NMR Relaxation

Ben Rosemeyer

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Moment dynamics

In a magnetic field $\mathbf{H}$, a moment follows the equation of motion

$$\frac{d\mathbf{m}}{dt} = \gamma \mathbf{m} \times \mathbf{H} \quad CLASSICAL \tag{1}$$

$$\frac{\hbar}{i}\frac{d\mathbf{m}}{dt} = [\mathcal{H}, \mathbf{m}] \quad QUANTUM \tag{2}$$

If the Hamiltonian $\mathcal{H} = -\mathbf{H} \cdot \mathbf{m}$ then the two equations have the same result. Further, we can go to a rotating frame of reference at $\boldsymbol{\omega}$ so that $\frac{d\mathbf{m}}{dt} = \frac{\partial \mathbf{m}}{\partial t} + \boldsymbol{\omega} \times \mathbf{m}$, and $\frac{\partial \mathbf{m}}{\partial t}$ is in the rotating frame.

If we choose $\mathbf{H} = H_1 \cos(\omega t)\hat{x} - H_1 \sin(\omega t)\hat{y} + H_0\hat{z}$, where $\boldsymbol{\omega} = -\omega\hat{z}$, then the effective field seen in the rotating frame is $\mathbf{H}_e = H_1\hat{x'} + (H_0 - \omega/\gamma)\hat{z}$. In the rotating frame we have

$$\frac{\partial \mathbf{m}}{\partial t} = \gamma \mathbf{m} \times \mathbf{H}_e \tag{3}$$

Tuning the constant applied field to $H_0 = \omega/\gamma$ results in a simple form $\frac{\partial \mathbf{m}}{\partial t} = \gamma H_1 \mathbf{m} \times \hat{x'}$. In a typical NMR experiment $H_0 = \omega/\gamma$ is large and initially there is no perturbing field H_1 so that $\mathbf{m}(t = 0) = m_0\hat{z}$. When a H_1 pulse is turned on $(t = 0)$ the moment beings to rotate in the $y - z$ plane at frequency $\omega_1 = \gamma H_1$ and when the H_1 pulse is turned off at time $t = t'$ the moment will be

$$\mathbf{m} = \cos(\omega_1 t')\hat{z} + \sin(\omega_1 t')\hat{y} \tag{4}$$

There are two types of pulses which are widely used; a π pulse $\omega_1 t' = \pi$ which flips the spin to $-\hat{z}$, and a $\pi/2$ pulse $\omega_1 t' = \pi/2$ which turns the spin to $\hat{y}$. After applying the pulse of interest the system of spins is probed at various times after t' to measure the rate at which the equilibrium $\mathbf{m} = m_0\hat{z}$ is recovered.

Decay types

There are two types of decay processes which are described by rates T_1 and T_2. T_1 is the recovery of the component parallel to the constant field $H_0\hat{z}$

$$\frac{dm_z}{dt} = (m_0 - m_z)/T1 \tag{5}$$

T_2 is the recovery of the transverse component which is zero in equilibrium.

$$\frac{dm_\perp}{dt} = -m_\perp/T2 \tag{6}$$

T_1 Transition Rate

A system of non-interacting nuclear moments in a material has an average total energy $U = Tr[\rho\mathcal{H}]$. $\rho = e^{-\mathcal{H}/T_s}/\mathcal{Z}$ ($\mathcal{Z} = Tr[e^{-\mathcal{H}/T_s}]$). The time derivative of the total energy is

$$\frac{dU}{dt} = \sum_i \frac{dp_i}{dt} E_i = \frac{dU}{dT_s}\frac{dT_s}{dt} \tag{7}$$

$p_i = e^{-E_i/T_s}/\mathcal{Z}$ and T_s is the spin temperature. The change in occupation probability

$$\frac{dp_i}{dt} = \sum_j W_{ji}p_j - W_{ij}p_i \tag{8}$$

W_{ji} is the transition probability per time for $j \to i$. The principle of detail balance assumes that all the terms in the above sum are zero in equilibrium, $\frac{p_i}{p_j} = \frac{W_{ji}}{W_{ij}}$. The LHS of this equation is the ratio of spin occupation probabilities, which can be defined using a spin temperature T_s, while the RHS is the ratio of transition rates and is defined in terms of a lattice temperature T_l ($T_s = T_l$ in equilibrium). The idea is that the nuclear spins are in contact with a reservoir at T_l, and spin transitions of the nuclei are allowed through energy exchange with the reservoir.

