November 2, 2010

Notes on quantum treatment of spin transitions

Reference: Charles P. Slichter, **Principles of Magnetic Resonance**, Harper & Row, 1963.

In the following, we will use the following Pauli spin matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{1}$$

In terms of these matrices, the electron magnetic moment can be written:

$$\vec{\mu} = \frac{g\mu_B}{2}\vec{\sigma} \equiv \mu_e(\sigma_x\hat{\mathbf{x}} + \sigma_y\hat{\mathbf{y}} + \sigma_z\hat{\mathbf{z}}), \tag{2}$$

where $g = -2.0023$ denotes the electron g-factor, $\mu_B = 5.788 \times 10^{-5}$ eV/T is the Bohr magneton, and $\mu_e = -5.795 \times 10^{-5}$ eV/T is the electron magnetic moment. This same formalism can also treat nuclear spin$-1/2$ systems, with $g_N\mu_N$ replacing $g\mu_B$. The nuclear magneton $\mu_N = 3.152 \times 10^{-8}$ eV/T and $g_{proton} = 5.586, g_{neutron} = -3.826$. In the following, we write the explicit formulas in terms of the electron intrinsic magnetic moment, but the same formulation could be applied to other spin$-1/2$ systems as indicated. The Hamiltonian which represents the interaction between the electron magnetic moment and a magnetic field $\mathbf{B}$ is given by

$$\mathcal{H} = -\vec{\mu}\cdot\mathbf{B}. \tag{3}$$

In magnetic resonance experiments, the magnetic field is generally composed of a constant component (B_0) taken to be in the $\hat{\mathbf{z}}$ direction and a rotating component (B_1) in the perpendicular direction taken to be in the $x - y$ plane. Suppose that the rotation frequency is denoted by Ω, the magnetic field can be written:

$$\mathbf{B} = B_1(\cos(\Omega t)\hat{\mathbf{x}} + \sin(\Omega t)\hat{\mathbf{y}}) + B_0\hat{\mathbf{z}}, \tag{4}$$

where it is generally assumed that $B_0 >> B_1$. For this field, the interaction Hamiltonian can be written:

$$\mathcal{H} = -\mu_e\mathbf{B}\cdot\vec{\sigma} \equiv -\mu_e \begin{pmatrix} B_0 & B_1 e^{-i\Omega t} \\ B_1 e^{i\Omega t} & -B_0 \end{pmatrix}. \tag{5}$$

We would like to solve the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial\Psi(t)}{\partial t} = \mathcal{H}(t)\Psi(t). \tag{6}$$

It turns out to be simpler to solve the equation by transforming it into the form of a time-independent Hamiltonian:

$$i\hbar\frac{\partial\Psi'(t)}{\partial t} = \begin{pmatrix} -\mu_e B_0 - \frac{\hbar\Omega}{2} & -\mu_e B_1 \\ -\mu_e B_1 & -(-\mu_e B_0 - \frac{\hbar\Omega}{2}) \end{pmatrix}\Psi'(t) \equiv \mathcal{H}_{\text{eff}}\Psi'(t). \tag{7}$$

Here, the transformed wavefunction Ψ' is defined to be

$$\Psi'(t) \equiv \begin{pmatrix} e^{i\Omega t/2} & 0 \\ 0 & e^{-i\Omega t/2} \end{pmatrix} \Psi(t), \tag{8}$$

and the time independent effective Hamiltonian is given by

$$\mathcal{H}_{\text{eff}} \equiv \begin{pmatrix} -\mu_e B_0 - \frac{\hbar\Omega}{2} & -\mu_e B_1 \\ -\mu_e B_1 & -(-\mu_e B_0 - \frac{\hbar\Omega}{2}) \end{pmatrix}. \tag{9}$$

