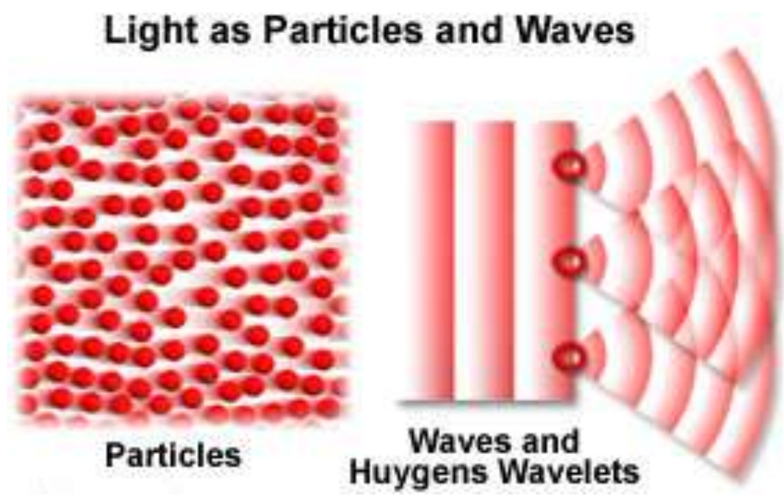
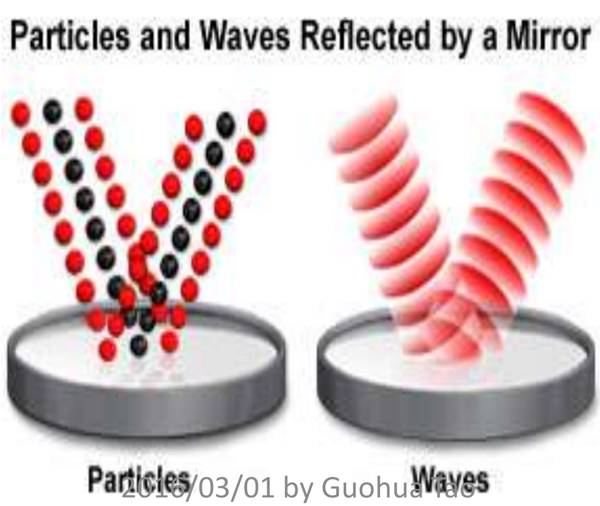
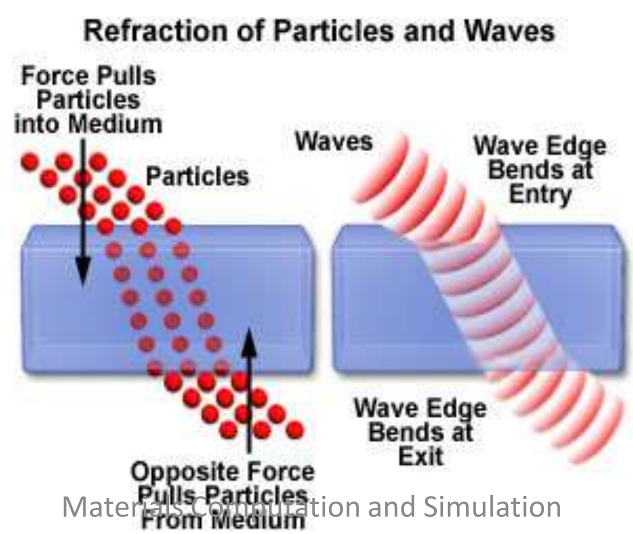
Chapter 2: Quantum theory and electronic structure

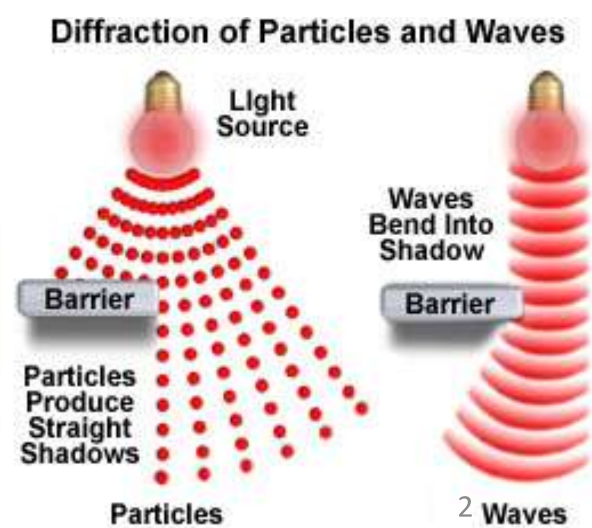
1. Background
2. Fundamental equations
3. Examples

