9. Quantum dynamics ...

or finding solutions for the Stationary Schrödinger eq.

$$\boxed{-\underbrace{\frac{\hbar^2}{2m^2}}_{\text{mass}}\nabla^2\psi_n(\vec{x}) + V(\vec{x})\underbrace{\psi_n(\vec{x})}_{\text{eigen function = state}} = \underbrace{E_n}_{\text{eigen values = energy}}\psi_n(\vec{x})}$$

for 1 particle moving in d-dim potential $V(x)$.

$\rightsquigarrow$ time dependent solutions from

$$\psi(t,\vec{x}) = \sum_n e^{-it E_n/\hbar \cdot t}\, \overbrace{c_n \psi_n(\vec{x})}^{\text{initial conditions}}$$

9.1. 1-d stationary Schrödinger eq.

*) also for separable systems like H-atom

$$(1)\quad -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad \text{can be written as}$$

$$\psi''(x) = f(x)\,\psi(x) \rightsquigarrow 2\ 1^{st} \text{ order equation} + RK \checkmark$$

But, we can do better $\rightsquigarrow$ <u>Numerov's algorithm</u>

Look at the sum (Taylor expand :-))

$$\psi(\underbrace{x_{k+1}}_{x_k+\Delta}) + \psi(\underbrace{x_{k-1}}_{x_k-\Delta}) = 2\psi(x_k) + \Delta^2\psi''(x_k) + \frac{1}{12}\Delta^4\psi^{(4)}(x_k) + \dots$$

and define the central difference

$$\delta g(x) = g(x+\Delta/2) - g(x-\Delta/2)$$

$$\delta^2 g(x) = \delta(\delta g(x)) = g(x+\Delta) - 2g(x) + g(x-\Delta)$$

$$\leadsto \quad \underbrace{\delta^2 \Psi_K}_{\Psi(x_K)} = \Delta^2 \underbrace{\Psi_K''}_{f_K \Psi_K} + \frac{1}{12}\Delta^4 \Psi_K^{(4)} + \mathcal{O}(\Delta^6)$$

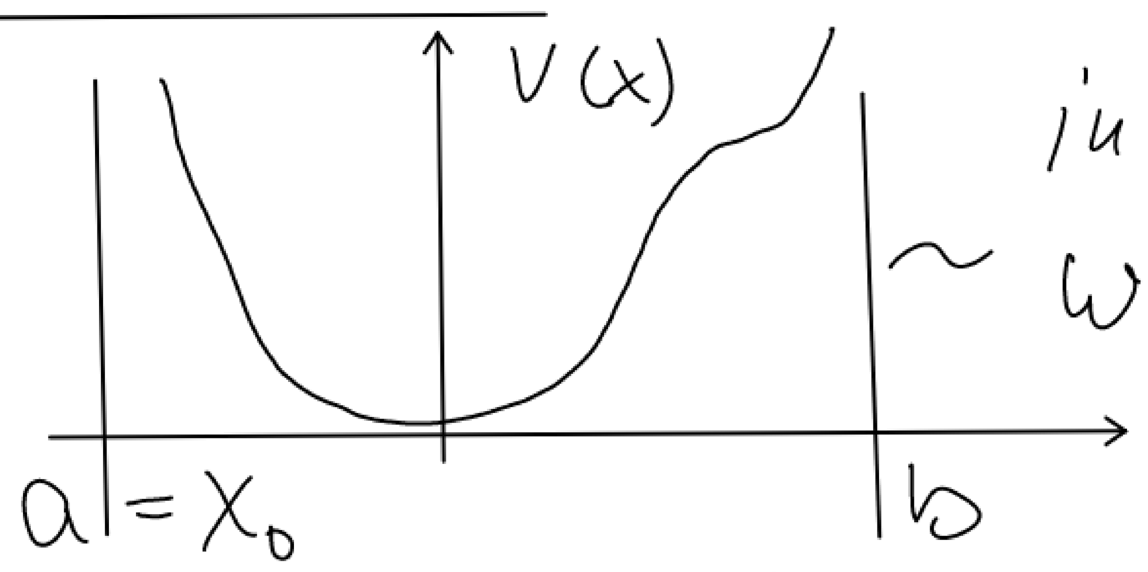
$$= \Delta^2 f_K \Psi_K + \frac{1}{12}\Delta^2 \delta^2 \Psi_K'' + \mathcal{O}(\Delta^6) \quad \text{or}$$

