Real space

$$\mathcal{H} = L^2(\mathbb{R}) := \left\{ f \;\middle|\; \int |f^2(x)|\, dx < \infty \,,\; f(x) \in \mathbb{C} \right\}$$

$$\langle \psi | \varphi \rangle := (\psi, \varphi) = \int \psi^*(x)\, \varphi(x)\, dx .$$

$$\|\psi\|_2^2 := \langle \psi | \psi \rangle = \int |\psi^*(x)|^2\, dx = 1 .$$

Position

$$(\hat{x}\psi)(x) = x\,\psi(x) \longrightarrow \hat{x}|\psi\rangle = |x\psi\rangle .$$

Eigen-decomposition.

$$\hat{x}|\psi\rangle = x_0 |\psi\rangle \longrightarrow (x - x_0)\,\psi(x) = 0 .$$

$$\longrightarrow \psi(x) = \begin{cases} 0 , & x \neq x_0 \\ \infty , & x = x_0 . \end{cases}$$ (why not finite?)

Dirac δ - function

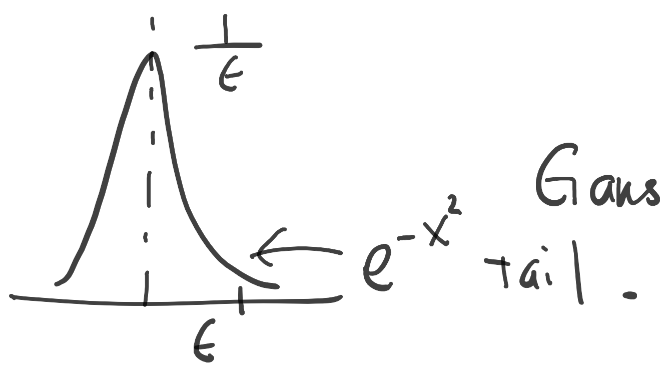
$$\int \delta(x-x_0)\, f(x)\, dx := f(x_0)\,.$$

Ex. $f(x) = 1$

$$\int \delta(x-x_0)\, dx = 1 \longrightarrow \text{normalization.}$$

limit.

$$\delta(x-x_0) = \lim_{\eta \to 0^+} \frac{1}{\sqrt{\pi \eta^2}} e^{-\frac{(x-x_0)^2}{\eta^2}}$$



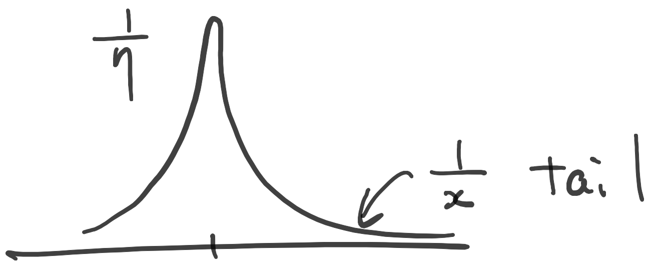
Gaussian broadening

Sokhotski-Plemelj formula

$$\lim_{\eta\to0^+}\frac{1}{(x-x_0)+i\eta} = -i\pi\,\delta(x-x_0) + \text{P.V.}\,\frac{1}{x-x_0}\,.$$

$$\frac{(x-x_0)-i\eta}{(x-x_0)^2+\eta^2}$$

Lorenztian broadening



Formal eigen decomposition

$$\hat{x}\,|x_0\rangle = x_0\,|x_0\rangle$$

Recall finite dimensional case

$$|\psi\rangle = \sum_{i=1}^{n} c_i |\varphi_i\rangle$$

$\langle \varphi_i | \psi \rangle = c_i \longrightarrow$ coefficient.

$$|\psi\rangle = \int |x\rangle \underline{\langle x|\psi\rangle}\, dx.$$

coefficient. or coordinate.

$\langle x | \psi \rangle =: \psi(x).$

wave function (real space representation)

Resolution of identity.

<u>Thm</u>. $A \in \mathbb{C}^{n\times n}$ Hermitian.

