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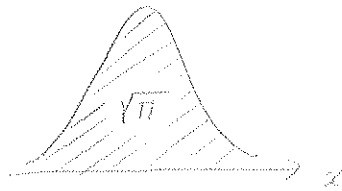
① Gaussian function —— extremely useful!

$$\int_{-\infty}^{+\infty} e^{-x^2}\,dx = \sqrt{\pi}$$



Proof

$$\int_{-\infty}^{+\infty} e^{-x^2}dx \cdot \int_{-\infty}^{+\infty} e^{-y^2}dy = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-\overbrace{(x^2+y^2)}^{r^2}}\,dx\,dy$$

Cartesian to radial, polar

$$= \int_{0}^{+\infty} e^{-r^2}\, 2\pi r\, dr$$

$$= \left[-\pi\, e^{-r^2}\right]_0^{\infty} = \pi$$

$$\int_{-\infty}^{+\infty} e^{-ax^2}dx = \int_{-\infty}^{+\infty} e^{-(\sqrt{a}\,x)^2}\frac{1}{\sqrt{a}}\,d(\sqrt{a}\,x) = \sqrt{\frac{\pi}{a}}$$

$$\left(\frac{1}{r} = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{+\infty} e^{-r^2u^2}du\right)$$

Gaussian expansion of Coulomb
S. F. Boys

$$\int_{-\infty}^{+\infty} e^{-ax^2+bx} = \int_{-\infty}^{+\infty} e^{-a\left(x-\frac{b}{2a}\right)^2+\frac{b^2}{4a}}\,dx$$

$$= \underbrace{\int_{-\infty}^{+\infty} e^{-a\left(x-\frac{b}{2a}\right)^2}dx}_{\sqrt{\frac{\pi}{a}}} \cdot e^{\frac{b^2}{4a}} = \sqrt{\frac{\pi}{a}}\; e^{\frac{b^2}{4a}}$$

$$\boxed{\int_{-\infty}^{+\infty} e^{-ax^2+ibx}\,dx = \sqrt{\frac{\pi}{a}}\; e^{-\frac{b^2}{4a}}}$$

Fourier transform of a Gaussian is a Gaussian

Normalized Gaussians $\quad \frac{1}{\sqrt{\pi}}\, e^{-x^2}$

$$\sqrt{\frac{a}{\pi}}\; e^{-ax^2}$$

② Fourier transform, delta function

$$\underbrace{F(t)}_{\text{time domain}} = \int_{-\infty}^{+\infty} \underbrace{f(\omega)}_{\text{freq domain}} e^{i\omega t}\, d\omega$$

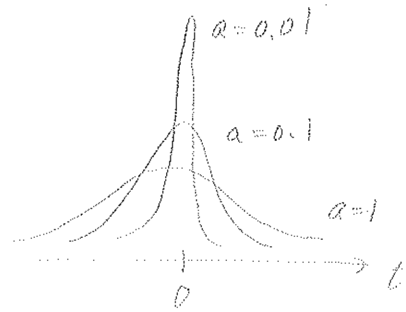
$$f(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F(t)\, e^{-i\omega t}\, dt$$

Substitute $f(\omega) = 1$ (no info about ω or energy)

$$F(t) = \int_{-\infty}^{+\infty} 1 \cdot e^{i\omega t}\, d\omega = \lim_{a\to 0} \int_{-\infty}^{+\infty} \underbrace{e^{-ax^2}}_{=1,\ \text{if } a=0} \cdot e^{i\omega t}\, d\omega$$

$$= \lim_{a\to 0} \sqrt{\frac{\pi}{a}}\, e^{-\frac{t^2}{4a}}$$

$$\boxed{\int_{-\infty}^{+\infty} e^{i\omega t}\, d\omega = 2\pi\delta(t)} \qquad = \lim_{a\to 0} 2\pi \underbrace{\sqrt{\frac{1}{4\pi a}}\, e^{-\frac{t^2}{4a}}}_{\text{normalized Gaussian}}$$



constant $\overset{FT}{\longleftrightarrow}$ delta

E-T uncertainty

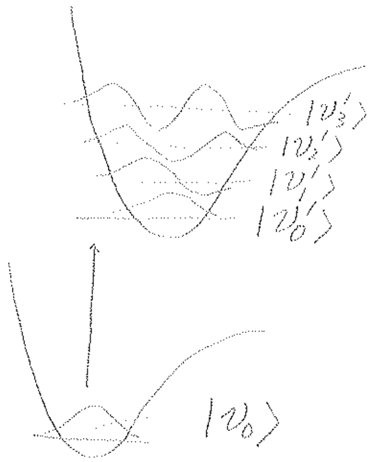
$$= 2\pi\,\delta(t) \quad \text{(time of event completely known)}$$

