Density matrix dynamics

Warm up: single particle

Let's start with the dynamics of a potentially mixed state of a single electron in a finite system. So we have discrete states labeled only by a band index n, and no wave-vector index yet. Let these orbitals (eigenstates of the unperturbed Hamiltonian) be denoted by the kets $|n\rangle$, and the density matrix operator $\hat{\rho} = \sum_{n'n} \rho_{n'n} |n'\rangle\langle n|$, also denoted by the matrix ρ or the matrix elements $\rho_{n'n}$ in this basis of the unperturbed eigenstates. The unperturbed Hamiltonian is $\hat{H}_0 = \sum_n \varepsilon_n |n\rangle\langle n|$, where ε_n are the unperturbed eignevalues.

We will first write time-dependent evolution in this basis. Consider a time-dependent perturbation $\hat{P}(t) = \sum_{n'n} P_{n'n}(t) |n'\rangle\langle n|$, which could be the dipole matrix elements for optical excitation in a specific polarization, for example. In particular, we could consider a time dependence of the form $P_{n'n}(t) = P_{n'n} 2\cos(\omega t) \frac{e^{-t^2/2\tau^2}}{\sqrt{\sqrt{\pi}\tau}}$ to describe a Gaussian pulse for the pump or probe. Note that the Gaussian is square normalized, such that the time dependence of the *intensity* integrates to 1, not the electric field.

Additionally, while $P_{n'n}(t)$ has the dimensions of $[E]$, $P_{n'n}$ has the dimensions of $\left[E\sqrt{t}\right]$. Therefore, if we are writing this as a dipole matrix element $P_{n'n} = \frac{e\vec{A}_0 \cdot \vec{p}_{n'n}}{m_e}$, then the polarization amplitude $\vec{A}_0$ has an extra $\sqrt{t}$ dimension relative to that of the usual vector potential. Further, we have to be careful if $\vec{A}_0$ is complex to describe circularly-polarized light. The overall vector potential is real: $\left(\vec{A}_0 e^{-i\omega t} + \vec{A}_0^* e^{i\omega t}\right) \frac{e^{-t^2/2\tau^2}}{\sqrt{\sqrt{\pi}\tau}}$, so that

$$
\begin{aligned}
P_{n'n}(t) &= \frac{e}{m_e}\left(\vec{A}_0 \cdot \vec{p}_{n'n} e^{-i\omega t} + \vec{A}_0^* \cdot \vec{p}_{n'n} e^{i\omega t}\right) \frac{e^{-t^2/2\tau^2}}{\sqrt{\sqrt{\pi}\tau}} \\
&= \frac{e}{m_e}\left(\vec{A}_0 \cdot \vec{p}_{n'n} e^{-i\omega t} + \left(\vec{A}_0 \cdot \vec{p}^*_{n'n}\right)^* e^{i\omega t}\right) \frac{e^{-t^2/2\tau^2}}{\sqrt{\sqrt{\pi}\tau}} \\
&= \frac{e}{m_e}\left(\vec{A}_0 \cdot \vec{p}_{n'n} e^{-i\omega t} + \left(\vec{A}_0 \cdot \vec{p}_{nn'}\right)^* e^{i\omega t}\right) \frac{e^{-t^2/2\tau^2}}{\sqrt{\sqrt{\pi}\tau}} \qquad \text{(since } \vec{p} \text{ is Hermitian)} \\
&= \left(P_{n'n} e^{-i\omega t} + P^*_{nn'} e^{i\omega t}\right) \frac{e^{-t^2/2\tau^2}}{\sqrt{\sqrt{\pi}\tau}}
\end{aligned}
$$

Now let us write the Liouville equation for time evolution (working in atomic units with $\hbar = 1$):

$$
\begin{aligned}
i\frac{\partial \hat{\rho}}{\partial t} &= [\hat{H}, \hat{\rho}] \\
&= \left[\hat{H}_0 + \hat{P}, \hat{\rho}\right] \\
&= \hat{H}_0\hat{\rho} - \hat{\rho}\hat{H}_0 + \hat{P}\hat{\rho} - \hat{\rho}\hat{P} \\
&= \sum_a \varepsilon_a |a\rangle\langle a| \sum_{n'n} \rho_{n'n} |n'\rangle\langle n| - \sum_{n'n} \rho_{n'n} |n'\rangle\langle n| \sum_a \varepsilon_a |a\rangle\langle a| \\
&\qquad + \sum_{ab} P_{ab}(t) |a\rangle\langle b| \sum_{n'n} \rho_{n'n} |n'\rangle\langle n| - \sum_{n'n} \rho_{n'n} |n'\rangle\langle n| \sum_{ab} P_{ab}(t) |a\rangle\langle b| \\
&= \sum_{n'n} \varepsilon_{n'} \rho_{n'n} |n'\rangle\langle n| - \sum_{n'n} \rho_{n'n} \varepsilon_n |n'\rangle\langle n| + \sum_{an'n} P_{an'}(t) \rho_{n'n} |a\rangle\langle n| - \sum_{n'nb} \rho_{n'n} P_{nb}(t) |n'\rangle\langle b| \\
&\qquad \text{(Using orthonormality of eigenstates)} \\
&= \sum_{n'n} \varepsilon_{n'} \rho_{n'n} |n'\rangle\langle n| - \sum_{n'n} \rho_{n'n} \varepsilon_n |n'\rangle\langle n| + \sum_{n'an} P_{n'a}(t) \rho_{an} |n'\rangle\langle n| - \sum_{n'na} \rho_{n'a} P_{an}(t) |n'\rangle\langle n| \\
&\qquad \text{(relabeling dummy indices)}
\end{aligned}
$$

$$
\begin{aligned}
&= \sum_{n'n} \left[(\varepsilon_{n'} - \varepsilon_n)\rho_{n'n} + \sum_a \left(P_{n'a}(t)\rho_{an} - \rho_{n'a}P_{an}(t) \right) \right] |n'\rangle\langle n| \\
\Rightarrow \qquad i\frac{\partial \rho_{n'n}}{\partial t} &= (\varepsilon_{n'} - \varepsilon_n)\rho_{n'n} + \sum_a \left(P_{n'a}(t)\rho_{an} - \rho_{n'a}P_{an}(t) \right)
\end{aligned}
$$

Above, we have just explicitly worked out the matrix version of the Liouville equation in the chosen basis, starting from the general operator version for completeness. Now, in principle we could numerically solve the above equation given an initial density matrix. However, it would be inefficient because even in the absence of a perturbation, the first term is strongly oscillatory and would need to be integrated numerically.