Corpuscles vs. Wave

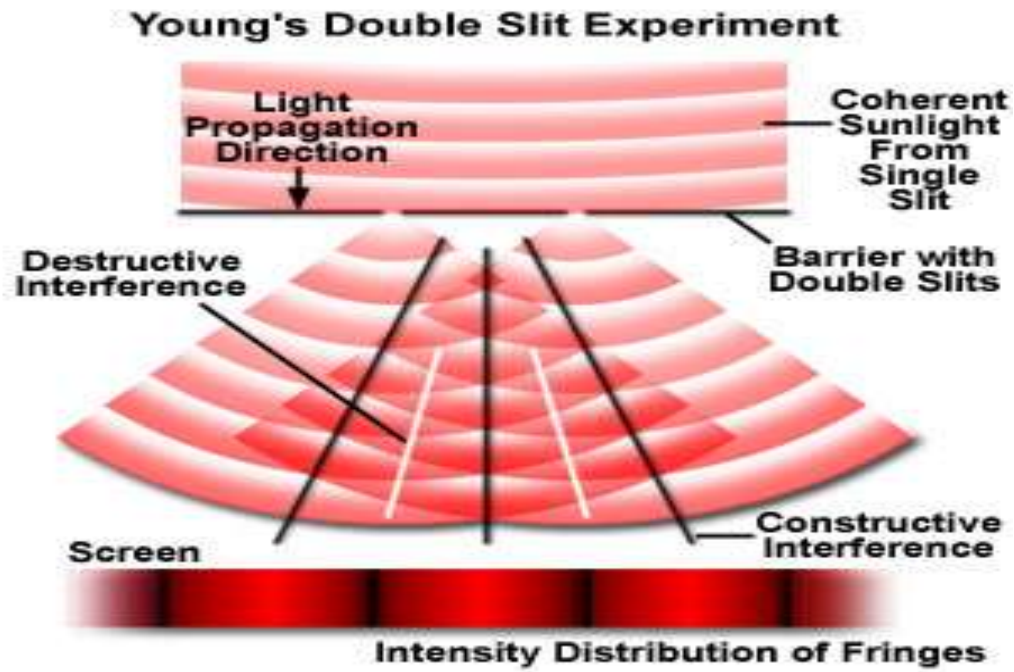






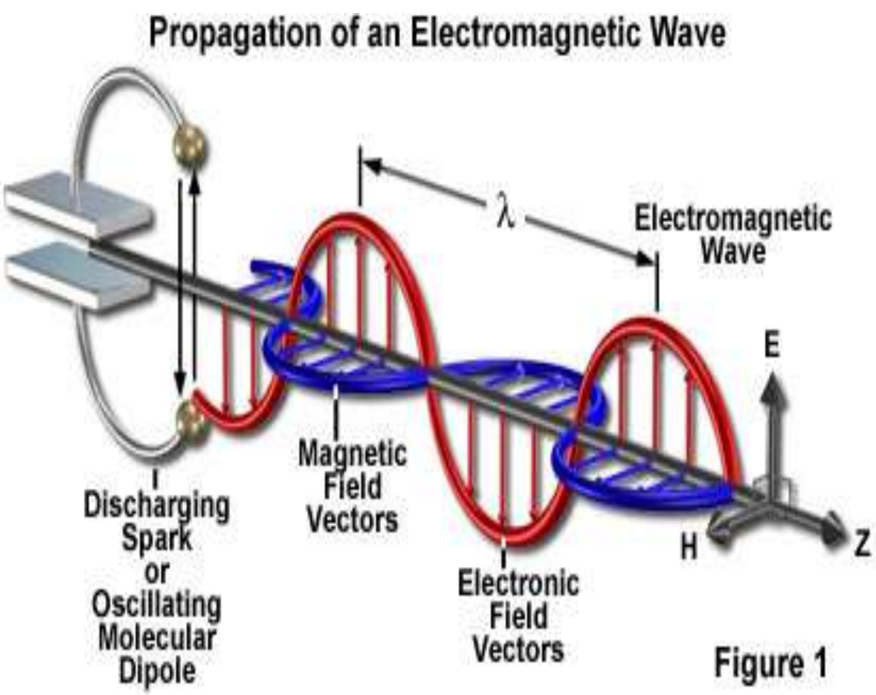


Experiments against Newton



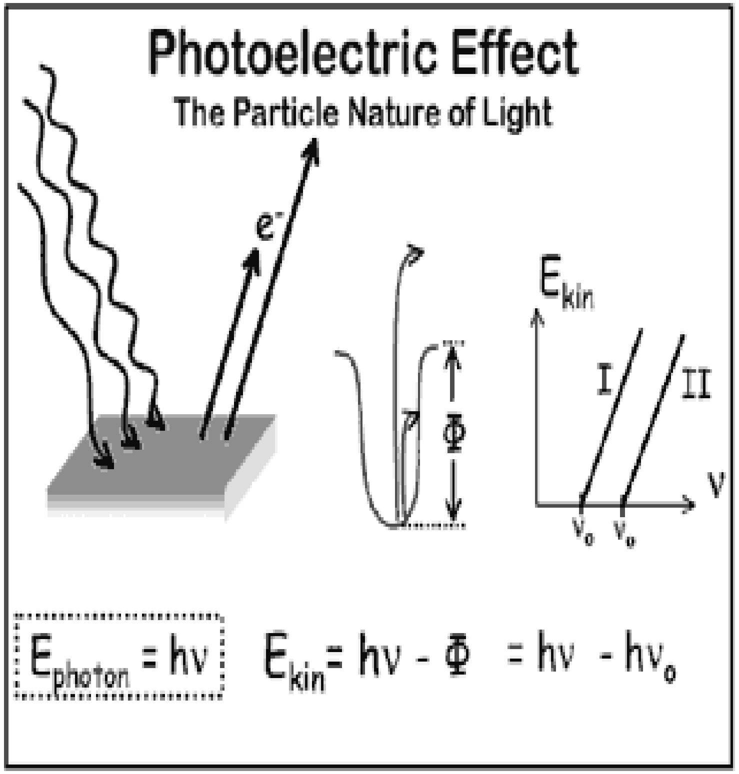
- Young's experiment
- Foucault found that the speed of light in water was lower than the speed of light in air.