Reverse

$$f(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} 2\pi\delta(t)\, e^{-i\omega t}\, dt = \frac{1}{2\pi} 2\pi = 1$$

remove $\int$ and $t \leftarrow 0$

③ Correlation function and spectra



Immediately after the transition

$$|w(0)\rangle = \sum_n |v_n'\rangle\, a_n$$

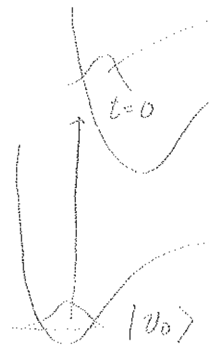
which is why FC factors are $|\langle v_n'|v_0\rangle|^2$

$$= \sum_n |v_n'\rangle \underbrace{\langle v_n'|v_0\rangle}_{=\,a_n}$$

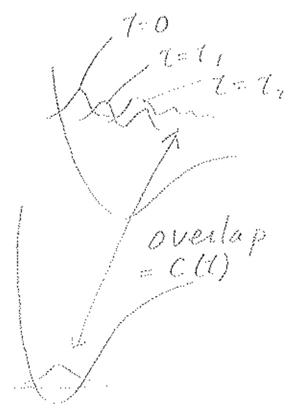
$\sum_n |v_n'\rangle\langle v_n'|$ → resolution of the identity

$$= |v_0\rangle$$

same shape, location as $|v_0\rangle$ but on a different surface!



$$|w(t)\rangle = \sum_n |v_n'\rangle \underbrace{e^{-iE_n't}}_{\text{hidden time dependence}} \langle v_n'|v_0\rangle$$



wave packet $|w\rangle$ changes its shape and location w/ time because $|v_0\rangle$ or $|w\rangle$ is not the s/n of time-independent SE for this PES

Correlation function

$$C(t) = \langle w(0)|w(t)\rangle$$

$$= \langle v_0| \left\{ \sum_n |v_n'\rangle e^{-iE_n't} \langle v_n'|v_0\rangle \right\}$$

$$= \sum_n \underbrace{\langle v_0|v_n'\rangle\langle v_n'|v_0\rangle}_{\text{F-C factor}} e^{-iE_n't}$$

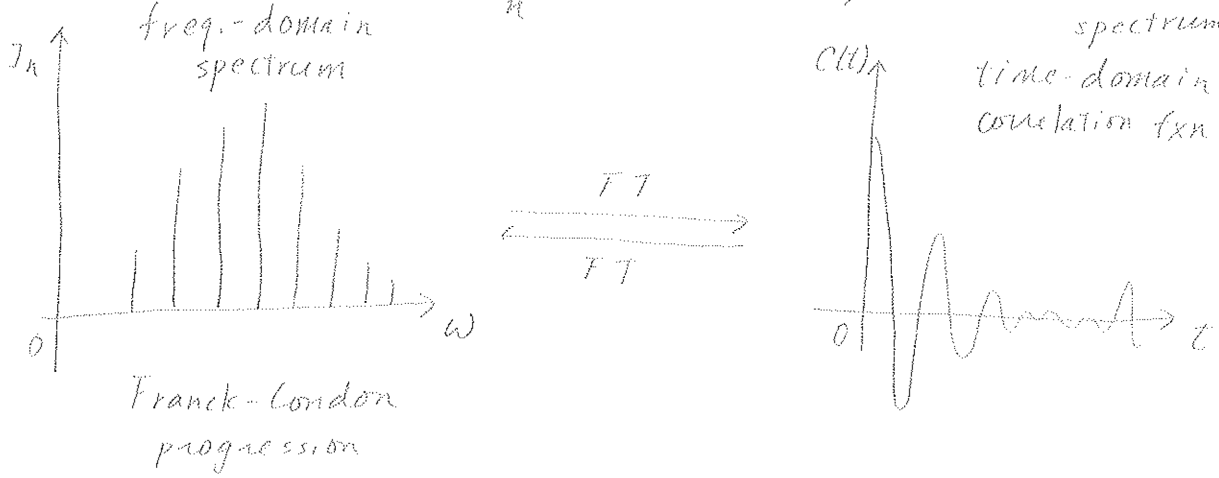
$$= \sum_n I_n^{F\text{-}C}\, e^{-iE_n't}$$