Instead, we should switch to the interaction picture, where we build the non-interacting time dependence into the states. Effectively our basis then switches from $|n'\rangle\langle n|$ to $e^{-i\varepsilon_{n'}t}|n'\rangle\langle n|e^{i\varepsilon_{n'}t} = e^{i(\varepsilon_n - \varepsilon_{n'})t}|n'\rangle\langle n|$. In the revised basis, the matrix equation becomes:

$$
\begin{aligned}
i\frac{\partial(\rho_{n'n}e^{i(\varepsilon_n - \varepsilon_{n'})t})}{\partial t} &= (\varepsilon_{n'} - \varepsilon_n)\rho_{n'n}e^{i(\varepsilon_n - \varepsilon_{n'})t} + \sum_a P_{n'a}(t)\rho_{an}e^{i(\varepsilon_n - \varepsilon_a)t} - \sum_b \rho_{n'b}e^{i(\varepsilon_b - \varepsilon_{n'})t}P_{bn}(t) \\
\Rightarrow \qquad i\frac{\partial \rho_{n'n}}{\partial t} &= \sum_a P_{n'a}(t)\rho_{an}e^{i(\varepsilon_{n'} - \varepsilon_a)t} - \sum_b \rho_{n'b}e^{i(\varepsilon_b - \varepsilon_n)t}P_{bn}(t)
\end{aligned}
$$

$$
\begin{aligned}
\text{Redefine:} \qquad P_{n'n}(t) &= e^{i(\varepsilon_{n'} - \varepsilon_n)t}(P_{n'n}e^{-i\omega t} + P^*_{nn'}e^{i\omega t})\frac{e^{-t^2/2\tau^2}}{\sqrt{\sqrt{\pi}\tau}} \qquad \text{(include } e^{i\Delta\varepsilon t} \text{ from above)} \\
\Rightarrow \qquad i\frac{\partial \rho_{n'n}}{\partial t} &= \sum_a \left(P_{n'a}(t)\rho_{an} - \rho_{n'a}P_{an}(t) \right)
\end{aligned}
$$

We will use the interaction picture henceforth; note that we have used the same notation and hence redefined the time dependence of the symbols above for convenience. Note that $P_{n'n}(t)$ is always Hermitian, even when $P_{n'n}$ is not (which will happen for complex polarizations).

We could integrate the above explicitly for describing a highly nonlinear response. However, it would be further useful to derive a perturbative form assuming that the density matrix does not change appreciably before to after, corresponding to a small net excitation probability. This would be applicable both for describing pumps in the linear power dependence regime, and probe response.

In the perturbative form, we can assume that the density matrix time dependence can be decomposed into a series in the perturbation strength. Then to get the density matrix up to first order, we can only keep it up to zeroth order in the RHS. Since this zeroth order ρ is constant in the interaction picture, we can write:

$$
\begin{aligned}
\Delta\rho_{n'n} &= -i\int_{-\infty}^{\infty} \mathrm{d}t \sum_a \left(P_{n'a}(t)\rho_{an} - \rho_{n'a}P_{an}(t) \right) \\
&= -i\int_{-\infty}^{\infty} \mathrm{d}t \, \frac{e^{-t^2/2\tau^2}}{\sqrt{\sqrt{\pi}\tau}} \sum_{a\pm} \left(P^{\pm}_{n'a}\rho_{an}e^{i(\varepsilon_{n'} - \varepsilon_a \pm \omega)t} - \rho_{n'a}P^{\pm}_{an}e^{i(\varepsilon_a - \varepsilon_n \pm \omega)t} \right) \\
&\qquad\qquad \text{(where } P^-_{n'n} \equiv P_{n'n} \text{ and } P^+_{n'n} \equiv P^*_{nn'}\text{)} \\
&= -i\int_{-\infty}^{\infty} \frac{\mathrm{d}t}{\sqrt{\sqrt{\pi}\tau}} \sum_{a\pm} \left(P^{\pm}_{n'a}\rho_{an}e^{i(\varepsilon_{n'} - \varepsilon_a \pm \omega)t - t^2/2\tau^2} - \rho_{n'a}P^{\pm}_{an}e^{i(\varepsilon_a - \varepsilon_n \pm \omega)t - t^2/2\tau^2} \right) \\
&= -i\sqrt{2\pi} \sum_{a\pm} \left(P^{\pm}_{n'a}\rho_{an}\, g^{1/2}_\tau(\varepsilon_{n'} - \varepsilon_a \pm \omega) - \rho_{n'a}P^{\pm}_{an}\, g^{1/2}_\tau(\varepsilon_a - \varepsilon_n \pm \omega) \right) \\
&\qquad \left(\text{Using} \int_{-\infty}^{\infty} \frac{\mathrm{d}t}{\sqrt{\sqrt{\pi}\tau}} \, e^{i\alpha t - t^2/2\tau^2} = \int_{-\infty}^{\infty} \frac{\mathrm{d}t}{\sqrt{\sqrt{\pi}\tau}} \, e^{-\tau^2\alpha^2/2 + (t - 2i\tau^2\alpha)^2/2\tau^2} = \frac{\sqrt{2\pi}\tau}{\sqrt{\sqrt{\pi}\tau}} e^{-\tau^2\alpha^2/2} \right. \\
&\qquad\qquad \left. = \sqrt{2\pi}\frac{e^{-\tau^2\alpha^2/2}}{\sqrt{\sqrt{\pi}/\tau}} = \sqrt{2\pi g_\tau(\alpha)}, \text{where } g_\tau(\alpha) \equiv \frac{e^{-\tau^2\alpha^2}}{\sqrt{\pi}/\tau} \text{ is a normalized Gaussian} \right)
\end{aligned}
$$

Let us see what this looks like if we start with a pure initial state i, so that the zeroth order $\rho_{n'n} = \rho_{ii}\delta_{in}\delta_{in'}$. Then we get:

$$\begin{aligned}
\rho_{n'n} &= \rho_{ii}\delta_{in}\delta_{in'} - i\sqrt{2\pi}\sum_{a\pm}\left(P^{\pm}_{n'a}\rho_{ii}\delta_{in}\delta_{ia}g_\tau^{1/2}(\varepsilon_{n'}-\varepsilon_a\pm\omega) - \rho_{ii}\delta_{ia}\delta_{in'}P^{\pm}_{an}g_\tau^{1/2}(\varepsilon_a-\varepsilon_n\pm\omega)\right)\\
&= \rho_{ii}\delta_{in}\delta_{in'} - i\sqrt{2\pi}\sum_{\pm}\left(P^{\pm}_{n'n}\rho_{ii}\delta_{in}g_\tau^{1/2}(\varepsilon_{n'}-\varepsilon_n\pm\omega) - \rho_{ii}\delta_{in'}P^{\pm}_{n'n}g_\tau^{1/2}(\varepsilon_{n'}-\varepsilon_n\pm\omega)\right)\\
&= \rho_{ii}\delta_{in}\delta_{in'} - i\sqrt{2\pi}\,\rho_{ii}(\delta_{in}-\delta_{in'})\sum_{\pm}P^{\pm}_{n'n}g_\tau^{1/2}(\varepsilon_{n'}-\varepsilon_n\pm\omega)
\end{aligned}$$

Note that ρ_{nn} does not change for any n, so at this order, we have not yet described any transitions. This is the coherent part of the dynamics where the optical pulse has linearlyc ombined the initial state with others. However this effect is only significant for energy conserving pairs, as one could expect.

