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0. Introduction

1. Differential equations

  1.1 Classical equation of motion (classical mechanics, pendulum)

  1.2 Partial differential equation relaxation methods (electromagnetism, diffusion)

  1.3 Partial differential equation in space-time (traffic flow, tsunami)

2. Eigenvalue problem

  2.1 Schrödinger equation and Hamiltonian (Harmonic oscillator, wave package)

  2.2 Quantum lattice model and Hibert space (Heisenberg model)

  2.3 Exact diagonalization of spin chain (Spin wave, Haldane conjecture, topology)

  2.4 Matrix product state and density matrix renormalization group (DMRG)

Content

Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(t,\overrightarrow{x}) = -\frac{\hbar^2}{2m}\Delta\psi(t,\overrightarrow{x}) + V(\overrightarrow{x})\psi(t,\overrightarrow{x}) = H(\overrightarrow{x})\psi(t,\overrightarrow{x}) \qquad \psi(t,\overrightarrow{x}) = e^{-it\frac{E}{\hbar}}\psi(\overrightarrow{x})$$

Animating Schrödinger's Equation

$$H(\overrightarrow{x})\psi(\overrightarrow{x}) = E\psi(\overrightarrow{x})$$

https://www.youtube.com/watch?v=Xj9PdeY64rA

Particle in a box   https://en.wikipedia.org/wiki/Particle_in_a_box

zero probability
= we will not find
the particle here
at t=1s

high probability
= very likely that
we will find the
particle here
at t=1s
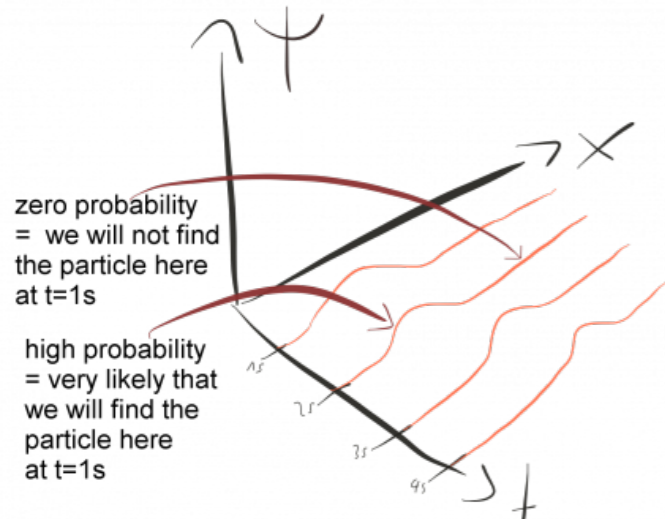
Quantum harmonic oscillator   https://en.wikipedia.org/wiki/Quantum_harmonic_oscillator

Hydrogen atom

Hydrogen (H)   Helium (He)
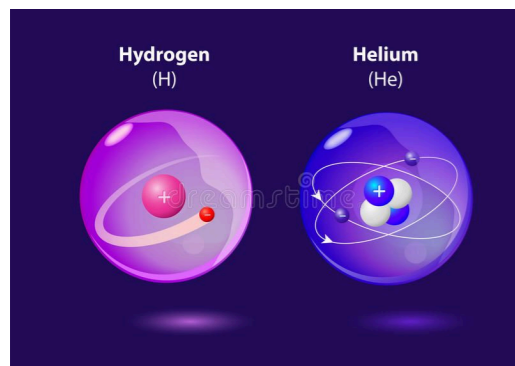
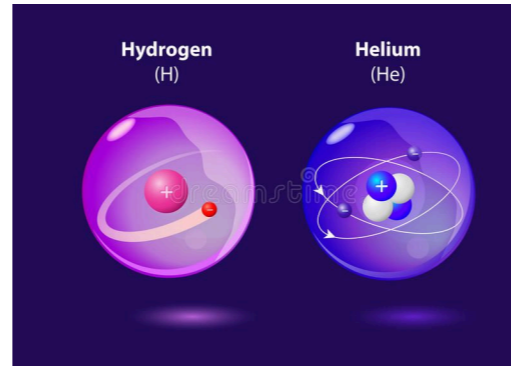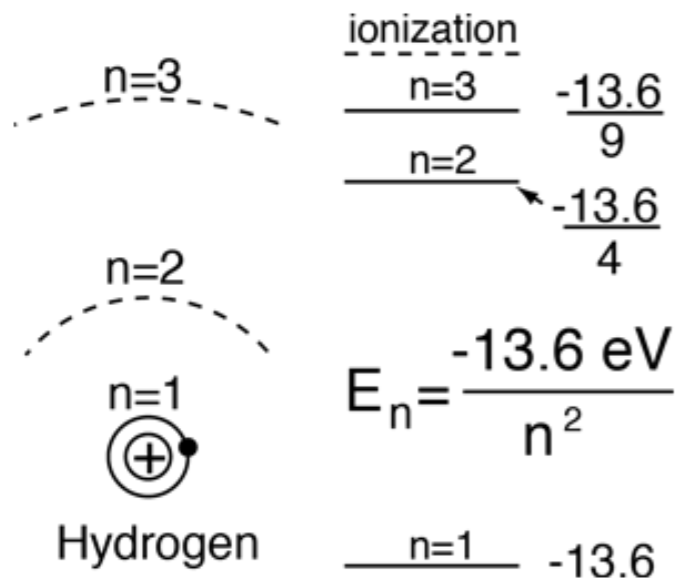$$\left(-\frac{\hbar^2}{2\mu}\Delta - \frac{e^2}{4\pi\epsilon_0 r}\right)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi) \qquad \mu = \frac{m_e M}{(m_e + M)}$$

