TIME-DEPENDENT PERTURBATION THEORY [SEC. 2]

If we can write:

$$\hat{H}(\underline{r},t) = H_0(\underline{r}) + \lambda V(\underline{r},t) \qquad (2.1)$$

λ is small

If the Hamiltonian is the sum of a stationary part ($\hat{H}_0$) and a small time-dependent perturbation, $\lambda V(\underline{r},t)$, then we can seek analytical solutions.

Assume we know the solutions of $\hat{H}_0$:

$$\hat{H}_0 \psi_n^{(0)}(\underline{r}) = E_n^{(0)} \psi_n^{(0)}(\underline{r}) \qquad (2.2)$$

unperturbed e'functions and eigenvalues

For the unperturbed case, the general solution of the TDSE:

$$\hat{H}_0 \Psi(\underline{r},t) = i\hbar \frac{\partial \Psi(\underline{r},t)}{\partial t} \qquad (2.3)$$

(as seen in Sec 1.2) reduces to the time-indep. conservative form:

$$\Psi(\underline{r},t) = \sum_n C_n^{(0)} \psi_n^{(0)} e^{-iE_n^{(0)}t/\hbar} \qquad (2.4)$$

the unperturbed prob amplitudes $C_n^{(0)} = \langle \psi_n^{(0)} | \Psi(\underline{r}, t=0) \rangle$

are constant in time.

[2.1] DIRAC'S METHOD OF VARIATION OF CONSTANTS.

If $\lambda V(\underline{r},t) \neq 0$, the energy is not conserved

NB unperturbed case is <u>conservative</u> since $\langle E \rangle = \langle \hat{H}_o \rangle$

$$\langle \Psi(t) H_o \Psi(t) \rangle = \sum_n |C_n^{(0)}|^2 E_n .$$

$\langle E \rangle$ is independent of time.

But even with the perturbation, we express the new solutions in terms of the unpert. functions $\psi_n^{(0)}(\underline{r})$, but now:

$$\Psi(\underline{r},t) = \sum_n C_n(t) \psi_n^{(0)} e^{-iE_n^{(0)}t/\hbar} \qquad (2.5)$$

... we allow the coefficients to vary with time.

We still need normalisation so $\sum_n |C_n(t)|^2 = 1$ (2.6)

From orthonormality of $\psi_n^{(0)}(\underline{r})$

$$\langle \psi_n^{(0)} | \Psi(\underline{r},t) \rangle = C_n(t) e^{-iE_n^0 t/\hbar} \qquad (2.7)$$

To calculate the $C_n(t)$, substitute eq (2.5) into the T.D.S.E ($i\hbar \partial\Psi/\partial t = H\Psi$) to obtain:

$$i\hbar \sum_n \dot{C}_n \psi_n^o e^{-iE_n^0 t/\hbar} + \sum_n C_n(t) \psi_n^{(0)} E_n^{(0)} e^{-iE_n^0 t/\hbar}$$

$$= \sum_n (H_o + \lambda V) C_n(t) \psi_n^o e^{-iE_n^o t/\hbar} \qquad (2.8)$$

but, $H_o \psi_n^{(0)} = E_n^o \psi_n^{(0)}$.

So the 2nd and 3rd terms cancel, giving:

$$i\hbar \sum \dot{c}_n \psi_n^{(0)} e^{-iE_n^0 t/\hbar} = \lambda \sum_n V(r,t)\, c_n\, \psi_n^0\, e^{-iE_n^0 t/\hbar}$$

(2.9)

Take the scalar product of (2.9) (both sides) with $\langle \psi_k^0 |$ i.e. $\psi_k^{0*}(r)$ to obtain:

$$i\hbar\, \dot{c}_k\, e^{-iE_k^0 t/\hbar} = \lambda \sum_n V_{kn}(t)\, c_n(t)\, e^{-iE_n^0 t/\hbar}$$

(2.10)

since $\langle \psi_k^0 | \psi_n^0 \rangle = \delta_{kn}$.

$$V_{kn}(t) = \langle \psi_k^0\ V(r,t)\ \psi_n^0 \rangle \qquad (2.11)$$

is 'THE MATRIX ELEMENT OF THE PERTURBATION'.

Hence,

$$\frac{dc_k(t)}{dt} = \frac{\lambda}{i\hbar} \sum_n V_{kn}(t)\, e^{i\omega_{kn} t}\, c_n(t)$$

(2.12a)

$\omega_{kn} = (E_k^0 - E_n^0)/\hbar \equiv$ the BOHR ANGULAR FREQUENCY.

