

# A primer on (spin) Hamiltonians

$$\hat{\mathcal{H}}|\psi\rangle = E|\psi\rangle$$

- This is a brief summary of how to “solve a Hamiltonian”
- Will do this in context of a spin Hamiltonian for  $s = 1/2$ , because this is a “simple” two-level system
- The general method is applicable to other forms of Hamiltonian.

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# States and Operators

$$\hat{O}|\psi\rangle = |\varphi\rangle$$

- Notation:
  - $|\ \ \rangle \Rightarrow$  a **function** (called a “ket” in Dirac notation).
  - $\hat{\ \ } \Rightarrow$  an **operator**. An instruction to perform on a function  $\rightarrow$  another function.
- If operation gives the same function multiplied by a scalar, i.e.  $\hat{O}|\psi\rangle = E|\psi\rangle$
- ...then  $|\psi\rangle$  is an **eigenfunction** of  $\hat{O}$  with associated **eigenvalue**  $E$ .
- Experimental observables are represented by operators. The **Hamiltonian operator** corresponds to the total energy.  $|\psi\rangle$  are the energy levels and  $E$  are their energies.
- A **spin Hamiltonian** operator gives spin states and relative energies. It involves operators that only act on spin functions.

# Spin states and spin operators

- For spin  $s$ , with  $m = +s, +(s - 1), \dots - s$ , define states as  $|s, m\rangle$
- Spin operators have the actions:

$$\hat{S}^2 |s, m\rangle = s(s + 1) |s, m\rangle \quad \rightarrow \text{magnitude of spin is } \sqrt{s(s + 1)}$$

$$\hat{S}_z |s, m\rangle = m |s, m\rangle \quad \rightarrow \text{component of spin along z axis is } m$$

$$\left. \begin{aligned} \hat{S}_x &= \frac{1}{2} (\hat{S}_+ + \hat{S}_-) \\ \hat{S}_y &= -\frac{i}{2} (\hat{S}_+ - \hat{S}_-) \end{aligned} \right\} \begin{aligned} \hat{S}_+ |s, m\rangle &= \sqrt{s(s + 1) - m(m + 1)} |s, m + 1\rangle \\ \hat{S}_- |s, m\rangle &= \sqrt{s(s + 1) - m(m - 1)} |s, m - 1\rangle \end{aligned}$$

Raising and lowering operators

Units of  $\hbar$  have been dropped from  $\hat{S}_z |s, m\rangle = m\hbar |s, m\rangle$ , etc

# Operations on spin 1/2

- For  $s = 1/2$ , have **basis states** (see next slide):

$$|s, m\rangle = |1/2, \pm 1/2\rangle = |\alpha\rangle, |\beta\rangle$$

- Then

$$\begin{aligned}\hat{s}_x|\alpha\rangle &= +\frac{1}{2}|\beta\rangle & \hat{s}_x|\beta\rangle &= +\frac{1}{2}|\alpha\rangle \\ \hat{s}_y|\alpha\rangle &= +\frac{i}{2}|\beta\rangle & \hat{s}_y|\beta\rangle &= -\frac{i}{2}|\alpha\rangle \\ \hat{s}_z|\alpha\rangle &= +\frac{1}{2}|\alpha\rangle & \hat{s}_z|\beta\rangle &= -\frac{1}{2}|\beta\rangle\end{aligned}$$

- Can already see  $|\alpha\rangle, |\beta\rangle$  are eigenfunctions of  $\hat{s}_z$  but not of  $\hat{s}_x, \hat{s}_y$

# General spin states

• Linear combinations of basis states  $|\psi\rangle = a|\alpha\rangle + b|\beta\rangle$

• Can represent ket as a column vector  $|\psi\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$

• Where the **basis states** are:  $|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$   $|\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

•  $a$  and  $b$  can be complex, and  $|\psi\rangle$  must be **normalised**:

$$(x + iy)^* = (x - iy)$$

**Complex conjugate;  $i^2 = -1$**

$$|a|^2 + |b|^2 = a^*a + b^*b = 1 \quad \dots\text{or}\dots \quad \langle\psi|\psi\rangle = (a^* \quad b^*) \begin{pmatrix} a \\ b \end{pmatrix} = a^*a + b^*b$$

• ...where the “bra”  $\langle\psi| = |\psi\rangle^\dagger$  (adjoint = complex conjugate and transpose), hence a row vector.  $\langle \quad | \quad \rangle$  (“bra(c)ket”) is an inner product (or dot product) of vectors.

