Notes on Dynamic Nuclear Polarization

1. Overhauser Effect

The following simple derivation shows that the enhancement in a electron nuclear DNP experiment, Overhauser is (γ_S/γ_I)~660.

1.1 Energy levels and transitions of a model four level system

Consider the Hamiltonian with electron and nuclear Zeeman terms and a hyperfine term of magnitude A.

$$H = \gamma_S \hbar B_0 S_Z - \gamma_I \hbar B_0 I_Z + A\vec{I} \bullet \vec{S}$$

The hyperfine term couples two spin-1/2 particles I=1/2 and S=1/2. We assume that

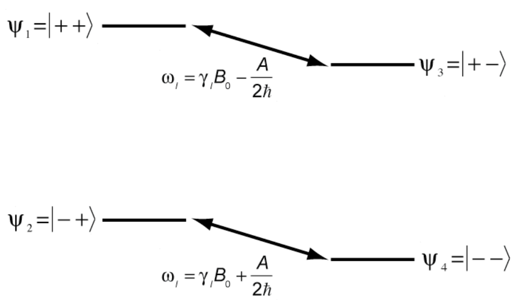
$$\gamma_S \hbar B_0 > A \quad and \quad \gamma_S >> |\gamma_S|$$

and therefore

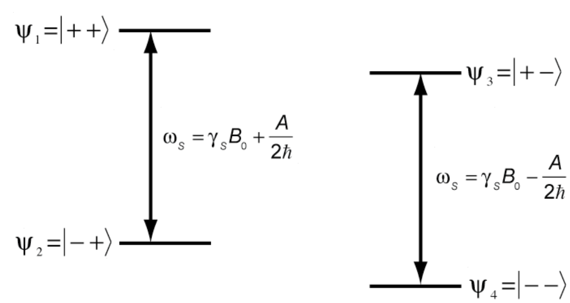
$$H = \gamma_S \hbar B_0 S_Z - \gamma_I \hbar B_0 I_Z + A I_Z S_Z$$

with m_S=±1/2 and m_I=±1/2 we obtain resonance frequencies and the transitions given below.

$$\omega_S = \gamma_S B_0 + \frac{A}{\hbar} m_I \quad and \quad \omega_I = \gamma_I B_0 - \frac{A}{\hbar} m_S$$



NMR transtions



EPR transitions

In the absence of applied alternating fields the populations are in thermal equilbrium

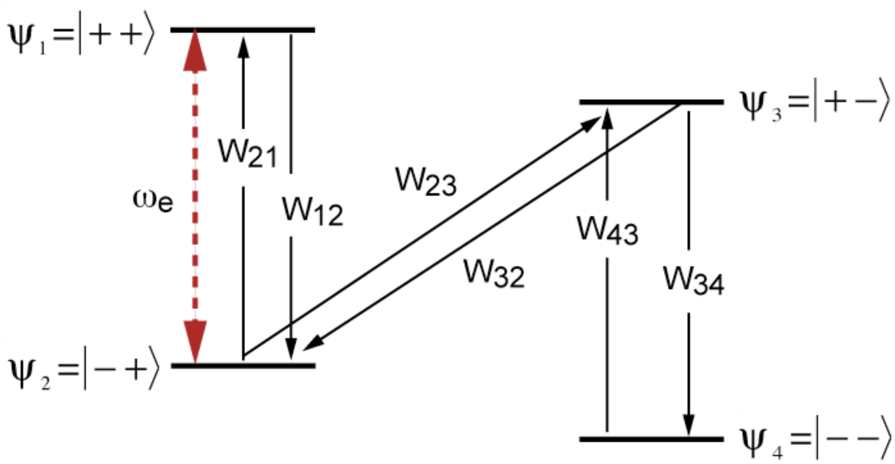
$$W_{\varepsilon\eta,\varepsilon'\eta'} P_{\varepsilon\eta} = W_{\varepsilon'\eta',\varepsilon\eta} P_{\varepsilon'\eta'}$$

where $W_{\varepsilon\eta,\varepsilon'\eta'}$ is the transition rate from state $|\varepsilon\eta\rangle \rightarrow |\varepsilon'\eta'\rangle$ and P_{ij}'s are the populations of the two states. This can be rewritten in terms of Boltzmann factors as

$$\frac{W_{\varepsilon\eta,\varepsilon'\eta'}}{W_{\varepsilon'\eta',\varepsilon\eta}} = \frac{P_{\varepsilon'\eta'}}{P_{\varepsilon\eta}} = e^{\left(E_{\varepsilon\eta} - E_{\varepsilon\eta}\right)/kT}$$

1.2 Overhauser effect *(A. Overhauser, 1953 and Carver and Slichter, 1953)*

Now consider the same system subject to irradiation of one of the electron transitions, ω_e, as illustrated below.