$$\frac{p_i}{p_j} = exp[-(E_i - E_j)/T_s] \tag{9}$$

$$\frac{W_{ji}}{W_{ij}} = exp[-(E_i - E_j)/T_l] \tag{10}$$

Using the above relations and expanding the exponentials for small E/T, $\frac{dU}{dt}$ to lowest order in energy/temperature is

$$\begin{aligned}
\frac{dU}{dt} &= \sum_{ij} E_i\big(e^{(E_i-E_j)/T_s}e^{-(E_i-E_j)/T_l} - 1\big)W_{ij}p_i && (11)\\
&= \sum_{ij} E_iW_{ij}\Big((1 + (E_i - E_j)/T_s)(1 - (E_i - E_j)/T_l) - 1\Big)(1 - E_i/T_s)/\mathcal{Z} && (12)\\
&= \frac{\big(1/T_s - 1/T_l\big)}{\mathcal{Z}} \sum_{ij} W_{ij}E_i(E_i - E_j) && (13)\\
&= \frac{\big(1/T_s - 1/T_l\big)}{2\mathcal{Z}} \sum_{ij} W_{ij}(E_i - E_j)^2 && (14)
\end{aligned}$$

The last step simply symmetrizes the sum. Additionally, the spin temperature derivative of energy to lowest order is

$$\begin{aligned}
\frac{dU}{dT_s} &= \Big[\sum_i (E_i^2/T_s^2)e^{-E_i/T_s}\Big]/\mathcal{Z} - \Big[\sum_i (E_i/T_s^2)e^{-E_i/T_s}\Big]\Big[\sum_i E_ie^{-E_i/T_s}\Big]/\mathcal{Z}^2 && (15)\\
&= \Big[\sum_i (E_i^2/T_s^2)e^{-E_i/T_s}\Big]/\mathcal{Z} - \frac{U^2}{T_s^2} && (16)\\
&\approx \frac{1}{T_s^2}\Big[\sum_i E_i^2\Big]/\mathcal{Z} && (17)
\end{aligned}$$

Note, $Tr[\mathcal{H}] = 0$ for a spin system.

Now equating $\frac{dU}{dt} = \frac{dU}{dT_s}\frac{dT_s}{dt}$

$$-\frac{1}{T_s^2}\frac{dT_s}{dt} = \frac{d}{dt}\frac{1}{T_s} = \big(1/T_l - 1/T_s\big)\frac{1}{2}\sum_{ij} W_{ij}(E_i - E_j)^2 / \Big[\sum_i E_i^2\Big] \tag{18}$$

By expanding the exponentials in E/T we assumed the nuclear spin energies to be much smaller than the thermal energy which is valid for ^{13}C. The gyromagnetic ratio of ^{13}C is only $\gamma = 6.728284 \times 10^7 \frac{rad}{Ts}$, producing a Zeeman level splitting of $\hbar\gamma H \approx 1\mu eV$ in a *large* 30 tesla field. Even at $1K$, the thermal energy $E_T \approx 10^{-4}$ is still 2 orders of magnitude larger.

In the presence of a magnetic field the magnetization and spin temperature are related through Curie-Weiss Law $T_s \propto H/M$ ($T_l \propto H/M_0$ in equilibrium). In this way we can write the rate equation for the magnetization recovery as follows

$$\frac{dM}{dt} = (M_0 - M)/T_1 \tag{19}$$

$$\frac{d}{dt}(1/T_s) = (1/T_l - 1/T_s)/T_1 \tag{20}$$

Where T_1 is the relaxation rate. Comparing this with the above equation gives

$$\frac{1}{T_1} = \frac{1}{2}\sum_{ij} W_{ij}(E_i - E_j)^2 / \Big[\sum_i E_i^2\Big] \tag{21}$$

For a spin 1/2 nuclei ($i = \{\uparrow, \downarrow\}$, $E_{\uparrow\downarrow} = \mp E_H$) the above equation reduces to

$$\frac{1}{T_1} = 2(W_{\uparrow\downarrow} + W_{\downarrow\uparrow}) \tag{22}$$

In time dependent perturbation theory, $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t)\Theta(t)$, the time translation operator in the interaction picture is

$$U(t) = Te^{-\frac{i}{\hbar}\int_0^t \mathcal{H}_1(t')dt'} \tag{23}$$

$$|\psi(t)\rangle_I = U(t)|\psi(0)\rangle = \sum_n |n\rangle\langle n|U(t)|\psi(0)\rangle \tag{24}$$

$$|\psi(t)\rangle_I = e^{-\frac{i}{\hbar}\mathcal{H}_1 t}|\psi(0)\rangle \tag{25}$$

Where T acts to order the time integrations in the expanded form of the exponential operator.

