We start with the following

$$\langle \psi^{00} | \hat{H}^{00} | \psi^{00} \rangle = E^{00}$$

$$\Rightarrow \hat{H}^{00} | \psi^{00} \rangle = E^{00} | \psi^{00} \rangle$$

We now express the perturbation series

$$\hat{H} = \hat{H}^{00} + \hat{H}^{10}\lambda_1 + \hat{H}^{01}\lambda_2 + \hat{H}^{11}\lambda_1\lambda_2 + \dots$$

$$E = E^{00} + E^{10}\lambda_1 + E^{01}\lambda_2 + E^{11}\lambda_1\lambda_2 + \dots$$

$$\psi = \psi^{00} + \psi^{10}\lambda_1 + \psi^{01}\lambda_2 + \psi^{11}\lambda_1\lambda_2 + \dots$$

If we're looking for E^{11}, then

$$E^{11} = \frac{\partial E}{\partial \lambda_1 \partial \lambda_2}$$

The new Schrödinger equation is:

$$(\hat{H}^{00} + \hat{H}^{10}\lambda_1 + \hat{H}^{01}\lambda_2 \; \hat{H}^{11}\lambda_1\lambda_2)(\psi^{00} + \psi^{10}\lambda_1 + \psi^{01}\lambda_2 + \psi^{11}\lambda_1\lambda_2) =$$

$$(E^{00} + E^{10}\lambda_1 + E^{01}\lambda_2 + E^{11}\lambda_1\lambda_2)(\psi^{00} + \psi^{10}\lambda_1 + \psi^{01}\lambda_2 + \psi^{11}\lambda_1\lambda_2)$$

Collect like terms in $\lambda_1\lambda_2$

$$\hat{H}^{00}\psi^{11}\lambda_1\lambda_2 + \hat{H}^{10}\psi^{01}\lambda_1\lambda_2 + \hat{H}^{01}\psi^{10}\lambda_1\lambda_2 + \hat{H}^{11}\psi^{00}\lambda_1\lambda_2 =$$

$$E^{00}\psi^{11}\lambda_1\lambda_2 + E^{10}\psi^{01}\lambda_1\lambda_2 + E^{01}\psi^{10}\lambda_1\lambda_2 + E^{11}\psi^{00}\lambda_1\lambda_2$$

Left multipy & integrate with ψ^{00}

$$\lambda_1\lambda_2 \left(\langle \psi^{00} | \hat{H}^{00} | \psi^{11} \rangle + \langle \psi^{00} | \hat{H}^{10} | \psi^{01} \rangle + \langle \psi^{00} | \hat{H}^{01} | \psi^{10} \rangle + \langle \psi^{00} | \hat{H}^{11} | \psi^{00} \rangle \right)$$

$$\lambda_1\lambda_2\left(\langle\Psi^{00}|\hat{H}^{00}|\Psi^{11}\rangle + \langle\Psi^{00}|\hat{H}^{10}|\Psi^{01}\rangle + \langle\Psi^{00}|\hat{H}^{01}|\Psi^{10}\rangle + \langle\Psi^{00}|\hat{H}^{11}|\Psi^{00}\rangle\right)$$

$$= \lambda_1\lambda_2\left(E^{00}\langle\Psi^{00}|\Psi^{11}\rangle + E^{10}\langle\Psi^{00}|\Psi^{01}\rangle + E^{01}\langle\Psi^{00}|\Psi^{10}\rangle + E^{11}\langle\Psi^{00}|\Psi^{00}\rangle\right)$$

Intermediate normalization gives us...

$$E^{11} = \langle\Psi^{00}|\hat{H}^{10}|\Psi^{01}\rangle + \langle\Psi^{00}|\hat{H}^{01}|\Psi^{10}\rangle + \langle\Psi^{00}|\hat{H}^{11}|\Psi^{00}\rangle$$