(see Appendix 1)

• Note, basis states are defined to be **orthonormal**:

$$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$$

**normalised**

$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$$

**orthogonal**

# (time independent) Schrödinger equation

- Given an operator  $\hat{\mathcal{H}}$ , want to find eigenfunctions and eigenvalues that meet:

$$\hat{\mathcal{H}}|\psi_i\rangle = E_i|\psi_i\rangle$$

- Pre-multiply both sides by  $\langle\alpha|$  and expand  $|\psi_i\rangle = a_i|\alpha\rangle + b_i|\beta\rangle$

$$\langle\alpha|\hat{\mathcal{H}}|\psi_i\rangle = E_i\langle\alpha|\psi_i\rangle$$

(see Appendix 2)

$$a_i\langle\alpha|\hat{\mathcal{H}}|\alpha\rangle + b_i\langle\alpha|\hat{\mathcal{H}}|\beta\rangle = a_iE_i$$

- Pre-multiply both sides by  $\langle\beta|$  and expand  $|\psi_i\rangle = a_i|\alpha\rangle + b_i|\beta\rangle$

$$\langle\beta|\hat{\mathcal{H}}|\psi_i\rangle = E_i\langle\beta|\psi_i\rangle$$

$$a_i\langle\beta|\hat{\mathcal{H}}|\alpha\rangle + b_i\langle\beta|\hat{\mathcal{H}}|\beta\rangle = b_iE_i$$

combine

$$\begin{pmatrix} \langle\alpha|\hat{\mathcal{H}}|\alpha\rangle & \langle\alpha|\hat{\mathcal{H}}|\beta\rangle \\ \langle\beta|\hat{\mathcal{H}}|\alpha\rangle & \langle\beta|\hat{\mathcal{H}}|\beta\rangle \end{pmatrix} \begin{pmatrix} a_i \\ b_i \end{pmatrix} = E_i \begin{pmatrix} a_i \\ b_i \end{pmatrix}$$

This is just  $\hat{\mathcal{H}}|\psi_i\rangle = E_i|\psi_i\rangle$  in matrix/vector form

# Hamiltonian matrix

- So Hamiltonian operator in matrix form is:

$$\hat{\mathcal{H}} = \begin{array}{cc} & \begin{array}{c} |\alpha\rangle \\ |\beta\rangle \end{array} \\ \begin{array}{c} \langle\alpha| \\ \langle\beta| \end{array} & \begin{array}{cc} \langle\alpha|\hat{\mathcal{H}}|\alpha\rangle & \langle\alpha|\hat{\mathcal{H}}|\beta\rangle \\ \langle\beta|\hat{\mathcal{H}}|\alpha\rangle & \langle\beta|\hat{\mathcal{H}}|\beta\rangle \end{array} \end{array}$$

- Entries  $\langle \quad | \hat{\mathcal{H}} | \quad \rangle$  are called **matrix elements**
  - $\langle\alpha|\hat{\mathcal{H}}|\alpha\rangle$  and  $\langle\beta|\hat{\mathcal{H}}|\beta\rangle$  are **diagonal** matrix elements
  - $\langle\alpha|\hat{\mathcal{H}}|\beta\rangle$  and  $\langle\beta|\hat{\mathcal{H}}|\alpha\rangle$  are **off-diagonal** matrix elements
- Each column associated with one basis ket
- Each row associated with one basis bra (in same order)
- Diagonal matrix element  $\langle\psi|\hat{\mathcal{H}}|\psi\rangle$  gives the **expectation value**: the average result of measurements represented by  $\hat{\mathcal{H}}$  on the system in the state  $|\psi\rangle$

# Solving the Hamiltonian

- Want solutions to

$$\begin{pmatrix} \langle \alpha | \hat{\mathcal{H}} | \alpha \rangle & \langle \alpha | \hat{\mathcal{H}} | \beta \rangle \\ \langle \beta | \hat{\mathcal{H}} | \alpha \rangle & \langle \beta | \hat{\mathcal{H}} | \beta \rangle \end{pmatrix} \begin{pmatrix} a_i \\ b_i \end{pmatrix} = E_i \begin{pmatrix} a_i \\ b_i \end{pmatrix}$$

- Rearrange...