Under irradiation we can write rate equations for the populations

$$\frac{dP_1}{dt} = P_2W_{21} - P_1W_{12} + (P_1 - P_2)W_e \tag{1}$$

$$\frac{dP_2}{dt} = P_1W_{12} - P_2W_{21} + P_3W_{32} - P_2W_{23} + (P_1 - P_2)\omega_e \tag{2}$$

$$\frac{dP_3}{dt} = P_2W_{23} - P_3W_{32} + P_4W_{43} - P_3W_{34} \tag{3}$$

$$\frac{dP_4}{dt} = P_3W_{34} - P_4W_{43} \tag{4}$$

The probabilities sum to unity $\sum_1^4 P_i = 1$. We solve the equations in the steady state when the driving field is strong $\omega_e >> W_{12}, W_{21}$ and saturates the $|1\rangle \rightarrow |2\rangle$ transition. Therefore,

$$P_1 = P_2$$

and (4) yields

$$P_3 = P_4 \frac{W_{43}}{W_{34}}$$

which is thermal equilibrium for $|3\rangle$ and $|4\rangle$. Equation (3) yields

$$P_3 = P_2 \frac{W_{23}}{W_{32}}$$

Since P_2 and P_3 and P_3 and P_4 are in equilibrium. Therefore, P_2 and P_4 are in equilibrium.

We define

$$P_j = P_i e^{\left(E_i - E_j\right)/kT} = p_i B_{ij}$$

Therefore,

$$P_1 = P_2 \qquad P_3 = P_2 B_{23} \qquad P_4 = P_2 B_{24}$$

and

$$P_1 = P_2 = \frac{1}{2 + B_{23} + B_{24}} \qquad P_3 = \frac{B_{23}}{2 + B_{23} + B_{24}} \qquad P_4 = \frac{B_{24}}{2 + B_{23} + B_{24}}.$$

The expectation value $\langle I_Z \rangle$ is

$$\langle I_Z \rangle = \sum_1^4 P_i \langle i | I_Z | i \rangle = \frac{1}{2}\left(P_1 + P_2 - P_3 - P_4\right)$$

$$\langle I_Z \rangle = \frac{1}{2}\left[\frac{2 - B_{23} - B_{24}}{2 + B_{23} + B_{24}}\right]$$

We evaluate this in the high temperature limit

$$B_{ij} = 1 + \frac{\left(E_i - E_j\right)}{kT}$$

and

$$\langle I_Z \rangle_{OV} = \frac{1}{2}\left(\frac{\left(E_3 - E_2\right) + \left(E_4 - E_2\right)}{4kT}\right).$$

Using

$$\left(E_3 - E_2\right) = \gamma_S \hbar B_0 + \gamma_I \hbar B_0 \qquad \left(E_4 - E_2\right) = \gamma_I \hbar B_0 + \frac{A}{2}$$

Therefore the Overhauser polarization is

$$\langle I_Z \rangle_{OV} = \frac{1}{2}\left(\frac{\gamma_S \hbar B_0 + 2\gamma_I \hbar B_0 + \frac{A}{2}}{4kT}\right) \approx \frac{1}{2}\left(\frac{\gamma_S \hbar B_0}{4kT}\right).$$

In the absence of a saturating microwave field

$$\langle I_Z \rangle_{Boltz} = \frac{1}{2}\left[\frac{1+B_{12}-B_{23}-B_{24}}{1+B_{21}+B_{23}+B_{24}}\right] = \frac{1}{2}\left(\frac{(E_2-E_1)+(E_3-E_2)+(E_4-E_2)}{4kT}\right)$$

Using

$$(E_2-E_1) = -\gamma_S \hbar B_0 - \frac{A}{2}$$

we find

$$\langle I_Z \rangle_{Boltz} = \frac{1}{2}\left(\frac{\gamma_I \hbar B_0}{2kT}\right)$$

and therefore,

$$\frac{\langle I_Z \rangle_{OV}}{\langle I_Z \rangle_{Boltz}} = \frac{\gamma_S}{2\gamma_I}$$

