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. That is also the way spin was historically introduced. 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:

$$\psi_{total}(r, s) = \sum_{nk} \psi_{space}^{(n)}(r) \otimes \psi_{spin}^{(k)}(s)$$

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:

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

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

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

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:

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

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:

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

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \quad \hat{S}_- \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \Rightarrow \hat{S}_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$
The remaining Cartesian operators can then be constructed from the raising and lowering operators using
the relations from the angular momentum theory:

\[ \hat{S}_x = \frac{\hat{S}_+ + \hat{S}_-}{2}, \quad \hat{S}_y = \frac{\hat{S}_+ - \hat{S}_-}{2i} \]  

(6)

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

\[
\begin{align*}
\hat{S}_x &= \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix}, \\
\hat{S}_y &= \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix}, \\
\hat{S}_z &= \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}
\end{align*}
\]  

(7)

These matrices are called Pauli matrices for spin \( \frac{1}{2} \). They are a two-dimensional matrix representation
of the corresponding spin operators. For spins greater than \( \frac{1}{2} \), they have larger dimensions, but may still be
constructed using the same method. For example, a spin-1 particle has:

\[
\begin{align*}
\hat{S}_x &= \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \\
\hat{S}_y &= \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & -i & 0 \end{pmatrix}, \\
\hat{S}_z &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}
\end{align*}
\]  

(8)

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

\[ [\hat{S}_x, \hat{S}_y] = i\hat{S}_z, \quad [\hat{S}_z, \hat{S}_x] = i\hat{S}_y, \quad [\hat{S}_y, \hat{S}_z] = i\hat{S}_x; \quad [\hat{S}_z^2, \hat{S}_{(x,y,z)}] = 0 \]  

(9)

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

\[
\begin{align*}
\hat{S}_z^{(1/2)} &= \begin{pmatrix} 3/4 & 0 \\ 0 & 3/4 \end{pmatrix}; \\
\hat{S}_z^{(i)} &= \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}
\end{align*}
\]  

(10)

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

**Connection between spin and magnetic moment**

Spin arises as a mathematical consequence of imposing Lorentz invariance (a requirement of special rel-
ativity) on quantum mechanics. The relevant mathematics is far beyond this course, but it may be shown
that, for a charged particle in an electromagnetic field, this necessarily yields a term that looks like an
interaction of a point dipole with the magnetic field. The direction of the dipole is aligned with the direc-
tion of the spin. A practical consequence is that the observables corresponding to the Pauli matrices are
proportional to the Cartesian components of the magnetic dipole:

\[ \hat{\mu}_x = \gamma \hat{S}_x, \quad \hat{\mu}_y = \gamma \hat{S}_y, \quad \hat{\mu}_z = \gamma \hat{S}_z \]  

(11)

The proportionality constant \( \gamma \) is known as the magnetogyric ratio. These relations are the reason why
the magnetization operators and the spin operators are often used interchangeably.

**Spin Hamiltonian approximation**

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 order:

\[ E = E_0 + \sum_n \frac{\partial E}{\partial s_n} s_n + \frac{1}{2} \sum_{nk} \frac{\partial^2 E}{\partial s_n \partial s_k} s_n s_k + \ldots \]  

(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 \textit{spin Hamiltonian}. 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:

\[
\hat{H}_Z = \hat{S} \cdot \mathbf{A} \cdot \mathbf{B} = \left( \hat{S}_x \right) \left( \hat{S}_y \right) \left( \hat{S}_z \right) \left( \begin{array}{ccc} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{array} \right) \left( \begin{array}{c} B_x \\ B_y \\ B_z \end{array} \right)
\]  

(13)

where \( \hat{S} \) is a vector of spin operators, \( \mathbf{B} \) 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:

\[
\hat{H}_{\text{HFC}} = \hat{S} \cdot \mathbf{A} \cdot \hat{\mathbf{L}} = \left( \hat{S}_x \right) \left( \hat{S}_y \right) \left( \hat{S}_z \right) \left( \begin{array}{ccc} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{array} \right) \left( \begin{array}{c} \hat{L}_x \\ \hat{L}_y \\ \hat{L}_z \end{array} \right)
\]  

(14)

where \( \hat{S} \) 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:

\[
\hat{H}_Q = \hat{\mathbf{S}} \cdot \mathbf{A} \cdot \hat{\mathbf{S}} = \left( \hat{S}_x \right) \left( \hat{S}_y \right) \left( \hat{S}_z \right) \left( \begin{array}{ccc} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{zy} & a_{zz} \end{array} \right) \left( \begin{array}{c} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{array} \right)
\]  

(15)

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