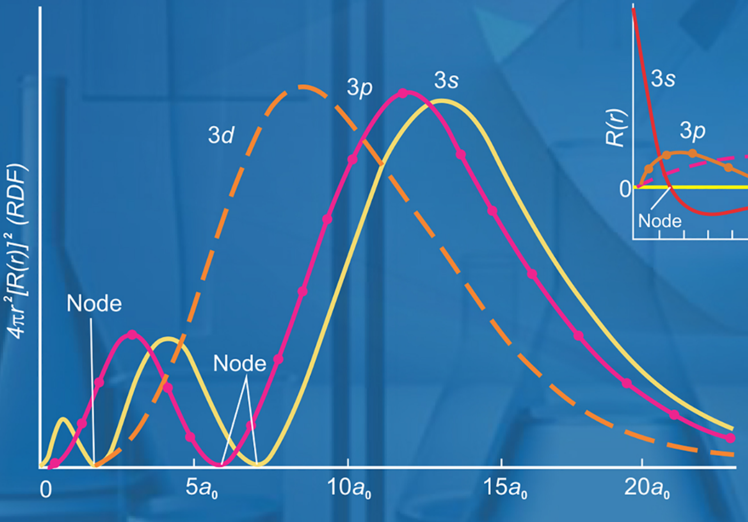
Volume 1

Third Edition

Fundamental Concepts of Inorganic Chemistry



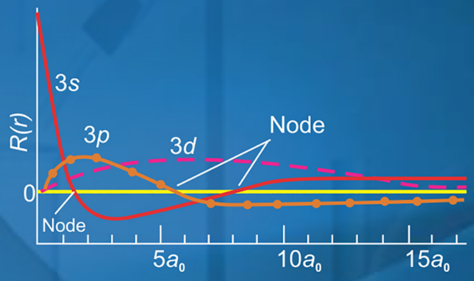


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Illustration 4: Say, $\widehat{A} = \frac{(\widehat{p_x})^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} = \widehat{E_x}$ (kinetic energy operator), $\widehat{B} = \widehat{p_x}$.

$$\widehat{A}\,\widehat{B}\psi_x = \widehat{E_x}\,\widehat{p_x}\,\psi_x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left(\frac{\hbar}{i}\frac{d\psi_x}{dx}\right) = -\frac{\hbar^3}{2mi}\frac{d^3\psi_x}{dx^3}$$

and

$$\widehat{B}\,\widehat{A}\,\psi_x = \frac{\hbar}{i}\frac{d}{dx}\left(-\frac{\hbar^2}{2m}\frac{d^2\psi_x}{dx^2}\right) = -\frac{\hbar^3}{2mi}\frac{d^3\psi_x}{dx^3}$$

i.e.

$$\left[\widehat{E_x}\,\widehat{p_x} - \widehat{p_x}\,\widehat{E_x}\right]\psi_x = 0, \text{ or } \left[\widehat{E_x}, \widehat{p_x}\right] = 0$$

$\therefore$ $\widehat{E_x}$ and $\widehat{p_x}$ commute.

Illustration 5: Evaluation of $\left[\hat{x}, \widehat{p_y}\right]$ and $\left[\hat{x}, \widehat{p_x}\right]$ for a particle in a two dimensional box.

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

Let

$$\psi = f(x)\,f(y)$$

$$\left[\hat{x}, \widehat{p_y}\right] f(x)f(y) = \left[\hat{x}, \frac{\hbar}{i}\frac{\partial}{\partial y}\right] f(x)f(y) = x\frac{\hbar}{i}\frac{\partial}{\partial y} f(x)f(y) - \frac{\hbar}{i}\frac{\partial}{\partial y} x f(x)f(y)$$

$$= \frac{\hbar}{i} x f(x)\, f'(y) - \frac{\hbar}{i} x f(x) f'(y) = 0$$

i.e. $\hat{x}$ $(= x)$ and $\widehat{p_y}$ commute.