Fourier transform

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty} C(t)\, e^{i\omega t}\, dt = \frac{1}{2\pi}\int_{-\infty}^{\infty} \sum_n I_n^{F\text{-}C}\, e^{i(\omega - E_n')t}\, dt$$

$$= \frac{2\pi}{2\pi} \sum_n I_n^{F\text{-}C}\, \delta(\omega - E_n')$$

$$= \sum_n I_n^{F\text{-}C}\, \delta(\omega - E_n')$$ ⟵ Franck-Condon spectrum



Two approaches to spectral simulation

a) — Compute $|v_0\rangle$, E_0

— Compute $|v_n'\rangle$, E_n', $n = 0, 1, 2, \cdots$

— Evaluate $|\langle v_n' | v_0\rangle|^2$, $\omega_n = E_n' - E_0$, $n = 0, 1, 2, \cdots$

b) — Compute $|v_0\rangle$, E_0

— Find time-evolution of $|w(t=0)\rangle = |v_0\rangle$ on the PES of the excited state by solving $\hat{H}|w\rangle = i\frac{\partial}{\partial t}|w\rangle$ (wave packet propagation)

— Evaluate $C(t) = \langle w(0) | w(t)\rangle$

— FT $C(t)$

(4) Various wavepackets

$$\underbrace{|w(t)\rangle}_{\text{wavepacket}} = \sum_n \underbrace{|v_n'\rangle}_{\text{energy eigenfunctions}} a_n \, e^{-iE_n' t}$$

Let us consider the simplest energy eigenfunctions: planewave

$$-\frac{1}{2m}\frac{\partial^2}{\partial x^2} e^{ikx} = \underbrace{\frac{k^2}{2m}}_{=E_k} e^{ikx}$$

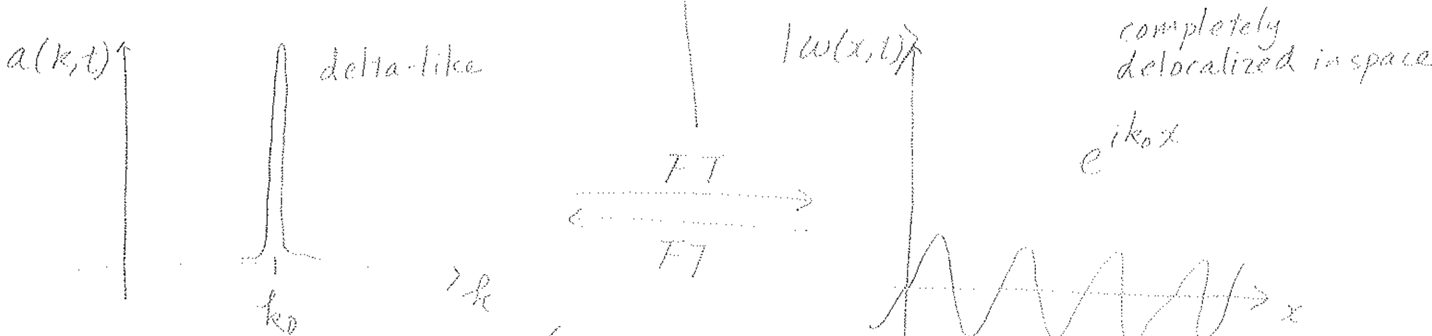
$$|w(t)\rangle = \sum_k e^{ikx - iE_k t} a_k$$

→ describes the composition of $|w\rangle$ in the momentum space (w/n in momentum space)