Maxwell's electromagnetic wave



- Maxwell predicted that all three, heat, light and electricity, are propagated in free space at the speed of light as electromagnetic disturbances.
- Hertz showed that light transmissions and electrically generated waves are of the same nature.

Photoelectric effect



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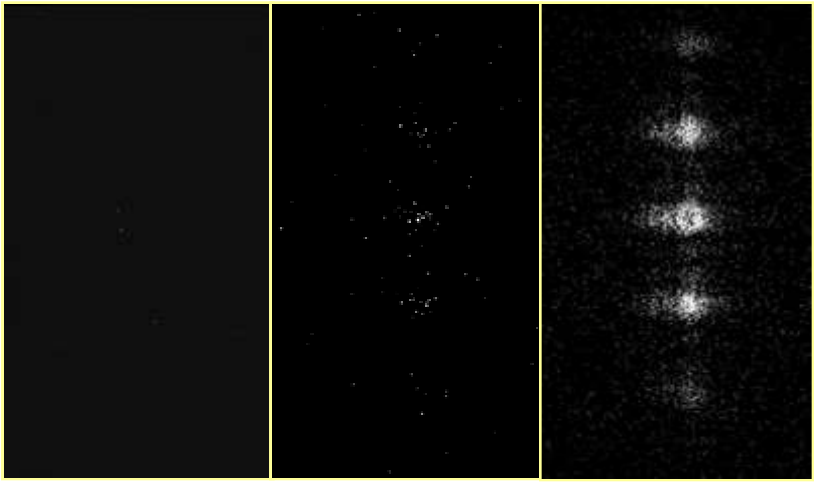
- Discovered by Heinrich Hertz (1887)
- Explained by Einstein (1905)
- Led to a belief in the physical reality of the light quanta

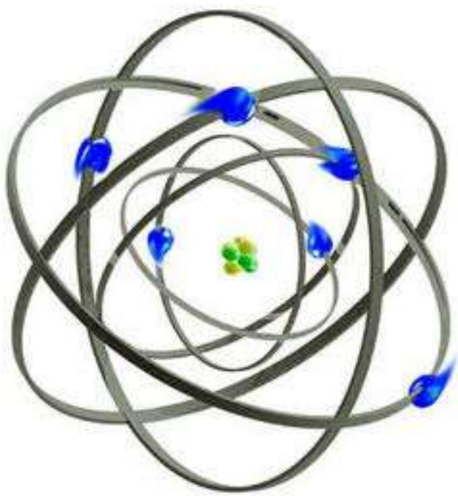
Wave-particle duality of light

- The act of observing light waves makes them collapse into particles.
- Would light always be a wave if nobody was there to observe it?



Single-photon two-slit experiment

Atomic model (1911)

