

## CHEM6154 - Week 21 - Lecture 2: Spin

A theory of spin may be obtained from algebraic considerations (see [https://youtu.be/\\_2hXRP6gZtM](https://youtu.be/_2hXRP6gZtM)), but – for lack of time – we use the analogy with angular momentum in this course. Although the algebraic properties are broadly similar, spin is different from angular momentum:

1. Spin can take half-integer values.
2. Spin vanishes in the classical limit ( $\hbar \rightarrow 0$ ).
3. At terrestrial energies, most nuclei are in their ground state, and therefore their spin does not change.
4. Spin is associated, in most cases, with a magnetic dipole.
5. Spin appears because Minkowski space-time of Special Relativity has more ways of rotating things than were available in Euclidean space-time.

Spin degrees of freedom create a finite number of independent copies of each spatial wavefunction. For example, for a spin-1/2 particle, a wavefunction becomes a pair of wavefunctions, each associated with a specific state of the spin. Such constructs are called *spinors*; they may be separated into the “space” and the “spin” part that are in a direct product relationship:

$$|\Psi_{\text{total}}(\vec{r}, s)\rangle = \sum_{nk} |\psi_{\text{space}}^{(n)}(\vec{r})\rangle \otimes |\psi_{\text{spin}}^{(k)}(s)\rangle \quad (1)$$

By analogy with angular momentum, the state space of a spin  $s$  is  $2s+1$  dimensional. The spin part of Equation (1) is therefore a vector with  $2s+1$  complex components. For spin  $\frac{1}{2}$ , we have:

$$\begin{pmatrix} c_{1/2} \\ c_{-1/2} \end{pmatrix} = c_{1/2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + c_{-1/2} \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad |c_{1/2}|^2 + |c_{-1/2}|^2 = 1 \quad (2)$$

Let us assign the two orthogonal vectors to the two projection states of the spin, that is:

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} = |\alpha\rangle, \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix} = |\beta\rangle \quad (3)$$

This fixes the basis and allows us to build matrix representations of the spin operators. In particular, the two spin projection states should be eigenvectors of the total spin operator  $\hat{S}^2$  and the projection operator  $\hat{S}_z$ , which we introduce using the angular momentum analogy:

$$\begin{aligned} \hat{S}^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= \frac{1}{2} \left( \frac{1}{2} + 1 \right) \begin{pmatrix} 1 \\ 0 \end{pmatrix}; & \hat{S}^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} &= \frac{1}{2} \left( \frac{1}{2} + 1 \right) \begin{pmatrix} 0 \\ 1 \end{pmatrix} & \Rightarrow & \hat{S}^2 = \begin{pmatrix} 3/4 & 0 \\ 0 & 3/4 \end{pmatrix} \\ \hat{S}_z \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= \frac{1}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix}; & \hat{S}_z \begin{pmatrix} 0 \\ 1 \end{pmatrix} &= -\frac{1}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} & \Rightarrow & \hat{S}_z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \end{aligned} \quad (4)$$

The basis vectors  $|\alpha\rangle$  and  $|\beta\rangle$  should be raised and lowered into each other. This yields matrix representations for the raising and lowering operators:

$$\begin{aligned} \hat{S}_+ \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= \begin{pmatrix} 0 \\ 0 \end{pmatrix}; & \hat{S}_+ \begin{pmatrix} 0 \\ 1 \end{pmatrix} &= \begin{pmatrix} 1 \\ 0 \end{pmatrix} & \Rightarrow & \hat{S}_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \\ \hat{S}_- \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= \begin{pmatrix} 0 \\ 1 \end{pmatrix}; & \hat{S}_- \begin{pmatrix} 0 \\ 1 \end{pmatrix} &= \begin{pmatrix} 0 \\ 0 \end{pmatrix} & \Rightarrow & \hat{S}_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \end{aligned} \quad (5)$$