$$\begin{pmatrix} \langle \alpha | \hat{\mathcal{H}} | \alpha \rangle - E_i & \langle \alpha | \hat{\mathcal{H}} | \beta \rangle \\ \langle \beta | \hat{\mathcal{H}} | \alpha \rangle & \langle \beta | \hat{\mathcal{H}} | \beta \rangle - E_i \end{pmatrix} \begin{pmatrix} a_i \\ b_i \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$(\hat{\mathcal{H}} - \mathbf{1}E_i)|\psi_i\rangle = 0$$

$$\mathbf{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Unit matrix

- There is a trivial, and useless, solution:  $a_i = b_i = 0$
- Non-trivial solutions are the eigenfunctions  $\begin{pmatrix} a_i \\ b_i \end{pmatrix}$  and eigenvalues  $E_i$
- Found when the **determinant**  $|\hat{\mathcal{H}} - \mathbf{1}E_i| = 0$

$$\det \begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

Matrix determinant

## Example: $\hat{\mathcal{H}} = \hat{s}_z$

- Evaluate matrix elements and construct Hamiltonian matrix

$$\hat{\mathcal{H}} = \begin{array}{c|cc} & |\alpha\rangle & |\beta\rangle \\ \hline \langle\alpha| & +1/2 & 0 \\ \langle\beta| & 0 & -1/2 \end{array} \quad \begin{array}{l} \langle\alpha|\hat{s}_z|\alpha\rangle = +\frac{1}{2}\langle\alpha|\alpha\rangle = +\frac{1}{2} \\ \langle\beta|\hat{s}_z|\alpha\rangle = +\frac{1}{2}\langle\beta|\alpha\rangle = 0 \end{array} \quad \begin{array}{l} \langle\alpha|\hat{s}_z|\beta\rangle = -\frac{1}{2}\langle\alpha|\beta\rangle = 0 \\ \langle\beta|\hat{s}_z|\beta\rangle = -\frac{1}{2}\langle\beta|\beta\rangle = -\frac{1}{2} \end{array}$$

- It is **diagonal**, i.e. all off-diagonal elements = 0
- Need to find solutions to:

$$\begin{vmatrix} +1/2 - E_i & 0 \\ 0 & -1/2 - E_i \end{vmatrix} = (+1/2 - E_i)(-1/2 - E_i) - 0 = 0$$

- eigenvalues:  $E_{1,2} = \pm \frac{1}{2}$
- $\hat{\mathcal{H}}$  matrix is only **diagonal** when the **basis states are eigenfunctions**
- Here,  $|\alpha\rangle$  and  $|\beta\rangle$  are eigenfunctions of  $\hat{s}_z$  (in fact, we used this as our definition)

## Example: $\hat{\mathcal{H}} = \hat{S}_x$

- Evaluate matrix elements and construct Hamiltonian matrix

$$\hat{\mathcal{H}} = \begin{array}{cc} & \begin{array}{c} |\alpha\rangle \\ |\beta\rangle \end{array} \\ \begin{array}{c} \langle\alpha| \\ \langle\beta| \end{array} & \begin{array}{cc} & \begin{array}{c} |\alpha\rangle \\ |\beta\rangle \end{array} \\ 0 & +1/2 \\ +1/2 & 0 \end{array} \end{array}$$
$$\begin{array}{ll} \langle\alpha|\hat{S}_x|\alpha\rangle = +\frac{1}{2}\langle\alpha|\beta\rangle = 0 & \langle\alpha|\hat{S}_x|\beta\rangle = +\frac{1}{2}\langle\alpha|\alpha\rangle = +1/2 \\ \langle\beta|\hat{S}_x|\alpha\rangle = +\frac{1}{2}\langle\beta|\beta\rangle = +1/2 & \langle\beta|\hat{S}_x|\beta\rangle = +\frac{1}{2}\langle\beta|\alpha\rangle = 0 \end{array}$$

- $\hat{\mathcal{H}}$  matrix *not* diagonal in this basis
- $|\alpha\rangle$  and  $|\beta\rangle$  are *not* eigenfunctions of  $\hat{S}_x$
- Need to find solutions to:

$$\begin{vmatrix} -E_i & +1/2 \\ +1/2 & -E_i \end{vmatrix} = (-E_i)(-E_i) - \left(+\frac{1}{2}\right)\left(+\frac{1}{2}\right) = 0$$

- eigenvalues:  $E_{1,2} = \pm\frac{1}{2}$

## Example: $\hat{\mathcal{H}} = \hat{S}_x$

- Substitute  $E_i$  back into  $(\hat{\mathcal{H}} - \mathbf{1}E_i)|\psi_i\rangle = 0$

$$\begin{pmatrix} -E_i & +1/2 \\ +1/2 & -E_i \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$
$$\begin{aligned} -E_i a + \frac{b}{2} &= 0 \\ +\frac{a}{2} - E_i b &= 0 \end{aligned}$$

