_{N,1} & A_{N,2} & \cdots & A_{N,N} \end{bmatrix} \begin{bmatrix} C_{i,1} \\ C_{i,2} \\ \vdots \\ C_{i,N} \end{bmatrix} = \begin{bmatrix} D_{i,1} \\ D_{i,2} \\ \vdots \\ D_{i,N} \end{bmatrix}$$

Solving the Schrödinger equation

- Solving the Schrödinger equation is therefore equivalent to finding the coefficients such that:

$$\begin{bmatrix} H_{1,1} & H_{1,2} & \cdots & H_{1,N} \\ H_{2,1} & H_{2,2} & \cdots & H_{2,N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N,1} & H_{N,2} & \cdots & H_{N,N} \end{bmatrix} \begin{bmatrix} C_{i,1} \\ C_{i,2} \\ \vdots \\ C_{i,N} \end{bmatrix} = E_i \begin{bmatrix} C_{i,1} \\ C_{i,2} \\ \vdots \\ C_{i,N} \end{bmatrix}$$

- $H_{a,b}$ are the ***matrix elements*** of the Hamiltonian matrix $\overline{\overline{\hat{H}}}$, found by evaluating the Hamiltonian operator over all basis states:

$$H_{a,b} = \langle \psi_a | \hat{H} | \psi_b \rangle \equiv \int_r \overline{\psi_a[\vec{r}]} \hat{H} \psi_b[\vec{r}] d\vec{r}$$

- The Schrödinger equation is an ***eigenvalue equation***, and the solution can be found by ***diagonalising*** the Hamiltonian matrix

FEED FORWARD: Hamiltonians

- The ***Hamiltonian operator*** $\hat{H}$ acts on a state/ket/wavefunction to yield a number and either the same or a different state/ket/wavefunction

- The ***Hamiltonian matrix*** $\hat{\hat{H}}$ is formed by evaluating all the matrix elements $H_{a,b} = \langle a|\hat{H}|b\rangle$ which involve the Hamiltonian operator acting on the ket $|b\rangle$ and then evaluation with the bra $\langle a|$

$$\hat{\hat{H}} = \begin{matrix} \\ \langle a| \\ \langle b| \\ \langle c| \end{matrix} \begin{matrix} \begin{matrix} |a\rangle & |b\rangle & |c\rangle \end{matrix} \\ \begin{bmatrix} \langle a|\hat{H}|a\rangle & \langle a|\hat{H}|b\rangle & \langle a|\hat{H}|c\rangle \\ \langle b|\hat{H}|a\rangle & \langle b|\hat{H}|b\rangle & \langle b|\hat{H}|c\rangle \\ \langle c|\hat{H}|a\rangle & \langle c|\hat{H}|b\rangle & \langle c|\hat{H}|c\rangle \end{bmatrix} \end{matrix}$$

Solving the Schrödinger equation

- Diagonalisation of a matrix is finding the matrix P such that $P^{-1}\hat{\hat{H}}P = D$, where D is a diagonal matrix:

$$D = \begin{bmatrix} E_1 & 0 & \cdots & 0 \\ 0 & E_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & E_N \end{bmatrix}$$

- The columns of P are the ***eigenvectors*** (wavefunctions), and the diagonal elements of D are the ***eigenvalues*** (energies)

$$P = \begin{bmatrix} C_{1,1} & C_{2,1} & \cdots & C_{N,1} \\ C_{1,2} & C_{2,2} & \cdots & C_{N,2} \\ \vdots & \vdots & \ddots & \vdots \\ C_{1,N} & C_{2,N} & \cdots & C_{N,N} \\ |\Psi_1\rangle & |\Psi_2\rangle & \cdots & |\Psi_N\rangle \end{bmatrix}$$

- Can be done by hand for 2×2, but usually we use computers!

Matrix diagonalisation

- Every operator, including the Hamiltonian, must correspond to a physical measurement
  - Therefore, all expectation values and eigenvalues must be ***real numbers***

- For this to be true, the Hamiltonian matrix must be ***hermitian***
  - This means that it is equal to its conjugate transpose:

$$\overline{\overline{\hat{H}}} = \overline{\overline{\hat{H}}}^{\dagger}$$

  - Because of this, the eigenvectors of the Hamiltonian are all orthogonal to each other! (But not to the original basis vectors)
  - Therefore, the eigenvectors are also a basis for the Hilbert space! They define the ***eigenbasis***!

Matrix diagonalisation

- Let's consider a simple 2D example:
  - Basis states: $|v_1\rangle = \begin{bmatrix}1\\0\end{bmatrix}, |v_2\rangle = \begin{bmatrix}0\\1\end{bmatrix}$
  - Hamiltonian matrix: $\overline{\overline{\hat{H}}} = \begin{bmatrix}a & b\\ b & a\end{bmatrix}$

- Diagonalisation gives:
  - Eigenvectors: $|\psi_1\rangle = \begin{bmatrix}\frac{1}{\sqrt{2}}\\ \frac{1}{\sqrt{2}}\end{bmatrix}, |\psi_2\rangle = \begin{bmatrix}\frac{1}{\sqrt{2}}\\ -\frac{1}{\sqrt{2}}\end{bmatrix}$
  - Eigenvalues: $E_1 = a + b, E_2 = a - b$

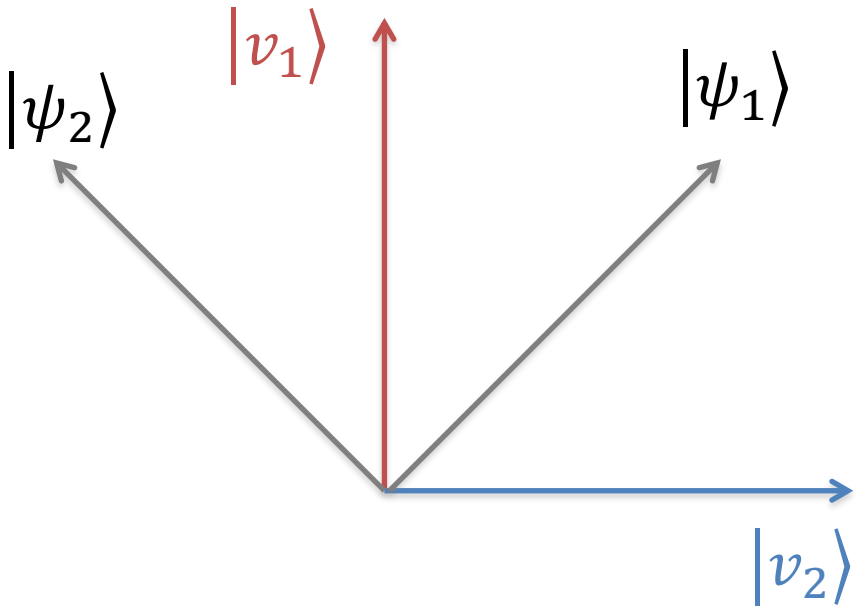
Matrix diagonalisation

- Plot the eigenvectors in our orthogonal 2D basis:

$$|\psi_1\rangle = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix}, |\psi_2\rangle = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{bmatrix}$$

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}|v_1\rangle + \frac{1}{\sqrt{2}}|v_2\rangle$$

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}|v_1\rangle - \frac{1}{\sqrt{2}}|v_2\rangle$$



Eigenvectors are orthogonal!

Eigenbasis is just rotated!

Diagonalisation is a rotation in the Hilbert space!