Module I, Lecture 05: Quantum Mechanical Theory of Spin

A formal theory of spin may be obtained from purely algebraic considerations (see Southampton's big Spin Dynamics course on http://spindynamics.org), but here we shall build it based on the analogy with the angular momentum theory, which is always taught in physics and chemistry programmes of modern universities. That is also the way spin was historically introduced into quantum mechanics. Although the algebraic properties are broadly similar, spin is different from angular momentum in the following ways:

1. Spin is an intrinsic and unchanging property (*e.g.* always ½ for a single electron).
2. Spin can take half-integer values (thereby confusing some philosophers).
3. Spin vanishes in the classical limit (*i.e.* when $\hbar \to 0$).
4. Spin is associated, in most cases, with a point magnetic dipole.
5. Spin has nothing to do with rotations in physical space.

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

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

By analogy with angular momentum, the state space of a spin s is $2s+1$ dimensional. The spin part of Equation (1) is therefore is a vector with $2s+1$ complex components. For spin ½, we have:

$$\begin{pmatrix} c_{1/2} \\ c_{-1/2} \end{pmatrix} = c_{1/2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} + c_{-1/2}\begin{pmatrix} 0 \\ 1 \end{pmatrix}, \qquad |c_{1/2}|^2 + |c_{-1/2}|^2 = 1 \tag{2}$$

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

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} = |\alpha\rangle, \qquad \begin{pmatrix} 0 \\ 1 \end{pmatrix} = |\beta\rangle \tag{3}$$

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. This information yields matrix representations for these operators:

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

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

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

The remaining Cartesian operators can then be constructed from the raising and lowering operators using the relations from the angular momentum theory:

$$\hat{S}_{\mathrm{X}} = \frac{\hat{S}_{+} + \hat{S}_{-}}{2} \qquad \hat{S}_{\mathrm{Y}} = \frac{\hat{S}_{+} - \hat{S}_{-}}{2i} \tag{6}$$

So the operators corresponding to the three Cartesian projections of spin ½ are:

$$\hat{S}_{\mathrm{X}} = \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \qquad \hat{S}_{\mathrm{Y}} = \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix} \qquad \hat{S}_{\mathrm{Z}} = \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \tag{7}$$

These matrices are called *Pauli matrices* for spin ½. They are a two-dimensional *matrix representation* of the corresponding spin operators. For spins greater than ½, they have larger dimensions, but may still be constructed using the same method. For example, a spin-1 particle has:

$$\hat{S}_{\mathrm{X}} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \hat{S}_{\mathrm{Y}} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad \hat{S}_{\mathrm{Z}} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{8}$$

It is easy to check by direct inspection that the matrices in Equations (7) and (8) obey the same commutation relations as the angular momentum projection operators:

$$[\hat{S}_{\mathrm{X}}, \hat{S}_{\mathrm{Y}}] = i\hat{S}_{\mathrm{Z}}; \quad [\hat{S}_{\mathrm{Z}}, \hat{S}_{\mathrm{X}}] = i\hat{S}_{\mathrm{Y}}; \quad [\hat{S}_{\mathrm{Y}}, \hat{S}_{\mathrm{Z}}] = i\hat{S}_{\mathrm{X}}; \quad [\hat{S}^2, \hat{S}_{\{\mathrm{X,Y,Z}\}}] = 0 \tag{9}$$

However, unlike angular momentum, the total spin operator is proportional to the unit operator:

$$\hat{S}^2_{(1/2)} = \begin{pmatrix} 3/4 & 0 \\ 0 & 3/4 \end{pmatrix}; \qquad \hat{S}^2_{(1)} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{10}$$

Multiplication properties are also different between spin and angular momentum operators.

Connection between spin and magnetic moment

It is not presently known why quarks have a spin and a magnetic dipole moment, and why the direction of the two happens to be aligned. A practical consequence of this alignment, however, is that the observables corresponding to the Pauli matrices are proportional to the Cartesian components of the particle's magnetic dipole, meaning that the magnetic dipole projection operators are proportional to the spin projection operators:

$$\hat{\mu}_{\mathrm{X}} = \gamma\hat{S}_{\mathrm{X}} \qquad \hat{\mu}_{\mathrm{Y}} = \gamma\hat{S}_{\mathrm{Y}} \qquad \hat{\mu}_{\mathrm{Z}} = \gamma\hat{S}_{\mathrm{Z}} \tag{11}$$

The proportionality constant γ is known as the *magnetogyric ratio*. These relations are the reason why the magnetization operators and the spin operators are often used interchangeably.