The probability amplitude of a transition from unperturbed states $I \to J$ at time t after the perturbation is turned on at $t = 0$ is $c_{IJ}(t) = \langle n|U(t)|\psi(0)\rangle$. To first order in the perturbation

$$c_{IJ}(t) = \frac{i}{\hbar}\int_0^t dt'\, \langle J|\mathcal{H}^1|I\rangle \tag{26}$$

$$\tag{27}$$

The most common perturbing Hamiltonian $\mathcal{H}_1$ is the hyperfine interaction, assuming a sum over repeated indecies $\alpha, \beta \in \{x, y, z\}$, $\mathcal{H}_1 = \int d\mathbf{x} I^\alpha(t) S^\beta(\mathbf{x}, t) A^{\alpha\beta}(\mathbf{x})$ where the spatial integration is over electron coordinates (The nuclear moment is considered fixed at the origin), and $S^\beta(\mathbf{x}, t) = \Psi^\dagger_\mu(\mathbf{x}, t)\Psi_\nu(\mathbf{x}, t)\sigma^\beta_{\mu\nu}$ is the electron spin operator and $\Psi_{s'}(\mathbf{x}, t)$ is the electron field operator (similarly for $I^\alpha(0, t) = I^\alpha(t)$ with nuclear spin operators $\Phi_\mu(\mathbf{x}, t)$). $A^{\alpha\beta}(\mathbf{x})$ is the hyperfine matrix element between nuclear spin α and electron spin β.

Assuming the unperturbed Hamiltonian has separable solutions for the nuclear moments and electrons, (ie nuclear spins and electrons are non-interacting) the matrix element for a particular $in's' \rightarrow jns$ $((i, n, s) =$(nuclear spin state, electron state, electron spin)) is

$$M_{in's',jns}(t) = \langle j|I^{\alpha}(t)|i\rangle \int d\mathbf{x}\, A^{\alpha\beta}(\mathbf{x})\langle ns|S^{\beta}(\mathbf{x},t)|n's'\rangle \tag{28}$$

Which gives a probability amplitude

$$c_{in's',jns}(t) = \frac{i}{\hbar}\int_0^t dt'\, M_{in's',jns}(t') \tag{29}$$

Then, the probability of a nuclear transition per time is found by summing over all the electron transition probabilities $|c_{in's',jns}(t)|^2$ weighted by the probability of the initial state $p_{n's'}$. In this way, we consider an initial state with probability $p_{n's'}$ coupling to *all* final states ns.

$$W_{ij} = \frac{1}{t}\sum_{n's'ns} p_{n's'}|c_{in's',jns}(t)|^2 \tag{30}$$

$$= \frac{1}{t}\sum_{nn',ss'}\int d\mathbf{x}d\mathbf{x}'\; A^{\alpha\beta}(\mathbf{x})A^{*\alpha'\beta'}(\mathbf{x}')\int_0^t dt'dt''\langle j|I^{\alpha}(t')|i\rangle\langle i|I^{\alpha'}(t'')|j\rangle\langle ns|S^{\beta}(\mathbf{x},t')|n's'\rangle\langle n's'|S^{\beta'}(\mathbf{x}',t'')|ns\rangle \tag{31}$$

$$= \frac{1}{t}\int d\mathbf{x}d\mathbf{x}'\; A^{\alpha\beta}(\mathbf{x})A^{*\alpha'\beta'}(\mathbf{x}')\int_0^t dt'dt''\langle j|I^{\alpha}(t')|i\rangle\langle i|I^{\alpha'}(t'')|j\rangle\Big\langle S^{\beta}(\mathbf{x},t')S^{\beta'}(\mathbf{x}',t'')\Big\rangle \tag{32}$$

$$= \langle j|I^{\alpha}|i\rangle\langle i|I^{\alpha'}|j\rangle\int d\mathbf{x}d\mathbf{x}'\; A^{\alpha\beta}(\mathbf{x})A^{*\alpha'\beta'}(\mathbf{x}')\int_{-t}^{t} d\tau\Big\langle S^{\beta}(\mathbf{x},\tau)S^{\beta'}(\mathbf{x}',0)\Big\rangle e^{i\omega\tau} \tag{33}$$

We have used $1 = \sum_{n's'}|n's'\rangle\langle n's'|$ and introduced $\Big\langle A\Big\rangle = \sum_{ns}\langle ns|A|ns\rangle = Tr[\rho A]$ as the thermal average of the unperturbed electron ensemble ($\mathcal{H}_0$, $\rho = e^{-\beta\mathcal{H}_0}/\mathcal{Z}_e$). $\omega = (E_j - E_i)/\hbar$ is the difference of nuclear energy states, and we used the cyclic property of the trace to write the time bit in terms of $\tau = t' - t''$

