

The Variation Principle

The variational method

The energy calculated using an approximate wave function cannot be less than the true energy of the system.

For the exact wave function ψ

$$E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$

but for a trial wave function χ

$$\frac{\langle \chi | \hat{H} | \chi \rangle}{\langle \chi | \chi \rangle} = \mathcal{E} \geq E$$

If χ is a function of one or more adjustable parameters these can be optimized to give a minimum value for \mathcal{E} .

If χ has the same form as ψ then \mathcal{E} can be optimized to give the true E .

Slater-type orbitals (STO):

$$\phi_{nlm} = N r^{n^*-1} e^{-(Z-\sigma)r/(n^*a_0)} Y_{lm} \quad \phi_{nlm} = N r^{n-1} e^{-Z^*r/a_0} Y_{lm}$$

Gaussian-type orbitals (GTO):

$$\phi_{ijk} = N x^i y^j z^k e^{-\alpha r^2}$$

Linear combination of atomic orbitals (LCAO):

$$\chi = \sum_i c_i \phi_i$$

The Variation Principle – Justification

Assume that a trial function χ can be written as a linear combination of the true eigenfunctions ψ_j .

$$\chi = \sum_j c_j \psi_j$$

where $\hat{H}\psi_j = E_j\psi_j$

Then

$$\begin{aligned}\langle \chi | \hat{H} | \chi \rangle &= \sum_i \sum_j c_i^* c_j \langle \psi_i | \hat{H} | \psi_j \rangle \\ &= \sum_i \sum_j c_i^* c_j E_j \langle i | j \rangle \\ &= \sum_j c_j^* c_j E_j \quad \text{since } \langle i | j \rangle = \delta_{ij}\end{aligned}$$

But $c_j^* c_j = |c_j|^2 \geq 0$

and $E_j \geq E_0$ where E_0 is the lowest energy eigenvalue

$$\mathcal{E} - E_0 = \frac{\langle \chi | \hat{H} | \chi \rangle}{\langle \chi | \chi \rangle} - E_0 = \frac{\sum_j c_j^* c_j E_j}{\sum_j c_j^* c_j} - E_0 \frac{\sum_j c_j^* c_j}{\sum_j c_j^* c_j} = \frac{\sum_j c_j^* c_j (E_j - E_0)}{\sum_j c_j^* c_j} \geq 0$$

i.e. $\mathcal{E} \geq E_0$

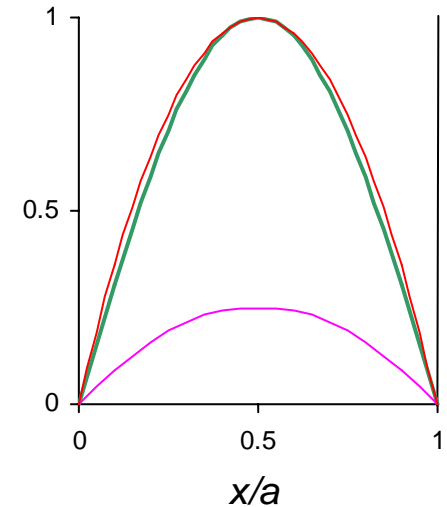
The Variation Method – An Example

This example tests a known problem with a trial function that does not have the same form as the known solution.

Problem: The particle in a box with infinitely high walls.

The known solution is a sine function.

Trial function: $\chi = x(a-x)/a^2$ an inverted parabola



$$\begin{aligned}\langle \chi | \hat{H} | \chi \rangle &= -\frac{\hbar^2}{2m} \int_0^a \left(\frac{x}{a} - \frac{x^2}{a^2} \right) \frac{d^2}{dx^2} \left(\frac{x}{a} - \frac{x^2}{a^2} \right) dx \\ &= -\frac{\hbar^2}{2ma^4} \int_0^a (ax - x^2)(-2) dx = \frac{\hbar^2}{6ma}\end{aligned}$$

$$\begin{aligned}\langle \chi | \chi \rangle &= \frac{1}{a^4} \int_0^a (ax - x^2)^2 dx \\ &= a \left(\frac{1}{3} - \frac{1}{2} + \frac{1}{5} \right) = \frac{a}{30}\end{aligned}$$

$$\mathcal{E} = \frac{\langle \chi | \hat{H} | \chi \rangle}{\langle \chi | \chi \rangle} = \frac{5\hbar^2}{ma^2} = \frac{10}{\pi^2} \left(\frac{\pi^2 \hbar^2}{2ma^2} \right) = 1.013E_0$$

only 1.3% higher
than the true value

Note: The only adjustment in this example was in the normalization (wave amplitude).

