CHEM20212
Computational Chemistry II:
Fundamentals of electronic structure theory

5 Spin Hamiltonians

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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

Spin Hamiltonians

- Previously, we have seen:

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

- However, what if we want to fit experimental data to a quantum mechanical model? How do we adapt an "*ab initio*" theory?
  - You can't! They are fixed!

- ***Spin Hamiltonians*** are model Hamiltonians that consider only the ***spin*** coordinates of the electrons
  - This is an approximation, but works very well for magnetism
  - Spatial part of the wavefunction is a parameter in the model
  - Useful for modelling experiments; not an "*ab initio*" theory!

A "how-to" guide

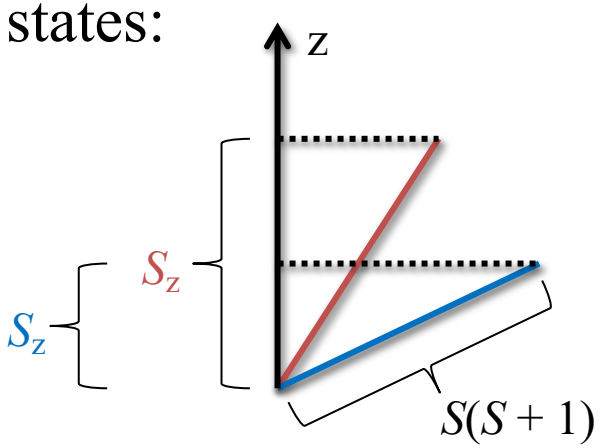
- The approach is as follows:
  - Define basis: $|q\rangle, |w\rangle, |e\rangle$ ...
  - Write Hamiltonian: $\hat{H} = -2J\hat{S}_A \cdot \hat{S}_B$ ...
  - Choose guess parameters: $J = -10$
  - Solve the Schrödinger equation: $\hat{H}\Psi = E\Psi$
  - Use wavefunction to calculate property: $\langle \hat{A} \rangle = \langle \Psi | \hat{A} | \Psi \rangle$
  - Does the calculation match experiment?

Repeat

A "how-to" guide

- For a given total spin S, there are $2S+1$ m_S states:
  $m_S = -S, -S+1, \ldots, S-1, S$

- These are the ***projections*** of S along the quantisation axis (*i.e.* S_z)



- These states are orthogonal and therefore define a basis:

$$|-S\rangle = \begin{bmatrix} 1 \\ 0 \\ \vdots \\ 0 \\ 0 \end{bmatrix}, |-S+1\rangle = \begin{bmatrix} 0 \\ 1 \\ \vdots \\ 0 \\ 0 \end{bmatrix}, \cdots, |S-1\rangle = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 1 \\ 0 \end{bmatrix}, |S\rangle = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix}$$

- Note that the Bra-Ket notation is general to physics, but that the problem and the basis states are very different here compared to Hückel theory!

A "how-to" guide

- Remember, the Hamiltonian matrix $\overline{\overline{\hat{H}}}$ is all the possible combinations of bras and kets within our basis:

$$\begin{array}{c} \\ \langle -S| \\ \langle -S+1| \\ \vdots \\ \langle S-1| \\ \langle S| \end{array} \begin{array}{c} \begin{array}{cccccc} |-S\rangle & |-S+1\rangle & \cdots & |S-1\rangle & |S\rangle \end{array} \\ \begin{bmatrix} \langle -S|\hat{H}|-S\rangle & \langle -S|\hat{H}|-S+1\rangle & \cdots & \langle -S|\hat{H}|S-1\rangle & \langle -S|\hat{H}|S\rangle \\ \langle -S+1|\hat{H}|-S\rangle & \langle -S+1|\hat{H}|-S+1\rangle & \cdots & \langle -S+1|\hat{H}|S-1\rangle & \langle -S+1|\hat{H}|S\rangle \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \langle S-1|\hat{H}|-S\rangle & \langle S-1|\hat{H}|-S+1\rangle & \cdots & \langle S-1|\hat{H}|S-1\rangle & \langle S-1|\hat{H}|S\rangle \\ \langle S|\hat{H}|-S\rangle & \langle S|\hat{H}|-S+1\rangle & \cdots & \langle S|\hat{H}|S-1\rangle & \langle S|\hat{H}|S\rangle \end{bmatrix} \end{array}$$