$$\left[\hat{x}, \widehat{p_x}\right] f(x)f(y) = \left[\hat{x}, \frac{\hbar}{i}\frac{\partial}{\partial x}\right] f(x)f(y)$$

$$= x\frac{\hbar}{i}\frac{\partial}{\partial x} f(x)f(y) - \frac{\hbar}{i}\frac{\partial}{\partial x} x f(x)f(y)$$

$$= x\frac{\hbar}{i} f'(x)f(y) - \left\{\frac{\hbar}{i} f(x)f(y) + \frac{\hbar}{i} x f'(x)f(y)\right\}$$

$$= -\frac{\hbar}{i} f(x)f(y) = i\hbar\, f(x)f(y)$$

i.e. $\left[\hat{x}, \widehat{p_x}\right] = i\hbar \neq 0$

Illustration 6: Evaluate $\left[\hat{x}^n, \widehat{p_x}\right]$ for a particle in a one dimensional box.

$$\left[\hat{x}^n, \widehat{p_x}\right]\psi_x = \hat{x}^n\,\widehat{p_x}\,\psi_x - \widehat{p_x}\,\hat{x}^n\,\psi_x;\ \hat{x} = x \text{ and } \widehat{p_x} = -i\hbar\frac{d}{dx}$$

$$= -i\hbar\, x^n \frac{d\psi_x}{dx} + i\hbar\frac{d}{dx}(x^n\,\psi_x)$$

$$= -i\hbar x^n \frac{d\psi_x}{dx} + i\hbar x^n \frac{d\psi_x}{dx} + i\hbar\, n\, x^{n-1}\psi_x$$

$$= i\hbar\, n\, x^{n-1}\,\psi_x,\ i.e.\ \left[\hat{x}^n, \widehat{p_x}\right] = i\hbar\, n\, x^{n-1}$$

Illustration 7: Evaluate $[\widehat{A}, \widehat{B}]$ when $\widehat{A} = \frac{d}{dx} + x^2$ and $\widehat{B} = \frac{d}{dx} - x^2$.

To evaluate $[\widehat{A}, \widehat{B}]$ let us apply the operator to an arbitrary function, $\psi = f(x)$, i.e.

$$[\hat{A},\hat{B}]f(x)=\hat{A}\hat{B}f(x)-\hat{B}\hat{A}f(x)$$

$$\hat{A}\hat{B}f(x)=\left(\frac{d}{dx}+x^2\right)\left(\frac{d}{dx}-x^2\right)f(x)=\left[\frac{d}{dx}+x^2\right]\left[\frac{d}{dx}f(x)-x^2f(x)\right]$$

$$=\frac{d^2}{dx^2}f(x)-\frac{d}{dx}x^2f(x)+x^2\frac{d}{dx}f(x)-x^4f(x)$$

$$\hat{B}\hat{A}f(x)=\left(\frac{d}{dx}-x^2\right)\left(\frac{d}{dx}+x^2\right)f(x)=\left(\frac{d}{dx}-x^2\right)\left[\frac{d}{dx}f(x)+x^2f(x)\right]$$

$$=\frac{d^2}{dx^2}f(x)+\frac{d}{dx}x^2f(x)-x^2\frac{d}{dx}f(x)-x^4f(x)$$

$$\hat{A}\hat{B}f(x)-\hat{B}\hat{A}f(x)=2x^2\frac{d}{dx}f(x)-2\frac{d}{dx}x^2f(x)=2x^2\frac{d}{dx}f(x)-2\times 2xf(x)-2x^2\frac{d}{dx}f(x)$$

$$=2x^2f'(x)-4xf(x)-2x^2f'(x)=-4xf(x)$$

Deleting the arbitrary function $f(x)$, we get the operator equation, $[\hat{A},\hat{B}]=-4x$