The Variation Method applied to the H Atom

This example tests a known problem with a trial function that **does** have the correct form.

In atomic units the Schrödinger equation for a 1-electron H-like atom is

$$-\frac{1}{2}\nabla^2\psi - \frac{Z}{r}\psi = E\psi$$

Trial function: $\chi = Ne^{-\alpha r}$ no angular part, so $\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}$

$$\nabla^2 e^{-\alpha r} = \alpha^2 e^{-\alpha r} - \frac{2\alpha}{r}e^{-\alpha r}$$

$$\langle\chi|\hat{H}|\chi\rangle = N^2 \int_0^\infty \left(-\frac{\alpha^2}{2} + \frac{\alpha}{r} - \frac{Z}{r} \right) e^{-2\alpha r} 4\pi r^2 dr = N^2 \pi \left[-\frac{1}{2\alpha} + \frac{1}{\alpha} - \frac{Z}{\alpha^2} \right] = \frac{N^2 \pi}{\alpha^2} \left[\frac{1}{2}\alpha - Z \right]$$

$$\langle\chi|\chi\rangle = N^2 \int_0^\infty 4\pi r^2 e^{-2\alpha r} dr = N^2 \frac{\pi}{\alpha^3}$$

$$\mathcal{E} = \frac{\langle\chi|\hat{H}|\chi\rangle}{\langle\chi|\chi\rangle} = \frac{1}{2}\alpha^2 - Z\alpha \quad \text{This function has a minimum value at } \alpha = Z$$

$$\mathcal{E} = -\frac{1}{2}Z^2 \quad \text{which is the exact value since the trial function had the correct form}$$

The Variation Method applied to the He Atom

This is a real problem with hitherto unknown solution.

The Schrödinger equation can be simplified with 1-electron H-like terms

$$-\frac{1}{2}\nabla_1^2\psi - \frac{Z}{r_1}\psi - \frac{1}{2}\nabla_2^2\psi - \frac{Z}{r_2}\psi + \frac{1}{r_{12}}\psi = E\psi$$

$$\hat{h}_1\psi + \hat{h}_2\psi + \frac{1}{r_{12}}\psi = E\psi$$

Trial function: $\chi = |1s_1 1s_2\rangle$ where $|1s\rangle = N e^{-\alpha r}$ **H-like**

$$\begin{aligned} \mathcal{E} &= \langle 1s_1 1s_2 | \hat{h}_1 | 1s_1 1s_2 \rangle + \langle 1s_1 1s_2 | \hat{h}_2 | 1s_1 1s_2 \rangle + \langle 1s_1 1s_2 | \frac{1}{r_{12}} | 1s_1 1s_2 \rangle \\ &= \langle 1s_1 | \hat{h}_1 | 1s_1 \rangle + \langle 1s_2 | \hat{h}_2 | 1s_2 \rangle + \langle 1s_1 1s_2 | \frac{1}{r_{12}} | 1s_1 1s_2 \rangle \\ &= \frac{1}{2}\alpha^2 - Z\alpha + \frac{1}{2}\alpha^2 - Z\alpha + \frac{5\alpha}{8} = \alpha^2 - 2\alpha\left(Z - \frac{5}{16}\right) \end{aligned}$$