Dalgarno's Interchange theorem gives us

$$E^{11} = \langle\Psi^{00}|\hat{H}^{11}|\Psi^{00}\rangle + 2\langle\Psi^{00}|\hat{H}^{10}|\Psi^{01}\rangle$$

for real systems

$$= \langle\Psi^{00}|\hat{H}^{11}|\Psi^{00}\rangle + \langle\Psi^{00}|\hat{H}^{10}|\Psi^{01}\rangle + \langle\Psi^{01}|\hat{H}^{10}|\Psi^{00}\rangle$$

more generally

We now remember our Time-Dependent Schrödinger equation

$$\hat{H}\Psi_0(t) = i\frac{\partial\Psi_0(t)}{\partial t}$$

If we now consider a time-dependent WF and TD perturbation in terms of a SINGLE perturbation, and we assume a seperable $\hat{H}^{(1)}$:

$$\hat{H}^{(1)} = \hat{A}(r)F(t)$$

$\psi^{(0)} \Rightarrow \psi^{(0)}(t)$

$$(\hat{H}^{(0)} + \lambda \hat{H}^{(1)})(\psi^{0}(t) + \lambda \psi^{(1)}(t)) = i \frac{\partial(\psi^{(0)} + \lambda\psi^{(1)}(t))}{\partial t}$$

Collect like terms

$$\lambda \hat{H}^{(0)} \psi^{(1)}(t) + \lambda \hat{H}^{(1)} \psi^{(0)}(t) = i\lambda \frac{\partial \psi^{(1)}(t)}{\partial t}$$

$$\hat{H}^{(0)} \psi^{(1)}(t) + \hat{H}^{(1)} \psi^{(0)}(t) = i \frac{\partial \psi^{(1)}(t)}{\partial t}$$

We now choose to expand $\psi^{(1)}(t)$ in terms of solutions to $\hat{H}^{(0)}\psi^{(0)}(t)$

$$\text{So } \psi_0^{(1)}(t) = \sum_{j \neq 0} C_j(t) \psi_j^{(0)}(t)$$

We also remember that for a time-independent operator:

$$\psi_0(t) = \psi_0 e^{-iE_0 t}$$

$$\text{So...} \quad \frac{\partial \psi^{(1)}(t)}{\partial t} = \frac{\partial \sum_j C_j \psi_j^{(0)}(t)}{\partial t}$$

$$= \sum_{j \neq 0} \left(\frac{\partial C_j}{\partial t} \psi_j^{(0)}(t) + C_j \frac{\partial \psi_j^{(0)}(t)}{\partial t} \right)$$

Note that $\frac{\partial \psi_j^{(0)}(t)}{\partial t} = -i \hat{H}^{0} \psi_j^{(0)}(t)$

$$i\frac{\partial\Psi^{(1)}}{\partial t}(t) = \sum_j \left(iC_j'\Psi_j^{(0)}(t) + C_j\hat{H}^{(0)}\Psi_j^{(0)}(t)\right)$$

$$= \hat{H}^{(0)}\Psi^{(1)}(t) + \hat{H}^{(1)}\Psi_0^{(0)}(t)$$

$$= \hat{H}^{(0)}\sum_j C_j\Psi_j^{(0)}(t) + \hat{H}^{(1)}\Psi_0^{(0)}(t)$$

So $\hat{H}^{(1)}\Psi_0^{(0)}(t) = \sum_j iC_j'\Psi_j^{(0)}(t)$

$\rightarrow$ Left multiply by $\Psi_j^{(0)}(t)$ and integrate

$$\langle\Psi_j^{(0)}(t)|\hat{H}^{(1)}|\Psi_0^{(0)}(t)\rangle = iC_j'$$

$$C_j' = -i\langle\Psi_j^{(0)}(t)|\hat{H}^{(1)}|\Psi_0^{(0)}(t)\rangle$$

$$= -i\langle\Psi_j^{(0)}(t)|\hat{A}F(t)|\Psi_0^{(0)}(t)\rangle$$

We also remember that $\Psi_0^{(0)}(t)$ and $\Psi_j^{(0)}(t)$ are solutions to the time-independent Hamiltonian $\hat{H}^{(0)}$, so $\Psi_0^{(0)}(t) = \Psi_0^{(0)}e^{-iE_0t}$ and $\Psi_j^{(0)}(t) = \Psi_j^{(0)}e^{-iE_jt}$, so

$$\langle\Psi_j^{(0)}(t)| = e^{iE_jt}\langle\Psi_j^{(0)}|$$

So $C_j' = -i\langle\Psi_j^{(0)}|\hat{A}|\Psi_0^{(0)}\rangle F(t)e^{i(E_j-E_0)t}$

and thus

$$dC_j(t) = -i\langle\Psi_j^{(0)}|\hat{A}|\Psi_0^{(0)}\rangle F(t)e^{i\Delta Et}\,dt$$