- For  $E_1 = +1/2$ , get  $a = b$ .
  - For  $E_2 = -1/2$ , get  $a = -b$ .
- } Normalisation  $|a|^2 + |b|^2 = 1$   
requires factor of  $1/\sqrt{2}$

- Acceptable solutions are:

$$|\psi_1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = (|\alpha\rangle + |\beta\rangle)/\sqrt{2}$$

$$|\psi_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = (|\alpha\rangle - |\beta\rangle)/\sqrt{2}$$

## Example: $\hat{\mathcal{H}} = \hat{S}_x$

- Have gone from...

$$\begin{array}{c}
 \hat{\mathcal{H}} = \begin{array}{cc} & \begin{array}{c} |\alpha\rangle \\ |\beta\rangle \end{array} \\ \begin{array}{c} \langle\alpha| \\ \langle\beta| \end{array} & \begin{array}{cc} 0 & +1/2 \\ +1/2 & 0 \end{array} \end{array}
 \end{array}
 \quad \dots\text{to}\dots \quad
 \begin{array}{c}
 \hat{\mathcal{H}}^D = \begin{array}{cc} & \begin{array}{c} |\alpha + \beta\rangle/\sqrt{2} \\ |\alpha - \beta\rangle/\sqrt{2} \end{array} \\ \begin{array}{c} \langle\alpha + \beta|/\sqrt{2} \\ \langle\alpha - \beta|/\sqrt{2} \end{array} & \begin{array}{cc} +1/2 & 0 \\ 0 & -1/2 \end{array} \end{array}
 \end{array}$$

- Have found a new basis (the eigenfunctions) in which  $\hat{\mathcal{H}}$  is diagonal
- Note **off-diagonal matrix elements** result in **mixing of the connected states**
- This process has also given the eigenvalues
- “Solving the Hamiltonian” is the process of **diagonalising  $\hat{\mathcal{H}}$**  (see Appendix 3)

# SUMMARY

- Define orthonormal set of basis functions, e.g.  $|m\rangle = |\alpha\rangle, |\beta\rangle$  for  $s = 1/2$
- ...and Hamiltonian describing interactions, e.g.  $\hat{\mathcal{H}} = \mu_B g_x B_x \hat{S}_x$ .
- Construct energy matrix form of  $\hat{\mathcal{H}}$  by evaluating all matrix elements  $\langle m' | \hat{\mathcal{H}} | m \rangle$

$$\hat{\mathcal{H}} = \begin{array}{cc} & \begin{array}{c} |\alpha\rangle \\ |\beta\rangle \end{array} \\ \begin{array}{c} \langle\alpha| \\ \langle\beta| \end{array} & \begin{array}{cc} 0 & +\mu_B g_x B_x / 2 \\ +\mu_B g_x B_x / 2 & 0 \end{array} \end{array}$$

- Diagonalise to get **eigenvalues** (energies) and **eigenfunctions** (states)

$$\begin{array}{cc} & \begin{array}{c} |\alpha + \beta\rangle / \sqrt{2} \\ |\alpha - \beta\rangle / \sqrt{2} \end{array} \\ \begin{array}{c} \langle\alpha + \beta| / \sqrt{2} \\ \langle\alpha - \beta| / \sqrt{2} \end{array} & \begin{array}{cc} +\mu_B g_x B_x / 2 & 0 \\ 0 & -\mu_B g_x B_x / 2 \end{array} \end{array}$$

# Appendix 1: Matrix algebra

- Matrix =  $m \times n$  array of numbers ( $m$  rows,  $n$  columns)
  - Square matrix  $m \times m$
  - Column vector  $m \times 1$
  - Row vector  $1 \times n$

- Adding/subtracting: must be same dimension

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \pm \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} = \begin{pmatrix} a_{11} \pm b_{11} & a_{12} \pm b_{12} \\ a_{21} \pm b_{21} & a_{22} \pm b_{22} \end{pmatrix}$$

- Multiplication by a scalar

$$x \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} x = \begin{pmatrix} xa_{11} & xa_{12} \\ xa_{21} & xa_{22} \end{pmatrix}$$

- Matrix adjoint = complex conjugate and transpose (swap rows and columns)