All quarks have spin ½. The spin and the magnetic dipole moment of composite particles, such as atomic nuclei, is derived from the alignment of quarks within the particle. A proton, for example, has two antiparallel *up* quarks and a *down* quark, leading to the overall spin ½. The exact alignment of quarks in more complicated nuclei is the subject of active current research, but the resulting overall spin is presently known for all stable isotopes. In view of Equation (11), we can conclude that all spin interactions in chemical systems are mediated by magnetic fields and fundamental symmetry constraints, such as the Pauli exclusion principle.

Spin Hamiltonian approximation

Magnetic resonance spectroscopy usually deals with nuclear spin interactions in diamagnetic molecules and electron spin interactions in molecules where the number of unpaired electrons is small and individual unpaired electrons are separated by considerable (over 10 Angstrom) distances. The contribution of such interactions to the total molecular energy is about 40 J/mol for an organic radical in a W-band ESR magnet and about 0.2 J/mol per nucleus for a diamagnetic molecule in a 600 MHz NMR magnet.

Compared to the typical C–H bond energy (400 kJ/mol), spin interaction energies are small enough for the Taylor series for the total molecular energy to converge at the second term:

$$E = E_0 + \sum_n \frac{\partial E}{\partial s_n} s_n + \frac{1}{2} \sum_{nk} \frac{\partial^2 E}{\partial s_n \partial s_k} s_n s_k + \ldots \tag{12}$$

where E_0 is the part of the total molecular energy E that does not depend on the state of our spins and $\{s_k\}$ is a complete set of spin coordinates of the system. The energy operator corresponding to the spin-dependent part of Equation (12) is known as the *spin Hamiltonian*. This approximation remains valid for as long as the interaction energy of the spins under consideration remains much smaller than the electronic structure energy of the full system. Spin interactions stronger than approximately 1 THz do affect electronic structure significantly and must be considered as magnetic interactions within the electronic structure problem. That having been said, actual excursions outside the validity range of the spin Hamiltonian approximation are very rare.

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 (12), 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:

$$\hat{H}_{\mathrm{Z}} = \hat{\vec{S}} \cdot \mathbf{A} \cdot \vec{B} = \begin{pmatrix} \hat{S}_{\mathrm{X}} & \hat{S}_{\mathrm{Y}} & \hat{S}_{\mathrm{Z}} \end{pmatrix} \begin{pmatrix} a_{\mathrm{XX}} & a_{\mathrm{XY}} & a_{\mathrm{XZ}} \\ a_{\mathrm{YX}} & a_{\mathrm{YY}} & a_{\mathrm{YZ}} \\ a_{\mathrm{ZX}} & a_{\mathrm{ZY}} & a_{\mathrm{ZZ}} \end{pmatrix} \begin{pmatrix} B_{\mathrm{X}} \\ B_{\mathrm{Y}} \\ B_{\mathrm{Z}} \end{pmatrix} \tag{13}$$

   where $\hat{\vec{S}}$ is a vector of spin operators, $\vec{B}$ 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:

$$\hat{H}_{\mathrm{HFC}} = \hat{\vec{S}} \cdot \mathbf{A} \cdot \hat{\vec{L}} = \begin{pmatrix} \hat{S}_{\mathrm{X}} & \hat{S}_{\mathrm{Y}} & \hat{S}_{\mathrm{Z}} \end{pmatrix} \begin{pmatrix} a_{\mathrm{XX}} & a_{\mathrm{XY}} & a_{\mathrm{XZ}} \\ a_{\mathrm{YX}} & a_{\mathrm{YY}} & a_{\mathrm{YZ}} \\ a_{\mathrm{ZX}} & a_{\mathrm{ZY}} & a_{\mathrm{ZZ}} \end{pmatrix} \begin{pmatrix} \hat{L}_{\mathrm{X}} \\ \hat{L}_{\mathrm{Y}} \\ \hat{L}_{\mathrm{Z}} \end{pmatrix} \tag{14}$$

   where $\hat{\vec{S}}$ and $\hat{\vec{L}}$ 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:

$$\hat{H}_{\mathrm{Q}} = \hat{\vec{S}} \cdot \mathbf{A} \cdot \hat{\vec{S}} = \begin{pmatrix} \hat{S}_{\mathrm{X}} & \hat{S}_{\mathrm{Y}} & \hat{S}_{\mathrm{Z}} \end{pmatrix} \begin{pmatrix} a_{\mathrm{XX}} & a_{\mathrm{XY}} & a_{\mathrm{XZ}} \\ a_{\mathrm{YX}} & a_{\mathrm{YY}} & a_{\mathrm{YZ}} \\ a_{\mathrm{ZX}} & a_{\mathrm{ZY}} & a_{\mathrm{ZZ}} \end{pmatrix} \begin{pmatrix} \hat{S}_{\mathrm{X}} \\ \hat{S}_{\mathrm{Y}} \\ \hat{S}_{\mathrm{Z}} \end{pmatrix} \tag{15}$$

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

To a good approximation, the matrix $\mathbf{A}$ is always real and symmetric, meaning that its eigenvalues are real and its eigenvectors orthogonal. Anti-symmetric terms have been predicted for some of the interactions, but their amplitudes are negligibly small.