The integral over electron coordinates can be evaluated using the Fourier transform of the interaction squared $A^{\alpha\beta}(\mathbf{x})A^{*\alpha'\beta'}(\mathbf{x}') = C^{\alpha\beta}_{\alpha'\beta'}(\mathbf{r},\mathbf{R})$, and defining center of mass and relative coordinates $\mathbf{R} = (\mathbf{x}+\mathbf{x}')/2$ and $\mathbf{r} = \mathbf{x} - \mathbf{x}'$. Additionally, we consider the limit of $t \rightarrow \infty$, which is to say that the perturbation was turned on in the very distant past.

$$W_{ij} = \langle j|I^{\alpha}|i\rangle\langle i|I^{\alpha'}|j\rangle\int d\mathbf{R}d\mathbf{q}\; C^{\alpha\beta}_{\alpha'\beta'}(\mathbf{q},\mathbf{R})\mathcal{S}^{\beta\beta'}(\mathbf{q},\mathbf{R},\omega) \tag{34}$$

$\mathcal{S}^{\beta\beta}(\mathbf{q},\mathbf{R},\omega) = \int_{-\infty}^{\infty} d\tau d\mathbf{r} e^{-i(\mathbf{q}\mathbf{r}-\omega\tau)}\Big\langle S^{\beta}(\mathbf{x},\tau)S^{\beta'}(\mathbf{x}',0)\Big\rangle$, and $C^{\alpha\beta}_{\alpha'\beta'}(\mathbf{q},\mathbf{R}) = \int d\mathbf{r}e^{-i\mathbf{q}\mathbf{r}}A^{\alpha\beta}(\mathbf{x})A^{*\alpha'\beta'}(\mathbf{x}')$.

We now turn to the fluctuation-dissipation theorem to show that $\mathcal{S}^{\beta\beta'}(\mathbf{q},\mathbf{R},\omega) = \frac{Im[\chi\beta\beta'(\mathbf{q},\mathbf{R},\omega)]}{1+e^{\omega/T}}$. Which requires the definitions of a few things in linear response (suppressing spatial coordinates).

$X^{\beta\beta'}(t) = i\big\langle[S^{\beta}(t), S^{\beta'}(0)]\big\rangle$ RESPONSE FUNCTION

$\mathcal{S}^{\beta\beta'}(t) = \big\langle S^{\beta}(t), S^{\beta'}(0)\big\rangle$ CORRELATION FUNCTION

$\chi^{\beta\beta'}(\omega) = \int dt\Theta(t)X^{\beta\beta'}(t)e^{i\omega t}$ RETARDED SUSCEPTIBILITY

The response and correlation functions are easily related $X^{\beta\beta'}(t) = i(\mathcal{S}^{\beta\beta'}(t) - \mathcal{S}^{\beta'\beta}(-t))$, and the transform of the response function is $X^{\beta\beta'}(\omega) = \int_{-\infty}^{\infty} dt e^{i(\omega' t + i\omega''|t|)} X^{\beta\beta'}(t)$, where ω' and $\omega'' > 0$ are the real and imaginary parts of ω respectively. Using this definition one finds that $X^{\beta\beta'}(\omega) = 2iIm[\chi^{\beta\beta'}(\omega)]$.

We now turn to the correlation function $\mathcal{S}$ and employ the cyclic nature of the trace to find $\mathcal{S}^{\beta\beta'}(t) = \mathcal{S}^{\beta'\beta}(-t - i\beta)$, and if $\mathcal{S}^{\beta\beta'}(t)$ is analytic for $Im[t] \leq \beta$, then this equality can be transformed $\mathcal{S}^{\beta\beta'}(\omega) = e^{\beta\omega}\mathcal{S}^{\beta'\beta}(-\omega)$. Using the relation between $\mathcal{S}$ and X we find

$$\mathcal{S}^{\beta\beta'}(\omega) = e^{\beta\omega}(\mathcal{S}^{\beta\beta'}(\omega) + iX^{\beta\beta'}(\omega)) \tag{35}$$

$$\Rightarrow \mathcal{S}^{\beta\beta'}(\omega) = \frac{2Im[\chi^{\beta\beta'}(\omega)]}{1 - e^{-\beta\omega}} \tag{36}$$