(2.12) represents a set of coupled linear differential equations! We can write it in compact matrix form:

$$\dot{\vec{C}} = 1/i\hbar\ \mathbb{V}\ \vec{C} \qquad (2.12b)$$

$$\begin{bmatrix}\dot C_1\\ \dot C_2\\ \vdots\\ \dot C_N\end{bmatrix} = \begin{bmatrix} V_{11} & V_{12}(t)e^{i\omega_{12}t} & V_{13}(t)e^{i\omega_{13}t} & \cdots \\ V_{21}e^{-i\omega_{12}t} & V_{22} & & \\ V_{31}e^{-i\omega_{13}t} & & V_{33} & \\ & & & V_{NN}\end{bmatrix} \cdot \begin{bmatrix}C_1\\ C_2\\ \vdots\\ C_N\end{bmatrix}$$

These equations can be solved numerically, without further assumption.

Perturbation theory means the further assumption that λ is small.

[2.2] PERTURBATION EXPANSION

Assume perturbation is weak and expand the coefficients C_n in powers of λ:

$$C_n = C_n^0 + \lambda C_n^{(1)} + \lambda^2 C_n^{(2)} \ldots = \sum_{j=0}^{\infty} \lambda^j C_n^{(j)} \qquad (2.13)$$

Subs into (2.12):

$$\sum_j \lambda^j \dot{C}_k^{(j)} = \frac{\lambda}{i\hbar} \sum_n V_{kn}(t) e^{i\omega_{kn}t} \sum_j \lambda^j C_n^{(j)} \qquad (2.14)$$

Equate powers of λ:

λ^0 (0-th ORDER) $\quad \dot{C}_k^{(0)} = 0$ (0-th order is time-indep.) 2.15(a)

λ^1 (1st ORDER) $\quad \dot{C}_k^{(1)} = \frac{1}{i\hbar} \sum_n V_{kn} e^{i\omega_{kn}t} C_n^0$ 2.15(b)

λ^2 (2nd ORDER $\quad \dot{C}_k^{(2)} = \frac{1}{i\hbar} \sum_n V_{kn} e^{i\omega_{kn}t} C_n^{(1)}$ 2.15(c)

In principle, we can integrate successively to any order.

1ST ORDER PERTURBATION CORRECTION.

Assume that initially (at $t=t_0$) the system is in a particular unperturbed state $\psi_i^{(0)}$

Then $\quad c_k^{(0)} = \delta_{ki} \quad$ or $\quad \delta(k-i)$

DISCRETE $\qquad$ CONTINUOUS.

Hence, in (2.15 b) we have:

$$\dot{c}_k^{(1)} = 1/i\hbar \, V_{ki} \, e^{i\omega_{ki}t}$$

Hence, we have a correction to the initial state $k=i$,

$$C_i^{(1)}(t) = 1/i\hbar \int_{t_0}^{t} V_{ii}(t')\,dt' \qquad (2.16)$$

and a transfer of amplitude into other eigenstates $i \neq k$

$$C_k^{(1)}(t) = 1/i\hbar \int_{t_0}^{t} V_{ki}(t')\, e^{i\omega_{ki}t'}\,dt' \qquad (2.17)$$

The constant of integration is chosen so that:

$$C_k^{(1)}(t) = \delta_{ki} \quad \text{at} \quad t = t_0$$

TO 1ST ORDER:

$$C_k = \delta_{ki} + \lambda\, C_k^{(1)} \qquad (2.18)$$

There has been a transfer of population to other eigenstates. The probability of finding the system, initially in state i, to now be in state $k \neq i$ is

$$P_{ki}^{(1)}(t) = |C_k(t)|^2 = |\lambda C_k^{(1)}|^2$$

$$= \frac{1}{\hbar^2} \left| \int_{t_0}^{t} \lambda V_{ki} e^{i\omega_{ki}t'} dt' \right|^2 \qquad (2.19)$$

While the change to the initial state i, in the perturbative regime is:

$$C_i(t) \simeq 1 + \lambda C_i^{(1)} \simeq \underbrace{1 + \frac{\lambda}{i\hbar} \int_{t_0}^{t} V_{ii}(t') dt'}$$

if we can approximate this by

$$\simeq \exp - \frac{i}{\hbar} \int_{t_0}^{t} \lambda V_{ii}(t') dt' \qquad (2.20)$$

then $|C_i(t)|^2 \simeq 1$ and the main effect of the perturbation is to change the phase of the initial quantum state.