Illustration 8: Find the condition for $\left(\hat{A}+\hat{B}\right)^2=\hat{A}^2+2\hat{A}\hat{B}+\hat{B}^2$

$$\left(\hat{A}+\hat{B}\right)^2=\left(\hat{A}+\hat{B}\right)\left(\hat{A}+\hat{B}\right)=\hat{A}^2+\hat{A}\hat{B}+\hat{B}\hat{A}+\hat{B}^2$$

$$=\hat{A}^2+2\hat{A}\hat{B}+\hat{B}^2,\text{ if }\hat{A}\hat{B}=\hat{B}\hat{A},\ i.e.\left[\hat{A},\hat{B}\right]=0$$

The condition is that $\hat{A}$ and $\hat{B}$ are to commute.

Illustration 9: Evaluate (i) $\left[x^3,\frac{d}{dx}\right]$; (ii) $\left[\hat{2},\frac{d}{dx}\right]$; (iii) $\left[\frac{d}{dx},\hat{x}\right]$.

To evaluate $[\hat{A},\hat{B}]$, let us apply this operator to an arbitrary function, $\psi=f(x)$

(i) $\left[x^3,\frac{d}{dx}\right]f(x)=\left[x^3\frac{d}{dx}-\frac{d}{dx}x^3\right]f(x)=x^3\frac{d}{dx}f(x)-\frac{d}{dx}x^3f(x)$

$$=x^3f'(x)-3x^2f(x)-x^3f'(x)=-3x^2f(x);\ i.e.\left[x^3,\frac{d}{dx}\right]=-3x^2$$

(ii) $\left[\hat{2},\frac{d}{dx}\right]f(x)=\hat{2}\frac{d}{dx}f(x)-\frac{d}{dx}\hat{2}f(x)=2f'(x)-2f'(x)=0;\ (\hat{2}=2)$

$i.e.\left[\hat{2},\frac{d}{dx}\right]=0$ ($\hat{2}$ and $\frac{d}{dx}$ operators are to commute)

(iii) $\left[\frac{d}{dx},\hat{x}\right]f(x)=\left[\frac{d}{dx}\hat{x}-\hat{x}\frac{d}{dx}\right]f(x)=\frac{d}{dx}xf(x)-x\frac{d}{dx}f(x)$

$$=f(x)+xf'(x)-xf'(x)=f(x);\ (cf.\ \hat{x}=x)$$

i.e. $\left[\frac{d}{dx},\hat{x}\right]=1;$ (the operators $\frac{d}{dx}$ and $\hat{x}$ are not to commute)

- **Linear operator:** $\hat{A}$ is a linear operator, it has the following **two properties:**

$$\hat{A}[f(x)+g(x)]=\hat{A}f(x)+\hat{A}g(x)\text{ and }\hat{A}[cf(x)]=c\hat{A}f(x);\ c=a\text{ constant}$$

It gives: $\hat{A}[c_1f(x)+c_2g(x)]=c_1\hat{A}f(x)+c_2\hat{A}g(x)$

Examples of linear operators: $\hat{x}^2, d/dx, d^2/dx, \hat{E}_k$, etc.

Differentiation and integration are the linear operators, but square root is not a linear operator.

$$\frac{d}{dx}(ax^n+bx^m)=\frac{d}{dx}(ax^n)+\frac{d}{dx}(bx^m)\quad\text{and}\quad\int(ax^n+bx^m)dx=\int ax^ndx+\int bx^mdx$$

$$\sqrt{f(x)+g(x)}\neq\sqrt{f(x)}+\sqrt{g(x)}$$

The adjoint of $\widehat{A}$ is denoted as $\widehat{A}^{\dagger}$ (read as A-dagger). It gives:

$$\langle \psi | \widehat{A} | \psi \rangle^* = \langle \psi | \widehat{A}^{\dagger} | \psi \rangle$$

For a Hermitian operator, $\widehat{A} = \widehat{A}^{\dagger}$. **Thus a Hermitian operator is self-adjoint.** $\widehat{A}$ is anti-Hermitian, if $\widehat{A} = -\widehat{A}^{\dagger}$. Thus the d/dx operator is anti-Hermitian.