$A v_i = a_i v_i$, $i=1,\cdots,n$. $V=[v_1,\cdots,v_n]$ unitary

i.e. $I = \sum_{i=1}^{n} v_i v_i^*$

Ex. $\hat{A}|\varphi_i\rangle = a_i|\varphi_i\rangle$

$\langle\psi|\hat{B}\hat{C}|\psi\rangle = \sum_{i=1}^{n}\langle\psi|\hat{B}|\varphi_i\rangle\langle\varphi_i|\hat{C}|\psi\rangle.$

Ex. $\quad 1 = \int dx \, |x\rangle\langle x|$

Domain

$$\psi(x) \in L^2(\mathbb{R}) \quad , \quad x\psi(x) \in L^2(\mathbb{R}) \ ?$$

e.g. $\quad \psi(x) = \dfrac{1}{|x| + 1}$

$$\mathrm{dom}\,\hat{x} = \left\{ \psi \in L^2(\mathbb{R}) \,\middle|\, \int_{\mathbb{R}} |x\,\psi(x)|^2 dx < \infty \right\}.$$

$$\subset L^2(\mathbb{R})$$

dense subset.

Momentum

$$\hat{p} = -i \frac{d}{dx}$$

$$(\hat{p}\psi)(x) = -i\psi'(x)$$

Formal eigen decomposition

$$\hat{p}\,|p_0\rangle = p_0\,|p_0\rangle , \quad p_0 \in \mathbb{R} .$$

$$-i \frac{d}{dx} \langle x|p_0\rangle = p_0 \langle x|p_0\rangle .$$

$$\Longrightarrow \langle x|p_0\rangle = c\, e^{i p_0 x}$$

$$p_0(x) \notin L^2(\mathbb{R}) \qquad (\text{exer})$$

Fourier transform

$\psi \in L^2(\mathbb{R})$.

$$(\mathcal{F}\psi)(p) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} e^{-ipx} \psi(x)\, dx.$$

$\varphi \in L^2(\mathbb{R})$

$$(\mathcal{F}^{-1}\varphi)(x) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} e^{ipx} \varphi(p)\, dp.$$

$\mathcal{F} \circ \mathcal{F}^{-1} = I$.

$$\frac{1}{2\pi} \int e^{-ipx} \int e^{+ip'x} \varphi(p')\, dp'\, dx = \varphi(p)$$

$$\Rightarrow \int \left(\frac{1}{2\pi} \int e^{i(p'-p)x} dx \right) \varphi(p')\, dp' = \varphi(p)$$

$$\Rightarrow \frac{1}{2\pi}\int e^{i(p'-p)x}\,dx = \delta(p'-p)$$

$$\langle p'|p\rangle = \int dx\,\langle p'|x\rangle\langle x|p\rangle$$

$$= |C|^2 \int dx\; e^{i(p'-p)x}$$

$$\Rightarrow C = \frac{1}{\sqrt{2\pi}}$$

$$\operatorname{dom}\hat{p} = H^1(\mathbb{R}) := \{\psi \mid \psi \in L^2(\mathbb{R}),\ \psi' \in L^2(\mathbb{R})\}.$$

Canonical commutation relation

$$[\hat{x}, \hat{p}]\psi(x) = -ix\psi'(x) + i(x\psi)'(x)$$
$$= -ix\psi'(x) + i\psi(x) + ix\psi'(x) = i\psi(x).$$

$$[\hat{x}, \hat{p}] = i.$$

Heisenberg uncertainty principle. any $\psi \in H^1(\mathbb{R})$

$$\langle \Delta x^2 \rangle \langle \Delta p^2 \rangle \geq \frac{1}{4} \langle [\hat{x}, \hat{p}] \rangle^2 = \frac{1}{4}$$

When is uncertainty minimized? (exer)

$\mathbb{R}^3$. $\quad \hat{x} \longrightarrow \hat{\vec{r}} = (\hat{x}, \hat{y}, \hat{z})^T$

$$\hat{p} \longrightarrow \hat{\vec{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)^T. \qquad \hat{\vec{p}} = -i\nabla_{\vec{r}}$$

$$[\hat{\vec{r}}_\alpha, \hat{\vec{p}}_\beta] = i\delta_{\alpha\beta}, \quad \alpha, \beta = x, y, z.$$

Hamiltonian (1D) particle in potential field.

