Time-dependent perturbation theory

used for spectroscopic transition

change in a molecules or atoms energy:

$$\Delta E = h\nu = \hbar\omega$$

$$H = H^0 + H'(t)$$

time dependent perturbation

e.g. $H'(t) = -\mu_z \, E\cos\omega t$

electric dipole of molecule

$$H\Psi = i\hbar \frac{\partial\Psi}{\partial t}$$

first order: $\Psi_0'(t) = \sum_n c_n(t)\Psi_n(t) =$

$$= \sum_n c_n(t)\Psi_n^0 e^{-iE_n^0 t/\hbar}$$

with $c_n(t) = \frac{1}{i\hbar}\int_0^t H'_{n0}(t) e^{i\omega_{n0}t} dt$

equals time independent perturbation for a very slow perturbation:

$$H'(t) = H'(1-e^{-t/\tau}) \qquad \tau \gg 1$$

$$c_n(t) = \frac{1}{i\hbar} H'_{n0}\int_0^t (1-e^{-t/\tau}) e^{i\omega_{n0}t} dt = \frac{1}{i\hbar} H'_{n0}\left\{ \frac{e^{i\omega_{n0}t}-1}{i\omega_{n0}} - \frac{e^{(i\omega_{n0}-1/\tau)t}-1}{i\omega_{n0}-1/\tau} \right.$$

$\tau \gg \frac{1}{\omega_{n0}}$, $t \gg \tau$

$$\Rightarrow c_n(t) = -\frac{H'_{n0}}{\underbrace{\hbar\omega_{n0}}_{=E_n^0-E_0^0}} e^{i\omega_{n0}t} = \frac{H_{n0}^0}{E_n^0 - E_0^0} e^{iE_n^0 t/\hbar} e^{-iE_0^0 t/\hbar}$$

equal time independent

rate of change of population of the state f due to transitions from state i

$$w_{f\leftarrow i} = \frac{d|c_f|^2}{dt} = c_f \frac{dc_f^*}{dt} + c_f^* \frac{dc_f}{dt}$$

$$w_{f\leftarrow i} \sim |H'_{fi}|^2$$

interaction of the electromagnetic field with the molecule:

$$\boxed{\begin{array}{l} w_{f\leftarrow i} \sim |\mu_{z,fi}|^2 \mathcal{E}^2 \\ \text{with } \mu_{z,fi} = \int \psi_f^* \mu_z \psi_i \, d\tau \\ \qquad\qquad \text{transition dipole moment} \end{array}}$$

exercises:

12.3

problems:

12.8, 12.10, 12.3, 12.26, 12.28

7. Atomic Spectra

- focus on electronic structure
- hydrogenic atom: one-electron atom or ion of general atomic number Z
  e.g. H, He^+, Li^{2+}

$\leftrightarrow$ many-electron atom

Spectra of hydrogenic atoms:

$$\Delta E = h\nu$$

$$\tilde{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{with } R_H = 109677 \frac{1}{cm}$$

Rydberg constant

Lyman series $n_1 = 1$

Balmer series $n_1 = 2$

Paschen series $n_1 = 3$

Explanation – the H-atom:

$$H = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$\Rightarrow$ Internal motion ~~for the~~ of the electron relative to the nucleus:

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

with $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_n}$ reduced mass

$\mu \simeq m_e$ since $m_e \ll m_n$

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

$$\Rightarrow \boxed{\psi(r,\theta,\phi) = \underbrace{R(r)}_{\text{radial}}\ \underbrace{Y(\theta,\phi)}_{\text{angular}}}$$

$$\Rightarrow \quad \Lambda^2 Y = -l(l+1)Y$$

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right) + V_{eff}\,R = ER$$

with $V_{eff} = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$

Coulomb interaction — attractive; centrifugal forces — repulsive

$$\boxed{E_n = -\frac{Z^2\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2} \qquad n = 1, 2}$$ bound state

$E > 0 \Rightarrow$ unbound states

ionization energy $= -hcR_H$

$$= \frac{Z^2\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2} = E_1$$

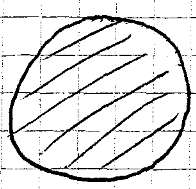
angular solutions $Y_{l,m_l}(\theta,\phi)$:

l: angular momentum quantum number l

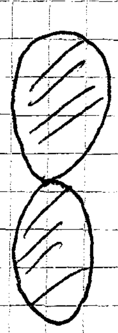
m_l: magnetic quantum number m_l

$Y_{l,m}(\theta, \phi)$: spherical harmonics

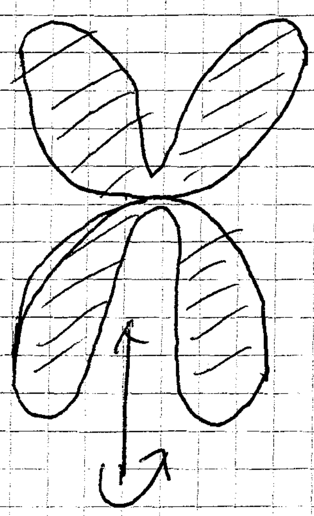
$l=0,\ m_l=0$: $\quad Y_{l,m} = \sqrt{\frac{1}{4\pi}}$



$l=1,\ m_l=\pm 0$: $\quad Y_{l,m} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$



$l=2,\ m_l=\pm 1$:



radial solution $R_{n,l}(r)$:

$$R_{n,l}(r) = N_{n,l} \left(\frac{\rho}{n}\right)^l L_{n,l}(\rho)\, e^{-\rho/2n}$$

associated Laguerre polynomial

with $\rho = \frac{2Zr}{a_0}$ $\quad a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2} = 52.9177$ pm

Bohr radius

Orbital

1s $(n=1 \;\; l=0)$ $\quad R_{n,l} = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$

2s $(n=2 \;\; l=0)$ $\quad R_{n,l} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{1}{2}\rho\right) e^{-\rho/4}$

2p $(n=2 \;\; l=1)$ $\quad R_{n,l} = \frac{1}{4\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \rho\, e^{-\rho/4}$

quantum number $n \Rightarrow$ energy E_n $\quad n = 1, 2, 3$

quantum number $l \Rightarrow$ |angular momentum|
$= \sqrt{l(l+1)}\,\hbar \quad l = 0, 1, 2, \ldots n-1$

quantum number $m_l \Rightarrow$ z-component of angular momentum $= m_l \hbar$

$m_l = 0, \pm 1, \pm 2, \ldots \pm l$