Use cosine rule to express r_{12} in terms of r_1 , r_2 and θ_2

This function has a minimum value at $\alpha = Z - \frac{5}{16}$

$$\mathcal{E} = -\left(Z - \frac{5}{16}\right)^2 = -2.85 \text{ Hartree}$$

$$E_{\text{He}} (\text{exact}) = -2.90 \text{ Hartree}$$

$$\text{cf. } 2E_{\text{H}} = -2.00 \text{ Hartree}$$

$$\mathcal{E}(\alpha = Z) = -2.75 \text{ Hartree}$$

Paired and Unpaired Electron Configurations

Example: the first excited state of He: 1s2s

If the spins are “paired” = singlet state
i.e. spin function antisymmetric
the orbital function must be symmetric

$$\phi = (1s2s + 2s1s) / \sqrt{2}$$

If the spins are “unpaired” = triplet state
i.e. spin function symmetric
the orbital function must be antisymmetric

$$\phi = (1s2s - 2s1s) / \sqrt{2}$$

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}}$$

$$\begin{aligned} \langle \hat{h}_1 \rangle_{\pm} &= \frac{1}{2} \langle 1s 2s | \hat{h}_1 | 1s 2s \rangle \pm \frac{1}{2} \langle 1s 2s | \hat{h}_1 | 2s 1s \rangle \pm \frac{1}{2} \langle 2s 1s | \hat{h}_1 | 1s 2s \rangle + \frac{1}{2} \langle 2s 1s | \hat{h}_1 | 2s 1s \rangle \\ &= \frac{1}{2} \langle 1s | \hat{h}_1 | 1s \rangle \pm 0 \pm 0 + \frac{1}{2} \langle 2s | \hat{h}_1 | 2s \rangle = \frac{1}{2} \epsilon_{1s} + \frac{1}{2} \epsilon_{2s} = \langle \hat{h}_2 \rangle_{\pm} \end{aligned}$$

$$\begin{aligned} \left\langle \frac{1}{r_{12}} \right\rangle_{\pm} &= \frac{1}{2} \langle 1s 2s | \frac{1}{r_{12}} | 1s 2s \rangle \pm \frac{1}{2} \langle 1s 2s | \frac{1}{r_{12}} | 2s 1s \rangle \pm \frac{1}{2} \langle 2s 1s | \frac{1}{r_{12}} | 1s 2s \rangle + \frac{1}{2} \langle 2s 1s | \frac{1}{r_{12}} | 2s 1s \rangle \\ &= \langle 1s 2s | \frac{1}{r_{12}} | 1s 2s \rangle \pm \langle 1s 2s | \frac{1}{r_{12}} | 2s 1s \rangle = J_{1s2s} \pm K_{1s2s} \end{aligned}$$

$$E_{\text{singlet}} = \epsilon_{1s} + \epsilon_{2s} + J_{1s2s} + K_{1s2s}$$

$$E_{\text{triplet}} = \epsilon_{1s} + \epsilon_{2s} + J_{1s2s} - K_{1s2s}$$

$$E_{\text{triplet}} < E_{\text{singlet}}$$

Coulomb integral

Exchange integral

because J and $K > 0$

The Exchange Interaction

The exchange integral K has no classical counterpart.

It introduces **correlation** into the spatial distribution of electrons.

Consider a two-electron system in the triplet state

$$\psi_T = \frac{1}{\sqrt{2}} [\phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2)]$$