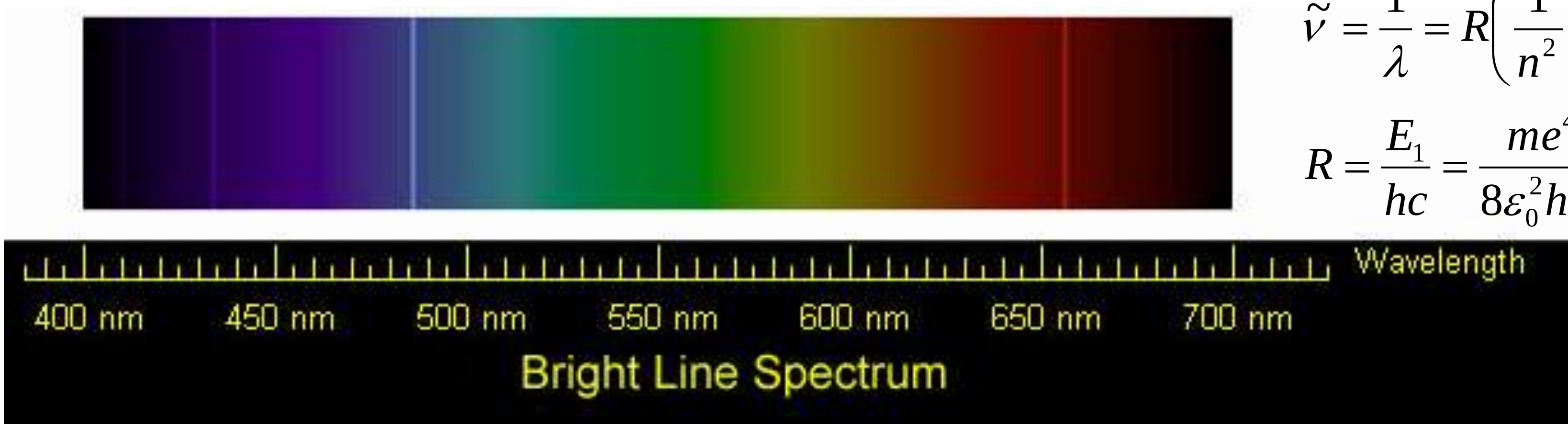


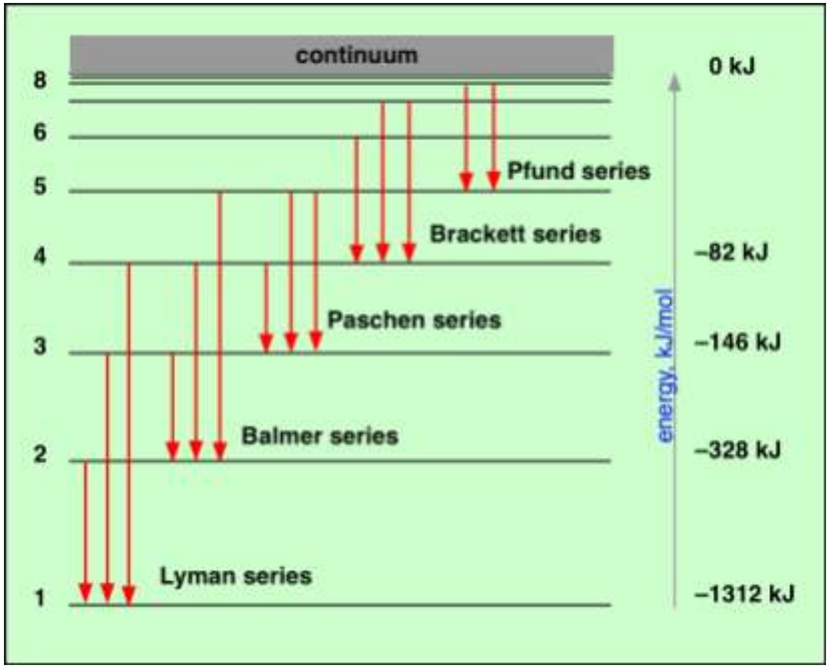
How electron moves around nucleus?

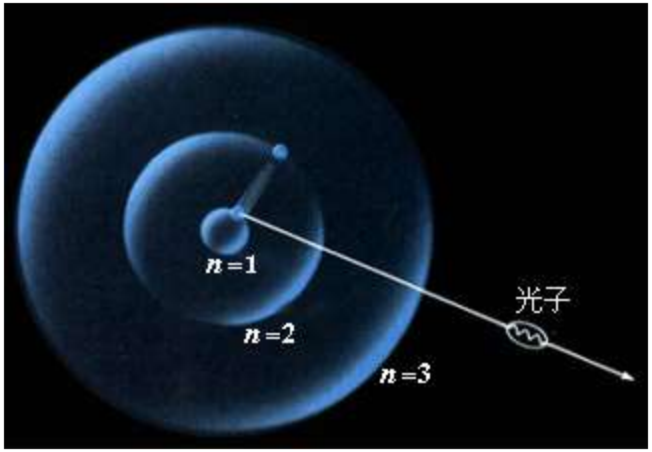
Atomic spectrum of Hydrogen

$$\tilde{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{k^2}\right)$$

$$R = \frac{E_1}{hc} = \frac{me^4}{8\varepsilon_0^2 h^3 c}$$







Semiclassical model for Hydrogen (1913)

Quantization of angular momentum

$$\tilde{\nu}=\frac{1}{\lambda}=R\left(\frac{1}{n^2}-\frac{1}{k^2}\right)$$

$$R=\frac{E_1}{hc}=\frac{me^4}{8\varepsilon_0^2h^3c}$$

Transition between states

$$\tilde{\nu}=\frac{1}{\lambda}=\frac{E_k-E_n}{hc}$$

$$L\equiv mvr=n\hbar$$

$$E=\frac{1}{2}mv^2-\frac{e^2}{r}$$

$$\frac{mv^2}{r}=\frac{e^2}{r^2}$$

$\Rightarrow$

$$v=\frac{e^2}{n\hbar}$$

$$r=\frac{n^2\hbar^2}{me^2}$$

$$E=-\frac{me^4}{2\hbar^2n^2}$$

Quantum theory

Fundamental equations:

$$i\hbar\frac{\partial}{\partial t}\left|\alpha,t_0;t\right\rangle = H\left|\alpha,t_0;t\right\rangle$$

