CHEM 455 Physical Chemistry

From Classical to Quantum Mechanics

| Blackbody radiation

Description	Equations
Energy quantization	$E = nh\nu$
Average energy of an oscillating dipole	$\langle E_{\text{osc}} \rangle = \dfrac{h\nu}{e^{h\nu/k_BT} - 1}$
Spectral radiation density of blackbody (Planck)	$\rho(\nu, T)\, d\nu = \dfrac{8\pi h\nu^3}{c^3} \dfrac{1}{e^{h\nu/k_BT} - 1}\, d\nu$
Spectral radiation density of blackbody (classical)	$\rho(\nu, T)\, d\nu = \dfrac{8\pi h\nu^3}{c^3} k_B T d\nu$

| Wave-particle duality

Description	Equations
Energy of light	$E = h\nu$
Photoelectric effect Kinetic energy of ejected photoelectron	$E_k = h\nu - \Phi$
de Broglie relation	$p = \dfrac{h}{\lambda}$
Kinetic energy	$E_k = \dfrac{1}{2}mv^2 = \dfrac{p^2}{2m}$

| Atomic spectra of hydrogen and Bohr's model

Description	Equations
Hydrogen emission lines $n_2 > n_1$	$\tilde{\nu} = \dfrac{1}{\lambda} = R_H \left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} \right)$
Bohr's radius	$r = \dfrac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$
Energy level in Bohr's model	$E_n = -\dfrac{m_e e^4}{8\varepsilon_0^2 h^2 n^2}$
Emission of hydrogen atom $n_2 > n_1$	$\nu = \dfrac{m_e e^4}{8\varepsilon_0^2 h^3} \left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} \right)$

| Waves

Description	Equations
Classical nondispersive wave equation	$\dfrac{\partial \Psi(x,t)}{\partial x^2} = \dfrac{1}{v^2} \dfrac{\partial \Psi(x,t)}{\partial t^2}$
Wave number	$k = \dfrac{2\pi}{\lambda}$
Frequency	$\nu = \dfrac{1}{T}$

Description	Equations
Angular frequency	$\omega = \dfrac{2\pi}{T} = 2\pi\nu$
Wave speed	$v = \lambda\nu$
Euler's formula	$e^{i\theta} = \cos\theta + i\sin\theta$
Solution of wave equation	$\Psi(x,t) = A\sin(kx - \omega t + \phi)$ $= \mathrm{Re}(Ae^{i(kx-\omega t+\phi')})$
Interfering traveling waves give standing wave	$\Psi(x,t) = A[\sin(kx-\omega t) + \sin(kx+\omega t)]$ $= 2A\sin(kx)\cos(\omega t)$ $= \psi(x)\cos(\omega t)$
Time-independent Schrodinger equation	$-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$
Time-dependent Schrodinger equation	$-\dfrac{\hbar^2}{2m}\dfrac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar\Psi(x,t)$
Stationary states are standing waves	$\Psi(x,t) = \psi(x)e^{-i(E/\hbar)t}$
Normalization	$\|f(x)\| = \int_D f^* f\, dx = 1$
Orthogonality	$\int_D f^* g\, dx = 0$
Use quantum mechanics when ...	1. $\lambda_{\text{particle}} \sim L_{\text{problem}}$ 2. $\Delta E \gtrsim k_b T$ (discrete energy spectrum)

Quantum-Mechanical Postulates

1. The state of a quantum-mechanical particle is completely specified by a wave function $\Psi(x,t)$. The probability that the particle will be found at time t_0 in a spatial interval of width dx centered at x_0 is given by $\Psi^*(x_0,t_0)\Psi(x_0,t_0)dx$
2. For every measurable property of a system, there exists a corresponding operator.
3. In any single measurement of the observable that corresponds to the operator $\hat{A}$, the only values that will ever be measured are the eigenvalues of that operator.
4. If the system is in a state described by the wave function $\Psi(x,t)$, and the value of the observatle a is measured once on each of many identically prepared systems, the average value (expectation value) of all of the measurements is given by

$$\langle a \rangle = \frac{\displaystyle\int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi\, dx}{\displaystyle\int_{-\infty}^{\infty} \Psi^* \Psi\, dx}$$