in spherical coordinates

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi$$

$$\psi_{n,l,m}(r,\theta,\phi) = \sqrt{\left(\frac{2}{na_0^*}\right)^3\frac{(n-l-1)!}{2n(n+l)!}}\, e^{-\rho/2}\rho^l L_{n-l-1}^{2l+1}(\rho)Y_l^m(\theta,\phi) \qquad E_n = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2}$$

$$n = 1, E_1 = 13.6ev = 1Rydberg$$

ionization

| n=3 | $-\dfrac{13.6}{9}$ |
| n=2 | $-\dfrac{13.6}{4}$ |

$$E_n = \frac{-13.6 \text{ eV}}{n^2}$$

Hydrogen

n=1   -13.6

Helium atom
Multi-electron problem
cannot be solved exactly

$$Z = 2$$

$$\left\{ -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right\} \psi(\mathbf{r_1}, \mathbf{r_2}) = E\,\psi(\mathbf{r_1}, \mathbf{r_2})$$

$$\psi(\mathbf{r_1}, \mathbf{r_2}) \neq \psi_{1s}(\mathbf{r_1})\psi_{1s}(\mathbf{r_2})$$

Electrons are fermions, not ideal particle

Ground state
$$\psi(1,2)_{1s^2} = \psi_{1s}(\mathbf{r_1})\psi_{1s}(\mathbf{r_2}) \times \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

excited state, singlet
$$\psi^+(1,2)_{1s2s} = \frac{1}{\sqrt{2}}(\psi_{1s}(\mathbf{r_1})\psi_{2s}(\mathbf{r_2}) + \psi_{2s}(\mathbf{r_1})\psi_{1s}(\mathbf{r_2})) \times \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

excited state, triplet
$$\psi^-(1,2)_{1s2s} = \frac{1}{\sqrt{2}}(\psi_{1s}(\mathbf{r_1})\psi_{2s}(\mathbf{r_2}) - \psi_{2s}(\mathbf{r_1})\psi_{1s}(\mathbf{r_2})) \times \begin{pmatrix} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}(\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\downarrow\downarrow\rangle \end{pmatrix}$$

$$E^\pm = \underbrace{I(1s) + I(2s)}_{\textbf{one electron integral}} + \underbrace{J(1s,2s)}_{\textbf{Coulomb integral}} \pm \underbrace{K(1s,2s)}_{\textbf{exchange integral}}$$

Triplet has lower energy
Hund's rule

Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(t,\vec{x}) = -\frac{\hbar^2}{2m}\Delta\psi(t,\vec{x}) + V(\vec{x})\psi(t,\vec{x}) = H(\vec{x})\psi(t,\vec{x}) \qquad \psi(t,\vec{x}) = e^{-it\frac{E}{\hbar}}\psi(\vec{x})$$

1d stationary Schrödinger equation $\quad H(\vec{x})\psi(\vec{x}) = E\psi(\vec{x}) \qquad (-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x))\psi(x) = E\psi(x)$