$$\boxed{\Psi_{K+1} - 2\Psi_K + \Psi_{K-1} = \Delta^2 f_K \Psi_K + \frac{1}{12}\Delta^2\left(f_{K+1}\Psi_{K+1} - 2 f_K \Psi_K + f_{K-1}\Psi_{K-1}\right) + \mathcal{O}(\Delta^6)}$$

5th order ?

boundary conditions ?

finite box



~ infinite potential wall

$$\Psi(a) = \Psi(b) = 0 \quad \leadsto \quad \Psi_0 = 0 \text{ and } \Psi_1 = 1$$

(always true after rescaling)

now find E such that $\Psi(b, E) = 0$ i.e. by bisection. (shooting method)

9.2. Schrödinger eq. in matrix form

Approximate state $|\Psi\rangle$ in a finite basis of orthonormal states $|\vec{k}\rangle$

$$|\Psi\rangle = \int dx^d \, \Psi(\vec{x}) \, |\vec{x}\rangle \quad \text{and}$$

$$|\vec{k}\rangle = \int dx^d \, \phi_k(\vec{x}) \, |\vec{x}\rangle$$

i.e. for a periodic potential

$$\phi_{\vec{k}}(\vec{x}) = \frac{1}{\sqrt{V}} \exp(i\vec{k}\vec{x})$$

normalization i.e. Volume of a box

Overlap

$$\boxed{C_{\vec{k}} = \langle \vec{k} | \Psi \rangle = \int dx^d \, \phi^*_{\vec{k}}(\vec{x}) \, \Psi(\vec{x})}$$