The exponential in the denominator can be expanded for small ω when the nuclear transitions are small and we arrive at

$$W_{ij} = 2T\langle j|I^\alpha|i\rangle\langle i|I^{\alpha'}|j\rangle \int d\mathbf{R}d\mathbf{q}\; C^{\alpha\beta}_{\alpha'\beta'}(\mathbf{q},\mathbf{R})\frac{Im[\chi^{\beta\beta'}(\mathbf{q},\mathbf{R},\omega)]}{\omega} \tag{37}$$

If the transition frequency ω is sufficiently small, the electron integral $K^{\alpha\beta}_{\alpha'\beta'}(\omega)$ becomes independent of the transition states i and j, and $W_{ij} = K^{\alpha\beta}_{\alpha'\beta'}\langle j|I^\alpha|i\rangle\langle i|I^{\alpha'}|j\rangle$. In this case, the relaxation rate equation is

$$\begin{aligned}
\frac{1}{T_1} &= \frac{1}{2}\sum_{ij} W_{ij}(E_i - E_j)^2 / \sum_i E_i^2 && (38)\\
&= \frac{K^{\alpha\beta}_{\alpha'\beta'}}{2}\sum_{ij}\langle j|I^\alpha|i\rangle\langle i|I^{\alpha'}|j\rangle(E_i - E_j)^2 / \sum_i E_i^2 && (39)\\
&= -\frac{K^{\alpha\beta}_{\alpha'\beta'}}{2}\sum_{ij}\langle j|[\mathcal{H}, I^\alpha]|i\rangle\langle i|[\mathcal{H}, I^{\alpha'}]|j\rangle / \sum_i E_i^2 && (40)\\
&= -\frac{K^{\alpha\beta}_{\alpha'\beta'}}{2} Tr\big[[\mathcal{H}, I^\alpha][\mathcal{H}, I^{\alpha'}]\big]/Tr[\mathcal{H}^2] && (41)
\end{aligned}$$

For the unperturbed nuclear Hamiltonian $\mathcal{H}_0 = \gamma\hbar H I^z$, so $Tr[\mathcal{H}^2] = (\gamma\hbar H)^2 Tr[I^{z2}]$, and using the commutator $[I^i, I^j] = i\epsilon_{ijk}I^k$, and product $I^a I^b = i\sum_c \epsilon_{abc}I^c + \delta_{ab}\mathcal{I}$ we see that $\alpha = \alpha'$

$$\begin{aligned}
\frac{1}{T_1} &= K^{\alpha\beta}_{\alpha\beta'} && (42)\\
&= 2T\int d\mathbf{R}d\mathbf{q}\; C^{\alpha\beta}_{\alpha\beta'}(\mathbf{q},\mathbf{R})\frac{Im[\chi^{\beta\beta'}(\mathbf{q},\mathbf{R},\omega)]}{\omega}\bigg|_{\omega\to 0} && (43)\\
&= \int d\mathbf{R}d\mathbf{q}\; C^{\alpha\beta}_{\alpha\beta'}(\mathbf{q},\mathbf{R})\mathcal{S}^{\beta\beta'}(\mathbf{q},\mathbf{R},\omega)\Big|_{\omega\to 0} && (44)
\end{aligned}$$

Having proceeded thus far with a general spin structure, we now focus on only the diagonal contributions from the hyperfine interaction $C^{\alpha\beta}_{\alpha\beta'} = C^\alpha\delta_{\alpha\beta}\delta_{\alpha\beta'}$, and now

$$1/T_1 = 2\int d\mathbf{R}d\mathbf{q}\; C^\alpha(\mathbf{q},\mathbf{R})\mathcal{S}^\alpha(\mathbf{q},\mathbf{R},\omega)\Big|_{\omega\to 0} \tag{45}$$

Another limit to consider is if the hyperfine interaction is purely S wave so that $C^{\alpha\beta}_{\alpha'\beta'}(\mathbf{r},\mathbf{R}) = C^{\alpha\beta}_{\alpha'\beta'}\delta(\mathbf{r})\delta(\mathbf{R})$, and in this case we can easily find W_{ij}

$$W_{ij} = \langle j|I^\alpha|i\rangle\langle i|I^{\alpha'}|j\rangle C^{\alpha\beta}_{\alpha'\beta'}\sigma^\beta_{\mu\nu}\sigma^{\beta'}_{\mu'\nu'}\int\limits_{-\infty}^{\infty} d\tau\left\langle \Psi^\dagger_\mu(\tau)\Psi_\nu(\tau)\Psi^\dagger_{\mu'}\Psi_{\nu'}\right\rangle e^{i\omega\tau} \tag{46}$$