We need to integrate up to second order in P to actually get transitions, as we will do next. Starting from the first order we had above, we can write the perturbative series more generally as:

$$\begin{aligned}
\rho^{(1)}_{n'n}(t_1) &= -i\int_{-\infty}^{t_1}\mathrm{d}t\,\frac{e^{-t^2/2\tau^2}}{\sqrt{\sqrt{\pi}\tau}}\sum_{a\pm}\left(P^{\pm}_{n'a}\rho^{(0)}_{an}e^{i(\varepsilon_{n'}-\varepsilon_a\pm\omega)t} - \rho^{(0)}_{n'a}P^{\pm}_{an}e^{i(\varepsilon_a-\varepsilon_n\pm\omega)t}\right)\\
\rho^{(2)}_{n'n}(t_2) &= -i\int_{-\infty}^{t_2}\mathrm{d}t_1\,\frac{e^{-t_1^2/2\tau^2}}{\sqrt{\sqrt{\pi}\tau}}\sum_{a\pm}\left(P^{\pm}_{n'a}\rho^{(1)}_{an}(t_1)e^{i(\varepsilon_{n'}-\varepsilon_a\pm\omega)t_1} - \rho^{(1)}_{n'a}(t_1)P^{\pm}_{an}e^{i(\varepsilon_a-\varepsilon_n\pm\omega)t_1}\right)\\
&\vdots
\end{aligned}$$

Let us specifically focus now on $\rho^{(2)}_{n'n} \equiv \rho^{(2)}_{n'n}(t_2\to\infty)$, the second order change in the density matrix after the pulse has passed:

$$\begin{aligned}
\rho^{(2)}_{n'n} &= -i\int_{-\infty}^{\infty}\mathrm{d}t_1\,\frac{e^{-t_1^2/2\tau^2}}{\sqrt{\sqrt{\pi}\tau}}\sum_{a,s_1=\pm}\left(P^{s_1}_{n'a}\rho^{(1)}_{an}(t_1)e^{i(\varepsilon_{n'}-\varepsilon_a+s_1\omega)t_1} - \rho^{(1)}_{n'a}(t_1)P^{s_1}_{an}e^{i(\varepsilon_a-\varepsilon_n+s_1\omega)t_1}\right)\\
&= -\int_{-\infty}^{\infty}\mathrm{d}t_1\int_{-\infty}^{t_1}\mathrm{d}t\,\frac{e^{-(t^2+t_1^2)/2\tau^2}}{\sqrt{\pi}\tau}\\
&\qquad\times\sum_{ab}\sum_{s_1s=\pm}\begin{pmatrix} P^{s_1}_{n'a}e^{i(\varepsilon_{n'}-\varepsilon_a+s_1\omega)t_1}\left(P^{s}_{ab}\rho^{(0)}_{bn}e^{i(\varepsilon_a-\varepsilon_b+s\omega)t} - \rho^{(0)}_{ab}P^{s}_{bn}e^{i(\varepsilon_b-\varepsilon_n+s\omega)t}\right)\\ -P^{s_1}_{an}e^{i(\varepsilon_a-\varepsilon_n+s_1\omega)t_1}\left(P^{s}_{n'b}\rho^{(0)}_{ba}e^{i(\varepsilon_{n'}-\varepsilon_b+s\omega)t} - \rho^{(0)}_{n'b}P^{s}_{ba}e^{i(\varepsilon_b-\varepsilon_a+s\omega)t}\right)\end{pmatrix}\\
&= \sum_{ab}\sum_{s_1s=\pm}\begin{pmatrix} -P^{s_1}_{n'a}P^{s}_{ab}\rho^{(0)}_{bn}I_2(\varepsilon_{n'}-\varepsilon_a+s_1\omega,\varepsilon_a-\varepsilon_b+s\omega)\\ +P^{s_1}_{n'a}\rho^{(0)}_{ab}P^{s}_{bn}I_2(\varepsilon_{n'}-\varepsilon_a+s_1\omega,\varepsilon_b-\varepsilon_n+s\omega)\\ +P^{s}_{n'b}\rho^{(0)}_{ba}P^{s_1}_{an}I_2(\varepsilon_a-\varepsilon_n+s_1\omega,\varepsilon_{n'}-\varepsilon_b+s\omega)\\ -\rho^{(0)}_{n'b}P^{s}_{ba}P^{s_1}_{an}I_2(\varepsilon_a-\varepsilon_n+s_1\omega,\varepsilon_b-\varepsilon_a+s\omega)\end{pmatrix}
\end{aligned}$$

with $$I_2(a,b) \equiv \int_{-\infty}^{\infty}\mathrm{d}t_1\int_{-\infty}^{t_1}\mathrm{d}t\,\frac{e^{-(t^2+t_1^2)/2\tau^2}}{\sqrt{\pi}\tau}e^{i(at_1+bt)}$$

Note that $I_2(-a,-b) = I_2^*(a,b)$ by definition. Consider the four terms in the sum above:

$$\begin{aligned}
A_{n'n} &\equiv \sum_{ab}\sum_{s_1s=\pm}P^{s_1}_{n'a}P^{s}_{ab}\rho^{(0)}_{bn}I_2(\varepsilon_{n'}-\varepsilon_a+s_1\omega,\varepsilon_a-\varepsilon_b+s\omega)\\
B_{n'n} &\equiv \sum_{ab}\sum_{s_1s=\pm}P^{s_1}_{n'a}\rho^{(0)}_{ab}P^{s}_{bn}I_2(\varepsilon_{n'}-\varepsilon_a+s_1\omega,\varepsilon_b-\varepsilon_n+s\omega)\\
C_{n'n} &\equiv \sum_{ab}\sum_{s_1s=\pm}P^{s}_{n'b}\rho^{(0)}_{ba}P^{s_1}_{an}I_2(\varepsilon_a-\varepsilon_n+s_1\omega,\varepsilon_{n'}-\varepsilon_b+s\omega)
\end{aligned}$$

$$
\begin{aligned}
&= \sum_{ab}\sum_{s_1 s=\pm} P^{-s}_{n'b}\rho^{(0)}_{ba}P^{-s_1}_{an} I_2(\varepsilon_a-\varepsilon_n-s_1\omega,\varepsilon_{n'}-\varepsilon_b-s\omega) \qquad \text{(Dummy } s\to -s, s_1\to -s_1\text{)}\\
&= \sum_{ab}\sum_{s_1 s=\pm} P^{s*}_{bn'}\rho^{(0)}_{ba}P^{s_1*}_{na} I_2(-(\varepsilon_n-\varepsilon_a+s_1\omega),-(\varepsilon_b-\varepsilon_{n'}+s\omega))\\
&= \sum_{ab}\sum_{s_1 s=\pm} P^{s_1 * s*}_{na}\rho^{(0)*}_{ab}P_{bn'} I^*_2(\varepsilon_n-\varepsilon_a+s_1\omega,\varepsilon_b-\varepsilon_{n'}+s\omega)\\
&= B^*_{nn'}
\end{aligned}
$$

$$
\begin{aligned}
D_{n'n} &\equiv \sum_{ab}\sum_{s_1 s=\pm} \rho^{(0)}_{n'b}P^{s}_{ba}P^{s_1}_{an} I_2(\varepsilon_a-\varepsilon_n+s_1\omega,\varepsilon_b-\varepsilon_a+s\omega)\\
&= \sum_{ab}\sum_{s_1 s=\pm} \rho^{(0)}_{n'b}P^{-s}_{ba}P^{-s_1}_{an} I_2(\varepsilon_a-\varepsilon_n-s_1\omega,\varepsilon_b-\varepsilon_a-s\omega) \qquad \text{(Dummy } s\to -s, s_1\to -s_1\text{)}\\
&= \sum_{ab}\sum_{s_1 s=\pm} \rho^{(0)*}_{bn'}P^{s*}_{ab}P^{s_1*}_{na} I_2(-(\varepsilon_n-\varepsilon_a+s_1\omega),-(\varepsilon_a-\varepsilon_b+s\omega))\\
&= \sum_{ab}\sum_{s_1 s=\pm} P^{s_1*}_{na}P^{s*}_{ab}\rho^{(0)*}_{bn'} I^*_2(\varepsilon_n-\varepsilon_a+s_1\omega,\varepsilon_a-\varepsilon_b+s\omega)\\
&= A^*_{nn'}
\end{aligned}
$$