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\psi(x) = 0 \qquad \frac{d^2\psi(x)}{dx^2} + k^2(x)\psi(x) = 0 \qquad \longrightarrow \qquad \psi''(x) = -k^2(x)\psi(x)$$

$$k^2(x) = \gamma^2(\epsilon - \nu(x)) \qquad \gamma^2 = \frac{2mV_0}{\hbar^2} \qquad \epsilon = \frac{E}{V_0} \qquad \nu(x) = \frac{V(x)}{V_0}$$

Numerov's algorithm

$$x = h \cdot r$$

$$\psi(r+1) = \psi(r) + h\psi'(r) + \frac{1}{2}h^2\psi''(r) + \frac{1}{6}h^3\psi^{(3)}(r) + \frac{1}{24}h^4\psi^{(4)}(r) + \cdots$$

$$\psi(r-1) = \psi(r) - h\psi'(r) + \frac{1}{2}h^2\psi''(r) - \frac{1}{6}h^3\psi^{(3)}(r) + \frac{1}{24}h^4\psi^{(4)}(r) + \cdots$$

$$\psi(r+1) + \psi(r-1) = 2\psi(r) + h^2\psi''(r) + \frac{1}{12}h^4\psi^{(4)}(r) + O(h^6) \qquad \psi^{(4)}(r) = \frac{\psi''(r+1) + \psi''(r-1) - 2\psi''(r)}{h^2} + O(h^2)$$

$$= 2\psi(r) + h^2\psi''(r) + \frac{1}{12}h^2(\psi''(r+1) + \psi''(r-1) - 2\psi''(r)) + O(h^6)$$

$$(1 + \frac{h^2}{12}k^2(r+1))\psi(r+1) = 2(1 + \frac{h^2}{12}k^2(r))\psi(r) - (1 + \frac{h^2}{12}k^2(r-1))\psi(r-1) - h^2k^2(r)\psi(r) + O(h^6)$$

$$= 2(1 - \frac{5}{12}h^2k^2(r))\psi(r) - (1 + \frac{h^2}{12}k^2(r-1))\psi(r-1) + O(h^6)$$

$$\psi(r+1) = \frac{2(1 - \frac{5}{12}h^2k^2(r))\psi(r) - (1 + \frac{1}{12}h^2k^2(r-1))\psi(r-1)}{1 + \frac{1}{12}h^2k^2(r+1)}$$

given $\psi(0)$ and $\psi(1)$

Matrix Numerov's algorithm

$$\psi(r+1) + \psi(r-1) = 2\psi(r) + h^2\psi''(r) + \frac{1}{12}h^2(\psi''(r+1) + \psi''(r-1) - 2\psi''(r)) + O(h^6)$$

$$\psi''(x) = -k^2(x)\psi(x)$$

$$\psi(r+1) - 2\psi(r) + \psi(r-1) = -\frac{h^2}{12}k^2(r+1)\psi(r+1) - \frac{10h^2}{12}k^2(r)\psi(r) - \frac{h^2}{12}k^2(r-1)\psi(r-1)$$

$$k^2(x) = \gamma^2(\epsilon - \nu(x)) \quad \gamma^2 = \frac{2mV_0}{\hbar^2} \quad \epsilon = \frac{E}{V_0} \quad \nu(x) = \frac{V(x)}{V_0}$$

$$-\frac{1}{\gamma^2}\left(\frac{\psi(r+1) - 2\psi(r) + \psi(r-1)}{h^2}\right) + \frac{\nu(r+1)\psi(r+1) + 10\nu(r)\psi(r) + \nu(r-1)\psi(r-1)}{12} = \epsilon\frac{\psi(r+1) + 10\psi(r) + \psi(r-1)}{12}$$

$$\Psi = \begin{pmatrix} \psi(1) \\ \psi(2) \\ \psi(3) \\ \vdots \\ \psi(N-1) \\ \psi(N) \end{pmatrix}$$

$$\mathbf{A} = \frac{1}{h^2}(\mathbb{I}_{-1} - 2\mathbb{I}_0 + \mathbb{I}_1)$$

$$\mathbf{B} = \frac{1}{12}(\mathbb{I}_{-1} + 10\mathbb{I}_0 + \mathbb{I}_1)$$

$$\underbrace{\left(-\frac{1}{\gamma^2}\mathbf{B}^{-1}\mathbf{A} + \nu\right)\Psi = \epsilon\Psi}_{\text{Hamiltonian matrix}}$$