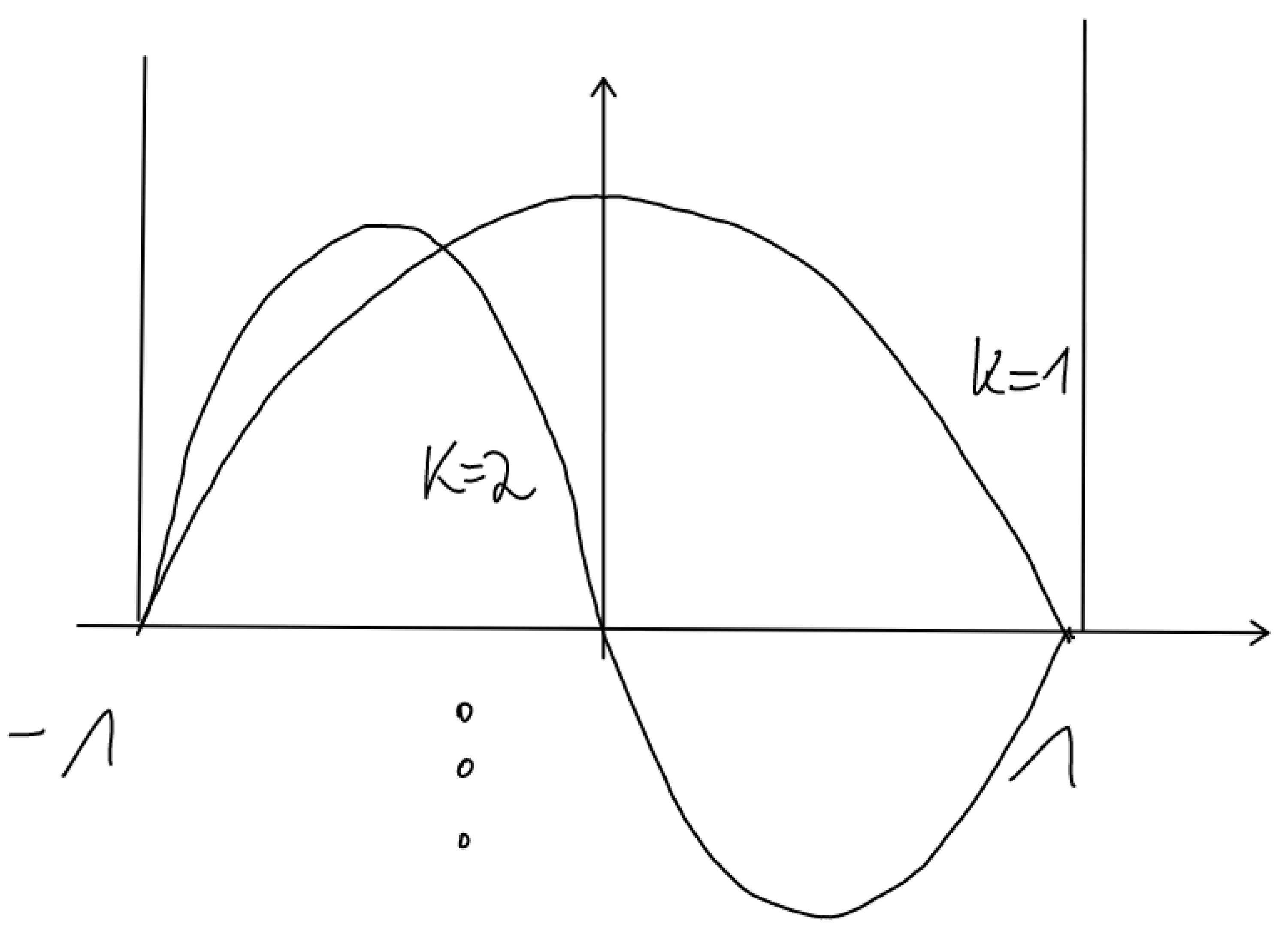
$|\psi\rangle = \sum_{\vec{k}} c_{\vec{k}} \, |\vec{k}\rangle$ we can also define

$H_{ke} = \langle k | H | \ell \rangle$ to get $\boxed{\sum_k c_k H_{\ell k} = E c_\ell}$

eigen value problem from last lecture

Example: $\phi_k(x) = \begin{cases} \cos(k\pi x/2) & \text{for odd } k \\ \sin(k\pi x/2) & \text{-''- even -''-} \end{cases}$