Giant spin approximation

Situations where spin interaction energies are comparable to the electronic structure energy and the expansion given in Equation (12) is too short are encountered in high-spin transition metal complexes and single-molecule magnets. Introduction of higher order terms into Equation (12) leads to the appearance of cubic and higher order terms in the spin Hamiltonian:

$$\hat{H} = \sum_{l} \sum_{m=-l}^{l} b_{lm} \hat{O}_{lm} \tag{16}$$

where $\hat{O}_{lm}$ are Stevens operators and b_{lm} are real coefficients with the dimension of energy. Stevens operators are spherical symmetry adapted polynomials of total spin operators, for example:

$$\hat{O}_{2,-2} = -\frac{i}{2}\left(\hat{S}_{+}^{2} - \hat{S}_{-}^{2}\right), \qquad \hat{O}_{2,2} = \frac{1}{2}\left(\hat{S}_{+}^{2} + \hat{S}_{-}^{2}\right) \tag{17}$$

Full tables and general expressions may be found in the literature. Equation (16) is essentially a symmetry adapted Taylor series from Equation (12). It rather infrequently yields any insight into the actual physics of the system, but as any sufficiently long Taylor series must, it fits the experimental data.

Building your spin Hamiltonian

Practical calculations start with a description of the molecule (types of spins and their spin quantum numbers) and a list of interaction tensors. The following procedure may be used to generate the spin Hamiltonian matrix from that description:

1. Hand-code the Pauli matrices for the spin quantum numbers that your system contains. This simply means transcribing Equations (7) and its equivalents for higher spin if appropriate. For spin-1/2 particles the corresponding Matlab code is:

```
% Define Pauli matrices
sigma_x=[0 1/2; 1/2 0];
sigma_y=[0 -1i/2; 1i/2 0];
sigma_z=[1/2 0; 0 -1/2];
unit=[1 0; 0 1];
```

2. Build Cartesian spin operators for each spin in the system. For the *k*-th spin in the system, this involves computing the following Kronecker products:

$$\hat{L}_{\mathrm{X}}^{(k)} = \hat{E} \otimes \hat{E} \otimes \ldots \otimes \hat{\sigma}_{\mathrm{X}} \otimes \ldots \otimes \hat{E}$$
$$\hat{L}_{\mathrm{Y}}^{(k)} = \hat{E} \otimes \hat{E} \otimes \ldots \otimes \hat{\sigma}_{\mathrm{Y}} \otimes \ldots \otimes \hat{E} \qquad (18)$$
$$\hat{L}_{\mathrm{Z}}^{(k)} = \hat{E} \otimes \hat{E} \otimes \ldots \otimes \hat{\sigma}_{\mathrm{Z}} \otimes \ldots \otimes \hat{E}$$

where the Pauli matrix appears in the *k*-th position and $\hat{E}$ is the unit matrix of appropriate (2x2 for spin-1/2, 3x3 for spin-1 and so on) dimension. Matlab code for generating these operators would in general involve a loop over the spins, but for a simple case of a two spin system:

```
% Calculate two-spin operators
Lx=kron(sigma_x,unit); Sx=kron(unit,sigma_x);
Ly=kron(sigma_y,unit); Sy=kron(unit,sigma_y);
Lz=kron(sigma_z,unit); Sz=kron(unit,sigma_z);
```

Note the descriptive variable names and a comment line above each code section – this is a very good practice that would save you hours of effort at the later stages of your projects.

3. Use Equations (13)-(15), along with the interaction tensors (which you should have as a part of the problem specification) to build individual terms in the Hamiltonian. Add up those terms. For a simple case of a two-spin system with Zeeman interactions at each spin and a *J*-coupling between the spins the Matlab code would be:

```
% Build the Hamiltonian
omega_L=2*pi*200; % 200Hz offset frequency for spin L
omega_S=2*pi*400; % 500Hz offset frequency for spin S
J=pi*40; % 40Hz scalar coupling
H=omega_L*Lz+omega_S*Sz+J*(Lx*Sx+Ly*Sy+Lz*Sz);
```

Note the use of angular frequencies for all interaction energies and the fact that *J*-coupling is multiplied by π rather than 2π. The resulting Hamiltonian should be a matrix of dimension $\prod_k (2s_k + 1)$ where the index k runs over the spins in the system and $2s_k + 1$ is the multiplicity of the k-th spin.

The calculations above may also be performed in Mathematica. The use of other languages (Fortran, C, Java, Python, *etc.*) is discouraged – run time is not usually an issue, but the programmer time is.