$$
\begin{aligned}
\Rightarrow \qquad \rho^{(2)}_{n'n} &= \sum_{ab}\sum_{s_1 s=\pm} (-A_{n'n}+B_{n'n}+C_{n'n}-D_{n'n})\\
&= \sum_{ab}\sum_{s_1 s=\pm} (-A_{n'n}+B_{n'n}+B^*_{nn'}-A^*_{nn'})\\
&= \sum_{ab}\sum_{s_1 s=\pm} (-A_{n'n}+B_{n'n})+h.c. \qquad \text{(explicitly Hermitian)}\\
&= \sum_{ab}\sum_{s_1 s=\pm} \begin{pmatrix} -P^{s_1}_{n'a}P^{s}_{ab}\rho^{(0)}_{bn} I_2(\varepsilon_{n'}-\varepsilon_a+s_1\omega,\varepsilon_a-\varepsilon_b+s\omega)\\ +P^{s_1}_{n'a}\rho^{(0)}_{ab}P^{s}_{bn} I_2(\varepsilon_{n'}-\varepsilon_a+s_1\omega,\varepsilon_b-\varepsilon_n+s\omega)\end{pmatrix}+h.c.
\end{aligned}
$$

$$
\text{with} \qquad I_2(a,b) \equiv \int_{-\infty}^{\infty}\mathrm{d}t_1\int_{-\infty}^{t_1}\mathrm{d}t\,\frac{e^{-(t^2+t_1^2)/2\tau^2}}{\sqrt{\pi}\tau}e^{i(at_1+bt)}
$$

Next, let us transform the double integral in $I_2(a,b)$ over t and t_1 into $x=\frac{t+t_1}{2\tau}$ and $y=\frac{t_1-t}{2\tau}$ in order to separate the limits of the integral. After transformation x can take all values in $(-\infty,\infty)$, while $y\geqslant 0$ by the limits of the previous integral. Finally, the Jacobian yields $\mathrm{d}x\mathrm{d}y=\left|\begin{smallmatrix} +1/2\tau & +1/2\tau \\ -1/2\tau & +1/2\tau\end{smallmatrix}\right|\mathrm{d}t\mathrm{d}t_1=\frac{1}{2\tau^2}\mathrm{d}t\mathrm{d}t_1$. Therefore:

$$
\begin{aligned}
I_2(a,b) &= 2\tau^2\int_{-\infty}^{\infty}\mathrm{d}x\int_0^{\infty}\mathrm{d}y\,\frac{e^{-(((x-y)\tau)^2+((x+y)\tau)^2)/2\tau^2}}{\sqrt{\pi}\tau}e^{i(a(x+y)\tau+b(x-y)\tau)}\\
&= 2\tau^2\int_{-\infty}^{\infty}\mathrm{d}x\int_0^{\infty}\mathrm{d}y\,\frac{e^{-(x^2+y^2)}}{\sqrt{\pi}\tau}e^{i(x\tau(a+b)+y\tau(a-b))}\\
&= \frac{2\tau}{\sqrt{\pi}}\int_{-\infty}^{\infty}\mathrm{d}x\,e^{-x^2+i\tau(a+b)x}\int_0^{\infty}\mathrm{d}y e^{-y^2+i\tau(a-b)y}\\
&= \frac{2\tau}{\sqrt{\pi}}\int_{-\infty}^{\infty}\mathrm{d}x\,e^{-\left(x+i\tau\left(\frac{a+b}{2}\right)\right)^2-\left(\tau\frac{a+b}{2}\right)^2}\int_0^{\infty}\mathrm{d}y e^{-\left(y+i\tau\left(\frac{a-b}{2}\right)\right)^2-\left(\tau\frac{a-b}{2}\right)^2}\\
&= \frac{2\tau}{\sqrt{\pi}}e^{-\left(\tau\frac{a+b}{2}\right)^2-\left(\tau\frac{a-b}{2}\right)^2}\int_{-\infty}^{\infty}\mathrm{d}x e^{-\left(x+i\tau\left(\frac{a+b}{2}\right)\right)^2}\int_0^{\infty}\mathrm{d}y e^{-\left(y+i\tau\left(\frac{a-b}{2}\right)\right)^2}\\
&= \frac{2\tau}{\sqrt{\pi}}e^{-\frac{\tau^2(a^2+b^2)}{2}}\int_{-\infty}^{\infty}\mathrm{d}x' e^{-(x')^2}\int_{i\tau\left(\frac{a-b}{2}\right)}^{\infty}\mathrm{d}y' e^{-(y')^2}\\
&= \frac{2\tau}{\sqrt{\pi}}e^{-\frac{\tau^2(a^2+b^2)}{2}}\cdot\sqrt{\pi}\cdot\frac{\sqrt{\pi}}{2}\mathrm{erfc}\left(i\tau\left(\frac{a-b}{2}\right)\right)\\
&= \tau\sqrt{\pi}e^{-\frac{\tau^2(a^2+b^2)}{2}}\left[1-\mathrm{erf}\left(i\tau\left(\frac{a-b}{2}\right)\right)\right]
\end{aligned}
$$

$$
\begin{aligned}
&= \tau\sqrt{\pi}e^{-\frac{\tau^2(a^2+b^2)}{2}}\left[1 - i\,\mathrm{erfi}\left(\tau\left(\frac{a-b}{2}\right)\right)\right] && (\mathrm{erfi}(x) \equiv -i\,\mathrm{erf}(ix)) \\
&= \tau\sqrt{\pi}e^{-\frac{\tau^2(a^2+b^2)}{2}}\left[1 - \frac{2i}{\sqrt{\pi}}\,e^{\tau^2\left(\frac{a-b}{2}\right)^2} D\left(\tau\left(\frac{a-b}{2}\right)\right)\right] && (\text{Dawson function}) \\
&= \tau\sqrt{\pi}e^{-\frac{\tau^2(a^2+b^2)}{2}} - 2i\tau\, e^{-\tau^2\left(\frac{a+b}{2}\right)^2} D\left(\tau\left(\frac{a-b}{2}\right)\right)
\end{aligned}
$$

The first term is purely real and the second purely imaginary. The real part drops off exponentially with a and b individually. The imaginary part drops off exponentially with $a+b$, but only polynomially as $a-b$ (the Dawson function $D(x) \sim 1/x$ for $x \to \infty$).

We can proceed with the above for exact dynamics with a Gaussian pulse, but we won't be able to achive any significant analytical simplification. (I tried!) Instead, let us focus on getting to the generalized Fermi Golden rule. To do this, consider a wide enough Gaussian pulse such that $\tau\Delta\varepsilon \gg 1$ for the smallest relevant level spacing $\Delta\varepsilon$, but simultaneously a short enough pulse that it explores the interesting dynamics of the system i.e. shorter than the spin dynamics etc. that we hope to explore. This is the usual intermediate time-frame approximation employed in conventional Fermi Golden rule derivations as well. Note that we will handle degeneracies explicitly by treating the case of $\Delta\varepsilon = 0$ separately. (This will lead to some initially confusing notations like $\delta_{\varepsilon_1\varepsilon_2}\delta(\varepsilon_1 - \varepsilon' - \omega)$, where the Kronecker δ identifies degeneracies and the Dirac δ measures enforces energy conservation.)