The remaining  $\hat{S}_x$  and  $\hat{S}_y$  operators are then constructed from raising and lowering operators:

$$\hat{S}_X = \frac{\hat{S}_+ + \hat{S}_-}{2} \quad \hat{S}_Y = \frac{\hat{S}_+ - \hat{S}_-}{2i} \quad (6)$$

So the operators corresponding to the three Cartesian projections of spin  $\frac{1}{2}$  are:

$$\hat{S}_X = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \quad \hat{S}_Y = \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix} \quad \hat{S}_Z = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \quad (7)$$

These matrices are called *Cartesian spin operators* for spin  $\frac{1}{2}$ ; they are a factor of  $\frac{1}{2}$  away from *Pauli matrices* used in relativistic quantum mechanics:

$$\hat{\sigma}_X = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \hat{\sigma}_Y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \hat{\sigma}_Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (8)$$

For spins greater than  $\frac{1}{2}$ , Cartesian spin operators have larger dimensions, but may still be constructed using the same method. For example, a spin-1 particle has:

$$\hat{S}_X = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \hat{S}_Y = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad \hat{S}_Z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (9)$$

It is easy to check by direct inspection that the matrices in Equations (7) and (9) obey the same commutation relations as the angular momentum projection operators:

$$[\hat{S}_X, \hat{S}_Y] = i\hat{S}_Z; \quad [\hat{S}_Z, \hat{S}_X] = i\hat{S}_Y; \quad [\hat{S}_Y, \hat{S}_Z] = i\hat{S}_X; \quad [\hat{S}^2, \hat{S}_{\{X,Y,Z\}}] = 0 \quad (10)$$

Unlike angular momentum, the spin squared operator is a multiple of the unit matrix:

$$\hat{S}_{(1/2)}^2 = \begin{pmatrix} 3/4 & 0 \\ 0 & 3/4 \end{pmatrix}; \quad \hat{S}_{(1)}^2 = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \quad (11)$$

Although commutation properties are the same, multiplication properties are different between spin and angular momentum operators, and also between operators of different spin.

### Connection between spin and magnetic moment

For free electrons, the proportionality between the magnetic moment operator and the spin operator:

$$\hat{\mu}_e = -g_e \mu_B \mathbf{S} \quad (12)$$

follows from Dirac's equation. Here,  $\mu_B = e\hbar/2m_e$  is Bohr magneton,  $m_e$  is the electron mass, and  $g_e$  is electron  $g$ -factor. For nuclei, the situation is more complicated because nuclear spin is itself an effective quantity (<https://youtu.be/lPc1jxo8-Uw>). However, so long as the nucleus stays in its ground state, its magnetic moment is also proportional to spin:

$$\hat{\mu}_X = \gamma \hat{S}_X \quad \hat{\mu}_Y = \gamma \hat{S}_Y \quad \hat{\mu}_Z = \gamma \hat{S}_Z \quad (13)$$

where the proportionality constant  $\gamma$  is called *magnetogyric ratio*. These relations are the reason why the magnetization operators and the spin operators are sometimes used interchangeably in magnetic resonance spectroscopy and imaging.

### Spin Hamiltonian approximation

Compared to the typical C–H bond energy (400 kJ/mol), energies of magnetic interactions involving electron and nuclear magnetic dipoles are small enough for the Taylor series for the total molecular energy with respect to the dipoles and the external field to converge at the second order:

$$E = E_0 + \sum_n \frac{\partial E}{\partial \mu_n} \mu_n + \sum_n \frac{\partial E}{\partial B_n} B_n + \frac{1}{2} \sum_{nk} \frac{\partial^2 E}{\partial B_n \partial \mu_k} B_n \mu_k + \frac{1}{2} \sum_{nk} \frac{\partial^2 E}{\partial \mu_n \partial \mu_k} \mu_n \mu_k + \frac{1}{2} \sum_{nk} \frac{\partial^2 E}{\partial B_n \partial B_k} B_n B_k \dots \quad (14)$$

here  $E_0$  is the part of the total molecular energy  $E$  that does not depend on the magnetic field and the magnetic moments,  $\{B_k\}$  are Cartesian components of the external field, and  $\{\mu_k\}$  are Cartesian components of all magnetic dipoles in the system. The quantum mechanical energy operator corresponding to the spin-dependent part of Equation (14) is called *spin Hamiltonian*.

