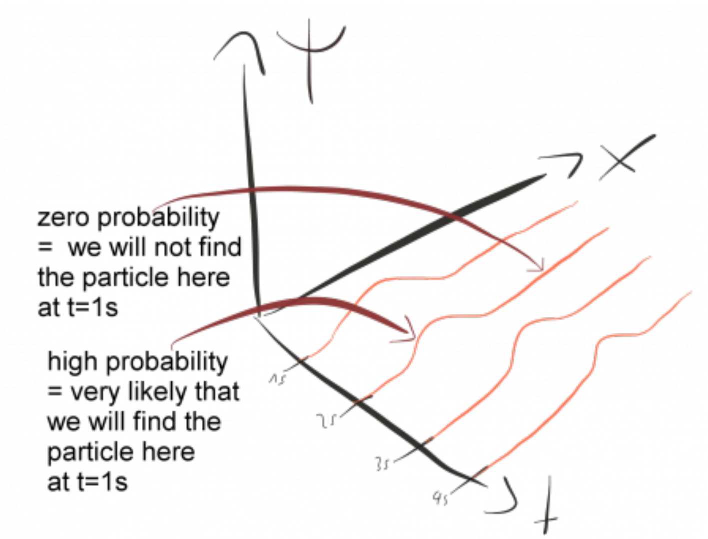
Content

Schrödinger equation

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

$$\psi(t,\overrightarrow{x}) = e^{-it\frac{E}{\hbar}}\psi(\overrightarrow{x})$$

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

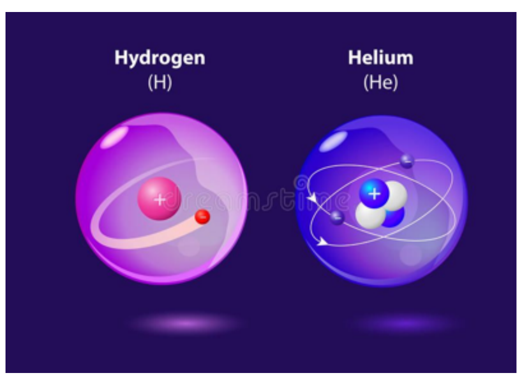


Animating Schrödinger's Equation

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

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

Quantum harmonic oscillator https://en.wikipedia.org/wiki/Quantum_harmonic_oscillator



Hydrogen atom

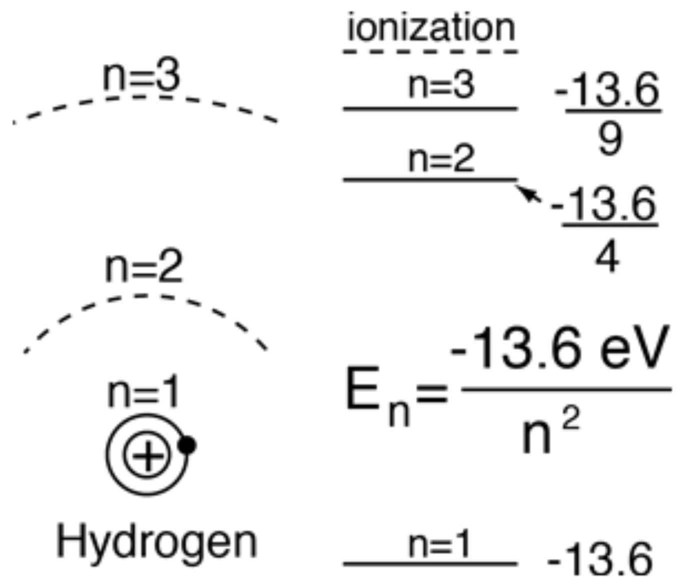
$$\left(-\frac{\hbar^2}{2\mu}\Delta - \frac{e^2}{4\pi\epsilon_0 r}\right)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi) \qquad \mu = \frac{m_e M}{(m_e + M)}$$