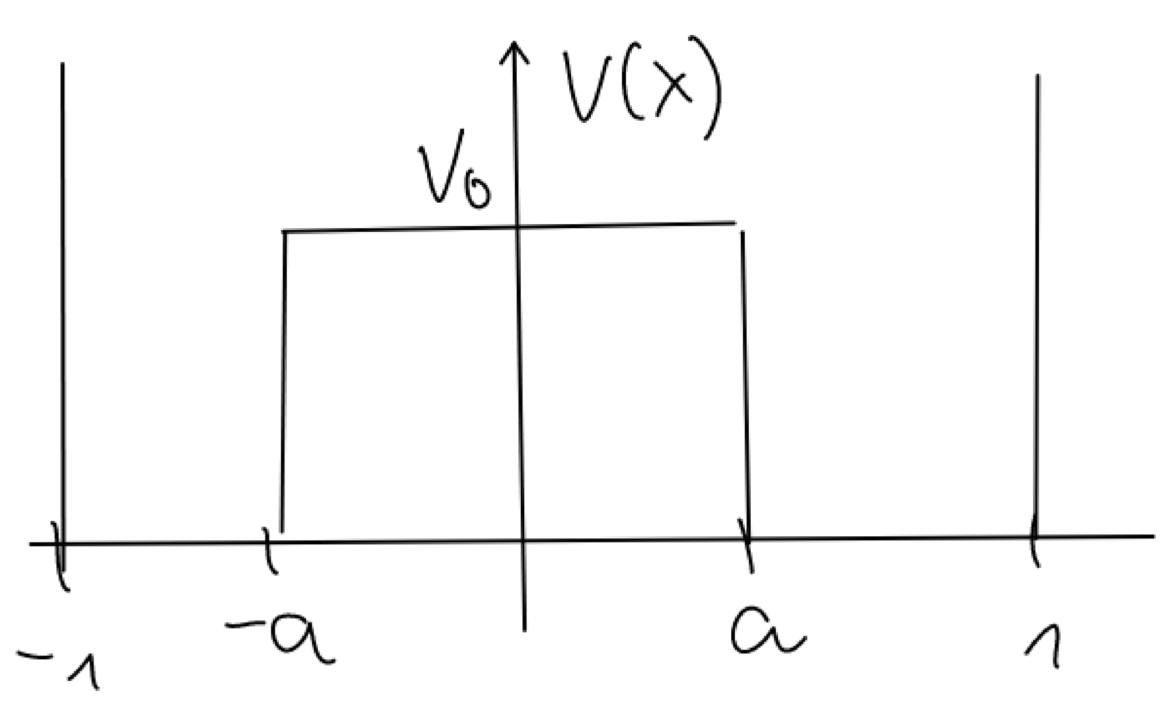
(a) momentum space



$$H_{\ell k} = \langle \ell | -\frac{1}{2}\frac{d^2}{dx^2} + V | k \rangle$$

$$= \underbrace{\frac{1}{8} k^2 \pi^2 \cdot \delta_{\ell k}}_{K_{\ell k}} + V_{\ell k}$$

$$V_{\ell k} = \int_{-1}^{1} dx \, \phi_\ell(x) \, V(x) \, \phi_k(x)$$



$$V_{\ell k} = V_0 a \begin{cases} si(k-\ell) + si(k+\ell) & k \text{ odd}, \ \ell \text{ odd} \\ si(k-\ell) - si(k+\ell) & \text{even even} \\ 0 & \text{otherwise} \end{cases}$$

with $si(\ell) = \sin(\tfrac{\pi}{2} a \ell) \big/ \tfrac{\pi}{2} a \ell$

Remarks: - Kinetic energy operator simple (already diag) but potential complicated ↯