Now let's write:

$$
\begin{aligned}
I_2(a,b) &= \tau\sqrt{\pi}e^{-\tau^2\left(\frac{a+b}{2}\right)^2} e^{-\tau^2\left(\frac{a-b}{2}\right)^2} - 2i\tau\, e^{-\tau^2\left(\frac{a+b}{2}\right)^2} D\left(\tau\left(\frac{a-b}{2}\right)\right) \\
&= \pi \cdot \frac{\tau}{\sqrt{\pi}} e^{-\tau^2\left(\frac{a+b}{2}\right)^2} \cdot \left[e^{-\tau^2\left(\frac{a-b}{2}\right)^2} - \frac{2i}{\sqrt{\pi}} D\left(\tau\left(\frac{a-b}{2}\right)\right)\right] \\
&\to \pi\delta\left(\frac{a+b}{2}\right)\left[\delta_{ab} - \frac{2i(1-\delta_{ab})}{\sqrt{\pi}\tau(a-b)}\right] && (\text{Dawson asymptotic form, as } \tau \to \infty) \\
&\to \pi\delta\left(\frac{a+b}{2}\right)\delta_{ab} && (\text{as } \tau \to \infty) \\
&= \pi\delta(a)\delta_{ab}
\end{aligned}
$$

Therefore, in the Fermi Golden rule regime, I_2 is non-zero only when $a = b$ (degeneracy / diagonal element of density matrix, as we will see below), and $a \sim 0$ (which will lead to energy conservation). If we want to restore the finite width Gaussian pulse approximately, we can set $\delta(a) \to g_\tau(a)$, a normalized Gaussian of width $1/\tau$ in frequency as defined above.

We have to be more careful about the first term, because we treated $a+b$ and $a-b$ differently (Kronecker vs Dirac delta), even though they were on the same footing before. Once we go back to $\rho^{(2)}$ where each a, b is of the form α, $\beta \pm \omega$, where α, β are differences between orbital energies. If we have $I_2(\alpha \pm \omega, \beta \pm \omega)$, the exact degeneracy can only be in the difference, and we should use the form above to get $\pi\delta(\alpha \pm \omega)\delta_{\alpha\beta}$. However, if we have $I_2(\alpha \pm \omega, \beta \mp \omega)$, then the exact degeneracy can only be in the sum (since ω is the continuous variable of interest), so that we should swap the roles of $a+b$ and $a-b$ in the derivation above to get the form $\pi\delta(\alpha \pm \omega)\delta_{\alpha,-\beta}$. Therefore:

$$
\begin{aligned}
I_1(\alpha,\beta) &= \sum_{s,s_1=\pm} I_2(\alpha + s_1\omega, \beta + s\omega) \\
&= \sum_{\pm} \left(I_2(\alpha \pm \omega, \beta \pm \omega) + I_2(\alpha \pm \omega, \beta \mp \omega)\right) \\
&\to \sum_{\pm} \left(\pi\delta(\alpha \pm \omega)\delta_{\alpha\beta} + \pi\delta(\alpha \pm \omega)\delta_{\alpha,-\beta}\right) && (\tau \to \infty) \\
&= \pi\delta(\alpha \pm \omega)(\delta_{\alpha\beta} + \delta_{\alpha,-\beta})
\end{aligned}
$$

Therefore, in the Fermi golden rule limit:

$$\begin{aligned}
\rho^{(2)}_{n'n} &= \sum_{ab}\sum_{s_1 s=\pm}\begin{pmatrix} -P^{s_1}_{n'a}P^{s}_{ab}\rho^{(0)}_{bn}I_2(\varepsilon_{n'}-\varepsilon_a+s_1\omega,\varepsilon_a-\varepsilon_b+s\omega) \\ +P^{s_1}_{n'a}\rho^{(0)}_{ab}P^{s}_{bn}I_2(\varepsilon_{n'}-\varepsilon_a+s_1\omega,\varepsilon_b-\varepsilon_n+s\omega)\end{pmatrix}+h.c. \\
&= \sum_{ab\pm}\begin{pmatrix} -P^{\pm}_{n'a}P^{\pm}_{ab}\rho^{(0)}_{bn}I_2(\varepsilon_{n'}-\varepsilon_a\pm\omega,\varepsilon_a-\varepsilon_b\pm\omega)-P^{\pm}_{n'a}P^{\mp}_{ab}\rho^{(0)}_{bn}I_2(\varepsilon_{n'}-\varepsilon_a\pm\omega,\varepsilon_a-\varepsilon_b\mp\omega) \\ +P^{\pm}_{n'a}\rho^{(0)}_{ab}P^{\pm}_{bn}I_2(\varepsilon_{n'}-\varepsilon_a\pm\omega,\varepsilon_b-\varepsilon_n\pm\omega)+P^{\pm}_{n'a}\rho^{(0)}_{ab}P^{\mp}_{bn}I_2(\varepsilon_{n'}-\varepsilon_a\pm\omega,\varepsilon_b-\varepsilon_n\mp\omega)\end{pmatrix}+h.c. \\
&\to \pi\sum_{ab\pm}\begin{pmatrix} -P^{\pm}_{n'a}P^{\pm}_{ab}\rho^{(0)}_{bn}\delta(\varepsilon_{n'}-\varepsilon_a\pm\omega)\delta_{\varepsilon_{n'}\varepsilon_a}\delta_{\varepsilon_a\varepsilon_b}-P^{\pm}_{n'a}P^{\mp}_{ab}\rho^{(0)}_{bn}\delta(\varepsilon_{n'}-\varepsilon_a\pm\omega)\delta_{\varepsilon_{n'}\varepsilon_b}\delta_{\varepsilon_a\varepsilon_a} \\ +P^{\pm}_{n'a}\rho^{(0)}_{ab}P^{\pm}_{bn}\delta(\varepsilon_{n'}-\varepsilon_a\pm\omega)\delta_{\varepsilon_{n'}\varepsilon_b}\delta_{\varepsilon_a\varepsilon_n}+P^{\pm}_{n'a}\rho^{(0)}_{ab}P^{\mp}_{bn}\delta(\varepsilon_{n'}-\varepsilon_a\pm\omega)\delta_{\varepsilon_{n'}\varepsilon_n}\delta_{\varepsilon_a\varepsilon_b}\end{pmatrix}+h.c. \\
&= \pi\sum_{ab\pm}\begin{pmatrix} -P^{\pm}_{n'a}P^{\mp}_{ab}\rho^{(0)}_{bn}\delta(\varepsilon_{n'}-\varepsilon_a\pm\omega)\delta_{\varepsilon_{n'}\varepsilon_b} \\ +P^{\pm}_{n'a}\rho^{(0)}_{ab}P^{\pm}_{bn}\delta(\varepsilon_{n'}-\varepsilon_a\pm\omega)\delta_{\varepsilon_{n'}\varepsilon_b}\delta_{\varepsilon_a\varepsilon_n} \\ +P^{\pm}_{n'a}\rho^{(0)}_{ab}P^{\mp}_{bn}\delta(\varepsilon_{n'}-\varepsilon_a\pm\omega)\delta_{\varepsilon_{n'}\varepsilon_n}\delta_{\varepsilon_a\varepsilon_b}\end{pmatrix}+h.c. \qquad (\text{Assuming}\,\omega\neq 0)
\end{aligned}$$