To evaluate C_j at time t, we can

choose to integrate from $-\infty$ rather than 0 to make the math easier in the future. Thus...

$$C_j(t) = -i\int_{-\infty}^{t} \langle\psi_j^{(0)}|\hat{A}|\psi_0^{(0)}\rangle F(t')\, e^{i\Delta E t'}\, dt'$$

We can now evaluate

$$\langle\psi_0^{(0,1)}|\hat{H}^{(1,0)}|\psi_0^{00}\rangle + \langle\psi_0^{00}|\hat{A}^{(1,0)}|\psi_0^{(0,1)}\rangle$$

$$= \sum_j -i\int_{-\infty}^{t}\left[\langle\psi_j|\hat{A}|\psi_0\rangle F(t')\, e^{i\Delta E t'}\, dt'\right]\langle\psi_j(t)|\hat{B}|\psi_0^{00}(t)\rangle$$

$$+ \sum_j \langle\psi_0^{00}(t)|\hat{B}|\psi_j(t)\rangle(-i)\int_{-\infty}^{t}\left[\langle\psi_j|\hat{A}|\psi_0\rangle F(t')\, e^{i\Delta E t'}\, dt'\right.$$

Limiting to the 1st term for now

$$-i\sum\int_{-\infty}^{t}\langle\psi_j|\hat{A}|\psi_0\rangle F(t')\, e^{i\Delta E t'}\, dt' \;\langle\psi_j|\hat{B}|\psi_0\rangle e^{-i\Delta E t}$$

$$= -i\sum\int_{-\infty}^{t} dt'\, F(t')\langle\psi_j|\hat{A}|\psi_0\rangle\langle\psi_j|\hat{B}|\psi_0\rangle\, e^{-i\Delta E(t-t')}$$

$$= -i\sum\int_{-\infty}^{\infty} dt'\, \Theta(t-t')\, F(t')\langle\psi_j|\hat{A}|\psi_0\rangle\langle\psi_j|\hat{B}|\psi_0\rangle\, e^{-i\Delta E(t-t')}$$

Θ here is the heavyside step function with $\Theta(x) = 0$ for $x < 0$, and 1 for $x > 0$

We now have the following

identities:

$$\mathcal{F}[\Theta(t-t')e^{-a(t-t')}] = \left(\frac{1}{a-i\omega}\right)$$

We also have the convolution theorem:

$$(f*g)(t) = \int_{-\infty}^{\infty} f(t')g(t-t')$$

and $\mathcal{F}[(f*g)(t)] = \mathcal{F}[f(t)]\,\mathcal{F}[g(t)]$

$$g(t) = \Theta(t)e^{-i\Delta E t}$$

$$\mathcal{F}[g(t)] = \frac{1}{i\Delta E - i\omega}$$

We now give a generic form to $F(t)$ and say $F(t) = e^{i\omega' t}$

$$\mathcal{F}[F(t)] = \int_{-\infty}^{\infty} e^{i\omega t} e^{i\omega' t} dt = \delta(\omega-\omega')$$

So the first term becomes

$$-i\sum_j \frac{\langle\psi_j|\hat{A}|\psi_0\rangle\langle\psi_0|\hat{B}|\psi_j\rangle}{i\Delta E - i\omega}$$

$$= \sum_j \frac{\langle A\rangle\langle B\rangle}{\omega - \Delta E}$$

In the same way, the 2^{nd} term can be shown to be

$$-\sum \langle A\rangle\langle B\rangle$$

$$j \qquad \omega + \Delta E$$

$$E'' = \sum_j \left[\frac{\langle \psi_0 | \hat{B} | \psi_j \rangle \langle \psi_j | \hat{A} | \psi_0 \rangle}{\omega - \Delta E} - \frac{\langle \psi_0 | \hat{B} | \psi_j \rangle \langle \psi_j | \hat{A} | \psi_0 \rangle}{\omega + \Delta E} \right]$$