  - ***Note:*** I've ordered the basis states from –*S* to *S*, but you could do any order (including *S*, –*S*) as long as you are consistent and the rows have the same order as the columns

- So how do we evaluate the $\langle m_S{}' | \hat{H} | m_S \rangle$ matrix elements?

Matrix elements

- $\langle m_S' | \hat{H} | m_S \rangle$ can be evaluated using some simple rules:

1. Operators act on kets from left to right
2. Operators do not always commute! $\hat{A}\hat{B} \neq \hat{B}\hat{A}$
3. If the ket is unchanged by the operator, it is an ***eigenstate*** of the operator (*a.k.a.* eigenket, eigenfunction, eigenvector).
4. If it does change, it is not an eigenstate.
5. Operators may or may not give a numerical factor.

- Generally,

$$\hat{A}|m_s\rangle = A|m_s'\rangle$$

Note that $|\psi\rangle$ is an eigenstate of $\hat{H}$!

$$\hat{H}|\psi\rangle = E_\psi|\psi\rangle$$

Matrix elements

- For a single spin S, the rules are:

$$\hat{S}_z|m_s\rangle = m_s|m_s\rangle$$

- m_S is sometimes called S_z
- It is the ***projection*** of S on the z-axis
- $|m_s\rangle$ is an eigenstates of $\hat{S}_z$

Not eigenstates of $\hat{S}_\pm$!

$$\hat{S}_+|m_s\rangle = \sqrt{S(S+1) - m_s(m_s+1)}\,|m_s+1\rangle$$

$$\hat{S}_-|m_s\rangle = \sqrt{S(S+1) - m_s(m_s-1)}\,|m_s-1\rangle$$

Matrix elements

- $S = 2$, $m_S = -2, -1, 0, +1, +2$, basis: $|-2\rangle, |-1\rangle, |0\rangle, |1\rangle, |2\rangle$

$$\hat{S}_z|-1\rangle = -1|-1\rangle$$

This is the $m_S = 0$ state, not zero!

$$\hat{S}_+|0\rangle = \sqrt{2(2+1) - 0(0+1)}|+1\rangle = \sqrt{6}|+1\rangle$$

$$\hat{S}_+|+2\rangle = \sqrt{2(2+1) - 2(2+1)}|+3\rangle = 0$$

Note that $\hat{S}_+|S\rangle = 0$!

$$\hat{S}_x|+1\rangle = \frac{1}{2}(\hat{S}_+ + \hat{S}_-)|+1\rangle$$

$$= \frac{1}{2}(\hat{S}_+|+1\rangle + \hat{S}_-|+1\rangle) = \frac{1}{2}(\sqrt{4}|+2\rangle + \sqrt{6}|0\rangle)$$

FEED FORWARD: Numbers inside bras/kets are ***labels*** not coefficients

Matrix elements

- $S = 2$, m_S = -2, -1, 0, +1, +2, basis: $|-2\rangle$, $|-1\rangle$, $|0\rangle$, $|1\rangle$, $|2\rangle$

$$\langle -1|\hat{S}_z|-1\rangle$$

- Remember:

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

- Generally,

$$\langle m_S'|m_S\rangle = \delta_{m_S',m_S}$$

- So:

$$\langle -1|\hat{S}_z|-1\rangle = -1$$

Matrix elements

- $S = 2$, m_S = -2, -1, 0, +1, +2, basis: $|-2\rangle$, $|-1\rangle$, $|0\rangle$, $|1\rangle$, $|2\rangle$

$$\langle m_S' | \hat{S}_{\pm} | m_S \rangle$$

$$= \langle m_S' | \sqrt{S(S+1) - m_s(m_s \pm 1)} | m_s \pm 1 \rangle$$

$$= \sqrt{S(S+1) - m_s(m_s \pm 1)} \langle m_S' | m_s \pm 1 \rangle$$

$$= \sqrt{S(S+1) - m_s(m_s \pm 1)} \delta_{m_S', m_S \pm 1}$$

Matrix elements

- So generally,

$$\langle m_S' | \hat{S}_z | m_s \rangle = m_s \delta_{m_S', m_S}$$

So where are these non-zero?

$$\langle m_S' | \hat{S}_+ | m_S \rangle$$

$$= \sqrt{S(S+1) - m_s(m_s+1)}\, \delta_{m_S', m_S+1}$$

$$\langle m_S' | \hat{S}_- | m_S \rangle$$

$$= \sqrt{S(S+1) - m_s(m_s-1)}\, \delta_{m_S', m_S-1}$$

Matrix elements

- So for our example, $S = 2$, m_S = -2, -1, 0, +1, +2

$$\begin{array}{c} \\ \langle -2| \\ \langle -1| \\ \langle 0| \\ \langle +1| \\ \langle +2| \end{array} \begin{array}{c} \begin{array}{ccccc} |-2\rangle & |-1\rangle & |0\rangle & |+1\rangle & |+2\rangle \end{array} \\ \begin{bmatrix} \langle -2|\hat{H}|-2\rangle & \langle -2|\hat{H}|-1\rangle & \langle -2|\hat{H}|0\rangle & \langle -2|\hat{H}|+1\rangle & \langle -2|\hat{H}|+2\rangle \\ \langle -1|\hat{H}|-2\rangle & \langle -1|\hat{H}|-1\rangle & \langle -1|\hat{H}|0\rangle & \langle -1|\hat{H}|+1\rangle & \langle -1|\hat{H}|+2\rangle \\ \langle 0|\hat{H}|-2\rangle & \langle 0|\hat{H}|-1\rangle & \langle 0|\hat{H}|0\rangle & \langle 0|\hat{H}|+1\rangle & \langle 0|\hat{H}|+2\rangle \\ \langle +1|\hat{H}|-2\rangle & \langle +1|\hat{H}|-1\rangle & \langle +1|\hat{H}|0\rangle & \langle +1|\hat{H}|+1\rangle & \langle +1|\hat{H}|+2\rangle \\ \langle +2|\hat{H}|-2\rangle & \langle +2|\hat{H}|-1\rangle & \langle +2|\hat{H}|0\rangle & \langle +2|\hat{H}|+1\rangle & \langle +2|\hat{H}|+2\rangle \end{bmatrix} \end{array}$$

- Where would $\langle m_S'|\hat{S}_z|m_s\rangle = m_s\delta_{m_S',m_S}$ be non-zero?

- What about:

$$\langle m_S'|\hat{S}_{\pm}|m_S\rangle = \sqrt{S(S+1) - m_s(m_s \pm 1)}\,\delta_{m_S',m_S\pm1}?$$

Pick this

so that this is 1

Example: $S = 1/2$

- Single electron in a magnetic field along x, so we define:

$$\hat{H} = B\hat{S}_x$$

- Single electron, $S = 1/2$

- What are our basis states?
  - $m_S = -1/2, +1/2$

$$\left|-\frac{1}{2}\right\rangle, \left|+\frac{1}{2}\right\rangle$$

- And what does the matrix look like?