3.4.8 Degenerate Wave Functions and their Linear Combination

If two eigenfunctions (say, ψ_1 and ψ_2) have the same same eigenvalue, then the eigenfunctions are said to be **degenerate**. If the eigenvalue is energy (E), then it corresponds to the Hamiltonian operator $(\widehat{H})$.

$$\widehat{H}\psi_1 = E\psi_1 \text{ and } \widehat{H}\psi_2 = E\psi_2$$

Under this condition, the **linear combination of ψ_1 and ψ_2 is also an eigenfunction,** because the above relations lead to:

$$\widehat{H}(c_1\psi_1 + c_2\psi_2) = E(c_1\psi_1 + c_2\psi_2); \; c_1 \text{ and } c_2 \text{ are constants.}$$

If there are n-eigenfunctions having the same eigenvalue (E), then the energy level is said to have the n-fold degeneracy.

Say ψ_1 and ψ_2 are two normalised wave functions for a given Hamiltonian operator, **then they must be orthogonal.** Let us construct the normalised wave function by the linear combination of ψ_1 and ψ_2.

$$\psi_3 = c_1\psi_1 + c_2\psi_2$$

then, $$\int \psi_3^* \psi_3 \, d\tau = \int (c_1^*\psi_1^* + c_2^*\psi_2^*)(c_1\psi_1 + c_2\psi_2)\, d\tau$$

$$= c_1^* c_1 \int \psi_1^* \psi_1 \, d\tau + c_2^* c_2 \int \psi_2^* \psi_2 \, d\tau + c_1^* c_2 \int \psi_1^* \psi_2 \, d\tau + c_2^* c_1 \int \psi_2^* \psi_1 \, d\tau$$

i.e. $$1 = c_1^* c_1 + c_2^* c_2 + c_1^* c_2 \times 0 + c_2^* c_1 \times 0; \text{ or } c_1^* c_1 + c_2^* c_2 = 1$$

$$\left(cf. \int \psi_1^* \psi_1 \, d\tau = 1, \int \psi_2^* \psi_2 \, d\tau = 1, \int \psi_1^* \psi_2 \, d\tau = 0, \int \psi_2^* \psi_1 \, d\tau = 0 \right)$$

The process can be extended for more than two wave functions.

3.5 SOME APPLICATIONS OF THE SCHRÖDINGER'S WAVE EQUATION

3.5.1 Free Particle in One Dimension

Let us consider a particle (say, an electron) of mass m which is allowed to move freely in one dimension without any restriction in a field. As there is no restriction in its movement, the potential energy may be assumed to be zero.

To find out the energy values (E) and wave functions (ψ) of the particle, we are to consider the Schrödinger's time independent wave equation. Here the potential energy, $V = 0$. Thus, the Schrödinger's wave equation in one dimension becomes,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0; \text{ or, } \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E\psi = 0; \text{ (as, } V = 0) \qquad \ldots(3.5.1.1)$$

The above time independent Schrödinger wave equation may be obtained from the equation, $\widehat{H}\psi = E\psi$ where the Hamiltonian operator $(\widehat{H})$ is given by:

$$\widehat{H_{\text{kin}}} = \widehat{H} = \frac{\widehat{p_x}^2}{2m}$$

$$= \left(\frac{2}{l}\right)\left(-\frac{h^2}{8\pi^2 m}\right)\left\{-\left(\frac{n\pi}{l}\right)^2\right\}\int_0^l \sin^2\left(\frac{n\pi x}{l}\right)dx$$

$$= \left(\frac{2}{l}\right)\left(\frac{h^2}{8\pi^2 m}\right)\left(\frac{n\pi}{l}\right)^2 \frac{1}{2}\int_0^l \left[1-\cos\left(\frac{2n\pi x}{l}\right)\right]dx$$

$$= \left(\frac{2}{l}\right)\left(\frac{h^2}{8\pi^2 m}\right)\left(\frac{n\pi}{l}\right)^2 \frac{1}{2}\left[x-\frac{l}{n\pi x}\sin\left(\frac{2n\pi x}{l}\right)\right]_0^l$$

$$= \left(\frac{2}{l}\right)\left(\frac{h^2}{8\pi^2 m}\right)\left(\frac{n\pi}{l}\right)^2 \left(\frac{1}{2}l\right) = \frac{n^2h^2}{8ml^2}$$