In the case of a normal metal we can write the electron wave functions as block waves $\Psi_\mu(\mathbf{x},t) = \sum_{\mathbf{k}}\phi_{\mathbf{k}\mu}(\mathbf{r})\hat{\psi}_{\mathbf{k}\mu}e^{-iE_{\mathbf{k}}t}$, $\phi_{\mathbf{k}\mu}(0)=\phi_{\mathbf{k}\mu}$

$$W_{ij} = \langle j|I^\alpha|i\rangle\langle i|I^{\alpha'}|j\rangle C^{\alpha\beta}_{\alpha'\beta'}\sigma^\beta_{\mu\nu}\sigma^{\beta'}_{\mu'\nu'}\phi^*_{\mathbf{k}\mu}\phi_{\mathbf{p}\nu}\phi^*_{\mathbf{k}'\mu'}\phi_{\mathbf{p}'\nu'}\int\limits_{-\infty}^{\infty} d\tau\left\langle \hat{\psi}^\dagger_{\mathbf{k}\mu}\hat{\psi}_{\mathbf{p}\nu}\hat{\psi}^\dagger_{\mathbf{k}'\mu'}\hat{\psi}_{\mathbf{p}'\nu'}\right\rangle e^{i(\omega+E_{\mathbf{k}\mu}-E_{\mathbf{p}\nu})\tau} \tag{47}$$

The trace can be done using Wicks Theorem, noting that the first term $\langle\hat{\psi}^\dagger_{\mathbf{k}\mu}\hat{\psi}_{\mathbf{p}\nu}\rangle\langle\hat{\psi}^\dagger_{\mathbf{k}'\mu'}\hat{\psi}_{\mathbf{p}'\nu'}\rangle$ vanishes, because it requires $\delta_{\mathbf{kp}}\delta_{\mu\nu}$ from the trace which leads to $\delta(\omega)$ from the time integration, and $\omega=0$ corresponds to no nuclear transition (i=j). Therefore,

$$W_{ij} = \langle j|I^\alpha|i\rangle\langle i|I^{\alpha'}|j\rangle C^{\alpha\beta}_{\alpha'\beta'}\sum_{\mathbf{kp}\mu\nu}\sigma^\beta_{\mu\nu}\sigma^{\beta'}_{\nu\mu}|\phi_{\mathbf{k}\mu}|^2|\phi_{\mathbf{p}\nu}|^2 f_{\mathbf{k}\mu}(1-f_{\mathbf{p}\nu})\delta(\omega+E_{\mathbf{k}\mu}-E_{\mathbf{p}\nu}) \tag{48}$$

If instead, the electron states are superconducting then the electron operator is written in the Bogoliubov transformation

$$\Psi_\mu(\mathbf{x},t) = \sum_{\mathbf{n}} u_{\mathbf{n}\mu\nu}(\mathbf{x})\hat{\gamma}_{\mathbf{n}\nu}(t) + v^*_{\mathbf{n}\mu\nu}(\mathbf{x})\hat{\gamma}^\dagger_{\mathbf{n}\nu}(t) \tag{49}$$

$$\left\langle\Psi^\dagger_\alpha(\tau)\Psi_\beta(\tau)\Psi^\dagger_{\alpha'}\Psi_{\beta'}\right\rangle = -\langle\Psi^\dagger_\alpha(t)\Psi^\dagger_{\alpha'}\rangle\langle\Psi_\beta(t)\Psi_{\beta'}\rangle + \langle\Psi^\dagger_\alpha(t)\Psi_{\beta'}\rangle\langle\Psi_\beta(t)\Psi^\dagger_{\alpha'}\rangle \tag{50}$$

$$= -\langle\Big(u^*_{\mathbf{n}\alpha\mu}\hat{\gamma}^\dagger_{\mathbf{n}\mu}(t) + v_{\mathbf{n}\alpha\mu}\hat{\gamma}_{\mathbf{n}\mu}(t)\Big)\Big(u^*_{\mathbf{n}'\alpha'\mu'}\hat{\gamma}^\dagger_{\mathbf{n}'\mu'} + v_{\mathbf{n}'\alpha'\mu'}\hat{\gamma}_{\mathbf{n}'\mu'}\Big)\rangle \tag{51}$$

$$\times\langle\Big(u_{\mathbf{m}\beta\nu}\hat{\gamma}_{\mathbf{m}\nu}(t) + v^*_{\mathbf{m}\beta\nu}\hat{\gamma}^\dagger_{\mathbf{m}\nu}(t)\Big)\Big(u_{\mathbf{m}'\beta'\nu'}\hat{\gamma}_{\mathbf{m}'\nu'} + v^*_{\mathbf{m}'\beta'\nu'}\hat{\gamma}^\dagger_{\mathbf{m}'\nu'}\Big)\rangle \tag{52}$$