5. The evolution in time of a quantum-mechanical system is governed by the time-dependent Schrödinger equation

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

| Operators

Description	1D	3D
Position	$\hat{x} = x$	$\hat{\mathbf{x}} = \mathbf{x}$
Linear momentum	$\hat{p}_x = -i\hbar\dfrac{d}{dx}$	$\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}$
Kinetic energy	$\hat{T} = \dfrac{\hat{p}_x^2}{2m} = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$	$\hat{\mathbf{T}} = -\dfrac{\hbar^2}{2m}\boldsymbol{\nabla}^2$
Potential energy	$\hat{V} = V(x)$	$\hat{\mathbf{V}} = V(\mathbf{x})$

Description	1D	3D
Total energy Hamiltonian	$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$	$\hat{\mathbf{H}} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{x})$

Simple Quantum Systems

Stationary states

Description	Equations
Time dependent Schrodinger equation	$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$
Time independent Schrodinger equation	$\hat{H}\psi_n(x) = E_n\psi_n(x)$
Stationary state wave function	$\Psi(x,t) = \psi(x)T(t)$
Time component of wave function	$T(t) = e^{iEt/\hbar}$
Probability of finding particle in an interval	$\text{Prob}(x, x+dx) = \lvert\Psi(x,t)\rvert^2 dx = \lvert\psi(x)\rvert^2 dx$
General solution as linear combination of stationary states	$\psi(x) = \sum_n c_n\phi_n(x)$
Expansion coefficients	$c_n = \langle\phi_n\lvert\psi\rangle = \int \phi_n^*\psi\, dx$
Normalization	$\sum_n c_n = 1$

Particle in a 1D box

Description	Equations
Time independent Schrodinger equation	$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x)$
Wave function $n = 0, 1, 2, \ldots$	$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$
Energy eigenvalues	$E_n = \frac{h^2}{8mL^2}n^2 = \frac{\hbar^2\pi^2}{2mL^2}n^2$

Particle in a 3D box

Description	Equations
Time independent Schrodinger equation	$\left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{x})\right]\psi(\mathbf{x}) = E\psi(\mathbf{x})$
Wave function $n_x = 0, 1, 2, \ldots$ $n_y = 0, 1, 2, \ldots$ $n_z = 0, 1, 2, \ldots$	$\psi_{nx,ny,nz}(\mathbf{x})$ $= \psi_{nx}(x)\psi_{ny}(y)\psi_{nz}(z)$ $= \sqrt{\frac{2}{L_x}}\sqrt{\frac{2}{L_y}}\sqrt{\frac{2}{L_z}}\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right)\sin\left(\frac{n_z\pi z}{L_z}\right)$
Energy eigenvalues	$E_n = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$

Finite potential well

Description	Equations

Description	Equations
Potential	$V(x) = \begin{cases} 0 & x \in [0, L] \\ V_0 & \text{elsewhere} \end{cases}$
Reflection probability	$R = \frac{(\sqrt{E} - \sqrt{E - V_0})^2}{(\sqrt{E} + \sqrt{E - V_0})^2}$
Transmission probability	$T = \frac{4\sqrt{E(E - V_0)}}{(\sqrt{E} - \sqrt{E - V_0})^2}$

Commutators and Uncertainty

Description	Equations
Commutator	$[A, B] = AB - BA$
Condition of commutation	$[A, B] = 0$
Standard deviation (uncertainty)	$\sigma_A = \sqrt{\langle (A - \langle A \rangle^2) \rangle} = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$
Heisenberg uncertainty principle (general)	$\sigma_A \sigma_B \geq \frac{1}{2} \lvert \langle [\hat{A}, \hat{B}] \rangle \rvert$
Heisenberg uncertainty principle (position-momentum)	$\sigma_x \sigma_p \geq \frac{\hbar}{2}$