$$\nu = \begin{pmatrix} \nu_1 & 0 & \cdots & 0 & 0 \\ 0 & \nu_2 & \cdots & 0 & 0 \\ \vdots & 0 & \ddots & \vdots & \\ 0 & 0 & \cdots & \nu_{N-1} & 0 \\ 0 & 0 & \cdots & 0 & \nu_N \end{pmatrix}$$

$$\psi(0) = \psi(N+1) = 0$$

boundary condition $\psi(1)$ has no left neighbour

boundary condition $\psi(N)$ has no right neighbour

Solution for square well

$$\nu(0) = \nu(L) = \infty$$

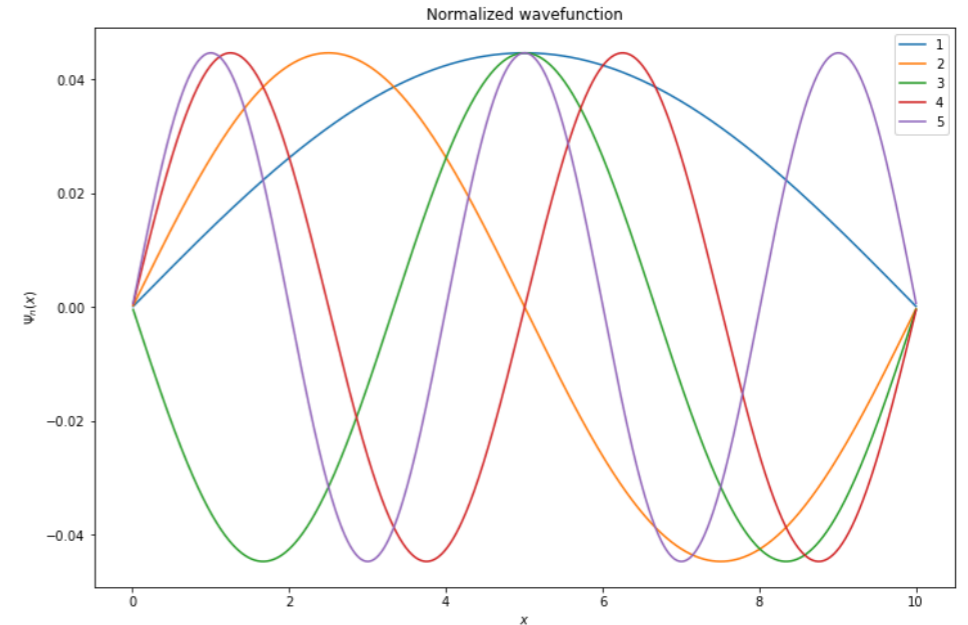$$\Psi'' + k^2\Psi = 0 \qquad k^2 = \gamma^2(\epsilon - \nu)$$

$$\frac{2m}{\hbar^2} = 1, \gamma^2 = 1 \quad \nu(x) = 0, x \in (0,L)$$

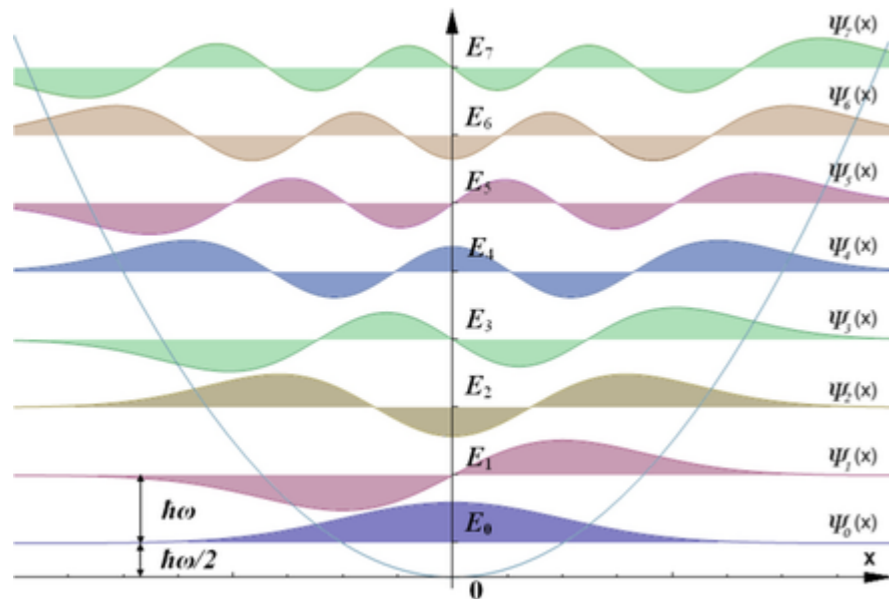$$\psi_n(x) = \sqrt{2}\sin(k_n x) = \sqrt{2}\sin(n\pi x) \qquad k_n = n\pi/L \qquad \psi(0) = \psi(L) = 0$$