The derivation of this result depends on the following identities:

$$\begin{pmatrix} B_0 & B_1 e^{-i\Omega t} \\ B_1 e^{i\Omega t} & -B_0 \end{pmatrix} = \begin{pmatrix} e^{-i\Omega t/2} & 0 \\ 0 & e^{i\Omega t/2} \end{pmatrix} \begin{pmatrix} B_0 & B_1 \\ B_1 & -B_0 \end{pmatrix} \begin{pmatrix} e^{i\Omega t/2} & 0 \\ 0 & e^{-i\Omega t/2} \end{pmatrix}, \tag{10}$$

and

$$i\hbar\frac{\partial\Psi(t)}{\partial t} = \begin{pmatrix} e^{-i\Omega t/2} & 0 \\ 0 & e^{i\Omega t/2} \end{pmatrix} \left\{ i\hbar\frac{\partial}{\partial t} - \begin{pmatrix} \frac{-\hbar\Omega}{2} & 0 \\ 0 & \frac{\hbar\Omega}{2} \end{pmatrix} \right\} \begin{pmatrix} e^{i\Omega t/2} & 0 \\ 0 & e^{-i\Omega t/2} \end{pmatrix} \Psi(t). \tag{11}$$

The transformed wave function Ψ' can be interpreted as representing the spin in a rotating coordinate system in which the effective Hamiltonian is now independent of time. Solving the differential equation (7), we find

$$\Psi'(t) = e^{-i\mathcal{H}_{\text{eff}} t/\hbar} \Psi'(0), \tag{12}$$

where $\Psi'(0)$ denotes the initial value of the transformed wave function and where the exponential function must be evaluated by taking its Taylor series expansion. Consider a general 2×2 matrix of the form

$$m \equiv \begin{pmatrix} a & b \\ b & -a \end{pmatrix}. \tag{13}$$

The exponential of m can be evaluated:

$$e^{-im} \equiv 1 - im - \frac{1}{2!}m^2 - \frac{1}{3!}m^2(-im) + \frac{1}{4!}(m^2)^2 \cdots \tag{14}$$

For our form of m, all even terms are diagonal,

$$m^2 = \begin{pmatrix} a^2 + b^2 & 0 \\ 0 & a^2 + b^2 \end{pmatrix} \equiv (a^2 + b^2) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{15}$$

and all odd terms are proportional to m itself, so that we can simplify the expansion by summing the odd and even terms separately:

$$e^{-im} = \cos(\sqrt{a^2 + b^2}) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - i\frac{\sin(\sqrt{a^2 + b^2})}{\sqrt{a^2 + b^2}} \begin{pmatrix} a & b \\ b & -a \end{pmatrix}. \tag{16}$$

The results can be put in a more convienient form by defining the simplifying notation, $\Omega_0 \equiv -2\mu_e B_0/\hbar$, $\Omega_1 \equiv -2\mu_e B_1/\hbar$, $\Omega_T \equiv \sqrt{(\Omega_0 - \Omega)^2 + \Omega_1^2}$, $\cos(\theta_0) \equiv (\Omega_0 - \Omega)/\Omega_T$, and $\sin(\theta_0) \equiv \Omega_1/\Omega_T$. In these terms, the full solution to the Schrödinger equation in the form

$$\Psi(t) = \begin{pmatrix} e^{-i\Omega t/2} & 0 \\ 0 & e^{i\Omega t/2} \end{pmatrix} \left\{ \cos(\Omega_T t/2) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - i\sin(\Omega_T t/2) \begin{pmatrix} \cos(\theta_0) & \sin(\theta_0) \\ \sin(\theta_0) & -\cos(\theta_0) \end{pmatrix} \right\} \Psi(0). \tag{17}$$

For the special value of the rotational frequency $\Omega = \Omega_0$, the general result 17 simplifies to

$$\Psi(t) = \begin{pmatrix} \mathrm{e}^{-i\Omega_0 t/2} & 0 \\ 0 & \mathrm{e}^{i\Omega_0 t/2} \end{pmatrix} \begin{pmatrix} \cos(\Omega_1 t/2) & -i\sin(\Omega_1 t/2) \\ -i\sin(\Omega_1 t/2) & \cos(\Omega_1 t/2) \end{pmatrix} \Psi(0). \tag{18}$$