$$+\langle\Big(u^*_{\mathbf{n}\alpha\mu}\hat{\gamma}^\dagger_{\mathbf{n}\mu}(t) + v_{\mathbf{n}\alpha\mu}\hat{\gamma}_{\mathbf{n}\mu}(t)\Big)\Big(u_{\mathbf{m}'\beta'\nu'}\hat{\gamma}_{\mathbf{m}'\nu'} + v^*_{\mathbf{m}'\beta'\nu'}\hat{\gamma}^\dagger_{\mathbf{m}'\nu'}\Big)\rangle \tag{53}$$

$$\times\langle\Big(u_{\mathbf{m}\beta\nu}\hat{\gamma}_{\mathbf{m}\nu}(t) + v^*_{\mathbf{m}\beta\nu}\hat{\gamma}^\dagger_{\mathbf{m}\nu}(t)\Big)\Big(u^*_{\mathbf{n}'\alpha'\mu'}\hat{\gamma}^\dagger_{\mathbf{n}'\mu'} + v_{\mathbf{n}'\alpha'\mu'}\hat{\gamma}_{\mathbf{n}'\mu'}\Big)\rangle \tag{54}$$

Now we can group Fermi function combinations

$$= f_{\mathbf{n}\mu}(1-f_{\mathbf{m}\nu})e^{i(E_{\mathbf{n}\mu}-E_{\mathbf{m}\nu})t}\big(-u^*_{\mathbf{n}\alpha\mu}v_{\mathbf{n}\alpha'\mu}u_{\mathbf{m}\beta\nu}v^*_{\mathbf{m}\beta'\nu} + u^*_{\mathbf{n}\alpha\mu}u_{\mathbf{n}\beta'\mu}u_{\mathbf{m}\beta\nu}u^*_{\mathbf{m}\alpha'\nu}\big) \tag{55}$$

$$+(1-f_{\mathbf{n}\mu})f_{\mathbf{m}\nu}e^{-i(E_{\mathbf{n}\mu}-E_{\mathbf{m}\nu})t}\big(-v_{\mathbf{n}\alpha\mu}u^*_{\mathbf{n}\alpha'\mu}v^*_{\mathbf{m}\beta\nu}u_{\mathbf{m}\beta'\nu} + v_{\mathbf{n}\alpha\mu}v^*_{\mathbf{n}\beta'\mu}v^*_{\mathbf{m}\beta\nu}v_{\mathbf{m}\alpha'\nu}\big) \tag{56}$$

$$+f_{\mathbf{n}\mu}f_{\mathbf{m}\nu}e^{i(E_{\mathbf{n}\mu}+E_{\mathbf{m}\nu})t}\big(-u^*_{\mathbf{n}\alpha\mu}v_{\mathbf{n}\alpha'\mu}v^*_{\mathbf{m}\beta\nu}v_{\mathbf{m}\beta'\nu} + u^*_{\mathbf{n}\alpha\mu}u_{\mathbf{n}\beta'\mu}v^*_{\mathbf{m}\beta\nu}v_{\mathbf{m}\alpha'\nu}\big) \tag{57}$$

$$+(1-f_{\mathbf{n}\mu})(1-f_{\mathbf{m}\nu})e^{-i(E_{\mathbf{n}\mu}+E_{\mathbf{m}\nu})t}\big(-v_{\mathbf{n}\alpha\mu}u^*_{\mathbf{n}\alpha'\mu}u_{\mathbf{m}\beta\nu}v^*_{\mathbf{m}\beta'\nu} + v_{\mathbf{n}\alpha\mu}v^*_{\mathbf{n}\beta'\mu}u_{\mathbf{m}\beta\nu}u^*_{\mathbf{m}\alpha'\nu}\big) \tag{58}$$