Example: $S = 1/2$

$$\left|-\frac{1}{2}\right\rangle \qquad \left|+\frac{1}{2}\right\rangle$$

$$\begin{matrix}\left\langle -\frac{1}{2}\right| \\ \left\langle +\frac{1}{2}\right|\end{matrix}\begin{bmatrix}\left\langle -\frac{1}{2}\right|\hat{H}\left|-\frac{1}{2}\right\rangle & \left\langle -\frac{1}{2}\right|\hat{H}\left|+\frac{1}{2}\right\rangle \\ \left\langle +\frac{1}{2}\right|\hat{H}\left|-\frac{1}{2}\right\rangle & \left\langle +\frac{1}{2}\right|\hat{H}\left|+\frac{1}{2}\right\rangle\end{bmatrix}$$

$$\langle m_S'|B\hat{S}_x|m_s\rangle = \langle m_S'|\frac{B}{2}(\hat{S}_+ + \hat{S}_-)|m_s\rangle$$

$$= \frac{B}{2}\left(\langle m_S'|\hat{S}_+|m_s\rangle + \langle m_S'|\hat{S}_-|m_s\rangle\right)$$

$$= \frac{B}{2}\begin{pmatrix}\sqrt{S(S+1)-m_s(m_s+1)}\,\delta_{m_S',m_S+1} \\ +\sqrt{S(S+1)-m_s(m_s-1)}\,\delta_{m_S',m_S-1}\end{pmatrix}$$

Example: $S = 1/2$

$$\begin{array}{c} \\ \left\langle -\frac{1}{2}\right| \\ \left\langle +\frac{1}{2}\right| \end{array} \begin{array}{c} \begin{array}{cc} \left|-\frac{1}{2}\right\rangle & \left|+\frac{1}{2}\right\rangle \end{array} \\ \begin{bmatrix} 0 & B/2 \\ B/2 & 0 \end{bmatrix} \end{array}$$

$$\langle m_S'|B\hat{S}_x|m_s\rangle = \langle m_S'|\frac{B}{2}(\hat{S}_+ + \hat{S}_-)|m_s\rangle$$

$$= \frac{B}{2}\left(\langle m_S'|\hat{S}_+|m_s\rangle + \langle m_S'|\hat{S}_-|m_s\rangle\right)$$

$$= \frac{B}{2}\begin{pmatrix} \sqrt{S(S+1) - m_s(m_s+1)}\,\delta_{m_S',m_S+1} \\ +\sqrt{S(S+1) - m_s(m_s-1)}\,\delta_{m_S',m_S-1} \end{pmatrix}$$

Example: $S = 1/2$

- Diagonalisation gives (recall this 2×2 result from L3 and L4):

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

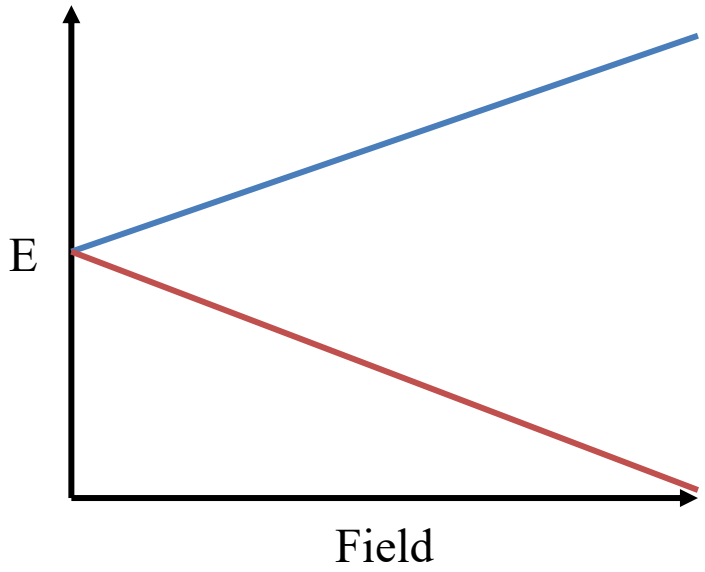
$$|\psi_1\rangle = \frac{1}{\sqrt{2}}\left|-\frac{1}{2}\right\rangle + \frac{1}{\sqrt{2}}\left|+\frac{1}{2}\right\rangle$$