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}^\dagger = \begin{pmatrix} a_{11}^* & a_{21}^* \\ a_{12}^* & a_{22}^* \end{pmatrix} \quad \begin{pmatrix} v_1 \\ v_2 \end{pmatrix}^\dagger = (v_1^* \quad v_2^*)$$

## Appendix 1: Matrix algebra cont.

- Multiplication: multiply (dot products of) rows of first matrix with columns of second. Only possible if no. of columns of first = no. of rows of second. Multiplication of  $m \times n$  with  $n \times p$  matrix  $\rightarrow m \times p$  matrix. Examples:

$$(w_1 \quad w_2) \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = (w_1 v_1 + w_2 v_2)$$

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{pmatrix} a_{11}v_1 + a_{12}v_2 \\ a_{21}v_1 + a_{22}v_2 \end{pmatrix}$$

$$(w_1 \quad w_2) \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} = (w_1 a_{11} + w_2 a_{21} \quad w_1 a_{12} + w_2 a_{22})$$

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} = \begin{pmatrix} a_{11}b_{11} + a_{12}b_{21} & a_{11}b_{12} + a_{12}b_{22} \\ a_{21}b_{11} + a_{22}b_{21} & a_{21}b_{12} + a_{22}b_{22} \end{pmatrix}$$

- Multiplication is associative:  $(AB)C = A(BC)$
- Multiplication, in general, is **not** commutative:  $AB \neq BA$

# Appendix 2: Expanding the Schrödinger equation

$$\hat{\mathcal{H}}|\psi_i\rangle = E_i|\psi_i\rangle$$

- e.g. pre-multiply both sides by  $\langle\alpha|$

$$\langle\alpha|\hat{\mathcal{H}}|\psi_i\rangle = \langle\alpha|E_i|\psi_i\rangle$$

$$\langle\alpha|\hat{\mathcal{H}}|\psi_i\rangle = E_i\langle\alpha|\psi_i\rangle$$

$E_i$  is just a scalar, so can come outside the bra-ket

- ...and expand  $|\psi_i\rangle = a_i|\alpha\rangle + b_i|\beta\rangle$

$$\langle\alpha|\hat{\mathcal{H}}|(a_i|\alpha\rangle + b_i|\beta\rangle)\rangle = E_i\langle\alpha|(a_i|\alpha\rangle + b_i|\beta\rangle)\rangle$$

$$a_i\langle\alpha|\hat{\mathcal{H}}|\alpha\rangle + b_i\langle\alpha|\hat{\mathcal{H}}|\beta\rangle = a_iE_i\langle\alpha|\alpha\rangle + b_iE_i\langle\alpha|\beta\rangle$$

$$a_i\langle\alpha|\hat{\mathcal{H}}|\alpha\rangle + b_i\langle\alpha|\hat{\mathcal{H}}|\beta\rangle = a_iE_i$$

$a_i$  and  $b_i$  are also scalars

## Appendix 3: for matrix enthusiasts

- The process of diagonalising  $\hat{\mathcal{H}} \rightarrow \hat{\mathcal{H}}^D$  is a **unitary transformation**...
- Find the matrix  $X$  such that  $X^{-1}\hat{\mathcal{H}}X = \hat{\mathcal{H}}^D$
- ...where  $X^{-1}$  is the **inverse** of  $X$  ( $X^{-1}X = XX^{-1} = \mathbf{1}$ )
- ...and  $X$  is **unitary** ( $X^{-1} = X^\dagger$ )
- Columns of  $X$  are the orthonormal eigenvectors of  $\hat{\mathcal{H}}$ , hence the basis states of  $\hat{\mathcal{H}}^D$

- For the example of  $\hat{\mathcal{H}} = \hat{s}_x$ 

$$X = X^\dagger = \begin{pmatrix} +1/\sqrt{2} & +1/\sqrt{2} \\ +1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix}$$

$$X^{-1}\hat{\mathcal{H}}X = \begin{pmatrix} +1/\sqrt{2} & +1/\sqrt{2} \\ +1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} 0 & +1/2 \\ +1/2 & 0 \end{pmatrix} \underbrace{\begin{pmatrix} +1/\sqrt{2} & +1/\sqrt{2} \\ +1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix}}_{\text{Eigenfunctions associated with eigenvalues}} = \underbrace{\begin{pmatrix} +1/2 & 0 \\ 0 & -1/2 \end{pmatrix}}_{\text{Eigenvalues}} = \hat{\mathcal{H}}^D$$