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0.0.1 Deriving Higher Order Corrections

Now, lets say we have some initial state $|\psi_i(0)\rangle = |i\rangle$, and we want to transition it into some other state. We should have in the schroedinger picture $|\psi_i(t)\rangle = U(t,0)|i\rangle$ or, in the interaction picture

$$|\psi_i(t)\rangle = U_0(t, t_0)U_I(t, t_0)|i\rangle$$

Now, recall our $d_f(t) = e^{\frac{i}{\hbar}E_f t} \langle f|\psi_i(t)\rangle$, so we can write

$$d_f(t) = e^{\frac{i}{\hbar}E_f t} \langle f | \psi_i(t) \rangle$$
$$= e^{\frac{i}{\hbar}E_f t} \langle f | U_0(t, t_0)U_I(t, t_0)) | i \rangle$$
$$= \langle f | U_i(t, t_0) | i \rangle$$

This gives us a formula for d_f .

$$d_f(t) = \delta_{fi} - \frac{i}{\hbar} \int_{t_0}^t \langle f | V_I(t_1) | i \rangle dt_1$$

and, if we want to go to second order,

$$d_f(t) = \delta_{fi} - \frac{i}{\hbar} \int_{t_0}^t \left\langle f | V_I(t_1) | i \right\rangle dt_1 - \frac{1}{\hbar^2} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \left\langle f | V_I(t_1) V_I(t_2) | i \right\rangle$$

in the second term, we're going to insert a unit matrix, resolution of identity, so that we have

$$d_{f}(t) = \delta_{fi} - \frac{i}{\hbar} \int_{t_{0}}^{t} \langle f | V_{I}(t_{1}) | i \rangle dt_{1} - \frac{1}{\hbar^{2}} \int_{t_{0}}^{t} dt_{1} \int_{t_{0}}^{t_{1}} dt_{2} \sum_{m} \langle f | V_{I}(t_{1}) | m \rangle \langle m | V_{I}(t_{2}) | i \rangle$$

if we now insert the form for V_I we derived earlier, we should have, letting $V_{fi}(t) = \langle f | V | i \rangle$,

$$d_f(t) = \delta_{fi} - \frac{i}{\hbar} \int_{t_0}^t dt_1 e^{i\omega_{fi}t_1} V_{fi} - \sum_m \frac{1}{\hbar^2} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 e^{i\omega_{fm}t_1} e^{i\omega_{mi}t_2} V_{fm}(t_1) V_{mi}(t_2)$$

This is really hinting at the path integral formulation of quantum mechancis, but we're gonna yeet that now.

0.1 Ex: Harmonic Perturbation

Consider our perturbation to be $V(t) = \hat{V}e^{-i\omega t + \varepsilon t}$ If we assume that $\langle f|\hat{V}|i\rangle = 0$, we can immediately compute that

$$d_{f}^{(2)} = -\frac{1}{\hbar^{2}} \sum_{m} \left\langle f \right| \hat{V} \left| m \right\rangle \left\langle m \right| \hat{V} \left| i \right\rangle \int_{-\infty}^{t} dt_{1} \int_{-\infty}^{t_{1}} dt_{2} e^{i(\omega_{fm} - \omega - i\varepsilon)t_{1}} e^{i(\omega_{mi} - \omega - i\varepsilon)t_{2}}$$

This is kind of a nasty integral, but we can get it by taking

$$d_{f}^{(2)} = \frac{1}{\hbar} e^{i(\omega_{fi} - 2\omega)} \frac{e^{2\varepsilon t}}{\omega_{fi} - 2\omega - 2i\varepsilon} \sum_{m} \frac{\left\langle f \mid V \mid m \right\rangle \left\langle m \mid V \mid i \right\rangle}{\omega_{mi} - \omega - i\varepsilon}$$

Then, we want the transition rate, which we find by taking the time derivative of the modulus as $\varepsilon \to 0$, which gives

$$\lim_{\varepsilon \to 0} W_{fi} = \lim_{\varepsilon \to 0} \frac{\mathrm{d}}{\mathrm{d}t} |d_f^{(2)}|^2 = \frac{2\pi}{\hbar^4} \left| \sum_m \frac{V_{fm} V_{mi}}{\omega_{mi} - \omega - i\varepsilon} \right|^2 \delta(\omega_{fi} - 2\omega)$$

where the δ appears since there is a lorenzian term in there. It's not super necessary to keep the ε in the denominator of the sum, but he's about to explain why we did.

$$W_{fi} = \frac{2\pi}{\hbar^4} \left| \sum_{m} \frac{V_{fm} V_{mi}}{\omega_{mi} - \omega} \right|^2 \delta(\omega_{fi} - 2\omega)$$

Basically, just watch out for resonances. Our interpretation of the intermediate terms should be in terms of paths,