$$E_n = \frac{n^2\pi^2}{L^2\gamma^2} \qquad n = 1,2,3,\cdots$$

$$n = 0,\ \psi_n(x) = 0 \qquad \text{trivial solution, no particle}$$

Normalized wavefunction

https://en.wikipedia.org/wiki/Particle_in_a_box

Solution for harmonic potential

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + \frac{1}{2}m\omega^2 x^2\psi = E\psi \qquad \nu(x) = \frac{1}{2}m\omega^2 x^2$$

$$-\frac{1}{2}\frac{d^2}{dx^2}\psi + \frac{1}{2}\left(\frac{m\omega}{\hbar}\right)^2 x^2\psi = \frac{m\omega}{\hbar}\frac{E}{\hbar\omega}\psi \qquad \frac{m\omega}{\hbar} = 1 \quad \epsilon = \frac{E}{\hbar\omega}$$

$$\left(-\frac{1}{2}\mathbf{B}^{-1}\mathbf{A} + \nu\right)\Psi = \epsilon\Psi \qquad \nu = \frac{1}{2}x^2$$

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}e^{-\frac{m\omega x^2}{2\hbar}}H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \qquad n = 0,1,2,\cdots$$

$$E_n = \hbar\omega(n + 1/2)$$

https://en.wikipedia.org/wiki/Quantum_harmonic_oscillator

Time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(t,\vec{x}) = -\frac{\hbar^2}{2m}\Delta\psi(t,\vec{x}) + V(\vec{x})\psi(t,\vec{x}) = H(\vec{x})\psi(t,\vec{x}) \qquad \psi(t,x) \rightarrow \psi(t_n, x_r) = \psi_r^n$$

FTCS scheme
$$i\hbar\frac{\psi_r^{n+1} - \psi_r^n}{\tau} = -\frac{\hbar^2}{2m}\frac{\psi_{r+1}^n + \psi_{r-1}^n - 2\psi_r^n}{h^2} + V(r)\psi_r^n = \sum_{s=1}^{N} H_{r,s}\psi_s^n \quad N \times N$$

$$\vec{\psi}^n = \begin{pmatrix} \psi_0^n \\ \psi_1^n \\ \psi_2^n \\ \vdots \\ \psi_{N-1}^n \end{pmatrix}$$

$$H_{r,s} = -\frac{\hbar^2}{2m}\frac{\delta_{r+1,s} + \delta_{r-1,s} - 2\delta_{r,s}}{h^2} + V(r)\delta_{r,s}$$

von Neumann stability analysis $\quad \psi_r^n = A^n e^{ikrh}$

$$\vec{\psi}^{n+1} = (1 - \frac{i\tau}{\hbar}H)\vec{\psi}^n$$

for the free case $\qquad V(x) = 0$

$$A = 1 - i\frac{\hbar\tau}{mh^2}(\cos(kh) - 1) \quad |A|^2 > 1$$

Fully-Implicit scheme
$$i\hbar\frac{\psi_r^{n+1} - \psi_r^n}{\tau} = \sum_{s=1}^{N} H_{r,s}\psi_s^{n+1}$$

$$\vec{\psi}^{n+1} = \vec{\psi}^n - \frac{i\tau}{\hbar}H\vec{\psi}^{n+1} \qquad (1 + \frac{i\tau}{\hbar}H)\vec{\psi}^{n+1} = \vec{\psi}^n \qquad \vec{\psi}^{n+1} = (1 + \frac{i\tau}{\hbar}H)^{-1}\vec{\psi}^n$$

von Neumann stability analysis $\quad \psi_r^n = A^n e^{ikrh}$

for the free case $\qquad V(x) = 0$

$$A = \frac{1}{1 + i\frac{\hbar\tau}{mh^2}(\cos(kh) - 1)} \quad |A| < 0$$

do not preserve the norm of wave function, not unitary

$$\langle\psi(0)|\psi(0)\rangle = 1 \qquad \psi(t) = e^{-itH/\hbar}\psi(0) \qquad \text{preserve the normalisation} \qquad H \text{ is an hermitian matrix}$$

$$H = H^\dagger$$

$$(e^{-itH/\hbar})^\dagger = e^{itH/\hbar} = (e^{-itH/h})^{-1} \qquad \langle\psi(t)|\psi(t)\rangle = \langle\psi(0)|\underbrace{e^{itH/\hbar}\cdot e^{-itH/\hbar}}_{=1}|\psi(0)\rangle$$

