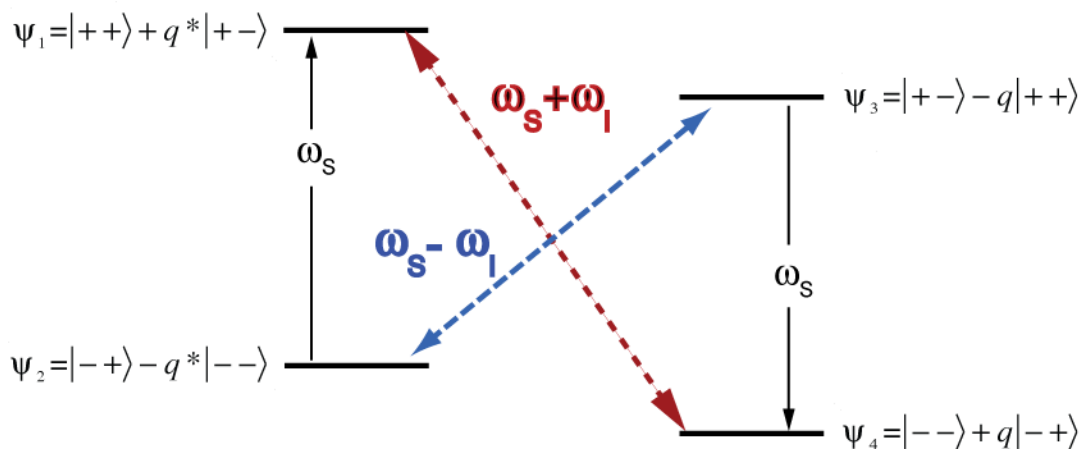


## State Mixing for the Solid Effect

If we use the pure spin states then transitions required for DNP are not allowed. Specifically, the zero and double quantum matrix elements vanish.

$$\langle ++|S_+|--\rangle = \langle +-|S_+|-+\rangle = 0$$

However, there are nearby states that mix into the pure states and the transitions become weakly allowed. We now perform the perturbation calculation that leads to the mixed states and shows the  $\omega_0^{-2}$  dependence of the solid effect. The calculation is based on the electron-nuclear dipolar Hamiltonian.



The full electron –nuclear dipolar Hamiltonian is

$$H_{IS} = \frac{\gamma_I \gamma_S \hbar}{r^3} (A + B + C + D + E + F)$$

where the terms are explicitly

$$A = (1 - 3 \cos^2 \theta) [S_Z I_Z]$$

$$B = -\frac{1}{4} (1 - 3 \cos^2 \theta) [S_- I_+ + S_+ I_-]$$

$$C = -\frac{3}{2} \sin \theta \cos \theta e^{-i\phi} [S_+ I_Z + S_Z I_+]$$

$$D = C^\dagger = -\frac{3}{2} \sin \theta \cos \theta e^{i\phi} [S_- I_Z + S_Z I_-]$$

$$E = -\frac{3}{4} \sin^2 \theta e^{-2i\phi} [S_+ I_+]$$

$$F = -\frac{3}{4} \sin^2 \theta e^{2i\phi} [S_- I_-]$$

To determine the form of the wavefunctions we use the standard formula from non-degenerate perturbation theory (see attached notes for the derivation) for the first order correction to the wave function. Here  $H' = H_{IS}$  is the perturbing Hamiltonian,  $\psi_m^0$  are the unperturbed wavefunctions and  $E_m^0$  are the associated energies.

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0$$

The terms in  $H_{IS}$  that perform the mixing are from the  $C$  and  $C^\dagger$  terms and are due to the operators  $S_Z I_+$  and  $S_Z I_-$ . So the Hamiltonian that we need to consider to calculate the energy levels of the system is of the form

$$H = \omega_{0S} S_Z - \omega_{0I} I_Z + C S_Z I_+ + C^* S_Z I_-$$

In order to appreciate in detail how these terms arise we consider an explicit example, specifically the correction  $\psi_3^1$  to  $\psi_3^0$ .

$$\psi_3^1 = \sum_{m \neq 3} \frac{\langle \psi_m^0 | H' | \psi_3^0 \rangle}{E_3^0 - E_m^0} \psi_m^0 = \frac{\langle \psi_1^0 | H' | \psi_3^0 \rangle}{E_3^0 - E_1^0} \psi_1^0 + \frac{\langle \psi_2^0 | H' | \psi_3^0 \rangle}{E_3^0 - E_2^0} \psi_2^0 + \frac{\langle \psi_4^0 | H' | \psi_3^0 \rangle}{E_4^0 - E_1^0} \psi_4^0$$

The energy denominators are

$$E_3^0 - E_1^0 = \left( \frac{1}{2} \gamma_S \hbar B_0 + \frac{1}{2} \gamma_I \hbar B_0 \right) - \left( \frac{1}{2} \gamma_S \hbar B_0 - \frac{1}{2} \gamma_I \hbar B_0 \right) = \gamma_I \hbar B_0 = \hbar \omega_{0I}$$

$$E_3^0 - E_2^0 = \left( \frac{1}{2} \gamma_S \hbar B_0 + \frac{1}{2} \gamma_I \hbar B_0 \right) - \left( -\frac{1}{2} \gamma_S \hbar B_0 - \frac{1}{2} \gamma_I \hbar B_0 \right) = \gamma_S \hbar B_0 = \hbar \omega_{0S}$$

$$E_4^0 - E_1^0 = \left( -\frac{1}{2} \gamma_S \hbar B_0 + \frac{1}{2} \gamma_I \hbar B_0 \right) - \left( \frac{1}{2} \gamma_S \hbar B_0 - \frac{1}{2} \gamma_I \hbar B_0 \right) = -\gamma_S \hbar B_0 + \gamma_I \hbar B_0 \approx -\hbar \omega_{0S}$$

Note that  $E_3^0 - E_2^0$  and  $E_4^0 - E_1^0$  are proportional to the electron resonance frequency and are proportional to  $\hbar \omega_{0S}$ , while  $E_3^0 - E_1^0 \approx \hbar \omega_{0I}$ . Thus, the first term in the perturbation expansion is  $\sim 10^3$  times larger than the second two. Thus, we drop the second and third terms.

For  $\psi_3^1$  the matrix element that does the mixing is of the form

$$q = -\frac{\gamma_I \gamma_S}{r^3} \frac{3}{2\omega_{0I}} \sin \theta \cos \theta e^{-i\phi} \langle + + | S_Z I_+ | + - \rangle$$

and therefore the wavefunction is

$$\psi_3 = | + - \rangle - q | + + \rangle.$$

Using similar arguments we find for the other three states

$$\psi_1 = |++\rangle + q^* |+-\rangle$$

$$\psi_2 = |-+\rangle - q^* |--\rangle$$

$$\psi_4 = |--\rangle + q | -+\rangle$$

We can now calculate the transition probabilities for the DQ and ZQ solid effect transitions, respectively, we obtain.

$$|\langle \psi_1 | S_+ | \psi_4 \rangle|^2 = |\langle (++) + q(+ -) | S_+ | (- -) + q(- +) \rangle|^2 = |2q| = 4q^2$$

$$|\langle \psi_2 | S_- | \psi_3 \rangle|^2 = |\langle (- +) - q(- -) | S_- | (+ -) + q(++) \rangle|^2 = |2q| = 4q^2$$

Ignoring numerical constants we note that

$$q^2 \sim \omega_{0I}^{-2}$$

which is the desired result – the solid effect scales as  $\omega_0^{-2}$ .