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}\left|-\frac{1}{2}\right\rangle - \frac{1}{\sqrt{2}}\left|+\frac{1}{2}\right\rangle$$

- With eigenvalues:

$$E_1 = -B/2\,, E_2 = B/2$$

  - Energies of spin states affected by magnetic field: ***Zeeman effect!***



Example: $S = 1$

- Ni(II) in an octahedral crystal field, we are interested in the zero-field splitting, so we define:

$$\hat{H} = D\hat{S}_z^{\,2}$$

- $3d^8$, ^3A ground term, $S = 1$

- What are our basis states?
  - $m_S = -1, 0, +1$

$$|-1\rangle, |0\rangle, |+1\rangle$$

- And what does the matrix look like?

Example: $S = 1$

$$\begin{array}{c} \\ \langle -1| \\ \langle 0| \\ \langle +1| \end{array} \begin{array}{c} \begin{array}{ccc} |-1\rangle & |0\rangle & |+1\rangle \end{array} \\ \begin{bmatrix} \langle -1|\hat{H}|-1\rangle & \langle -1|\hat{H}|0\rangle & \langle -1|\hat{H}|+1\rangle \\ \langle 0|\hat{H}|-1\rangle & \langle 0|\hat{H}|0\rangle & \langle 0|\hat{H}|+1\rangle \\ \langle +1|\hat{H}|-1\rangle & \langle +1|\hat{H}|0\rangle & \langle +1|\hat{H}|+1\rangle \end{bmatrix} \end{array}$$

- So what are the matrix elements?

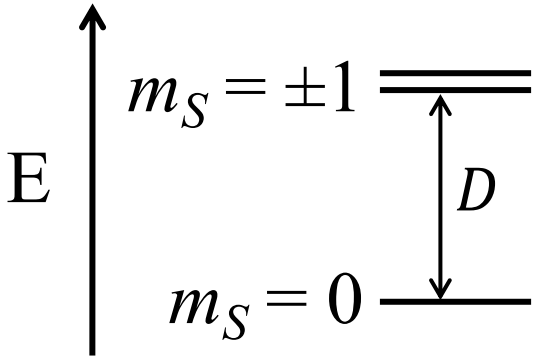
$$\begin{aligned} \langle m_S'|D\hat{S}_z{}^2|m_s\rangle &= \langle m_S'|D\hat{S}_z\hat{S}_z|m_s\rangle \\ &= \langle m_S'|D\hat{S}_z m_s|m_s\rangle \\ &= Dm_s\langle m_S'|\hat{S}_z|m_s\rangle \\ &= Dm_s m_s\delta_{m_S',m_S} \end{aligned}$$

Example: $S = 1$

$$\begin{array}{c} \\ \langle -1| \\ \langle 0| \\ \langle +1| \end{array} \begin{array}{c} \begin{array}{ccc} |-1\rangle & |0\rangle & |+1\rangle \end{array} \\ \begin{bmatrix} D & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & D \end{bmatrix} \end{array}$$

- Next step: diagonalisation…but our matrix is already diagonal! Therefore our existing basis is the eigenbasis of our Hamiltonian!

- The states $|\pm 1\rangle$ are degenerate with eigenvalue D, while $|0\rangle$ is non-degenerate with eigenvalue 0.



Writing Hamiltonians

- We have a library of operators to build Hamiltonians: what we choose depends on the problem we have in the lab!
  - Magnetic coupling: $\hat{H} = -2J\hat{S}_A \cdot \hat{S}_B$
  - Magnetic anisotropy: $\hat{H} = D\hat{S}_z{}^2$
  - Spin-orbit coupling: $\hat{H} = \lambda\hat{L} \cdot \hat{S}$
  - Magnetic fields: $\hat{H} = \mu_B gB \cdot \hat{S}$
- I will give you the Hamiltonian in questions: you are not expected to memorise these!