FTCS scheme $\qquad e^{-i\tau H/\hbar} \approx (1 - \dfrac{i\tau}{\hbar}H)$

breaks the unitarity

Fully-Implicit scheme $\qquad e^{-i\tau H/\hbar} \approx (1 + \dfrac{i\tau}{\hbar}H)^{-1}$

$$(e^{-ix})^\dagger = e^{ix} = (e^{-ix})^{-1} \qquad \text{but} \qquad (1 \pm ix)^\dagger = 1 \mp ix \neq 1/(1 \pm ix)$$

Crank-Nicolson scheme $\qquad i\hbar\dfrac{\psi_r^{n+1} - \psi_r^n}{\tau} = \displaystyle\sum_{s=1}^{N} H_{r,s}\dfrac{1}{2}(\underbrace{\psi_s^n}_{FTCS} + \underbrace{\psi_s^{n+1}}_{Fully-implicit})$

unitary discretisation scheme

$$(1 + \dfrac{i\tau}{2\hbar}H)\vec{\psi}^{n+1} = (1 - \dfrac{i\tau}{2\hbar}H)\vec{\psi}^n \qquad\qquad \vec{\psi}^{n+1} = \vec{\psi}^n - \dfrac{i\tau}{2\hbar}H(\vec{\psi}^n + \vec{\psi}^{n+1})$$

$$\underbrace{\vec{\psi}^{n+1} = (1 + \dfrac{i\tau}{2\hbar}H)^{-1}(1 - \dfrac{i\tau}{2\hbar}H)\vec{\psi}^n}_{unitary} \qquad (\dfrac{1-ix}{1+ix})^\dagger = \dfrac{1+ix}{1-ix} = (\dfrac{1-ix}{1+ix})^{-1}$$

Chap.20.2.

http://numerical.recipes/book/book.html

Can you see it? $\quad \left|\dfrac{1-ix}{1+ix}\right| = 1$

Operator splitting
$$H = -\frac{\hbar^2}{2m}(\Delta_x + \Delta_y + \Delta_z + V(\vec{x})) = H_{kin} + H_{pot}$$

$$\psi(t + \tau) = U(\tau)\psi(t) = e^{-i\frac{\tau}{\hbar}H}\psi(t) \qquad e^{-i\frac{\tau}{\hbar}H}|\psi\rangle \rightarrow e^{-i\frac{\tau}{\hbar}H_{kin}}e^{-i\frac{\tau}{\hbar}H_{pot}}|\psi\rangle$$

Trotter-Suzuki decomposition $\quad e^{\tau(A+B)} = e^{\tau A} \cdot e^{\tau B} + O(\tau^2) \qquad$ in the eigen basis $\quad e^{-i\frac{\tau}{\hbar}V(\vec{x})}\psi(\vec{x})$

Baker-Campbell-Hausdorff $\quad e^X e^Y = e^{X+Y+\frac{1}{2}[X,Y]+\frac{1}{12}([X,[X,Y]]-[Y,[X,Y]])+\cdots}$

$$e^{-i\frac{\tau}{\hbar}\frac{\hbar^2 k_x^2}{2m}}\psi(k_x)$$

But the Eigen bases for H_kin and H_pot are different

Spectral methods $\qquad i\hbar\frac{\partial}{\partial t}\vec{\Psi}(t) = H\vec{\Psi}(t) \qquad H\vec{\Psi} = E\vec{\Psi} \qquad \vec{\Psi}(t) = e^{-itE/\hbar}\vec{\Psi}(0)$

If one knows all the eigenvalues $\quad E_n$ and corresponding eigenstates $\quad \vec{\phi}_n$ of the $\quad H$

$$\vec{\Psi}(t = 0) = \sum_n c_n \vec{\phi}_n$$

$$\vec{\Psi}(t) = \sum_n c_n e^{-i\frac{t}{\hbar}E_n}\vec{\phi}_n$$

All these point to the diagonalization of the Hamiltonian matrix