Spectroscopy

Dimer model

Description	Equations
Hamiltonian of dimer	$\mathbf{H}_{\text{dimer}} = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + V(\lvert \mathbf{x}_1 - \mathbf{x}_2 \rvert)$
Total mass	$M = m_1 + m_2$
Reduced mass	$\mu = \frac{m_1 m_2}{m_1 + m_2}$
Position in center of mass (COM) coordinate	$\mathbf{X} = \frac{m_1 \mathbf{x}_1 + m_2 \mathbf{x}_2}{M}$
Momentum in center of mass (COM) coordinate	$\mathbf{\Pi} = \mathbf{p}_1 + \mathbf{p}_2$
Position in relative coordinate	$\mathbf{x} = \mathbf{x}_1 - \mathbf{x}_2 \equiv \mathbf{r}$
Momentum in relative coordinate	$\mathbf{p} = \frac{m_1 \mathbf{p}_1 + m_2 \mathbf{p}_2}{M}$
Hamiltonian of dimer	$\mathbf{H}_{\text{dimer}} = \mathbf{H}_{\text{free}} + \mathbf{H}_{\text{int}} = \underbrace{\frac{\mathbf{\Pi}^2}{2M}}_{\text{COM coord}} + \underbrace{\frac{\mathbf{p}^2}{2\mu} + V(\lvert \mathbf{x} \rvert)}_{\text{rel coord}}$
Free particle Hamiltonian	$\mathbf{H}_{\text{free}} = \frac{\mathbf{\Pi}^2}{2M}$
Internal Hamiltonian	$\mathbf{H}_{\text{int}} = \frac{\mathbf{p}^2}{2\mu} + V(\lvert \mathbf{x} \rvert)$
Dimer wave function	$\Psi_{\text{dimer}} = \Phi(\mathbf{X}) \psi(\mathbf{x})$
Free particle (COM) wave function	$\Phi(\mathbf{X}) = e^{\pm i \mathbf{\Pi} \mathbf{X} / \hbar}$

Description	Equations
Internal Hamiltonian Schrodinger equation	$\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{x}}^2 + V(\mathbf{r})\right]\psi(\mathbf{x}) = E\psi(\mathbf{x})$
Laplacian in spherical coordinate $\theta \in [0, \pi]$ $\phi \in [0, 2\pi]$	$\nabla^2 = \underbrace{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)}_{\text{radial breathing KE, vibration}} + \underbrace{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}}_{\text{angular breathing KE, rotation}}$
Dimer Hamiltonian	$\hat{H}_{\text{dimer}} = \hat{H}_{\text{COM}} + \hat{H}_{\text{vib}} + \hat{H}_{\text{rot}}$
Dimer total energy (see below)	$E = \frac{\Pi^2}{2M} + \hbar\omega_0(n+\frac{1}{2}) + \frac{\hbar^2 l(l+1)}{2I}$

Vibration: quantum harmonic oscillator

Description	Equations
Vibrational Schrodinger equation	$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + V(r)\right]\psi(\mathbf{x}) = E\psi(\mathbf{x})$
Wave function	$\psi(\mathbf{x}) = R(r)Y(\theta,\phi)$
Harmonic approximation	$V(r) \approx \frac{1}{2}kr^2$
Spring constant	$k = \mu\omega_0^2$
Vibrational Schrodinger equation	$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{2}kr^2\right]\psi(r) = E\psi(r)$
Wave function $n = 0, 1, 2, \dots$	$\psi(r) = \frac{1}{\sqrt{2^2 n!}}\left(\frac{\alpha}{\pi}\right)^{1/4} H_n(\sqrt{\alpha}r)e^{-\alpha r^2/2}$
Hermite polynomials	$H_n(r) = (-)^n e^{x^2}\left(\frac{d^n}{dx^n}\right)e^{-x^2}$
Constant	$\alpha = \frac{m\omega_0}{\hbar}$
Energy eigenvalue $n = 0, 1, 2, \dots$	$E_n = (n+\frac{1}{2})\hbar\omega_0$
Transition dipole moment	$\vec{\mu}_{fi} = \frac{d\vec{\mu}(x_0)}{dx}\langle\psi_f\|\hat{x}\|\psi_i\rangle$
Vibrational selection rule	$\Delta n = \pm 1$

Rotation: rigid rotor

Classical rigid rotor

Description	Equations
Angular momentum	$\mathbf{L} = \mathbf{x}\times\mathbf{p} = I\vec{\omega}$
Linear velocity	$\vec{v} = R_0\vec{\omega}$
Moment of inertia	$I = mR_0^2$
Rotational kinetic energy	$E = \frac{1}{2}I\omega^2 = \frac{L^2}{2I}$