The above expression is valid for an arbitrary starting density matrix and arbitrary degeneracy structure. For simplicity, if we consider the non-degenerate case, for which $\delta_{\varepsilon_a\varepsilon_n}=\delta_{an}$ etc., starting from a pure initial state i with $\rho^{(0)}_{n'n}=\delta_{in}\delta_{in'}$:

$$\begin{aligned}
\rho^{(2)}_{n'n} &= \pi\sum_{ab\pm}\begin{pmatrix} -P^{\pm}_{n'a}P^{\mp}_{ab}\delta_{ib}\delta_{in}\delta(\varepsilon_{n'}-\varepsilon_a\pm\omega)\delta_{\varepsilon_{n'}\varepsilon_b} \\ +P^{\pm}_{n'a}\delta_{ia}\delta_{ib}P^{\pm}_{bn}\delta(\varepsilon_{n'}-\varepsilon_a\pm\omega)\delta_{\varepsilon_{n'}\varepsilon_b}\delta_{\varepsilon_a\varepsilon_n} \\ +P^{\pm}_{n'a}\delta_{ia}\delta_{ib}P^{\mp}_{bn}\delta(\varepsilon_{n'}-\varepsilon_a\pm\omega)\delta_{\varepsilon_{n'}\varepsilon_n}\delta_{\varepsilon_a\varepsilon_b}\end{pmatrix}+h.c. \\
&= \pi\sum_{\pm}\begin{pmatrix} -\delta_{in}\delta_{in'}\sum_a P^{\pm}_{ia}P^{\mp}_{ai}\delta(\varepsilon_i-\varepsilon_a\pm\omega) \\ +P^{\pm}_{n'i}P^{\pm}_{in}\delta(\varepsilon_{n'}-\varepsilon_i\pm\omega)\delta_{n'i}\delta_{ni} \\ +P^{\pm}_{n'i}P^{\mp}_{in}\delta(\varepsilon_{n'}-\varepsilon_i\pm\omega)\delta_{n'n}\end{pmatrix}+h.c \\
&= \pi\sum_{\pm}\left(P^{\pm}_{n'i}P^{\mp}_{in}\delta(\varepsilon_{n'}-\varepsilon_i\pm\omega)\delta_{n'n}-\sum_a P^{\pm}_{ia}P^{\mp}_{ai}\delta(\varepsilon_i-\varepsilon_a\pm\omega)\delta_{in}\delta_{in'}\right)+h.c \qquad (\omega\neq 0) \\
&= 2\pi\sum_{\pm}\left(\mathrm{Re}[P^{\pm}_{ni}P^{\mp}_{in}]\delta(\varepsilon_n-\varepsilon_i\pm\omega)\delta_{n'n}-\sum_a \mathrm{Re}[P^{\pm}_{ia}P^{\mp}_{ai}]\delta(\varepsilon_i-\varepsilon_a\pm\omega)\delta_{in}\delta_{in'}\right) \\
&= 2\pi\sum_{\pm}\left(|P^{\pm}_{ni}|^2\delta(\varepsilon_n-\varepsilon_i\pm\omega)\delta_{n'n}-\sum_a |P^{\pm}_{ia}|^2\delta(\varepsilon_i-\varepsilon_a\pm\omega)\delta_{in}\delta_{in'}\right) \\
&= 2\pi\sum_{\pm}\left(|P^{\pm}_{ni}|^2\delta(\varepsilon_n-\varepsilon_i\pm\omega)\delta_{n'n}-\sum_a |P^{\mp}_{ia}|^2\delta(\varepsilon_a-\varepsilon_i\pm\omega)\delta_{in}\delta_{in'}\right) \qquad (+\leftrightarrow-\,\text{in second term}) \\
&= 2\pi\sum_{\pm}\left(|P^{\pm}_{ni}|^2\delta(\varepsilon_n-\varepsilon_i\pm\omega)\delta_{n'n}-\sum_a |P^{\pm}_{ai}|^2\delta(\varepsilon_a-\varepsilon_i\pm\omega)\delta_{in}\delta_{in'}\right),
\end{aligned}$$

which is exactly Fermi's Golden rule. The first term is the increase of population for each final state n (on the diagonal $n=n'$), while the second term is the reduction in population of the initial state due to transitions to any final state. The previous expression is then the density matrix version of Fermi's Golden rule that fully accounts for degeneracies and relative phases within degenerate subspaces.

Many-electron systems and semiconductor simplifications

While we derived everything above for a one-electron system for conceptual simplicity, it is in fact completely general to many-electron systems if we interpret ε_n and $|n\rangle$ to denote eigen-energies and eigenstates of the many-body system instead. The only issue is that this formalism will be impractical in general due to the (exponentially) large number of states that will need to be tracked. Therefore, we need a practical approximate framework to deal with the dynamics.

Formally, we now need to work in a many body formalism where each state $|n\rangle = a^\dagger_{c_1}...a_{v_1}...|0\rangle$, which corresponds to a number of electrons (in conduction band orbitals labeled by $c_1, ...$) and holes (in valence orbitals labeled by $v_1, ...$) relative to the ground state $|0\rangle$ with a perfectly filled valence band and perfectly empty conduction band. Our first strategy is to only consider weak excitations such that the probability of double excitations is small. We therefore only need to work with ensembles of single electron-hole pair states. This limits the set of basis states to $|0\rangle$ and $|cv\rangle \equiv a^\dagger_c a_v|0\rangle$ for all c, v in the empty and occupied bands respectively. The corresponding eigen-energies are 0 and $\varepsilon_c - \varepsilon_v$ respectively. This is the seentially the space of 2-particle reduced density matrices (2DM).

However, this is still an unfeasibly large space to work in for the full dynamics, and also mostly unnecessary for describing the coherent/incoherent dynamics within each band which we are primarily interested in. Therefore, we will seek to switch from representations in terms of electron-hole pairs to separate single-particle pictures in the conduction and valence space. We will then spend most of our effort on 1-particle density matrices (1DM) each for electrons and holes. We would only need to consider both electrons and holes in describing the optical response for the pump and probe, and we would need ways to switch between the 1-DM and 2-DM pictures.

The key strategy to density matrix reduction (2DM $\rightarrow$ 1DM) is to trace out over the other sector. For instance, to get the electron (conduction) 1DM from the 2DM $\rho_{c'v',cv}$, we would perform:

$$\begin{aligned}
\rho^{(c)}_{c'c} &= \sum_{v'v} \rho_{c'v',cv} \\
\rho^{(c)}_{c'0} &= \sum_{v'} \rho_{c'v',0} \\
\rho^{(c)}_{0c} &= \sum_{v} \rho_{0,cv} \\
\rho^{(c)}_{00} &= \rho_{0,0}
\end{aligned}$$

where we must also account for the ground state (with no conduction or valence electrons) separately.