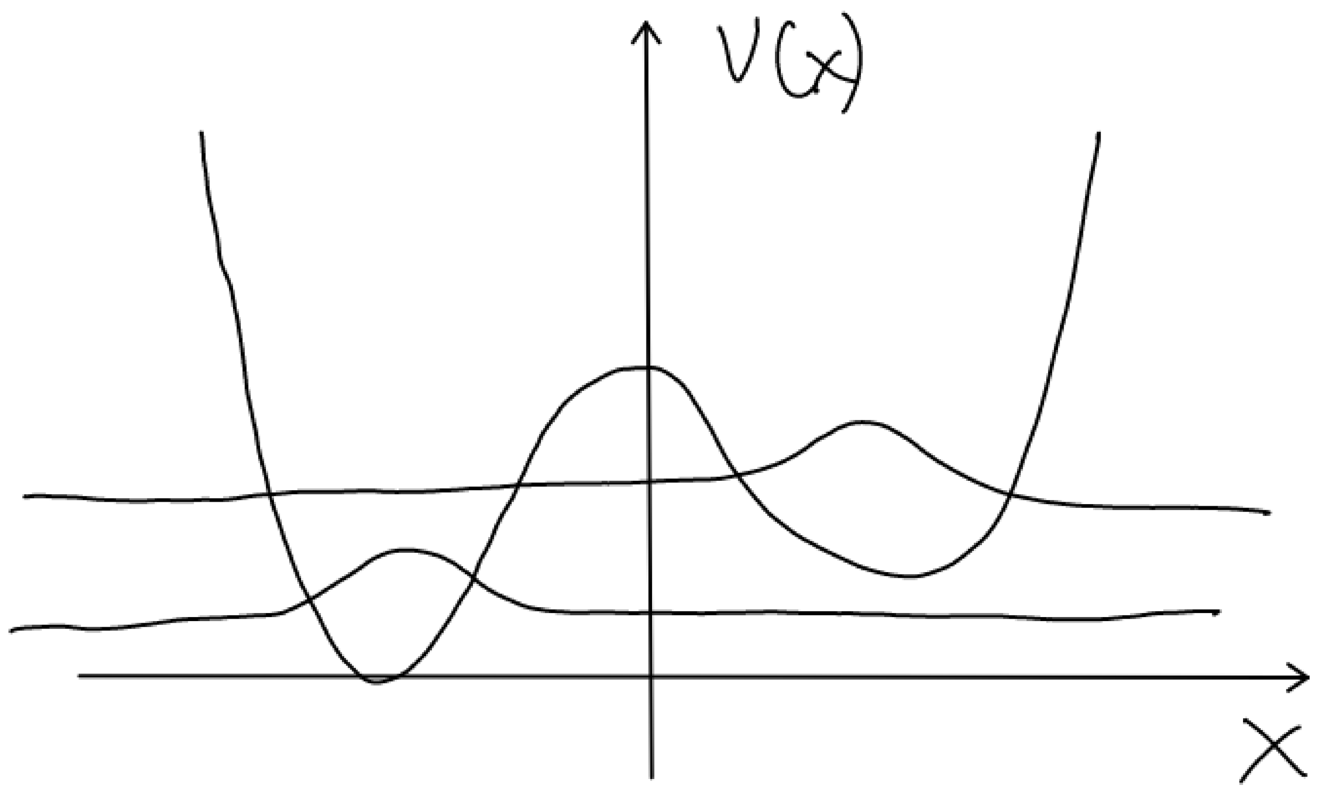
For alternative (b) position space remember $\delta^2\psi$ give rise to

$\frac{d}{dx^2}\psi_k \approx \psi_{k+1} - 2\psi_k + \psi_{k-1}$ and we get

$$K_{\ell k} = -\frac{1}{2}\left(\delta_{\ell k-1} - 2\delta_{\ell k} + \delta_{\ell k+1}\right) = \underbrace{\begin{pmatrix} 1 & -1/2 & & 0 \\ -1/2 & 1 & \ddots & \\ & \ddots & 1 & \ddots \\ 0 & & \ddots & 1 \end{pmatrix}}_{\text{tri-diag}}$$

while $V_{ek} = \delta_{ek} V_k$.