2ND ORDER AMPLITUDES

Sometimes we need to go to higher order, eg 1) if 1st-order correction vanishes b) if λ not small enough, so $C_n = C_n^{(0)} + \lambda C_n^{(1)} + \lambda^2 C_n^{(2)} \ldots$ falls off slowly with increase in order.)

We go back to 2.15(c)

$$\dot{C}_k^{(2)} = \frac{1}{i\hbar} \sum_n V_{kn}(t) e^{i\omega_{kn} t} C_n^{(1)}(t)$$

where, $$C_n^{(1)}(t) = \frac{1}{i\hbar} \int_{t_0}^{t} V_{ni}(t') e^{i\omega_{ni} t'} dt'$$ where $C_n^{(0)} = \delta_{ni}$

$$C_k^{(2)}(t) = \frac{1}{i\hbar} \int_{t_0}^{t} \sum_n V_{kn}(t'') e^{i\omega_{kn} t''} C_n^{(1)}(t'')\, dt''$$

now subs. the $C_n^{(1)}(t'')$

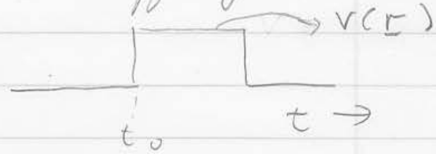
$$= \frac{1}{i\hbar} \int_{t_0}^{t} \sum_n V_{kn}(t'') e^{i\omega_{kn} t''} \frac{1}{i\hbar} \int_{t_0}^{t''} V_{ni}(t') e^{i\omega_{ni} t'} dt'\, dt''$$

$$= -\frac{1}{\hbar^2} \int_{t_0}^{t} dt'' \int_{t_0}^{t''} dt' \sum_n V_{kn}(t'') V_{ni}(t') e^{i\omega_{kn} t''} e^{i\omega_{ni} t'} \qquad (2.21)$$

So, even if matrix element $V_{ki} = 0$ (no direct coupling from initial to final state) we can go $i \to k$ via intermediate states n

[2.3] A CONSTANT PERTURBATION

A simple example is given by a perturbation $V(\underline{r})$ which is switched on at $t = t_0$ and off again at t but is constant in between



For convenience, choose $t_0 = 0$ and $\lambda = 1$ so

$$\hat{H} = \begin{cases} H_0 & t' < 0 \\ H_0 + V(\underline{r}) & 0 < t' < t \\ H_0 & t' > t \end{cases}$$

If our system is in state $\psi_i^{\circ}(\underline{r})$ at $t' < 0$, at a later time $t' > t$ (ie after switch-off) the amplitude for state k is

$$C_k^{(1)} = \frac{1}{i\hbar} \int_0^t V_{ki}\, e^{i\omega_{ki} t'}\, dt' \qquad k \neq i \qquad (2.22)$$

$V_{ki} = \int \psi_k^*(\underline{r})\, V(\underline{r})\, \psi_i(\underline{r})\, d\underline{r}$ is just a number...

$$\text{so} \quad C_{ki}^{(1)} = \frac{V_{ki}}{i\hbar} \int_0^t e^{i\omega_{ki} t'}\, dt'$$

$$= \frac{V_{ki}}{\hbar\omega_{ki}} \left[1 - e^{i\omega_{ki} t} \right] \qquad (2.23)$$

The corresponding probability, to 1st order

$$P_{ki}^{(1)}(t) = \left| C_k^{(1)}(t) \right|^2.$$

$$= \frac{1}{\hbar^2} |V_{ki}|^2 \frac{(1-e^{i\omega_{ki}t})(1-e^{-i\omega_{ki}t})}{\omega_{ki}^2}$$

$$P_k = \frac{4}{\hbar^2} |V_{ki}|^2 \frac{\sin^2 \omega_{ki} t/2}{\omega_{ki}^2} \qquad (2.24)$$