Quantum rigid rotor

Description	Equations
Angular momentum operator	$\hat{\mathbf{L}} = \hat{\mathbf{x}} \times \hat{\mathbf{p}}$
z-component of angular momentum operator	$L_x = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$
Magnitude of angular momentum operator	$\hat{\mathbf{L}}^2 = L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\right]$
Components of $\hat{\mathbf{L}}$ does not commute	$[\hat{L}_i, \hat{L}_j] = i\hbar\hat{L}_k$
Components of $\hat{\mathbf{L}}$ commute with its magnitude	$[\hat{L}_i, L^2] = 0$

Description	Equations
Rotational Schrodinger equation	$-\frac{\hbar^2}{2\mu R_0^2}\left[\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi) = EY(\theta,\phi)$
Spherical harmonics	$Y_l^m(\theta,\phi) = (-)^m\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi}$
Legendre polynomial	$P_l^m(x) = \frac{1}{2^l l!}(1-x^2)^{m/2}\frac{d^{(l+m)}}{dx^{(l+m)}}(x^2-1)^l$
Energy eigenvalues $l = 0, 1, 2, \ldots$	$E_l = \frac{\hbar^2}{2I}l(l+1)$
Angular momentum eigenvalues $l = 0, 1, 2, \ldots$	$L^2Y = \hbar^2 l(l+1)Y$
z-component eigenvalues $m = -l, \ldots, 0, \ldots, l$	$L_zY = \hbar m Y$
Transition dipole moment	$\mu_{fi} = \langle\psi_f\|\mu_z\cos\theta\|\psi_i\rangle$
Rotational selection rule	$\Delta l = \pm 1, \Delta m = 0$

Hydrogen atom

Description	Equations
Hydrogen atom Schrodinger equation	$\left[-\frac{\hbar}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\vec{L}}{2m_e r^2} - \frac{e^2}{r}\right]\psi(x) = E\psi(x)$
Effective potential	$V_{\text{eff}} = \frac{\hbar l(l+1)}{2mr^2} - \frac{e^2}{r}$
Wave function $n = 1, 2, \ldots$	$\psi_{nlm}(x) = R_{nl}(r)Y_l^m(\theta,\phi)$
Energy eigenvalues $n = 1, 2, \ldots$	$E_n = -\frac{e^2}{2a_0}\frac{1}{n^2} = -\frac{me^4}{2\hbar^2}\frac{1}{n^2} - \frac{R_H}{n^2}$
Rydberg's constant	$R_H = 2.179 \times 10^{-18}\,\text{J} = 13.6\,\text{eV}$
Bohr's radius	$a_0 = \frac{\hbar^2}{me^2}$
Radial probability distribution	$P_{nl}(r)dr = r^2R_{nl}^2(r)dr$

Many Electron and Proton System

| Many electron atom

Description	Equations
Helium Schrodinger equation	$\left[\underbrace{-\frac{\hbar^2}{2m}\nabla_1^2}_{\text{KE of } e_1^-}\overbrace{-\frac{\hbar^2}{2m}\nabla_2^2}^{\text{KE of } e_2^-}\underbrace{-\frac{2e^2}{\lvert\mathbf{x}_1\rvert}}_{e_1^-\text{-N attraction}}\overbrace{-\frac{2e^2}{\lvert\mathbf{x}_2\rvert}}^{e_2^-\text{-N attraction}}+\underbrace{\frac{e^2}{\lvert\mathbf{x}_1-\mathbf{x}_2\rvert}}_{e_1^-\text{-}e_2^-\text{ repulsion}}\right]\psi(\mathbf{x}_1,\mathbf{x}_2)=E\psi(\mathbf{x}_1,\mathbf{x}_2)$
Orbital approximation	$\psi(\mathbf{x}_1,\mathbf{x}_2,\dots,\mathbf{x}_n)=\phi(\mathbf{x}_1)\phi(\mathbf{x}_2)\dots\phi(\mathbf{x}_n)$
Hartree orbital equations	$\left[-\frac{\hbar^2\nabla_i^2}{2m}-\frac{Ze^2}{\lvert\mathbf{x}\rvert}+\sum_{j=1,j\neq i}^{N}\int\frac{e^2\phi_j^*(\mathbf{x}')\phi_j(\mathbf{x}')}{\lvert\mathbf{x}-\mathbf{x}'\rvert}d^3\mathbf{x}'\right]\phi_i(\mathbf{x})=\varepsilon_{ii}\phi_i(\mathbf{x})$