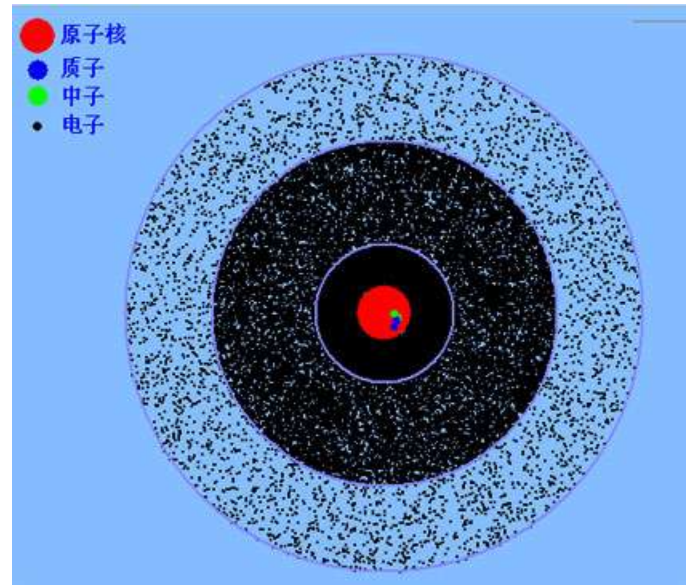
Schrodinger

$$H\left|\Psi\right\rangle = E\left|\Psi\right\rangle$$

$$\left|\Psi(t)\right\rangle = e^{-\frac{i}{\hbar}\int_0^t H(t')dt'}\left|\Psi\right\rangle$$

$$\frac{dA^{(H)}(t)}{dt} = \frac{1}{i\hbar}\left[A^{(H)}, H^{(H)}\right]$$

Heisenberg



Hamiltonian for the atomic system:

$$\hat{H} = \underbrace{-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{\left|R_I - R_J\right|}}_{\text{Nuclear}} \underbrace{- \frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{\left|r_i - R_I\right|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{\left|r_i - r_j\right|}}_{\text{Electronic}}$$

Nuclear Electronic

Examples

1. 1 D box
2. Harmonic oscillator
3. H atom
4. Double well
5. Coherent state

1D box

A free particle of mass *m*

$$H=\frac{\mathbf{p}^2}{2m}=\frac{p_x^2+p_y^2+p_z^2}{2m}$$

$$\frac{dp_i}{dt}=\frac{1}{i\hbar}[p_i,H]=0$$

$$\frac{dx_i}{dt}=\frac{1}{i\hbar}[x_i,H]=\frac{1}{i\hbar}\frac{1}{2m}i\hbar\frac{\partial}{\partial p_i}\left(\sum_{j=1}^{3}p_j^2\right)=\frac{p_i}{m}=\frac{p_i(0)}{m}$$

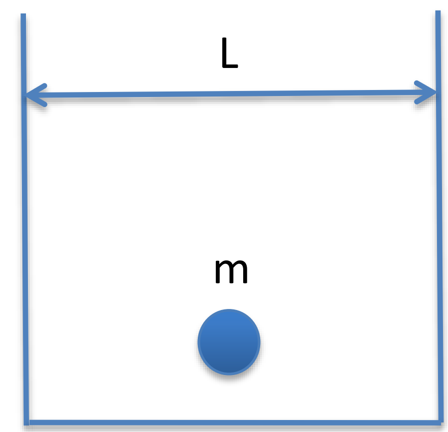
$$[x_i(t),x_i(0)]=?$$

$$\left\langle(\Delta x_i)^2\right\rangle_t\left\langle(\Delta x_i)^2\right\rangle_{t=0}\geq ?$$

$$H|\Psi\rangle=-\frac{\hbar^2}{2m}\nabla^2|\Psi\rangle=E|\Psi\rangle$$

$$|\Psi(t)\rangle=e^{-\frac{i}{\hbar}\int_0^t H(t')dt'}|\Psi\rangle$$

$$|\Psi\rangle=\frac{1}{\sqrt{2\pi}}e^{ikx-i\omega t},k=\frac{p}{\hbar},\omega=\frac{E}{\hbar}=\frac{p^2}{2m\hbar}=\frac{\hbar k^2}{2m}$$



1D box

$$V(x)=\begin{cases}0, & 0<x<L\\ \infty & \text{outside box}\end{cases}$$

$$\Psi(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right),n=1,2,3......$$

$$E_n=\frac{n^2h^2}{8mL^2}$$

$$\varepsilon_{n_x n_y n_z}=\frac{h^2(l_x^2+l_y^2+l_z^2)}{8mL^2}$$
$$l_x,l_y,l_z=1,2,3...$$

Examples

1. 1 D box
2. **Harmonic oscillator**
3. H atom
4. Double well
5. Coherent state

Harmonic oscillator

Harmonic oscillator:

$$H=\frac{\mathbf{p}^2}{2m}+V(\mathbf{x}) \qquad V(x)=\frac{1}{2}m\omega^2x^2$$

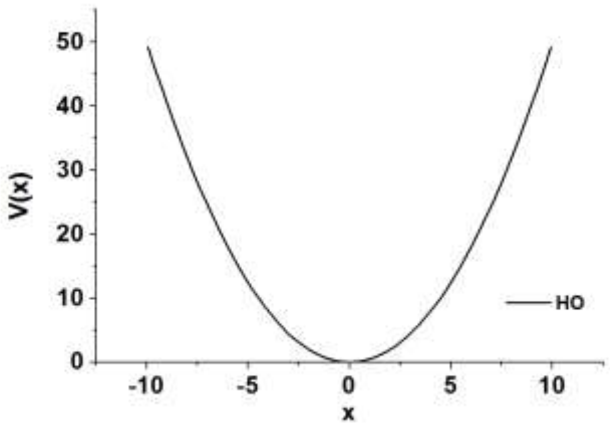
$$m\frac{d^2x}{dt^2}=\frac{dp}{dt}=-\nabla V(x)=-m\omega^2x \quad\longrightarrow\quad x(t)=x(0)\cos\omega t+\frac{p(0)}{m\omega}\sin\omega t$$

$$p(t)=-m\omega x(0)\sin\omega t+p(0)\cos\omega t$$

$$H|\Psi\rangle=E|\Psi\rangle \qquad [X,P]=i\hbar$$

$$|\Psi(t)\rangle=e^{-\frac{i}{\hbar}\int_0^t H(t')dt'}|\Psi\rangle$$

$$H|\Psi\rangle=\left(-\frac{\hbar^2}{2m}\nabla^2+\frac{1}{2}m\omega^2X^2\right)|\Psi\rangle=E|\Psi\rangle$$



