$$E_q^{(2)} = \sum_{k \neq q} \frac{\left| < \psi_k^{(0)} \mid \hat{H}^{(1)} \mid \phi_q^{(0)} > \right|^2}{E_q^{(0)} - E_k^{(0)}}$$

k is **not** part of the degenerate set

$$\therefore E_1^{(2)} = \frac{\left| H_{31}^{(1)} \right|^2}{E_1^{(0)} - E_3^{(0)}} = \frac{\left| < \psi_3^{(0)} \mid \hat{H}^{(1)} \mid \frac{1}{\sqrt{2}} \left(\psi_1^{(0)} + \psi_2^{(0)} \right) > \right|^2}{20 - 30}$$

$$= \frac{\left| \frac{1}{\sqrt{2}} H_{31}^{(1)} + \frac{1}{\sqrt{2}} H_{32}^{(1)} \right|^2}{-10} = \frac{\left| 0 + \frac{2}{\sqrt{2}} \right|^2}{-10} = -\frac{2}{10} = -\frac{1}{5} = -0.2$$

$$\therefore E_2^{(2)} = \frac{\left| H_{32}^{(1)} \right|^2}{E_2^{(0)} - E_3^{(0)}} = \frac{\left| < \psi_3^{(0)} \mid \hat{H}^{(1)} \mid \frac{1}{\sqrt{2}} \left(\psi_1^{(0)} - \psi_2^{(0)} \right) > \right|^2}{20 - 30}$$

$$= \frac{\left| \frac{1}{\sqrt{2}} H_{31}^{(1)} - \frac{1}{\sqrt{2}} H_{32}^{(1)} \right|^2}{-10} = \frac{\left| 0 - \frac{2}{\sqrt{2}} \right|^2}{-10} = -\frac{2}{10} = -\frac{1}{5} = -0.2$$

$$\therefore E_3^{(2)} = \frac{\left|H_{13}^{(1)}\right|^2}{E_3^{(0)} - E_1^{(0)}} + \frac{\left|H_{23}^{(1)}\right|^2}{E_3^{(0)} - E_2^{(0)}} = \frac{\left| < \frac{1}{\sqrt{2}}\left(\psi_1^{(0)} + \psi_2^{(0)}\right) | \hat{H}^{(1)} | \psi_3^{(0)} > \right|^2}{30-20} + \frac{\left| < \frac{1}{\sqrt{2}}\left(\psi_1^{(0)} - \psi_2^{(0)}\right) | \hat{H}^{(1)} | \psi_3^{(0)} > \right|^2}{30-20}$$

$$= \frac{\left|\frac{1}{\sqrt{2}} H_{13}^{(1)} + \frac{1}{\sqrt{2}} H_{23}^{(1)}\right|^2}{10} + \frac{\left|\frac{1}{\sqrt{2}} H_{13}^{(1)} - \frac{1}{\sqrt{2}} H_{23}^{(1)}\right|^2}{10} = \frac{\left|\frac{2}{\sqrt{2}}\right|^2}{10} + \frac{\left|-\frac{2}{\sqrt{2}}\right|^2}{10} = \frac{4}{10} = 0.4$$

Summary:

$$E_1 = E_1^{(0)} + E_1^{(1)} + E_1^{(2)} = 20 + 1 - 0.2 = 20.8$$

$$E_2 = E_2^{(0)} + E_2^{(1)} + E_2^{(2)} = 20 - 1 - 0.2 = 18.8$$

$$E_3 = E_3^{(0)} + E_3^{(1)} + E_3^{(2)} = 30 + 0 + 0.4 = 30.4$$

2.5. Time-dependent Perturbation Theory

a) General Observations

Can take unperturbed problem and make a static perturbation

$$\hat{H} \rightarrow \hat{H}^{(0)} + \hat{H}^{(1)}$$

which can be solved by diagonalizing the perturbation Hamiltonian

Now consider a time-dependent perturbation:

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

$\mathbf{H}^{(0)}$ could in fact include a static perturbation term. Regardless, it is given that:

$$\hat{H}^{(0)}\phi_k = E_k^{(0)}\phi_k$$

and Φ_k is the "perturbed" or unperturbed **stationary state**.

Earlier we argued that the state could be characterized by an expansion of the form:

$$\Omega(\vec{r},t) = \sum_{i=1}^{\infty} a_i(t)\phi_i$$

which must satisfy

$$\hat{H}(t)\Omega(\vec{r},t) = -\frac{\hbar}{i}\frac{\partial\Omega(\vec{r},t)}{\partial t}$$

Goal: to find a(t) since |a(t)|^2 is the transition probability.

b) Set up the problem

Have: $$\hat{H}(t)\Omega(\vec{r},t) = -\frac{\hbar}{i}\frac{\partial\Omega(\vec{r},t)}{\partial t} \qquad (a)$$

with $$\hat{H}(t) = \hat{H}^{(0)} + \hat{H}^{(1)}(t) \qquad (b)$$

$$\hat{H}^{(0)}\phi_k = E_k\phi_k \qquad (c)$$

$$\Omega(\vec{r},t) = \sum_{k=1}^{\infty} a_k(t)\phi(\vec{r},t) \qquad (d)$$

$$\phi(\vec{r},t) = \psi_k(\vec{r})e^{-\frac{iE_k t}{\hbar}} \qquad (e)$$

To solve this we substitute expansion into time-dependent Schrodinger Equation and solve for selected initial conditions.

Reasonable choices: at t = 0 all molecules are in a particular state j.
i.e. $a_k(o) = \delta_{kj}$; that is, $a_j(0) = 1$; $a_{k \neq j}(0) = 0$.

This makes sense for electronic transitions or vibrational transitions where the Boltzmann Distributions:

Excited state population → N_e

Ground state population → N_g

$$\frac{N_e}{N_g} \approx e^{-\frac{(E_e - E_g)}{kT}}$$

$\sim 10^{-16} - 10^{-160} \sim 0$

Therefore, $N_g >> N_e$

(**Note:** not necessarily true for rotational energy levels at room temperature).

c) Exact Solution

Derivation ahead

Preamble: dot convention for time derivatives:

$$\frac{\partial f}{\partial t} = \dot{f};\ \frac{\partial^2 f}{\partial t^2} = \ddot{f};\ \frac{\partial^3 f}{\partial t^3} = \dddot{f};\ etc.$$

Therefore we can write the time dependent Schrodinger wave equation as:

$$\hat{H}(t)\Omega(\vec{r},t) = -\frac{\hbar}{i}\dot{\Omega}(\vec{r},t)$$

$$\Rightarrow \left(\hat{H}^{(0)} + \hat{H}^{(1)}(t)\right)\left[\sum_{k=1}^{\infty} a_k(t)\phi(\vec{r},t)\right] = -\frac{\hbar}{i}\frac{\partial\left[\sum_{k=1}^{\infty} a_k(t)\phi(\vec{r},t)\right]}{\partial t}$$

$$\Rightarrow \sum_{k=1}^{\infty} a_k(t)\hat{H}^{(0)}\phi_k + \sum_{k=1}^{\infty} a_k(t)\hat{H}^{(1)}(t)\phi_k = -\frac{\hbar}{i}\sum_{k=1}^{\infty}\frac{\partial\left[a_k(t)\psi_k e^{-\frac{iE_k^{(0)}t}{\hbar}}\right]}{\partial t}$$