***Problem 19* :** Find the energy of a particle in a one dimensional box of length l from the Wilson-Sommerfeld quantisation principle.

***Solution* :** The particle is moving back and forth within the one dimensional box of length l. Thus in one period, it covers the $2l$ length.

The Wilson-Sommerfeld quantisation principle states:

$\oint p_x\,dx = nh$; $\oint$ indicates the integration taken over one period of motion; p_x denotes the momentum along the x-direction and **it is a constant as no force is acting on the particle.**

i.e. $$p_x\oint dx = nh \quad \text{or,}\quad p_x \times 2l = nh \quad \text{or,}\quad p_x = \frac{nh}{2l}$$

It gives: $E_{\text{kin}} = \dfrac{p_x^2}{2m} = \dfrac{n^2h^2}{8ml^2}$

***Problem 20a* :** Find $\widehat{A}^2$ when the operator $\widehat{A}$ is defined as:

(i) $\widehat{A} = x\dfrac{d}{dx}$, (ii) $\widehat{A} = \dfrac{d}{dx} + x$, (iii) $\widehat{A} = \dfrac{\hbar}{i}\dfrac{d}{dx}$, (iv) $\widehat{A} = \dfrac{\hbar}{i}\dfrac{d}{dx} + x$

***Solution* :** $\widehat{A}^2, \widehat{A}\widehat{A}$ (i.e. square of an operator is the product of the operator with itself). To evaluate $\widehat{A}^2$, we apply this operator to an arbitrary function, $\psi = f(x)$.

(i) $$\widehat{A}^2\psi = x\frac{d}{dx}\left(x\frac{d}{dx}\right)f(x) = x\frac{d}{dx}[xf'(x)] = x[f'(x) + xf''(x)]$$

$$= \left[x\frac{d}{dx} + x^2\frac{d^2}{dx^2}\right]f(x) = \left[x\frac{d}{dx} + x^2\frac{d^2}{dx^2}\right]\psi$$

$$i.e.\ \widehat{A}^2 = x\frac{d}{dx} + x^2\frac{d^2}{dx^2} = x\widehat{D} + x^2\widehat{D}^2, \widehat{D} = \frac{d}{dx}, \widehat{D}^2 = \frac{d^2}{dx^2}$$

(ii) $$\widehat{A}^2\psi = \left(\frac{d}{dx} + x\right)\left(\frac{d}{dx} + x\right)f(x) = \left(\frac{d}{dx} + x\right)[f'(x) + xf(x)]$$

$$= \frac{d}{dx}f'(x) + \frac{d}{dx}xf(x) + xf'(x) + x^2f(x)$$

$$= f''(x) + f(x) + xf'(x) + xf'(x) + x^2f(x)$$

$$= \left(\frac{d^2}{dx^2} + 2x\frac{d}{dx} + x^2 + 1\right)f(x) = \left(\frac{d^2}{dx^2} + 2x\frac{d}{dx} + x^2 + 1\right)\psi$$

$$i.e.\ \widehat{A}^2 = \frac{d^2}{dx^2} + 2x\frac{d}{dx} + x^2 + 1 = \widehat{D}^2 + 2x\widehat{D} + x^2 + 1$$

