$$V(x) = \frac{1}{2} k x^2$$

$$E_n = h\nu\left(\frac{1}{2} + n\right)$$

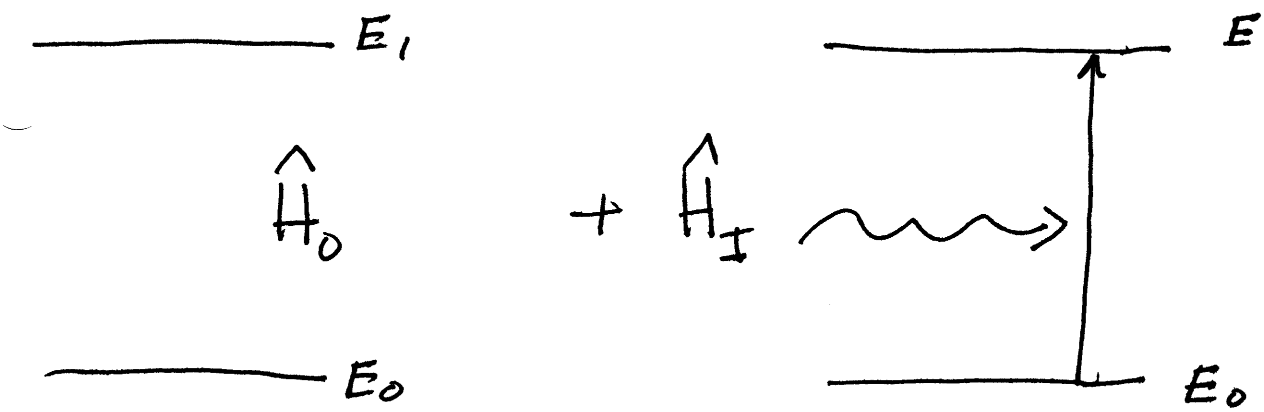
MORSE POTENTIAL

$$V_M(x) = D_e \left[1 - e^{-\alpha(x - x_e)}\right]^2$$

$$E_n = h\nu\left(\frac{1}{2} + n\right)\left[1 - \frac{h\nu}{4D_e}\left(\frac{1}{2} + n\right)\right]$$

$$\alpha = \sqrt{\frac{k}{D_e}}$$

$$k = \left.\frac{d^2 V_M}{dx^2}\right|_{x = x_e}$$



FIRST

$$\hat{H}_0 \phi_i = E_i \phi_i$$

$$\hat{H}_0 \left(\phi_i e^{-\frac{i}{\hbar} E_i t} \right) = i\hbar \frac{\partial}{\partial t} \left(\phi_i e^{-\frac{i}{\hbar} E_i t} \right)$$

ADD THE INTERACTION $\hat{H}_I(x,t)$

$$\hat{H} = \hat{H}_0(x) + \hat{H}_I(x,t)$$

$$\hat{H} \Phi(x,t) = i\hbar \frac{\partial}{\partial t} \Phi(x,t)$$

$$\Phi(x,t) = a_0(t)\, \phi_0(x)\, e^{-\frac{i}{\hbar} E_0 t} + a_1(t)\, \phi_1(x)\, e^{-\frac{i}{\hbar} E_1 t}$$

WITH IC

$$a_0(0) = 1$$

$$a_1(0) = 0$$

$$\cancel{a_0 (\hat{H}_0 \phi_0) e^{-\frac{i}{\hbar}E_0 t}} + \cancel{a_1 (\hat{H}_0 \phi_1) e^{-\frac{i}{\hbar}E_1 t}} +$$

$$a_0 (\hat{H}_I \phi_0) e^{-\frac{i}{\hbar}E_0 t} + a_1 (\hat{H}_I \phi_1) e^{-\frac{i}{\hbar}E_1 t} =$$

$$\cancel{a_0 \phi_0 \left(i\hbar \frac{\partial}{\partial t} e^{-\frac{i}{\hbar}E_0 t} \right)} + \cancel{a_1 \phi_1 \left(i\hbar \frac{\partial}{\partial t} e^{-\frac{i}{\hbar}E_1 t} \right)} +$$

$$i\hbar \left(\frac{da_0}{dt} \right) \phi_0 e^{-\frac{i}{\hbar}E_0 t} + i\hbar \left(\frac{da_1}{dt} \right) \phi_1 e^{-\frac{i}{\hbar}E_1 t}$$

$\times \phi_0$ AND INTEGRATE

$$\langle i | \hat{H}_I | j \rangle \equiv \int_\Omega \phi_i^*(x) \left(\hat{H}_I(x,t) \phi_j(x) \right) dx$$

$$a_0 \langle 0 | \hat{H}_I | 0 \rangle e^{-\frac{i}{\hbar}E_0 t} + a_1 \langle 0 | \hat{H}_I | 1 \rangle e^{-\frac{i}{\hbar}E_1 t} =$$

$$i\hbar \left(\frac{da_0}{dt} \right) \overbrace{\langle 0 | 0 \rangle}^{=1} e^{-\frac{i}{\hbar}E_0 t} + i\hbar \left(\frac{da_1}{dt} \right) \cancelto{0}{\langle 0 | 1 \rangle} e^{-\frac{i}{\hbar}E_1 t}$$

$$\boxed{i\hbar \frac{da_0}{dt} = \langle 0 | \hat{H}_I | 0 \rangle a_0 + e^{-\frac{i}{\hbar}(E_1 - E_0)t} \langle 0 | \hat{H}_I | 1 \rangle a_1}$$

$$\boxed{i\hbar \frac{da_1}{dt} = \langle 1 | \hat{H}_I | 0 \rangle e^{\frac{i}{\hbar}(E_1 - E_0)t} a_0 + \langle 1 | \hat{H}_I | 1 \rangle a_2}$$