$$\hat{H} = \frac{\hat{p}^2}{2} + V(\hat{x}) = -\frac{1}{2}\frac{d^2}{dx^2} + V(\hat{x})$$

$$\left(V(\hat{x})\psi\right)(x) = V(x)\psi(x)$$

3D.

$$\hat{H} = \frac{1}{2}\hat{\vec{p}}^2 + V(\hat{\vec{r}}) = -\frac{1}{2}\Delta_{\vec{r}} + V(\hat{\vec{r}})$$

$$\Delta_{\vec{r}} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Schrödinger eq.

$$i\partial_t \psi(\vec{r}) = \left(-\frac{1}{2}\Delta + V(\vec{r})\right)\psi(\vec{r})$$

$$\left(-\frac{1}{2}\Delta + V(\vec{r})\right)\psi(\vec{r}) = E\psi(\vec{r})$$

Exer. Find eigendecomposition of harmonic oscillator in 1D.

$$\left(-\frac{1}{2}\frac{d^2}{dx^2} + \omega^2 x^2\right)\psi_n(x) = E_n\psi_n(x).$$

Angular momentum.

$$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} = \hat{\vec{r}} \times \left(-i \nabla_{\vec{r}}\right)$$

$$\hat{\vec{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Direct computation.

$$[\hat{L}_x, \hat{L}_y] = i \hat{L}_z ,$$

$$[\hat{L}_y, \hat{L}_z] = i \hat{L}_x$$

$$[\hat{L}_z, \hat{L}_x] = i \hat{L}_y$$

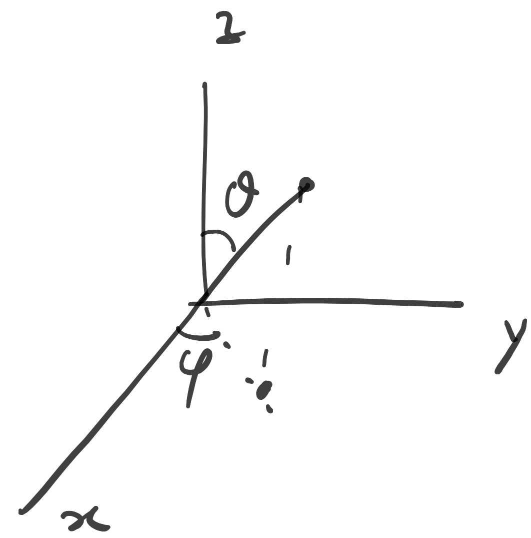
$$[\hat{\vec{L}}^2, \hat{L}_\alpha] = 0 . \quad \alpha = x, y, z .$$

spherical coordinates.

$$x = r\sin\theta\cos\varphi$$

$$y = r\sin\theta\sin\varphi$$

$$z = r\cos\theta$$



$$\hat{L}^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

Eigenfunctions : spherical harmonics.

$$\hat{L}^2 Y_{lm}(\theta,\varphi) = l(l+1)\,Y_{lm}(\theta,\varphi)$$

$l = 0, 1, 2, \cdots,$ $\quad m = -l, -l+1, \cdots, l.$

s p d

Hydrogen atom. $r = |\vec{r}|$

$$\left(-\frac{1}{2}\Delta_{\vec{r}} - \frac{1}{r}\right)\psi(\vec{r}) = E\,\psi(\vec{r})$$

Spherical coordinates.

$$\Delta_{\vec{r}} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\hat{\vec{L}}^2$$

$$\psi(r,\theta,\varphi) = R(r)\,Y_{lm}(\theta,\varphi)$$

Ground state. $l=0$, $m=0$.

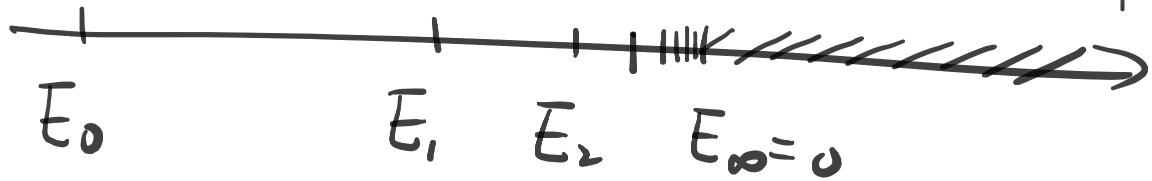
$$\psi_0(\vec{r}) = R(r) = \sqrt{\frac{1}{4\pi}}\, e^{-r}. \qquad E_0 = -\frac{1}{2}.$$