Introduce

$$\hat{X}=\sqrt{\frac{m\omega}{\hbar}}X \qquad [\hat{X},\hat{P}]=i$$

$$\hat{P}=\sqrt{\frac{1}{m\hbar\omega}}P \qquad H=\hbar\omega\hat{H},\ \hat{H}=\frac{1}{2}\left(\hat{X}^2+\hat{P}^2\right)$$

Define

$$a=\frac{1}{\sqrt{2}}\left(\hat{X}+i\hat{P}\right) \qquad a^+=\frac{1}{\sqrt{2}}\left(\hat{X}-i\hat{P}\right)$$

$$\longrightarrow \quad \hat{X}=\frac{1}{\sqrt{2}}\left(a^++a\right) \qquad \hat{P}=\frac{i}{\sqrt{2}}\left(a^+-a\right)$$

Operators

$$[a,a^{+}]=\left[\frac{1}{\sqrt{2}}(\hat{X}+i\hat{P}),\frac{1}{\sqrt{2}}(\hat{X}-i\hat{P})\right]=1$$

$$a^{+}a=\frac{1}{2}(\hat{X}^{2}+\hat{P}^{2}-1)$$

$$\hat{H}=a^{+}a+\frac{1}{2}=aa^{+}-\frac{1}{2}\equiv N+\frac{1}{2}$$

$$[N,a]=[a^{+}a,a]=-a$$

$$[N,a^{+}]=[a^{+}a,a]=a^{+}$$

Look for

$$N|\varphi_{v}^{i}\rangle=v|\varphi_{v}^{i}\rangle$$

1. $v\geq 0$ $\quad \left\| a|\varphi_{v}^{i}\rangle \right\|^{2}=\langle\varphi_{v}^{i}|N|\varphi_{v}^{i}\rangle\geq 0$

2. $a|\varphi_{v=0}^{i}\rangle=0$

   $N\left[a|\varphi_{v}^{i}\rangle\right]=(v-1)\left[a|\varphi_{v}^{i}\rangle\right]$

3. $a^{+}|\varphi_{v}^{i}\rangle>0$

   $N\left[a^{+}|\varphi_{v}^{i}\rangle\right]=(v+1)\left[a^{+}|\varphi_{v}^{i}\rangle\right]$

Destruction and creation operators

$$v=n$$

$$a^{n+1}|\varphi_{n}^{i}\rangle=0$$

$$E_{n}=\left(n+\frac{1}{2}\right)\hbar\omega,\ \ \mathrm{n}=0,1,2,......$$

Eigen state

Solve for ground state

$$a|\varphi_0^i\rangle = 0$$

$$\langle x'|p|\alpha\rangle = -i\hbar\frac{\partial}{\partial x'}\langle x'|\alpha\rangle$$

$$\frac{1}{\sqrt{2}}\left[\sqrt{\frac{m\omega}{\hbar}}X + \frac{i}{\sqrt{m\omega\hbar}}P\right]|\varphi_0^i\rangle = 0 \Longrightarrow \left[\sqrt{\frac{m\omega}{\hbar}}x + \frac{i}{\sqrt{m\omega\hbar}}\left(-i\hbar\frac{d}{dx}\right)\right]\varphi_0^i(x) = 0$$

$$\varphi_0^i(x) = ce^{-\frac{1}{2}\frac{m\omega}{\hbar}x^2}$$

Linear first-order ODEs:

$$\frac{dy}{dx} + p(x)y = q(x) \qquad y(x) = e^{-\int p(x)dx}\left[\int q(x)e^{\int p(x)dx}dx + C\right]$$

$$N = a^+a$$

$$N|\varphi_{n+1}^i\rangle = a^+a|\varphi_{n+1}^i\rangle = a^+\left[c^i|\varphi_n\rangle\right] \Rightarrow |\varphi_{n+1}^i\rangle = \frac{c^i}{n+1}a^+|\varphi_n\rangle$$

Non-degenerate

$$N\left[a|\varphi_v^i\rangle\right] = (v-1)\left[a|\varphi_v^i\rangle\right]$$

$$N\left[a^+|\varphi_v^i\rangle\right] = (v+1)\left[a^+|\varphi_v^i\rangle\right]$$