Assuming that the interaction promotes A transition (3)

$$\langle i | \hat{H}_I(t) | i \rangle = 0,$$

THEREFORE WE GET

$$i\hbar \frac{da_0}{dt} = \langle 0 | \hat{H}_I(t) | 1 \rangle a_1(t) e^{-\frac{i}{\hbar}(E_1 - E_0)t}$$

$$i\hbar \frac{da_1}{dt} = \langle 1 | \hat{H}_I(t) | 0 \rangle a_0(t) e^{\frac{i}{\hbar}(E_1 - E_0)t}.$$

We now consider the following interaction

$$\hat{H}_I(t) = g\,\underline{\mu} \cdot \underline{E}(t) = g\,\underline{\mu} \cdot |E_0|\,\hat{\imath}\,\cos(\omega t)$$

WHERE $\underline{\mu}$ IS THE DIPOLE MOMENT

$$\underline{\mu} \simeq q\,\underline{r} = q(\hat{\imath}x + \hat{\jmath}y + \hat{k}z)$$

IN THIS CASE THE INTERACTION HAMILTONIAN REDUCES TO

$$\hat{H}_I(t) = g\,q\,x\,|E_0|\cos(\omega t)$$

$$\hat{H}_I(t) = h(x)\cdot\cos(\omega t) = h\,f_\omega(t).$$

WITH THIS DEFINITIONS WE GET FOR THE λ_i ~~OR~~ COEFFICIENTS

$$\boxed{\begin{aligned} i\hbar \frac{da_0}{dt} &= h_{01}\, f_w(t)\, e^{-i\omega_{10} t}\, a_1(t) \\ i\hbar \frac{da_1}{dt} &= h_{10}\, f_w(t)\, e^{i\omega_{10} t}\, a_0(t) \end{aligned}}$$

$\hbar\omega = h\nu$

$= \frac{h}{2\pi}\frac{2\pi}{T}$

$\frac{\Delta E}{\hbar} = \frac{E_1 - E_0}{\hbar} \equiv \omega_{10}$

NOW WE INTEGRATE EQ. ( )

$$a_0(t) = 1 + \frac{h_{01}}{i\hbar}\int_0^t f_w(s)\, e^{-i\omega_{10} s}\, a_1(s)\, ds$$

WHICH WE CAN USE IN EQ. ( )

$$a_1(t) = \frac{h_{10}}{i\hbar}\int_0^t f_w(s')\, e^{+i\omega_{10} s'}\, a_0(s')\, ds'$$

OR

$$a_1(t) = \frac{h_{10}}{i\hbar}\int_0^t f_w(s)\, e^{i\omega_{10} s}\, ds \; +$$

$h(s, \omega, \omega_{10}) \equiv f_w(s)\, e^{i\omega_{10} s}$

$$+ \frac{|h_{01}|^2}{(i\hbar)^2}\int_0^t f_w(s')\, e^{i\omega_{10} s'}\int_0^{s'} f_w(s)\, e^{-i\omega_{10} s}\, a_1(s)\, ds\, ds'$$

$$h_{01} \equiv \langle 0 | h(t) | 1 \rangle$$

$$\frac{E_1 - E_0}{\hbar} = \omega_{10}$$

$$h\nu = \frac{h}{2\pi} 2\pi\nu = \frac{h}{2\pi} \frac{2\pi}{T} = \hbar\omega$$

$$\int_0^t \frac{da_0}{dt} dt \quad \frac{h_{01}}{i\hbar} \int_0^t f_w(t') e^{-i\omega_{10}t'} a_1(t') \, dt'$$

$$a_0(t) - a_0(0) = \left(\frac{h_{01}}{i\hbar}\right) \int_0^t f_w(s) e^{-i\omega_{10}s} a_1(s) \, ds$$

$$h_{01} h_{10} = |h_{01}|^2$$

DEF

$$G_{10}(t_f, t_i, w) \equiv \int_{t_i}^{t_f} f_w(s') e^{i\omega_{10}s'} ds' \equiv \int_{t_i}^{t_f} g_{10}(w, s') ds'$$

$$a_1(t) = \frac{h_{10}}{i\hbar} G_{10}(t, 0, w)$$
$$+ \frac{|h_{10}|^2}{(i\hbar)^2} \int_0^t G_{10}(t, s, w) f_w(s) e^{-i\omega_{10}s} a_1(s)\, ds$$

FIRST APPROXIMATION $a_0(t) \simeq 1$

AND $a_1(t) \simeq 0$

$$\Rightarrow a_1(t) \simeq \frac{h_{10}}{i\hbar}\, G_{10}(t,0;\omega)$$

THEREFORE THE OCCUPATION PROBABILITY OF THE EXCITED STATE IS GIVEN BY

$$P_1^{(1)}(t,\omega) = \frac{|h_{10}|^2}{\hbar^2}\, |G_{10}(t,0;\omega)|^2$$

WITH

$$G_{10}(t,0;\omega) = \int_0^t f_\omega(s)\, e^{i\omega_{10} s}\, ds$$

WHERE

$$f_\omega(s) = \frac{1}{2}\left[e^{i\omega s} + e^{-i\omega s}\right] = \cos(\omega s)$$

$$G_{10}(t,0;\omega) = \frac{1}{2i}\left[\frac{e^{i(\omega+\omega_{10})t} - 1}{\omega+\omega_{10}} + \frac{e^{i(\omega-\omega_{10})t} - 1}{\omega-\omega_{10}}\right]$$