(iii) $\widehat{A}^2\psi = \widehat{A}\widehat{A}\psi = \frac{\hbar}{i}\frac{d}{dx}\left(\frac{\hbar}{i}\frac{d}{dx}\right)\psi = \frac{\hbar^2}{i^2}\frac{d^2}{dx^2}\psi = -\hbar^2\frac{d^2}{dx^2}\psi,$ *i.e.* $\widehat{A}^2 = -\hbar^2\frac{d^2}{dx^2}$

(iv) $$\widehat{A}^2\psi = \left(\frac{\hbar}{i}\frac{d}{dx}+x\right)\left(\frac{\hbar}{i}\frac{d}{dx}+x\right)f(x) = \left(\frac{\hbar}{i}\frac{d}{dx}+x\right)\left[\frac{\hbar}{i}\frac{d}{dx}f(x)+xf(x)\right]$$

$$= \frac{\hbar^2}{i^2}\frac{d^2}{dx^2}f(x)+\frac{\hbar}{i}\frac{d}{dx}xf(x)+x\frac{\hbar}{i}\frac{d}{dx}f(x)+x^2f(x)$$

$$= \frac{\hbar^2}{i^2}\frac{d^2}{dx^2}f(x)+\frac{\hbar}{i}f(x)+\frac{\hbar}{i}x\frac{d}{dx}f(x)+x\frac{\hbar}{i}\frac{d}{dx}f(x)+x^2f(x)$$

$$= \left[-\hbar^2\frac{d^2}{dx^2}+\frac{\hbar}{i}+2\frac{\hbar}{i}x\frac{d}{dx}+x^2\right]f(x), (i^2=-1)$$

i.e. $\widehat{A}^2 = -\hbar^2\frac{d^2}{dx^2}+\frac{\hbar}{i}+2\frac{\hbar}{i}x\frac{d}{dx}+x^2$

Problem 20b **:** The wave function, $\psi = A\exp\left\{-\frac{i}{\hbar}(Et-px)\right\}$ is valid for a particle moving with velocity u ($\ll c$), in presence of a field of force for which the potential energy of the particle is $V(x, t)$. Show the operator for the total energy is:

$$i\hbar\frac{d}{dt} = -\frac{\hbar^2}{2m}\frac{d}{dx^2}+\widehat{V}$$

Solution **:** $\psi = A\exp\left\{-\frac{i}{\hbar}(Et-px)\right\}$

i.e. $$\frac{d\psi}{dt} = A\left(-\frac{iE}{\hbar}\right)\exp\left\{-\frac{i}{\hbar}(Et-px)\right\} = -\left(\frac{iE}{\hbar}\right)\psi$$

i.e. $$-\frac{\hbar}{i}\frac{d}{dt}\psi = E\psi, \quad (cf.\ \text{Schrödinger Eqn. } \widehat{H}\psi = E\psi)$$

∴ The operator for total energy is $-\frac{\hbar}{i}\frac{d}{dt}$, *i.e.* $i\hbar\frac{d}{dt}$

Under the condition, $u << c$, $E = E_{\text{kin}} + E_{\text{pot}} = \frac{p^2}{2m}+V$

∴ The operator for total energy is $= \frac{\widehat{p}^2}{2m}+\widehat{V}$

For the particle moving along the x-direction,

$$\widehat{p_x} \text{ (operator for momentum)} = \frac{\hbar}{i}\frac{d}{dx}$$

∴ $$i\hbar\frac{d}{dt} = \frac{1}{2m}\widehat{p_x}^2+\widehat{V} = \frac{\hbar^2}{2mi^2}\frac{d^2}{dx^2}+\widehat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\widehat{V}$$

Problem 20c **:** Justify the momentum operator for the function $\exp(ipx/\hbar)$, p = momentum

Solution **:** $\widehat{p_x}\exp(ipx/\hbar) = \frac{\hbar}{i}\frac{d}{dx}[\exp(ipx/\hbar)] = \frac{\hbar}{i}\frac{ip}{\hbar}\exp(ipx/\hbar)$

$$= p\exp(ipx/\hbar)$$

∴ $\widehat{p_x}$ is the operator for momentum.