Probability density

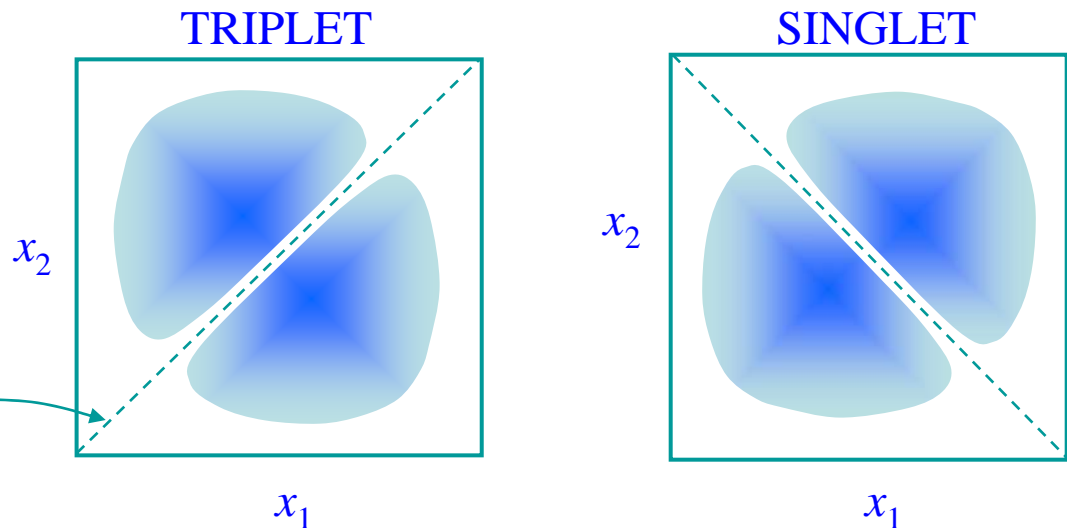
$$P(r_1, r_2) = \frac{1}{2} [\phi_1^*(r_1)\phi_1(r_1)\phi_2^*(r_2)\phi_2(r_2) + \phi_2^*(r_1)\phi_2(r_1)\phi_1^*(r_2)\phi_1(r_2)] - \frac{1}{2} [\phi_1^*(r_1)\phi_2(r_1)\phi_2^*(r_2)\phi_1(r_2) + \phi_2^*(r_1)\phi_1(r_1)\phi_1^*(r_2)\phi_2(r_2)]$$

If $r_1 = r_2$ the terms cancel and $P = 0$.

⇒ It is not possible to find two electrons at the same place in a triplet state.

e.g. 2 particles in a 1-D box, one with $n = 1$, the other $n = 2$

The node at $x_1 = x_2$ is known as the **Fermi hole**.



The Self-consistent Field Method

Think of the probability distribution of an individual electron as its charge density.

Then the potential energy that electron 1 experiences at r_1 due to electron 2 is

$$V_1^{\text{eff}}(r_1) = \left\langle \phi^*(r_2) \left| \frac{1}{r_{12}} \right| \phi(r_2) \right\rangle$$

Define a one-electron Hamiltonian

$$\hat{H}_1^{\text{eff}}(r_1) = -\frac{1}{2} \nabla_1^2 \psi - \frac{Z}{r_1} \psi + V_1^{\text{eff}}(r_1)$$

In principle, the Schrödinger equation can be solved to find the orbital energy ε_1 and the wave function ϕ .

$$\hat{H}_1^{\text{eff}}(r_1) \phi(r_1) = \varepsilon_1 \phi(r_1)$$

Problem: We don't know the electrostatic potential because it depends on $\phi^*(r_2)\phi(r_2)$ (and others if more than 2 electrons).

Procedure: Guess the form of $\phi(r)$ and use it as an estimate of V_1 .

Solve the S eqn to get $\phi_1(r)$ which can be used for V_2 .

Solve the S eqn to get $\phi_2(r)$ which can be used for V_1 .

Iterate until the $\phi(r)$ are self-consistent (i.e. input = output)

Such orbitals are **Hartree-Fock** orbitals.

Variation of Linear Combinations of Orbitals – 1

Take a trial function χ written as a linear combination of independent functions ψ_j .

$$\chi = \sum_j c_j \psi_j$$

In general, the basis set functions are not orthogonal.

$$\langle \chi | \hat{H} | \chi \rangle = \sum_j c_j \langle \chi | \hat{H} | \psi_j \rangle = \sum_i \sum_j c_i^* c_j \langle \psi_i | \hat{H} | \psi_j \rangle = \sum_i \sum_j c_i^* c_j \langle i | \hat{H} | j \rangle = \sum_i \sum_j c_i^* c_j \hat{H}_{ij}$$