Pump response

The simplest treatment of optical response will involve directly solving, numerically or using the second-order perturbation theory result for Gaussian pulses, the 2DM dynamics of the system at each k point, and then reduce it to the electron and hole 1DMs. For this the momentum matrix elements in terms of the orbital ones will be:

$$\begin{aligned}
P_{c'v',cv} &= \langle 0|a^\dagger_{v'}a_{c'}\left(\sum_{n'n} P_{n'n}a^\dagger_{n'}a_n\right)a^\dagger_c a_v|0\rangle \\
&= \sum_{n'n} P_{n'n}\langle 0|a^\dagger_{v'}a_{c'}a^\dagger_{n'}a_n a^\dagger_c a_v|0\rangle \\
&= \sum_{n'n} P_{n'n}\langle 0|a^\dagger_{v'}(\delta_{c'n'} - a^\dagger_{n'}a_{c'})a_n a^\dagger_c a_v|0\rangle \\
&= \sum_{n} P_{c'n}\langle 0|a^\dagger_{v'}a_n a^\dagger_c a_v|0\rangle - \sum_{n'n} P_{n'n}\langle 0|a^\dagger_{v'}a^\dagger_{n'}a_{c'}a_n a^\dagger_c a_v|0\rangle \\
&= \sum_{n} P_{c'n}\langle 0|(\delta_{v'n} - a_n a^\dagger_{v'})a^\dagger_c a_v|0\rangle + \sum_{n'n} P_{n'n}\langle 0|a^\dagger_{v'}a^\dagger_{n'}a_n a_{c'}a^\dagger_c a_v|0\rangle \\
&= \sum_{n} P_{c'v'}\langle 0|a^\dagger_c a_v|0\rangle - \sum_{n} P_{c'n}\langle 0|a_n a^\dagger_{v'}a^\dagger_c a_v|0\rangle + \sum_{n'n} P_{n'n}\langle 0|a^\dagger_{v'}a^\dagger_{n'}a_n(\delta_{c'c} - a^\dagger_c a_{c'})a_v|0\rangle \\
&= 0 + \sum_{n} P_{c'n}\langle 0|a_n a^\dagger_c a^\dagger_{v'}a_v|0\rangle + \delta_{c'c}\sum_{n'n} P_{n'n}\langle 0|a^\dagger_{v'}a^\dagger_{n'}a_n a_v|0\rangle - \sum_{n'n} P_{n'n}\langle 0|a^\dagger_{v'}a^\dagger_{n'}a_n a^\dagger_c a_{c'}a_v|0\rangle \\
&\qquad\qquad \text{(first term zero because } a_c|0\rangle = 0) \\
&= \sum_{n} P_{c'n}\langle 0|a_n a^\dagger_c(\delta_{v'v} - a_v a^\dagger_{v'})|0\rangle - \delta_{c'c}\sum_{n'n} P_{n'n}\langle 0|a^\dagger_{n'}a^\dagger_{v'}a_n a_v|0\rangle + \sum_{n'n} P_{n'n}\langle 0|a^\dagger_{v'}a^\dagger_{n'}a_n a^\dagger_c a_v a_{c'}|0\rangle
\end{aligned}$$

$$
\begin{aligned}
&= \delta_{v'v}\sum_n P_{c'n}\langle 0|a_n a_c^\dagger|0\rangle - \sum_n P_{c'n}\langle 0|a_n a_c^\dagger a_v a_{v'}^\dagger|0\rangle - \delta_{c'c}\sum_{n'n} P_{n'n}\langle 0|a_{n'}^\dagger(\delta_{v'n} - a_n a_{v'}^\dagger)a_v|0\rangle + 0 \\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(last term zero because } a_{c'}|0\rangle = 0) \\
&= \delta_{v'v}\sum_n P_{c'n}\delta_{nc} - 0 - \delta_{c'c}\sum_{n'} P_{n'v'}\langle 0|a_{n'}^\dagger a_v|0\rangle + \delta_{c'c}\sum_{n'n} P_{n'n}\langle 0|a_{n'}^\dagger a_n a_{v'}^\dagger a_v|0\rangle \\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(second term zero because } a_{v'}^\dagger|0\rangle = 0) \\
&= \delta_{v'v}P_{c'c} - \delta_{c'c}\sum_{n'} P_{n'v'}\delta_{n'v} + \delta_{c'c}\sum_{n'n} P_{n'n}\langle 0|a_{n'}^\dagger a_n(\delta_{v'v} - a_v a_{v'}^\dagger)|0\rangle \\
&= \delta_{v'v}P_{c'c} - \delta_{c'c}P_{vv'} + \delta_{c'c}\delta_{v'v}\sum_{n'n} P_{n'n}\langle 0|a_{n'}^\dagger a_n|0\rangle - \delta_{c'c}\sum_{n'n} P_{n'n}\langle 0|a_{n'}^\dagger a_n a_v a_{v'}^\dagger|0\rangle \\
&= \delta_{v'v}P_{c'c} - \delta_{c'c}P_{vv'} + \delta_{c'c}\delta_{v'v}\langle 0|\hat{P}|0\rangle - 0 \qquad \text{(last term zero because } a_{v'}^\dagger|0\rangle = 0) \\
&= \delta_{v'v}P_{c'c} - \delta_{c'c}P_{vv'} + \delta_{c'c}\delta_{v'v}P_0 \qquad \text{(with } P_0 \equiv \langle 0|\hat{P}|0\rangle)
\end{aligned}
$$

$$
\begin{aligned}
P_{0,cv} &\equiv \langle 0|\Big(\sum_{n'n} P_{n'n}a_{n'}^\dagger a_n\Big)a_c^\dagger a_v|0\rangle \\
&= \sum_{n'n} P_{n'n}\langle 0|a_{n'}^\dagger(\delta_{nc} - a_c^\dagger a_n)a_v|0\rangle \\
&= \sum_{n'} P_{n'c}\langle 0|a_{n'}^\dagger a_v|0\rangle - \sum_{n'n} P_{n'n}\langle 0|a_{n'}^\dagger a_c^\dagger a_n a_v|0\rangle \\
&= \sum_{n'} P_{n'c}\delta_{n'v} + \sum_{n'n} P_{n'n}\langle 0|a_c^\dagger a_{n'}^\dagger a_n a_v|0\rangle \\
&= P_{vc} \qquad \text{(last term zero because } a_c|0\rangle = 0)
\end{aligned}
$$

$$
\begin{aligned}
P_{c'v',0} &= \langle 0|a_{v'}^\dagger a_{c'}\Big(\sum_{n'n} P_{n'n}a_{n'}^\dagger a_n\Big)|0\rangle \\
&= \sum_{n'n} P_{n'n}\langle 0|a_{v'}^\dagger(\delta_{n'c'} - a_{n'}^\dagger a_{c'})a_n|0\rangle \\
&= \sum_{n} P_{c'n}\langle 0|a_{v'}^\dagger a_n|0\rangle - \sum_{n'n} P_{n'n}\langle 0|a_{v'}^\dagger a_{n'}^\dagger a_{c'} a_n|0\rangle \\
&= \sum_{n} P_{c'n}\delta_{v'n} + \sum_{n'n} P_{n'n}\langle 0|a_{v'}^\dagger a_{n'}^\dagger a_n a_{c'}|0\rangle \\
&= P_{c'v'} \qquad \text{(last term zero because } a_{c'}|0\rangle = 0)
\end{aligned}
$$

$$
\begin{aligned}
P_{0,0} &\equiv \langle 0|\Big(\sum_{n'n} P_{n'n}a_{n'}^\dagger a_n\Big)|0\rangle \\
&= P_0
\end{aligned}
$$

Note that the constant contribution P_0 to all diagonal entries above will not contribute to the dynamics since $P_0\mathbb{1}$ commutes with ρ and hence drops out of the Liouville equation. We can therefore set $P_0 = 0$ from the beginning for convenience.