Eigen vector

$$|\varphi_n\rangle = c_n a^+|\varphi_{n-1}\rangle \qquad \langle\varphi_n|\varphi_n\rangle = |c_n|^2\langle\varphi_{n-1}|aa^+|\varphi_{n-1}\rangle$$

$$= |c_n|^2\langle\varphi_{n-1}|a^+a+1|\varphi_{n-1}\rangle = |c_n|^2 n = 1$$

$$\Longrightarrow c_n = \frac{1}{\sqrt{n}}$$

$$|\varphi_n\rangle = \frac{1}{\sqrt{n}}a^+|\varphi_{n-1}\rangle = \frac{1}{\sqrt{n!}}(a^+)^n|\varphi_0\rangle$$

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Action

Lower and upper operators

$$a^+|\varphi_n\rangle = \sqrt{n+1}|\varphi_{n+1}\rangle$$
$$a|\varphi_n\rangle = \sqrt{n}|\varphi_{n-1}\rangle$$

Adjoint Eq.

$$\langle\varphi_n|a = \sqrt{n+1}\langle\varphi_{n+1}|$$
$$\langle\varphi_n|a^+ = \sqrt{n}\langle\varphi_{n-1}|$$

$$X|\varphi_n\rangle = \sqrt{\frac{\hbar}{m\omega}}\frac{1}{\sqrt{2}}(a^+ + a)|\varphi_n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n+1}|\varphi_{n+1}\rangle + \sqrt{n}|\varphi_{n-1}\rangle\right)$$
$$P|\varphi_n\rangle = \sqrt{m\hbar\omega}\frac{i}{\sqrt{2}}(a^+ - a)|\varphi_n\rangle = i\sqrt{\frac{m\omega\hbar}{2}}\left(\sqrt{n+1}|\varphi_{n+1}\rangle - \sqrt{n}|\varphi_{n-1}\rangle\right)$$

$$\langle\varphi_n|X|\varphi_n\rangle = 0$$
$$\langle\varphi_n|P|\varphi_n\rangle = 0$$

$$X^2 = \frac{\hbar}{2m\omega}(a^+ + a)(a^+ + a) = \frac{\hbar}{2m\omega}\left[(a^+)^2 + a^+a + aa^+ + a^2\right]$$
$$\langle\varphi_n|X^2|\varphi_n\rangle = \langle\varphi_n|\frac{\hbar}{2m\omega}(a^+a + aa^+)|\varphi_n\rangle = \left(n+\frac{1}{2}\right)\frac{\hbar}{m\omega}$$
$$P^2 = -\frac{m\omega\hbar}{2}(a^+ - a)(a^+ - a) = -\frac{m\omega\hbar}{2}\left[(a^+)^2 - a^+a - aa^+ + a^2\right]$$
$$\langle\varphi_n|P^2|\varphi_n\rangle = \langle\varphi_n|\frac{m\omega\hbar}{2}(a^+a + aa^+)|\varphi_n\rangle = \left(n+\frac{1}{2}\right)m\omega\hbar$$

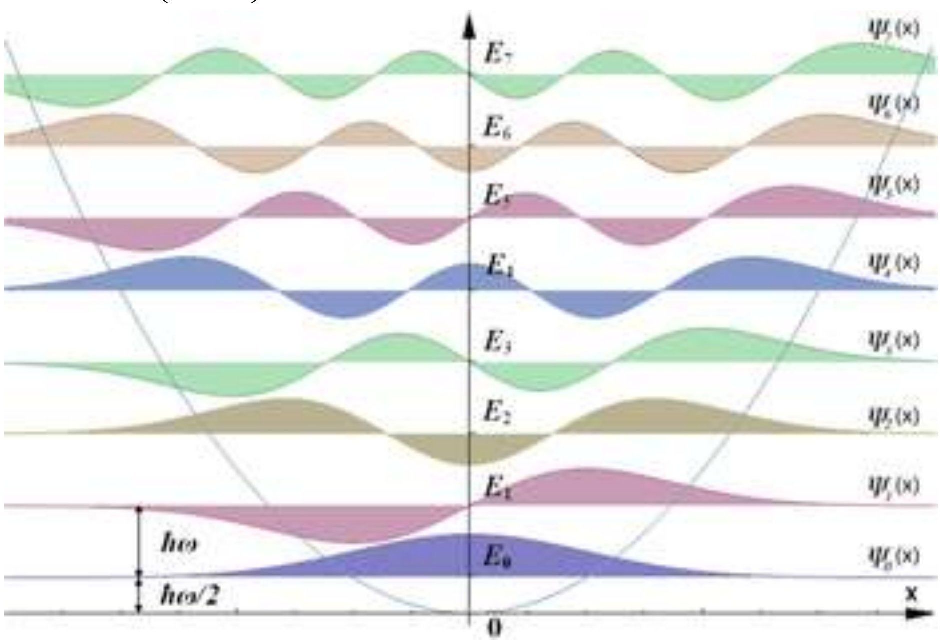
$$\Rightarrow (\Delta X)(\Delta P) = \left(n+\frac{1}{2}\right)\hbar$$