$$[\hat{x}, \widehat{p_x}]\,\psi(x) = x\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x) + \left(i\hbar\frac{\partial}{\partial x}\right)x\psi(x)$$

$$= i\hbar\left[-x\frac{\partial\psi(x)}{\partial x} + x\frac{\partial\psi(x)}{\partial x} + \psi(x)\right]$$

$$= i\hbar\psi(x) \neq 0$$

$$[\hat{t}, \widehat{E}]\,\psi(x,t) = t\widehat{E}\,\psi(x,t) - \widehat{E}\,t\psi(x,t) = t\,i\hbar\frac{\partial}{\partial t}\psi(x,t) - i\hbar\frac{\partial}{\partial t}t\psi(x,t)$$

$$= i\hbar t\frac{\partial}{\partial t}\psi(x,t) - i\hbar t\frac{\partial}{\partial t}\psi(x,t) - i\hbar\psi(x,t);\ \widehat{E} = i\hbar\frac{\partial}{\partial t}$$

$$= -i\hbar\psi(x,t) \neq 0.$$

For $[\hat{x}, \widehat{p_x}] \neq 0$ and $[t, \widehat{E}] \neq 0$ and the corresponding conjugate observables cannot be simultaneously measured without any uncertainty. **These are in conformity with the demand of the uncertainty principle**. But, x and p_y (y-component of the momentum) can be measured precisely at the same time as $[\hat{x}, \widehat{p_y}] = 0$.

Problem 20i **:** Show that E_x (kinetic energy along the x-direction) and p_x (momentum along the x-direction) for a moving particle can be determined simultaneously and precisely.

Solution **:** The required condition is: $[\widehat{E_x}, \widehat{p_x}] = 0$, *i.e.* $\widehat{E_x}$ and $\widehat{p_x}$ commute.

$$\widehat{E_x} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \text{ and } \widehat{p_x} = \frac{\hbar}{i}\frac{d}{dx}$$

$$\widehat{E_x}\,\widehat{p_x}\,\psi_x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left(\frac{\hbar}{i}\frac{d\psi_x}{dx}\right) = -\frac{\hbar^3}{2mi}\frac{d^3\psi_x}{dx^3}$$

$$\widehat{p_x}\,\widehat{E_x}\,\psi_x = \frac{\hbar}{i}\frac{d}{dx}\left(-\frac{\hbar^2}{2m}\frac{d\psi_x}{dx}\right) = -\frac{\hbar^3}{2mi}\frac{d^3\psi_x}{dx^3}$$

$$[\widehat{E_x}, \widehat{p_x}]\,\psi_x = \widehat{E_x}\,\widehat{p_x}\,\psi_x - \widehat{p_x}\,\widehat{E_x}\,\psi_x = 0,\ i.e.\ [\widehat{E_x}, \widehat{p_x}] = 0$$

$\therefore$ E_x and p_x can be determined simultaneously.

Problem 20j **:** Find the eigenfunction of the linear momentum operator. Indicate the implication of the result.

Solution: The condition is: $\widehat{p_x}\psi_x = p_x\psi_x$

i.e. $-i\hbar\dfrac{d}{dx}\psi_x = p_x\psi_x$ where p_x = eigenvalue and ψ_x = eigenfunction.

It gives: $\dfrac{d\psi_x}{\psi_x} = \dfrac{ip_x}{\hbar}dx$

On integration, we get: $\ln\psi_x = \dfrac{ip_x x}{\hbar} + \ln A$, A = constant, $\ln A$ = integration constant

i.e. $\psi_x = A\exp(ip_x x/\hbar)$;

ψ_x must be finite in the domain $-\infty$ to $+\infty$. This is possible, if p_x is real. Thus all the real values of p_x are the eigenvalues of the linear momentum. It implies that the **linear momentum is not quantised**.