Next, consider the Fermi's Golden rule limit of the density matrix after optical excitation starting at the pure Fermi sea initial state $|0\rangle\langle 0|$ i.e. $\rho_{00}^{(0)} = 1$, $\rho_{0,cv}^{(0)} = 0$, $\rho_{c'v',0}^{(0)} = 0$ and $\rho_{c'v',cv} = 0$. With the shorthand indices n, a, b etc. referring to 0 or cv:

$$
\begin{aligned}
\rho_{n'n}^{(2)} &= \pi\sum_{\pm}\begin{pmatrix} -\sum_a P_{0a}^{\pm}P_{a0}^{\mp}\delta(\varepsilon_0 - \varepsilon_a \pm \omega)\delta_{n'0}\delta_{n0} \\ +P_{n'0}^{\pm}P_{0n}^{\pm}\delta(\varepsilon_{n'} - \varepsilon_0 \pm \omega)\delta_{n'0}\delta_{n0} \\ +P_{n'0}^{\pm}P_{0n}^{\mp}\delta(\varepsilon_{n'} - \varepsilon_0 \pm \omega)\delta_{n'n} \end{pmatrix} + h.c. \\
&= \pi\sum_{\pm}\left(P_{n'0}^{\pm}P_{0n}^{\mp}\delta(\varepsilon_{n'} - \varepsilon_0 \pm \omega)\delta_{\varepsilon_{n'}\varepsilon_n} - \sum_a P_{0a}^{\pm}P_{a0}^{\mp}\delta(\varepsilon_0 - \varepsilon_a \pm \omega)\delta_{n'0}\delta_{n0}\right) + h.c. \qquad \text{(Assuming } \omega \neq 0) \\
&= 2\pi\sum_{\pm}\left(P_{n'0}^{\pm}P_{0n}^{\mp}\delta(\varepsilon_{n'} - \varepsilon_0 \pm \omega)\delta_{\varepsilon_{n'}\varepsilon_n} - \sum_a |P_{0a}^{\pm}|^2\delta(\varepsilon_0 - \varepsilon_a \pm \omega)\delta_{n'0}\delta_{n0}\right)
\end{aligned}
$$

Substituting $a \to cv$ explicitly, and separating the diagonal and off-diagonal elements as above:

$$\begin{aligned}
\rho^{(2)}_{0,cv} &= 0 = \rho^{(2)}_{c'v',0} && \text{(none at second order, first order not considered in FG limit)} \\
\rho^{(2)}_{c'v',cv} &= 2\pi \sum_{\pm} P^{\pm}_{c'v',0} P^{\mp}_{0,cv} \delta((\varepsilon_c - \varepsilon_v) - 0 \pm \omega) \delta_{\varepsilon_{c'} - \varepsilon_{v'}, \varepsilon_c - \varepsilon_v} \\
&= 2\pi P^{-}_{c'v'} P^{+}_{vc} \delta(\varepsilon_c - \varepsilon_v - \omega) \delta_{\varepsilon_{c'} - \varepsilon_{v'}, \varepsilon_c - \varepsilon_v} \\
&= 2\pi P_{c'v'} P^{*}_{cv} \delta(\varepsilon_c - \varepsilon_v - \omega) \delta_{\varepsilon_{c'} - \varepsilon_{v'}, \varepsilon_c - \varepsilon_v} \\
\rho^{(2)}_{0,0} &= -2\pi \sum_{a\pm} |P_{0a}|^2 \delta(\varepsilon_0 - \varepsilon_a \pm \omega) \\
&= -\sum_{cv} \rho^{(2)}_{cv,cv} && \text{(also obvious by particle number conservation)}
\end{aligned}$$

We can then easily reduce to the 1-DMs for c and v separately as outlined above.

Finally, we can calculate the dielectric function based on the absorbed energy:

$$\begin{aligned}
\Delta E_{\text{abs}} &= \text{Tr}[H_0 \Delta\rho] \\
&= \sum_{cv} (\varepsilon_c - \varepsilon_v) \rho^{(2)}_{cv,cv} && \text{(general)} \\
&= 2\pi \sum_{cv} (\varepsilon_c - \varepsilon_v) |P_{cv}|^2 \delta(\varepsilon_c - \varepsilon_v - \omega) && \text{(FG limit)} \\
&= \frac{2\pi}{\hbar} \sum_{cv} (\varepsilon_c - \varepsilon_v) \left| \frac{e\vec{A}_0 \cdot \vec{p}_{cv}}{m_e} \right|^2 \delta(\varepsilon_c - \varepsilon_v - \hbar\omega) && \text{(Restoring } \hbar \text{ etc. by dim. analysis)} \\
\text{Im}\epsilon(\omega) &= C(\omega) \Delta E_{\text{abs}} && (C \text{ is some frequency dependent proportionality factor}) \\
&= \frac{4\pi^2 e^2}{m_e^2 \omega^2 \Omega} \sum_{cv} \delta(\varepsilon_c - \varepsilon_v - \hbar\omega) |\vec{\lambda} \cdot \vec{p}_{cv}|^2 && \text{(ACS Nano, dropping BZ average)} \\
&= \frac{4\pi^2}{\hbar\omega^3} \sum_{cv} (\varepsilon_c - \varepsilon_v) \left| \frac{e\vec{\lambda} \cdot \vec{p}_{cv}}{m_e} \right|^2 \delta(\varepsilon_c - \varepsilon_v - \hbar\omega) && \text{(Note } \lambda \text{ must be unit vector)} \\
\Rightarrow \quad C(\omega) &= \frac{2\pi}{\omega^3 \left|\vec{A}_0\right|^2} && \left(\text{Matching expressions, accounting for arbitrary } \left|\vec{A}_0\right|\right) \\
\Rightarrow \quad \text{Im}\epsilon(\omega) &= \frac{2\pi}{\omega^3 \left|\vec{A}_0\right|^2} \text{Tr}[H_0 \rho^{(2)}] && \text{(Since diagonal part of } \rho \text{ changes only at second order)}
\end{aligned}$$

Dimensions check: vector potentials typically have dimensions $[Vs\,/\,m]$ since $\vec{E} = \partial\vec{A}\,/\,\partial t$. However due to the pulse normalization above, A_0 has dimensions $[Vs^{3/2}\,/\,m]$ and therefore the denominator $\omega^3 \left|\vec{A}_0\right|^2$ has the dimensions of $[(V\,/\,m)^2]$. $\text{Tr}[H\rho]$ has the dimensions of energy, so that the final quantity has the dimenions of energy/electric-field-squared, which is correct for dielectric constant.

Probe response

We essentially need to do the same as above, but starting at a different density matrix, $\rho^{(0)} + \rho^{(2)}$ (using either the general FG expression or the full Gaussian pulse expression, but not the simplified one already assuming that we start at the Fermi sea). Let $\text{Im}\epsilon(\omega)[\rho^{(0)}]$ denote the dielectric function obtained using the final result of the previous section, by first evaluating the change in the density $\rho^{(2)}$ matrix and then calculating the

absorbed energy. Note that due to the linearity of the Liouville equation, $\rho^{(2)}$ is a linear functional of $\rho^{(0)}$, and hence $\mathrm{Im}\epsilon(\omega)[\rho^{(0)}]$ is a linear functional of $\rho^{(2)}$ and, in turn, $\rho^{(0)}$. Therefore, we can write:

$$\begin{aligned}\Delta\mathrm{Im}\epsilon(\omega) &= \mathrm{Im}\epsilon(\omega)[\rho^{(0)}+\rho^{(2)}]-\mathrm{Im}\epsilon(\omega)[\rho^{(0)}] \\ &= \mathrm{Im}\epsilon(\omega)[\rho^{(2)}],\end{aligned}$$

which means that we can calculate the *change in dielectric function* sensed by the probe, simply by following the prescription for $\mathrm{Im}\epsilon(\omega)$, but using the *change in density matrix* due to the pump as the initial ρ. (This is assuming we keep the 2-particle version i.e. the $0+cv$ basis, and not the reduced 1-DM bases, yet.)