Note that since \hat{H} is Hermitian, $\hat{H}_{ij} = \hat{H}_{ji}$

$$\langle \chi | \chi \rangle = \sum_i \sum_j c_i^* c_j \langle \psi_i | \psi_j \rangle = \sum_i \sum_j c_i^* c_j S_{ij} \quad S_{ij} \text{ is an overlap integral}$$

$$\mathcal{E} = \frac{\langle \chi | \hat{H} | \chi \rangle}{\langle \chi | \chi \rangle} = \frac{\sum_i \sum_j c_i^* c_j \hat{H}_{ij}}{\sum_i \sum_j c_i^* c_j S_{ij}} \quad \text{needs to be minimized by adjusting the coefficients } c_i.$$

Rewriting,
$$\sum_i \sum_j c_i^* c_j \hat{H}_{ij} - \mathcal{E} \sum_i \sum_j c_i^* c_j S_{ij} = 0$$

or
$$\sum_i \sum_j c_i^* c_j (\hat{H}_{ij} - \mathcal{E} S_{ij}) = 0$$

Variation of Linear Combinations of Orbitals – 2

$$\sum_i \sum_j c_i c_j (H_{ij} - \mathcal{E} S_{ij}) = 0$$

coefficients
assumed real

Differentiate
with respect to c_1

$$2c_1(H_{11} - \mathcal{E} S_{11}) + \sum_{j \neq 1} c_j (H_{1j} - \mathcal{E} S_{1j}) - \frac{\partial \mathcal{E}}{\partial c_1} \sum_i \sum_j c_i c_j S_{ij} = 0$$

For $\frac{\partial \mathcal{E}}{\partial c_1} = 0$,

$$2c_1(H_{11} - \mathcal{E} S_{11}) + \sum_{j \neq 1} c_j (H_{1j} - \mathcal{E} S_{1j}) = 0$$

In general, $\frac{\partial \mathcal{E}}{\partial c_i} = 0 \Rightarrow 2 \sum_j c_j (H_{ij} - \mathcal{E} S_{ij}) = 0$ $H_{ij} = H_{ji}$, $S_{ij} = S_{ji}$

The set of n Secular Equations $\sum_j c_j (H_{ij} - \mathcal{E} S_{ij}) = 0$ for $i = 1, 2, 3, \dots, n$

has non-trivial solutions provided $\det |H_{ij} - \mathcal{E} S_{ij}| = 0$ a trivial solution
has all $c_j = 0$.

Note: The above condition is also apparent if Cramer's rule is used to solve the set of n simultaneous equations. This is more obvious from the matrix formulation.

Simplifying the Secular Determinant

$$\det |H_{ij} - \mathcal{E} S_{ij}| = \begin{vmatrix} H_{11} - \mathcal{E} S_{11} & H_{12} - \mathcal{E} S_{12} & \dots & H_{1n} - \mathcal{E} S_{1n} \\ H_{21} - \mathcal{E} S_{21} & H_{22} - \mathcal{E} S_{22} & \dots & H_{2n} - \mathcal{E} S_{2n} \\ \vdots & \vdots & \ddots & \dots \\ H_{n1} - \mathcal{E} S_{n1} & H_{n2} - \mathcal{E} S_{n2} & \dots & H_{nn} - \mathcal{E} S_{nn} \end{vmatrix} = 0$$

In principle, by manipulating rows and columns it is possible to achieve a diagonal form:

$$\begin{vmatrix} g_{11} - \mathcal{E} & 0 & \dots & 0 \\ 0 & g_{22} - \mathcal{E} & \dots & 0 \\ \vdots & \vdots & \ddots & \dots \\ 0 & 0 & \dots & g_{nn} - \mathcal{E} \end{vmatrix} = 0$$

Evaluation of the determinant gives an equation of order n in \mathcal{E}

$$(g_{11} - \mathcal{E})(g_{22} - \mathcal{E}) \dots (g_{nn} - \mathcal{E}) = 0$$

which can be solved to give n eigenvalues, each corresponding to one of n eigenfunctions.

These **orthogonal** eigenfunctions are linear combinations of the original basis set ψ .

Diagonalization is conveniently achieved using matrix algebra.

Variation of Linear Combinations – Example

Problem: The particle in a box with infinitely high walls... again!