Problem 20k **:** Evaluate the commutator $\left[\dfrac{\partial^2}{\partial x^2}, x\right]$ and then $[\widehat{p_x^{\,2}}, x]$.

***Solution* :** $\left[\frac{\partial^2}{\partial x^2}, x\right] f(x) = \frac{\partial^2}{\partial x^2} x f(x) - x \frac{\partial^2}{\partial x^2} f(x)$

$$= \frac{\partial}{\partial x}\left[f(x) + x f'(x)\right] - x f''(x);\ f'(x) = \frac{\partial}{\partial x} f(x) \text{ and } f''(x) = \frac{\partial^2}{\partial x^2} f(x)$$

$$= f'(x) + f'(x) + x f''(x) - x f''(x)$$

$$= 2f'(x) = 2\frac{\partial}{\partial x} f(x)$$

It gives: $\left[\frac{\partial^2}{\partial x^2}, x\right] = 2\frac{\partial}{\partial x}$

Multiplying both sides of the above expression by $(-i\hbar)^2$, we get:

$$\left[(-i\hbar)^2 \frac{\partial^2}{\partial x^2}, x\right] = -2i\hbar\left(-i\hbar\frac{\partial}{\partial x}\right)$$

or $\quad [\widehat{p_x}^2, x] = -2i\hbar\,\widehat{p_x};\left(\widehat{p_x} = -i\hbar\frac{\partial}{\partial x}\right)$

***Problem 20l* :** Find the value of $[\hat{x}, \widehat{p_x}^n]$.

***Solution* :** We have the relation,

$$[\hat{A}, \hat{B}\hat{C}] = \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} = \hat{A}\hat{B}\hat{C} - \hat{B}\hat{A}\hat{C} + \hat{B}\hat{A}\hat{C} - \hat{B}\hat{C}\hat{A}$$

$$= [\hat{A}\hat{B} - \hat{B}\hat{A}]\hat{C} + \hat{B}[\hat{A}\hat{C} - \hat{C}\hat{A}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$$

By using the above relation, we can write:

$$[\hat{x}, \widehat{p_x}^n] = [\hat{x}, \widehat{p_x}\,\widehat{p_x}^{n-1}] = [\hat{x}, \widehat{p_x}]\,\widehat{p_x}^{n-1} + \widehat{p_x}[\hat{x}, \widehat{p_x}^{n-1}]$$

$$= i\hbar\,\widehat{p_x}^{n-1} + \widehat{p_x}[\hat{x}, \widehat{p_x}\,\widehat{p_x}^{n-2}],\ [\hat{x}, \widehat{p_x}] = i\hbar \text{ (see **Solved Problem** 20h)}$$

$$= i\hbar\,\widehat{p_x}^{n-1} + \widehat{p_x}\left\{[x, \widehat{p_x}]\,\widehat{p_x}^{n-2} + \widehat{p_x}[\hat{x}, \widehat{p_x}^{n-2}]\right\}$$

$$= i\hbar\,\widehat{p_x}^{n-1} + \widehat{p_x}\left\{i\hbar\,\widehat{p_x}^{n-2} + \widehat{p_x}[\hat{x}, \widehat{p_x}\,\widehat{p_x}^{n-3}]\right\}$$

$$= i\hbar\,\widehat{p_x}^{n-1} + i\hbar\,\widehat{p_x}^{n-1} + \widehat{p_x}^2[\hat{x}, \widehat{p_x}\,\widehat{p_x}^{n-3}]$$

$$= \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$= n i\hbar\,\widehat{p_x}^{n-1}$$

For $n = 2$, *i.e.* $[x, \widehat{p_x}^2] = 2i\hbar\,\widehat{p_x}$. (*cf.* **Solved Problem** 20k)

Problems on Hermitian operators: See text.

***Problem 21* :** Show that the eigen functions of a particle in a one dimensional box are not the eigen functions to the momentum operator but to the kinetic energy operator.