$$E_n = -\frac{1}{2n^2}, \quad n = 1, 2, 3, \cdots.$$

$$n = k + l, \quad k = 1, 2, \cdots, \Rightarrow 0 \le l \le n-1$$

$$\psi_{nlm}(\vec{r}) = R_{kl}(r)\, Y_{lm}(\theta, \varphi)$$

essential spectrum (why no L^2 eigenfunction?)



Ex. H_2^+

$$H = -\frac{1}{2}\Delta_{\vec{r}} - \frac{1}{|\vec{r}|} - \frac{1}{|\vec{r}-\vec{R}|}$$

$$\psi(\vec{r}) \approx c_1 \psi_{100}(\vec{r}) + c_2 \psi_{100}(\vec{r}-\vec{R})$$

LCAO. $\cong \mathbb{C}^2$.

Galerkin projection

$$\begin{pmatrix} \varepsilon & -t \\ -t & \varepsilon \end{pmatrix} c = E \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix} c$$

$$\varepsilon = \int \psi_{100}(\vec{r}) \left(H \psi_{100}(\vec{r}) \right) d\vec{r}$$

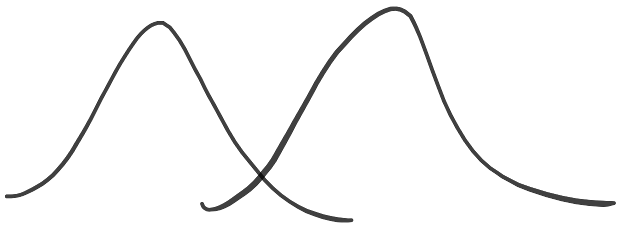
$$-t = \int \psi_{100}(\vec{r}) \left(H \psi_{100}(\vec{r}-\vec{R}) \right) d\vec{r}$$

$$s = \int \psi_{100}(\vec{r}) \psi_{100}(\vec{r}-\vec{R}) \, d\vec{r}$$

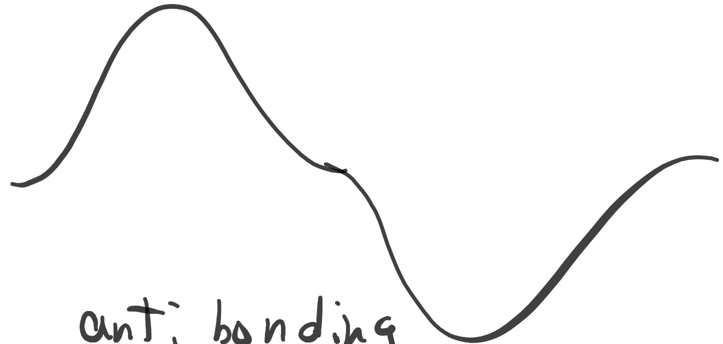
$$E_g = \frac{\varepsilon - t}{1+s}, \qquad c_g = \frac{1}{\sqrt{2(1+s)}} (1, 1)^T$$

(exer)

$$E_e = \frac{\varepsilon + t}{1-s}, \qquad c_e = \frac{1}{\sqrt{2(1-s)}} (1, -1)^T$$



(covalent) bonding

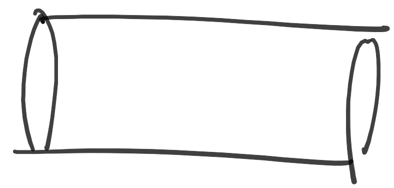


anti bonding

Notebook 1D.

1) soft Coulomb.

app. 1D cylinder



$$U_c(x) = \frac{1}{\epsilon_0 (x^2 + K^2)}$$

2) $$-U_c''(x) + K^2 U_c(x) = \frac{4\pi}{\epsilon_0}\delta(x). \Rightarrow U_c(x) = \frac{2\pi}{K\epsilon_0} e^{-K|x|}$$

① easy for boundary. pbc.

Yukawa.

② screening behavior.