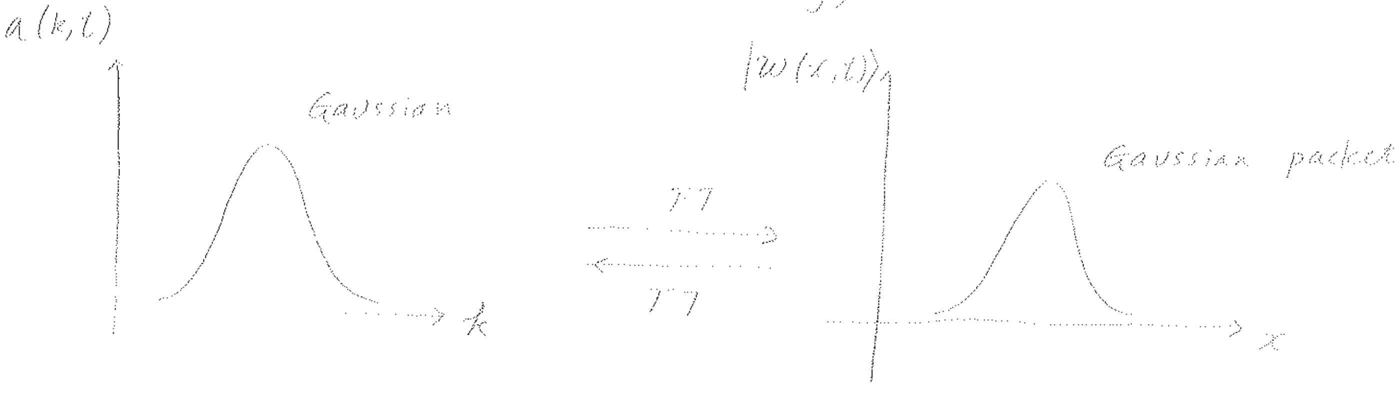
fxn of x and t

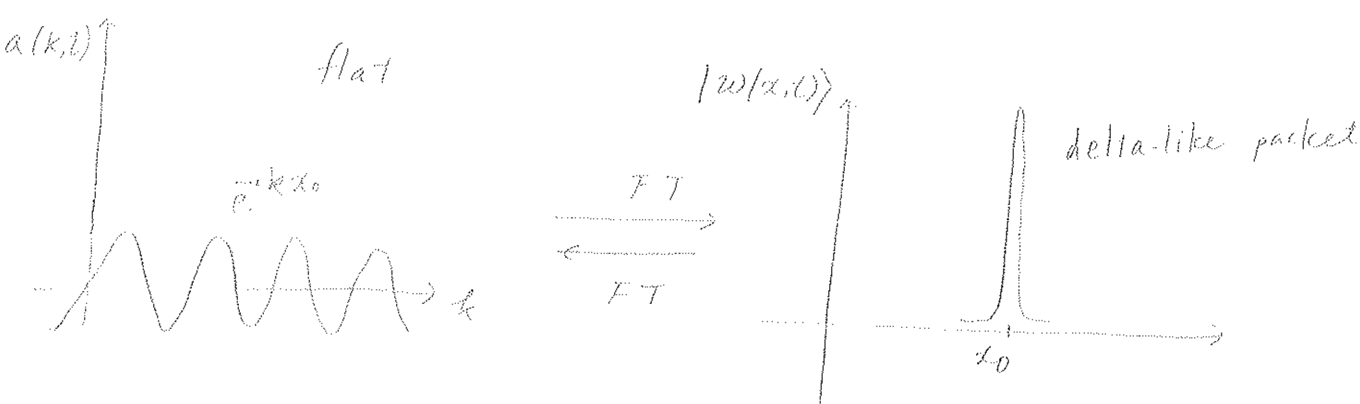
fxn of space

$$= \int_{-\infty}^{\infty} a(k,t)\, e^{ikx}\, dk$$



(p-x uncertainty)





How does a wave packet behave?

— has group velocity

— classically (Ehrenfest theorem)

Op. / Space	position	momentum
position	$\hat{x}$	$-i\frac{\partial}{\partial x}$
momentum	$i\frac{\partial}{\partial k}$	$\hat{k}$

→ familiar space

i) $|w\rangle$ with well-defined position

$$|w\rangle = \delta(x-x_0)$$
$$= \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ik(x-x_0)}\,dk$$
$$= \frac{1}{2\pi}\int_{-\infty}^{+\infty} \underbrace{e^{-ikx_0}}_{a(k) \equiv \text{momentum space w/fn}} e^{ikx}\,dk$$

in position space $\hat{x}\,\delta(x-x_0) = x_0\,\delta(x-x_0)$

in momentum space $i\frac{\partial}{\partial k} e^{-ikx_0} = x_0\, e^{-ikx_0}$

ii) $|w\rangle$ with well-defined momentum

$$|w\rangle = e^{ik_0 x}$$
$$= \int_{-\infty}^{+\infty} \underbrace{\delta(k-k_0)}_{a(k) \equiv \text{momentum space w/fn}} e^{ikx}\,dk$$

in position space $-i\frac{\partial}{\partial x} e^{ik_0 x} = k_0\, e^{ik_0 x}$

in momentum space $\hat{k}\,\delta(k-k_0) = k_0\,\delta(k-k_0)$