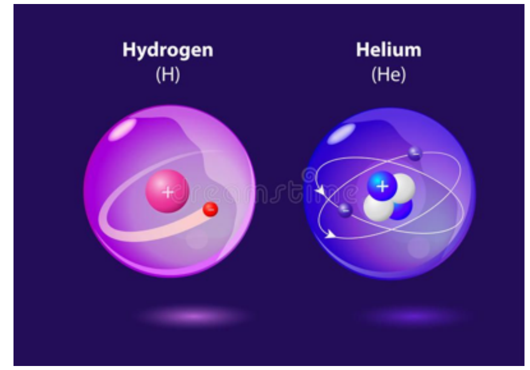
in spherical coordinates

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

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

$$\rho = \frac{2r}{na_0^*} \qquad n = 1, E_1 = 13.6ev = 1Rydberg$$





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

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

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

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

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

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

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

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

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

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

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

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

$$\Big(-\frac{1}{\gamma^2}\mathbf{B}^{-1}\mathbf{A}+\nu\Big)\Psi=\epsilon\Psi$$

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

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

Solution for square well

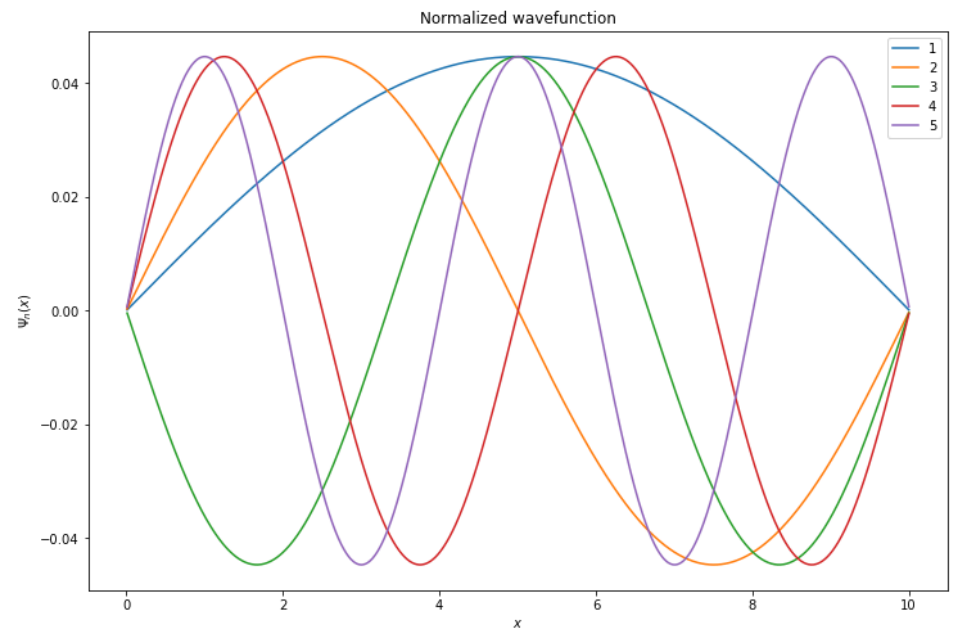
$$\Psi'' + k^2\Psi = 0 \qquad k^2 = \gamma^2(\epsilon - \nu) \qquad \frac{2m}{\hbar^2} = 1, \gamma^2 = 1 \quad \nu(x) = 0, x \in (0, L)$$

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

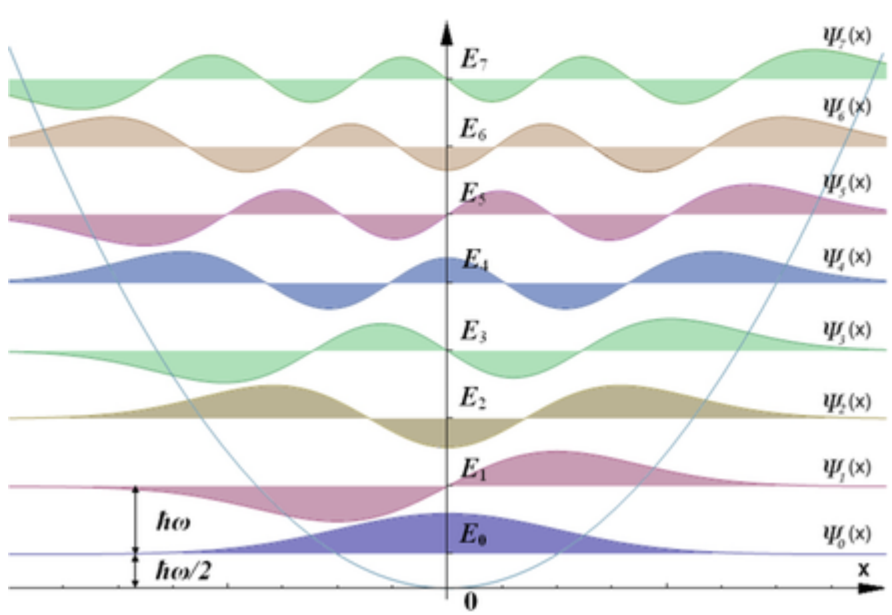
$$E_n = \frac{n^2\pi^2}{L^2\gamma^2} \qquad n = 1,2,3,\cdots$$

$n = 0,\ \psi_n(x) = 0$ trivial solution, no particle

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



Solution for harmonic potential



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

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

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

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

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

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

Time-dependent Schrödinger equation

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

$$\psi(t,x) \to \psi(t_n, x_r) = \psi_r^n$$

FTCS scheme

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

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

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

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

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

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

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

Fully-Implicit scheme

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

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

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

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

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

do not preserve the norm of wave function, not unitary

$\langle \psi(0) | \psi(0) \rangle = 1$ $\qquad \psi(t) = e^{-itH/\hbar}\psi(0)$ $\qquad$ preserve the normalisation $\qquad H$ 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 $\qquad e^{-i\tau H/\hbar} \approx (1 - \frac{i\tau}{\hbar}H)$

breaks the unitarity

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

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

Crank-Nicolson scheme

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

unitary discretisation scheme

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

Chap.20.2.

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

unitary

Can you see it? $\qquad |\frac{1 - ix}{1 + ix}| = 1$

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

Operator splitting

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

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

Trotter-Suzuki decomposition $e^{\tau(A+B)} = e^{\tau A} \cdot e^{\tau B} + O(\tau^2)$

in the eigen basis $e^{-i\frac{\tau}{\hbar}V(\overrightarrow{x})}\psi(\overrightarrow{x})$

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

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

But the Eigen bases for H_kin and H_pot are different

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

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

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

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

All these point to the diagonalization of the Hamiltonian matrix