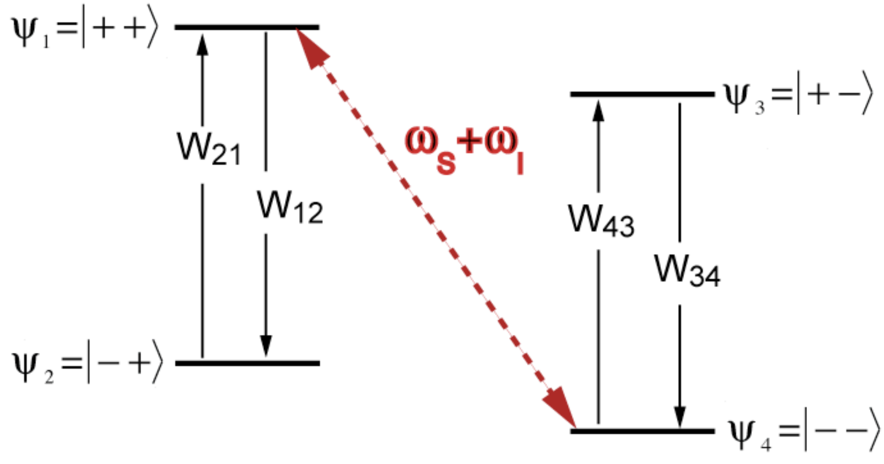
If both EPR transitions are irradiated

$$\boxed{\frac{\langle I_Z \rangle_{OV}}{\langle I_Z \rangle_{Boltz}} = \frac{\gamma_S}{\gamma_I}}$$

which is the desired result.

2. Solid effect -- DNP with forbidden transitions *(Jefferies and Abragam)*

Similar arguments can be extended to the Solid Effect that is based on forbidden transitions.



The solid effect utilizes zero and double quantum transitions that require operators of the form

$$\langle +- | S_+ I_- + S_- I_+ | -+ \rangle \neq 0 \qquad \langle ++ | S_+ I_+ + S_- I_- | -- \rangle \neq 0$$

However, in the DNP experiment we excite these nomally DQ and ZQ transitions with a microwave field. This is represented be S_+. In a separate note we show how this is accomplished.

Assume that we have admixtures of states which permit excitation of these transitions. We saturate the $|1\rangle \rightarrow |4\rangle$ transition with microwaves $\omega_S + \omega_I$. Thus, $P_1 = P_4$. Proceeding as before

$$P_2 = P_1 B_{12} \qquad P_3 = P_4 B_{43}$$

$$P_1 = P_4 = \frac{1}{2 + B_{12} + B_{43}} \qquad P_2 = \frac{B_{12}}{2 + B_{12} + B_{43}} \qquad P_3 = \frac{B_{43}}{2 + B_{12} + B_{43}}$$

$$\langle I_Z \rangle = \frac{1}{2}\left[\frac{B_{12} - B_{43}}{2 + B_{12} + B_{43}}\right]$$

$$\langle I_Z \rangle_{SE} = \frac{1}{2}\left(\frac{(E_1 - E_2) - (E_4 - E_3)}{4kT}\right)$$

$$E_1 = \frac{1}{2}\gamma_S \hbar B_0 - \frac{1}{2}\gamma_I \hbar B_0 - \frac{A}{4} \qquad E_2 = -\frac{1}{2}\gamma_S \hbar B_0 - \frac{1}{2}\gamma_I \hbar B_0 + \frac{A}{4}$$

$$\boxed{(E_1 - E_2) = \gamma_S \hbar B_0}$$

$$E_3 = \frac{1}{2}\gamma_S \hbar B_0 + \frac{1}{2}\gamma_I \hbar B_0 + \frac{A}{4} \qquad E_4 = -\frac{1}{2}\gamma_S \hbar B_0 + \frac{1}{2}\gamma_I \hbar B_0 + \frac{A}{4}$$

$$\boxed{(E_4 - E_3) = -\gamma_S \hbar B_0}$$

$$\langle I_Z \rangle_{SE} = \frac{1}{2}\left(\frac{\gamma_S \hbar B_0}{2kT}\right)$$

Which is the desired result for the solid effect

$$\boxed{\frac{\langle I_Z \rangle_{SE}}{\langle I_Z \rangle_{Boltz}} = \frac{\gamma_S}{\gamma_I}}$$