Wave functions

$$\varphi_n(x)=\sqrt{\frac{1}{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\xi^2/2}H_n(\xi)$$

$$=\left[\frac{1}{2^n n!}\left(\frac{\hbar}{m\omega}\right)^n\right]^{1/2}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\left[\frac{m\omega}{\hbar}x-\frac{d}{dx}\right]^n e^{-\frac{1}{2}\frac{m\omega}{\hbar}x^2}$$

$$E_n=h\omega\left(n+\frac{1}{2}\right), n=1,2,3......$$



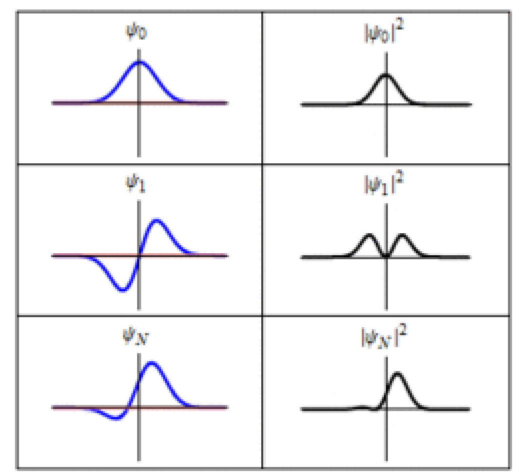
$$H_n(\xi)=(-1)^n e^{\xi^2}\frac{\partial^n}{\partial\xi^n}e^{-\xi^2},\quad \xi=\sqrt{\frac{m\omega}{\hbar}}x$$

$$\int_{-\infty}^{\infty}H_{n'}(\xi)H_n(\xi)e^{-\xi^2}d\xi=\pi^{1/2}2^n!\delta_{nn'}$$

$$\frac{d^2}{d\xi^2}H_n-2\xi\frac{dH_n}{d\xi}+2nH_n=0$$

$$H_0(\xi)=1, H_1(\xi)=2\xi, H_2(\xi)=4\xi^2-2$$

$$H_3(\xi)=8\xi^3-12\xi, H_4(\xi)=16\xi^4-48\xi^2+12$$



Examples

1. 1 D box
2. Harmonic oscillator
3. **H atom**
4. Double well
5. Coherent state

H atom

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla_r^2 - \frac{Ze^2}{|r-R|}$$

In the COM frame

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{r} \qquad \mu = \frac{m_e m_p}{m_e + m_p} \approx m_e\left(1 - \frac{m_e}{m_p}\right)$$

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

Spherical polar coordinates:

$$\frac{1}{r^2\sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{\partial^2\psi}{\partial\varphi^2}\right] + \frac{2\mu}{\hbar^2}\left(\frac{Ze^2}{r} + E\right)\psi = 0$$

$$\psi(r,\theta,\varphi) = \sum_{n,l,m} R_{n,l}(r)Y_l^m(\theta,\varphi) \qquad \psi_{n,l,m}(r,\theta,\varphi) = \frac{1}{r}u_{n,l}(r)Y_l^m(\theta,\varphi)$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{r}\right]u_{n,l}(r) = E_{n,l}u_{n,l}(r),$$

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + l(l+1)\right]Y_l^m(\theta,\varphi) = 0, \quad -i\frac{\partial}{\partial\varphi}Y_l^m(\theta,\varphi) = mY_l^m(\theta,\varphi)$$

H atom

$$R_{nl}(r)=-\left\{\left(\frac{2Z}{na_0}\right)^3\frac{(n-l-1)!}{2n[(n+1)!]^3}\right\}^{1/2}e^{-\rho/2}\rho^l L_{n+l}^{2l+1}(\rho)$$

$$L_p^q(\rho)=\frac{d^q}{d\rho^q}L_p(\rho)$$

$$L_p(\rho)=e^{\rho}\frac{d^p}{d\rho^p}\left(\rho^p e^{-\rho}\right)$$

$$\rho=\left(\frac{8\mu|E|}{\hbar^2}\right)^{1/2}r$$

$$\int e^{-\rho}\rho^{2l}\left[L_{n+l}^{2l+1}(\rho)\right]^2\rho^2 d\rho=\frac{2n[(n+l)!]^3}{(n-l-1)!}$$

$$Y_l^m(\theta,\varphi)=(-1)^m\sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi}$$

$$Y_l^m(\theta,\varphi)=(-1)^{|m|}Y_l^{|m|}*(\theta,\varphi),\quad (m<0)$$

$$P_l^m(\cos\theta)=\left(1-\cos^2\theta\right)^{m/2}\frac{d^m}{d(\cos\theta)^m}P_l(\cos\theta)$$

$$P_l(\cos\theta)=\frac{(-1)^l}{2^l l!}\frac{d^l\left(1-\cos^2\theta\right)^l}{d(\cos\theta)^l}$$

$$R_{10}(r)=\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}2e^{-Zr/a_0}$$

$$R_{20}(r)=\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}(2-Zr/a_0)e^{-Zr/2a_0}$$

$$R_{10}(r)=\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\frac{Zr}{\sqrt{3}a_0}e^{-Zr/a_0}$$

$$E_n=-\frac{Z^2e^2}{2n^2a_0}$$

$$a_0=\frac{\hbar^2}{m_e e^2}$$

$$\rho=\frac{2Zr}{na_0},n\geq l+1$$

Bohr model

$$v=\frac{e^2}{n\hbar}$$

$$r=\frac{n^2\hbar^2}{me^2}$$

$$E=-\frac{me^4}{2\hbar^2n^2}$$

H atom