$$i \neq k$$

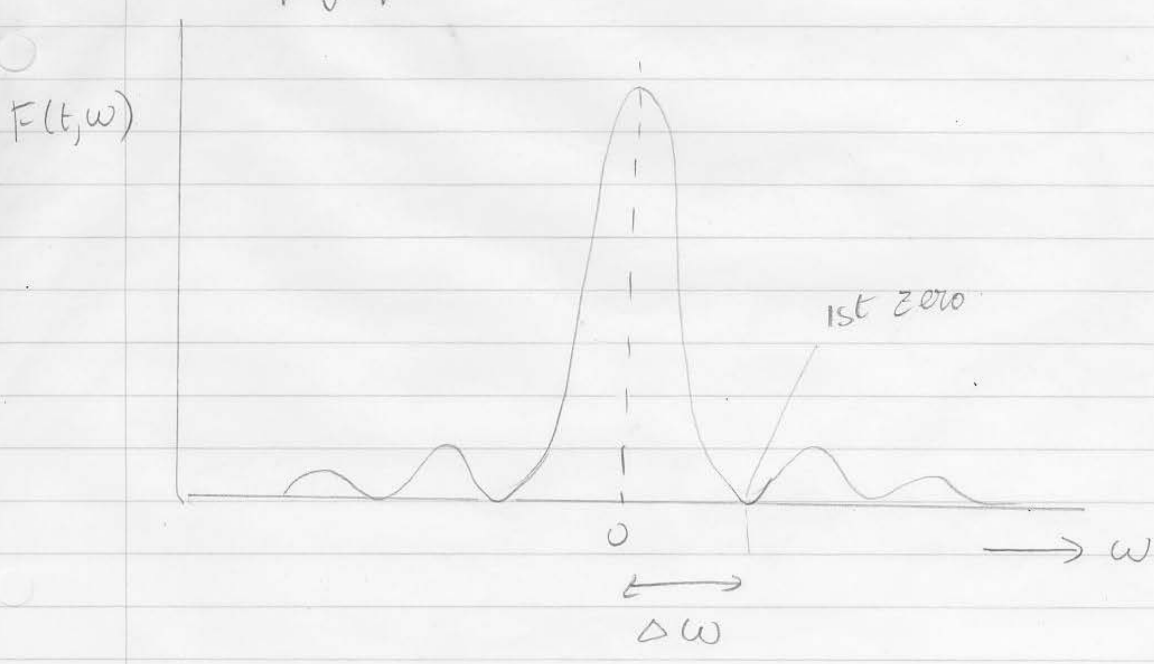
so,
we write

$$P_{ik}^{(1)}(t) = \frac{2}{\hbar^2} |V_{ki}|^2 F(t, \omega_{ki}) \qquad (2.25)$$

the function $F(t,\omega) = 2 \dfrac{\sin^2 \omega t/2}{\omega^2}$

$$F(t,\omega) = t^2/2 \frac{\sin^2 \omega t/2}{(\omega t/2)^2} = t^2/2 \left(\operatorname{sinc} \frac{\omega t}{2}\right)^2 \qquad (2.26)$$

F is sharply peaked about $\omega = 0$



1) width of central peak $\Delta \omega = 2\pi/t$ (1st zero of $\sin \omega t$)

2) height of the peak $= t^2/2$

3) with increasing time, peak gets taller and thinner.

in fact, $\lim_{t \to \infty} F(t,\omega) = \pi t \, \delta(\omega)$ (see I.4)

(2.27)

So, for short times (short lived perturbation), P_{ik} the probability, allows almost any energy jump.

For long times, jumps with $\omega_{ik} = E_i - E_k = 0$ are increasingly favoured.

This is a version of the energy-time uncertainty relation

$t \equiv \Delta t \rightarrow$ length of perturbation

$$\Delta \omega = 2\pi/t = \frac{2\pi}{\Delta t} \qquad \Delta E = \hbar \Delta \omega = \frac{2\pi \hbar}{\Delta t}$$

$$\text{so, } \Rightarrow \Delta E \Delta t \gtrsim h$$

(2.28)

From eq (2.25), the probability at time t

$$P_{ik}^{(1)}(t) = \frac{2}{\hbar^2} |V_{ki}|^2 \underbrace{F(t, \omega_{ki})}_{\pi t \, \delta(\omega_{ki})}$$

Now, $\delta(\omega_{ki}) = \hbar \, \delta(E_i - E_k)$

(From the property of the Dirac delta function

$$\delta(ax) = \frac{1}{|a|} \delta(x) \qquad \text{(eq I.4d)}$$

and $\hbar \omega_{ik} = E_i - E_k$)

So

$$P_{ik}^{(1)}(t) = \frac{2\pi t}{\hbar} |V_{ki}|^2 \delta(E_k - E_i) \qquad (2.29)$$

We can define a transition probability per unit time, a transition rate

$$\Gamma = \frac{2\pi}{\hbar} |V_{ki}|^2 \delta(E_k - E_i) \qquad (2.30)$$

'Fermi's golden rule'.