Basis set: $f_1 = z(1-z)$ and $f_2 = z^2(1-z^2)$ where $z = x/a$

Trial functions: $\chi = c_1 f_1 + c_2 f_2$ two sets of coefficients, two functions, two energies

Task: Solve
$$\begin{vmatrix} H_{11} - \mathcal{E} S_{11} & H_{12} - \mathcal{E} S_{12} \\ H_{21} - \mathcal{E} S_{21} & H_{22} - \mathcal{E} S_{22} \end{vmatrix} = 0$$

$$S_{11} = \int_0^1 z^2 (1-z)^2 dz = \frac{1}{3} - \frac{1}{2} + \frac{1}{5} = \frac{1}{30}, \quad S_{12} = S_{21} = \frac{1}{4} - \frac{3}{5} + \frac{1}{2} - \frac{1}{7} = \frac{1}{140}, \quad S_{22} = \frac{1}{630}$$

$$H_{11} = -\frac{1}{2} \int_0^1 (z - z^2) \frac{d^2}{dz^2} (z - z^2) dz = \frac{1}{6}, \quad H_{12} = H_{21} = \frac{1}{3} - \frac{1}{2} + \frac{1}{5} = \frac{1}{30}, \quad H_{22} = \frac{1}{105}$$

$$\begin{vmatrix} \frac{1}{6} - \frac{1}{30} \mathcal{E} & \frac{1}{30} - \frac{1}{140} \mathcal{E} \\ \frac{1}{30} - \frac{1}{140} \mathcal{E} & \frac{1}{105} - \frac{1}{630} \mathcal{E} \end{vmatrix} = 0 \quad \Rightarrow \quad \begin{vmatrix} 70 - 14\mathcal{E} & 14 - 3\mathcal{E} \\ 42 - 9\mathcal{E} & 12 - 2\mathcal{E} \end{vmatrix} = 0 \quad \Rightarrow \quad \mathcal{E}^2 - 56\mathcal{E} + 252 = 0$$

$$\mathcal{E} = 28 \pm \sqrt{532} = \begin{cases} 4.93487 \text{ a.u.} = 1.0000147 (\pi^2 \hbar^2 / 2ma^2) & E_1 = 1 \\ 51.0651 \text{ a.u.} = 10.3480 (\pi^2 \hbar^2 / 2ma^2) & E_3 = 9 \end{cases} \quad \begin{array}{l} \text{N.B. the basis} \\ \text{set has only} \\ \text{even functions} \end{array}$$

Matrices in Quantum Mechanics

The **unit** matrix \mathbb{I} has $\mathbb{I}_{ij} = \delta_{ij}$

A **diagonal** matrix has all $A_{ij} = 0, \quad i \neq j$

The **transpose** has rows and columns switched $A_{ij}^T = A_{ji}$ **reflect elements about the diagonal**

The **adjoint** = complex conjugate of transpose $A_{ij}^\dagger = A_{ji}^*$

A **unitary** matrix has $A^{-1} = A^\dagger \Leftrightarrow A^\dagger A = I$

A **Hermitian** matrix is self adjoint $A_{ij}^\dagger = A_{ij} \Leftrightarrow A_{ji}^* = A_{ij}$

A **Hermitian** matrix has **real eigenvalues**

The **eigenvectors** of a **Hermitian** matrix belonging to **distinct eigenvalues** are **orthogonal**.

Any **Hermitian** matrix can be **diagonalized**. **The eigenvectors “span” the space.**

Hermitian matrices **commute** if they are diagonalized in the **same basis**.

Integrals, Brackets and Matrices

$$\int \psi_1^* \psi_2 \, d\tau \equiv \langle \psi_1 | \psi_2 \rangle \equiv (\psi_1^T) \cdot (\psi_2) \equiv (\dots c_i \dots) \begin{pmatrix} \vdots \\ c_j \\ \vdots \end{pmatrix}$$

$$\int \psi_1^* \hat{H} \psi_2 \, d\tau \equiv \langle \psi_1 | \hat{H} | \psi_2 \rangle \equiv (\dots c_i \dots) \begin{pmatrix} \vdots \\ \dots H_{ij} \dots \\ \vdots \end{pmatrix} \begin{pmatrix} \vdots \\ c_j \\ \vdots \end{pmatrix}$$

$$\psi_1 = \sum_i c_i \phi_i, \quad \psi_2 = \sum_j c_j \phi_j, \quad H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle \equiv \int \phi_i^* \hat{H} \phi_j \, d\tau$$

Matrix Representation of Spin Operators

Consider a simple spin-1/2 system, such as an electron, a proton, or a muon.