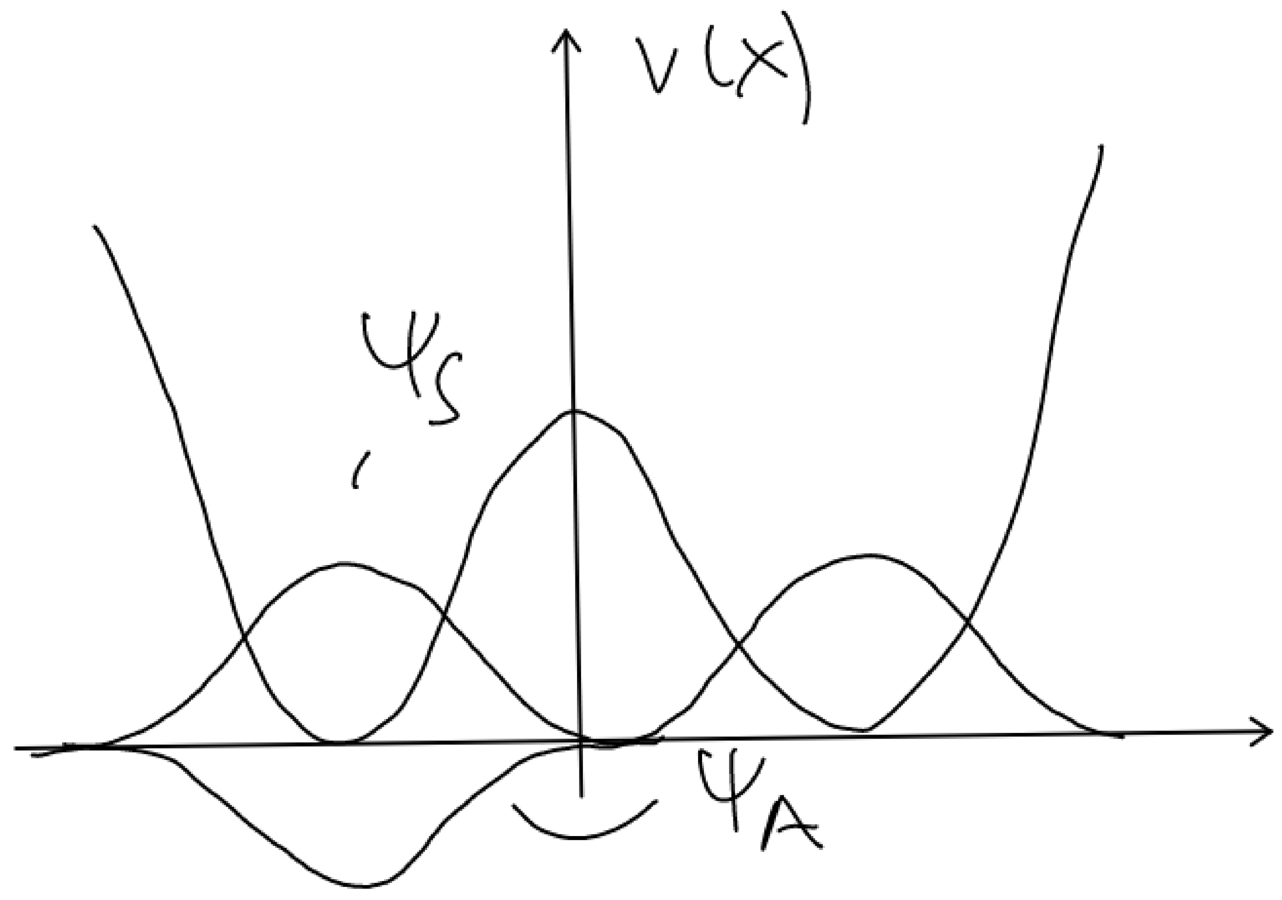
9.3. Tunneling in the double well



$V(x) = x^4 - x^2 + \mu \cdot x$

observation, eigenstates with lowest energies in wells

$\rightsquigarrow \mu \to 0$ still two eigenstates with <u>different</u> energies $\Delta E = E_1 - E_0$



$\psi_S = e^{-iE_0 t} \psi_S$

$\psi_A = e^{-iE_1 t} \psi_A$

$\psi_{L/R} = \frac{1}{\sqrt{2}} \left(\psi_S -/+ \psi_A \right)$

$$\psi(t) = \frac{1}{\sqrt{2}} \left(e^{-iE_0 t} \psi_S + e^{-iE_1 t} \psi_A \right)$$

$$= \frac{1}{\sqrt{2}} e^{-iE_0 t} \left(\psi_S + e^{-i\Delta E t} \psi_A \right)$$

sign flip for going from left to right?

tunnel time

$$e^{-i\Delta E \cdot T} = -1$$

$$\rightsquigarrow \boxed{T = \frac{\pi}{\Delta E}}$$