### Algebraic classification of spin interaction Hamiltonians

Physical mechanisms of spin interactions vary greatly, but the resulting terms in the spin Hamiltonian can only have three generic algebraic forms: as per Equation (14), they can either be linear, or bilinear, or quadratic in spin operators corresponding to the coordinates  $\{s_k\}$ . The Hamiltonian operator of NMR and ESR systems can therefore only have three generic algebraic types of interaction terms:

1. [Linear in spin](#): these come from couplings to some “external” vectors, such as magnetic field and orbital angular momentum. Nuclear Zeeman interaction, electron Zeeman interaction, spin-rotation coupling and spin-orbit coupling belong to this type. For nuclear Zeeman interaction:

$$\hat{H}_Z = \hat{\mathbf{S}} \cdot \mathbf{A} \cdot \vec{\mathbf{B}} = \begin{pmatrix} \hat{S}_X & \hat{S}_Y & \hat{S}_Z \end{pmatrix} \begin{pmatrix} a_{XX} & a_{XY} & a_{XZ} \\ a_{YX} & a_{YY} & a_{YZ} \\ a_{ZX} & a_{ZY} & a_{ZZ} \end{pmatrix} \begin{pmatrix} B_X \\ B_Y \\ B_Z \end{pmatrix} \quad (15)$$

where  $\hat{\mathbf{S}}$  is a vector of spin operators,  $\vec{\mathbf{B}}$  is the magnetic field vector and  $\mathbf{A}$  is the Zeeman interaction tensor.

2. [Bilinear in spin](#): these come from couplings between spins.  $J$ -coupling, dipolar coupling, exchange interaction and hyperfine coupling belong to this type. For hyperfine coupling:

$$\hat{H}_{\text{HFC}} = \hat{\mathbf{S}} \cdot \mathbf{A} \cdot \hat{\mathbf{L}} = \begin{pmatrix} \hat{S}_X & \hat{S}_Y & \hat{S}_Z \end{pmatrix} \begin{pmatrix} a_{XX} & a_{XY} & a_{XZ} \\ a_{YX} & a_{YY} & a_{YZ} \\ a_{ZX} & a_{ZY} & a_{ZZ} \end{pmatrix} \begin{pmatrix} \hat{L}_X \\ \hat{L}_Y \\ \hat{L}_Z \end{pmatrix} \quad (16)$$

where  $\hat{\mathbf{S}}$  and  $\hat{\mathbf{L}}$  are spin operator vectors for and  $\mathbf{A}$  is the hyperfine coupling tensor.

3. [Quadratic in spin](#): these are often caused indirectly by other interactions, but manifest themselves algebraically as coupling between a spin and itself. Nuclear quadrupolar interaction and electron zero-field splitting belong to this type. For nuclear quadrupolar interaction:

$$\hat{H}_Q = \hat{\mathbf{S}} \cdot \mathbf{A} \cdot \hat{\mathbf{S}} = \begin{pmatrix} \hat{S}_X & \hat{S}_Y & \hat{S}_Z \end{pmatrix} \begin{pmatrix} a_{XX} & a_{XY} & a_{XZ} \\ a_{YX} & a_{YY} & a_{YZ} \\ a_{ZX} & a_{ZY} & a_{ZZ} \end{pmatrix} \begin{pmatrix} \hat{S}_X \\ \hat{S}_Y \\ \hat{S}_Z \end{pmatrix} \quad (17)$$

where  $\hat{\mathbf{S}}$  is a vector of spin operators and  $\mathbf{A}$  is the quadrupolar coupling tensor.