Take as basis set, the eigenfunctions of \hat{S}_z : $\hat{S}_z|\alpha\rangle = \frac{1}{2}|\alpha\rangle$ $\hat{S}_z|\beta\rangle = -\frac{1}{2}|\beta\rangle$

The matrix elements are $\langle\alpha|\hat{S}_z|\alpha\rangle = \frac{1}{2}$ $\langle\beta|\hat{S}_z|\beta\rangle = -\frac{1}{2}$ \Rightarrow $\hat{S}_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
 $\langle\alpha|\hat{S}_z|\beta\rangle = \frac{1}{2}\langle\alpha|\beta\rangle = 0$ $\langle\beta|\hat{S}_z|\alpha\rangle = 0$

Similarly, $\hat{S}^2|\alpha\rangle = s(s+1)|\alpha\rangle = \frac{3}{4}|\alpha\rangle$ \Rightarrow $\hat{S}^2 = \frac{3}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ $\hat{S}^2\hat{S}_z = \frac{3}{8}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \hat{S}_z\hat{S}^2$
 $\hat{S}^2|\beta\rangle = \frac{3}{4}|\beta\rangle$
 $[\hat{S}^2, \hat{S}_z] = 0$

$\hat{S}_x|\alpha\rangle = \frac{1}{2}|\beta\rangle$ $\hat{S}_x|\beta\rangle = \frac{1}{2}|\alpha\rangle$ $\hat{S}_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ $\hat{S}_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ α and β are **not**
 $\hat{S}_y|\alpha\rangle = \frac{1}{2}i|\beta\rangle$ $\hat{S}_y|\beta\rangle = -\frac{1}{2}i|\alpha\rangle$ eigenfunctions
of \hat{S}_x and \hat{S}_y

$\hat{S}_x\hat{S}_y = \frac{1}{4}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{1}{4}i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
 $\hat{S}_y\hat{S}_x = \frac{1}{4}i\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$ \Rightarrow $[\hat{S}_x, \hat{S}_y] = \frac{1}{2}i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = i\hat{S}_z$

Matrix Diagonalization of a Spin Operator

$$\hat{S}_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{Set up the secular equation:} \quad \det \begin{pmatrix} 0-\lambda & \frac{1}{2} \\ \frac{1}{2} & 0-\lambda \end{pmatrix} = \lambda^2 - \frac{1}{4} = 0 \quad \text{and solve:} \quad \lambda = \pm \frac{1}{2}$$

To find the coefficients of the eigenvectors, write out the simultaneous equations for each eigenvalue. Solve for coefficients and normalize

For $\lambda = -\frac{1}{2}$

$$\begin{aligned} (0 + \frac{1}{2})c_{11} + \frac{1}{2}c_{12} &= 0 & c_{11} &= -c_{12} & c_{11}^2 + c_{12}^2 &= 1 & c_{11} &= \frac{1}{\sqrt{2}} = -c_{12} \\ \frac{1}{2}c_{11} + (0 + \frac{1}{2})c_{12} &= 0 & & & & & & \end{aligned}$$

For $\lambda = \frac{1}{2}$

$$\begin{aligned} (0 - \frac{1}{2})c_{21} + \frac{1}{2}c_{22} &= 0 & c_{21} &= c_{22} & c_{21}^2 + c_{22}^2 &= 1 & c_{21} &= \frac{1}{\sqrt{2}} = c_{22} \\ \frac{1}{2}c_{21} + (0 - \frac{1}{2})c_{22} &= 0 & & & & & & \end{aligned}$$

$$\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad \frac{1}{4} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

or

$$\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad \frac{1}{4} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

arbitrary labelling of wave functions

↑
 \hat{S}_x is diagonal in the new basis