Using the relation for negative energies ($E_{n\mu} =\!\rightarrow -E_{n\mu}$, $(u_{\mathbf{n}\alpha\beta}, v_{\mathbf{n}\alpha\beta}) \rightarrow (v^*_{\mathbf{n}\alpha\beta}, u^*_{\mathbf{n}\alpha\beta})$) it is possible to show that all the above contributions are the same

$$= 4f_{\mathbf{n}\mu}(1-f_{\mathbf{m}\nu})e^{i(E_{\mathbf{n}\mu}-E_{\mathbf{m}\nu})t}\big(-u^*_{\mathbf{n}\alpha\mu}v_{\mathbf{n}\alpha'\mu}u_{\mathbf{m}\beta\nu}v^*_{\mathbf{m}\beta'\nu} + u^*_{\mathbf{n}\alpha\mu}u_{\mathbf{n}\beta'\mu}u_{\mathbf{m}\beta\nu}u^*_{\mathbf{m}\alpha'\nu}\big) \tag{59}$$

$$= 4f_{\mathbf{n}\alpha}(1-f_{\mathbf{m}\beta})e^{i(E_{\mathbf{n}\alpha}-E_{\mathbf{m}\beta})t}\big(-\sigma(\alpha)\sigma(\beta)\delta_{\alpha'\bar{\alpha}}\delta_{\beta'\bar{\beta}}u^*_{\mathbf{n}}v_{\mathbf{n}}u_{\mathbf{m}}v^*_{\mathbf{m}} + \delta_{\beta'\alpha}\delta_{\beta\alpha'}u^*_{\mathbf{n}}u_{\mathbf{n}}u_{\mathbf{m}}u^*_{\mathbf{m}}\big) \tag{60}$$

In a singlet superconductor the amplitudes are known $u_{\mathbf{n}\alpha\beta} = u_{vn}\delta_{\alpha\beta}$, $v_{\mathbf{n}\alpha\beta} = -v_{\mathbf{n}}\sigma(\alpha)\delta_{\alpha\bar{\beta}}$

$$W_{ij} = 4\langle j|I^{\alpha}|i\rangle\langle i|I^{\alpha'}|j\rangle C^{\alpha\beta}_{\alpha'\beta'} \sum_{\mathbf{nm}\mu\nu} \sigma^{\beta}_{\mu\nu} f_{\mathbf{n}\mu}(1-f_{\mathbf{m}\nu})\big(-\sigma(\mu)\sigma(\nu)\sigma^{\beta'}_{\bar{\mu}\bar{\nu}} u^*_{\mathbf{n}} v_{\mathbf{n}} u_{\mathbf{m}} v^*_{\mathbf{m}} + \sigma^{\beta'}_{\nu\mu}|u_{\mathbf{n}}|^2|u_{\mathbf{m}}|^2\big)\delta(\omega + E_{\mathbf{n}\mu} - E_{\mathbf{m}\nu}) \quad (61)$$

If there is no magnetic field the spin sums can be evaluated easily for a diagonal $\beta = \beta'$ elements ($\beta \neq \beta'$ is zero ?), and from BCS we know that $u_{\mathbf{n}}V^*_{\mathbf{n}} = \Delta/(2E_{\mathbf{n}})$

$$W_{ij} = 8\langle j|I^{\alpha}|i\rangle\langle i|I^{\alpha'}|j\rangle C^{\alpha\beta}_{\alpha'\beta'} \sum_{\mathbf{nm}} f_{\mathbf{n}}(1-f_{\mathbf{m}})\big(|\Delta|^2/(4E_{\mathbf{n}}E_{\mathbf{m}}) + |u_{\mathbf{n}}|^2|u_{\mathbf{m}}|^2\big)\delta(\omega + E_{\mathbf{n}\mu} - E_{\mathbf{m}\nu}) \quad (62)$$

From BCS we also know that

$$|u_{\mathbf{n}}|^2|u_{\mathbf{m}}|^2 = \frac{1}{4}(1+\xi_{\mathbf{n}}/E_{\mathbf{n}})(1+\xi_{\mathbf{m}}/E_{\mathbf{m}}) = \frac{1}{4}(1+\xi_{\mathbf{n}}/E_{\mathbf{n}} + \xi_{\mathbf{m}}/E_{\mathbf{m}} + \xi_{\mathbf{n}}\xi_{\mathbf{m}}/(E_{\mathbf{n}}E_{\mathbf{m}})) \quad (63)$$

Near the Fermi surface there will be both particles ($\xi > 0$) and holes ($\xi < 0$) which both have the same total energy $E = \sqrt{\xi^2 + \Delta^2}$. Therefore the last three terms above do not contribute to the total integration and can be removed. The final result is

$$W_{ij} = 2\langle j|I^{\alpha}|i\rangle\langle i|I^{\alpha'}|j\rangle C^{\alpha\beta}_{\alpha'\beta'} \sum_{\mathbf{nm}} f_{\mathbf{n}}(1-f_{\mathbf{m}})\big(|\Delta|^2/(E_{\mathbf{n}}E_{\mathbf{m}}) + 1\big)\delta(\omega + E_{\mathbf{n}\mu} - E_{\mathbf{m}\nu}) \quad (64)$$