| Spin

Description	Equations
Components of $\hat{\mathbf{S}}$ does not commute	$[\hat{S}_i,\hat{S}_j]=i\hbar\hat{S}_k$
Components of $\hat{\mathbf{S}}$ commute with its magnitude	$[\hat{S}_i,S^2]=0$
Eigenvalue of $\hat{\mathbf{S}}^2$	$\hat{\mathbf{S}}^2\leftrightarrow\hbar^2s(s+1)$
Eigenvalue of $\hat{S}_z$	$\hat{S}_z\leftrightarrow\hbar m_s$

| Electron spin

Description	Equations
Electron spin	$s=\frac{1}{2}$
Spin up function	$\alpha(m_s)=\begin{cases}1 & m_s=+\frac{1}{2}\\0 & m_s=-\frac{1}{2}\end{cases}$
Spin down function	$\beta(m_s)=\begin{cases}0 & m_s=+\frac{1}{2}\\1 & m_s=-\frac{1}{2}\end{cases}$
α is eigenfunction of $\hat{S}_z$	$\hat{S}_z\alpha=+\frac{1}{2}\hbar\alpha$
β is eigenfunction of $\hat{S}_z$	$\hat{S}_z\beta=-\frac{1}{2}\hbar\beta$
α,β are eigenfunctions of $\hat{S}^2$	$\hat{S}^2\alpha=\hbar^2s(s+1)\alpha=\frac{3}{4}\hbar^2\alpha$ $\hat{S}^2\beta=\hbar^2s(s+1)\beta=\frac{3}{4}\hbar^2\beta$
Normalization	$\sum_{m_s}\alpha^*\alpha=\sum_{m_s}\beta^*\beta=1$
Orthogonality	$\sum_{m_s}\alpha^*\beta=\sum_{m_s}\beta^*\alpha=0$

| Identical particles

Description	Equations
Spin-spin permutation operator	$P_{ij}\psi(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_i,\dots,\mathbf{r}_j,\dots,\mathbf{r}_N)=$ $\psi(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_j,\dots,\mathbf{r}_i,\dots,\mathbf{r}_N)$

Description	Equations
Doing nothing	$P_{ij} P_{ij} = 1$
Symmetric eigenvalue	$\lambda = 1$
Anti-symmetric eigenvalue	$\lambda = -1$
Fermions (e.g. electron)	$\frac{1}{2}$-integer spin, anti-symmetric
Bosons	integer spin, symmetric
Pauli exclusion principle	$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_N) =$ $-\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_N) = 0$
Slater determinant	$\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$
Hartree-Fock orbital equations	$\left[-\frac{\hbar^2\nabla^2}{2m} - \frac{Ze^2}{\vert\mathbf{x}\vert}\right]\phi_i(\mathbf{r}) +$ $\sum_{j=1}^{N}\left[\phi_i(\mathbf{r})\int\frac{e^2\phi_j^*(\mathbf{r})\phi_j(\mathbf{r})}{\vert\mathbf{x}-\mathbf{x}'\vert}d^3r' - \phi_j(\mathbf{r})\int\frac{e^2\phi_j^*(\mathbf{r})\phi_i(\mathbf{r})}{\vert\mathbf{x}-\mathbf{x}'\vert}d^3r'\right] =$ $\varepsilon_i\phi_i(\mathbf{r})$
Molecular orbital by linear combination of atomic orbitals (MO-LCAO)	$\psi(\mathbf{x}) = c_1\phi_1(\mathbf{x}) + c_2\phi_2(\mathbf{x})$ $\mathrm{MO} = c_1(\mathrm{AO}) + c_2(\mathrm{AO})$
Variational principle	$E = \frac{\langle\psi\vert H\vert\psi\rangle}{\langle\psi\vert\psi\rangle}$