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

Prove

**Example**

\[
\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x
\]

\[
[\hat{L}_z, \hat{p}_y] = [xp_y - yp_x, p_y] = [xp_y, p_y] - [yp_x, p_y] = -[y, p_y]p_x
\]

\[
0 = y[p_x, p_y] + [y, p_y]p_x
\]

\[
\hat{L}_z, \hat{p}_y = -i\hbar\hat{p}_x
\]
Problems

Page 696

16.16 (a)
16.18
III. Quantum operators and observables

- Operator algebra
- Classical correspondence
- Particle on a ring
- Expectation and Interpretation of wave function
III-3. Particle on a ring

\[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi(x, y) + V(x, y)\psi(x, y) = E\psi(x, y)\]

\[V(x, y) = \begin{cases} 0, & x^2 + y^2 = R^2 \\ \infty, & \text{otherwise} \end{cases}\]

\[x = R\cos\phi, \quad y = R\sin\phi\]

\[\psi(x, y) = \Theta(\phi)\]

\[\frac{\partial^2 \psi(x, y)}{\partial x^2} = \frac{d^2\Theta}{d\phi^2}\left(\frac{\partial\phi}{\partial x}\right)^2 + \frac{d\Theta}{d\phi}\left(\frac{\partial^2 \phi}{\partial x^2}\right)\]

\[\frac{\partial^2 \psi(x, y)}{\partial y^2} = \frac{d^2\Theta}{d\phi^2}\left(\frac{\partial\phi}{\partial y}\right)^2 + \frac{d\Theta}{d\phi}\left(\frac{\partial^2 \phi}{\partial y^2}\right)\]

\[\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi = \frac{1}{R^2} \frac{d^2}{d\phi^2} \Theta\]
\[
- \frac{\hbar^2}{2 \mu R^2} \frac{d^2}{d\phi^2} \Theta(\phi) = E \Theta(\phi)
\]

\[
\Theta(\phi + 2\pi) = \Theta(\phi)
\]

\[
\psi(\phi) = Ae^{ik\phi}
\]

\[
k = \sqrt{\frac{2IE}{\hbar^2}}
\]

\[
k = \sqrt{\frac{2IE}{\hbar^2}} = m, \implies E_m = \frac{m^2 \hbar^2}{2I}
\]

\[
m = 0, \pm 1, \pm 2, \ldots
\]

\[
I = \mu R^2
\]

Momentum of inertia
Application for Benzene again

Six free electrons

C-C bond = 140 pm

R = 140 pm

The first absorption line

\[ \Delta E = \frac{\left(2^2 - 1^2\right)\hbar^2}{2m_eR^2} = \hbar \nu = h \tilde{\nu}c \]

\[ \lambda = 1 / \tilde{\nu} = 212 \, \text{nm} \]

\[ m_e = 9.1094 \times 10^{-31} \, \text{kg} \]

\[ \hbar = 1.0546 \times 10^{-34} \, \text{J} \cdot \text{s} \]
Connection to angular momentum

\[ L_z = xp_y - yp_x = \frac{\hbar}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = \frac{\hbar}{i} \frac{d}{d\phi} \]

\[ L_z e^{im\phi} = m \hbar e^{im\phi} \]

Sign indicates direction of rotation

\[ L_z e^{-im\phi} = -m \hbar e^{-im\phi} \]

Kinetic energy (particle on a ring)

\[ \hat{T} = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) = -\frac{\hbar^2}{2\mu R^2} \frac{\partial^2}{\partial \phi^2} = \frac{L_z^2}{2\mu R^2} \]
Kinetic energy for a particle moving on a spherical surface is given by

\[ T = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = \frac{\hbar^2}{2\mu R^2} \]

\[ L^2 = L_x^2 + L_y^2 + L_z^2 \]

Prove

\[ L^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \]

Start from \[ \psi(x, y, z) = \Theta(\theta, \phi) \]
III-4. Expectation and Interpretation of wave function

From the Schrödinger equation

\[ \Psi(x, y, z, t) = \psi(x, y, z) \]

Wave function for determining state of a system

From the classical mechanics

\[ \hat{A} = A(x, y, z; \frac{\hbar}{i} \frac{\partial}{\partial x}, \frac{\hbar}{i} \frac{\partial}{\partial y}, \frac{\hbar}{i} \frac{\partial}{\partial z}) \]

Operator for calculating observable in this state

Expectation value

\[ \langle A \rangle = \frac{\int \Psi^* \hat{A} \Psi \, dx dy dz}{\int \Psi^* \Psi \, dx dy dz} \]

Wave function has statistical interpretation
### Statistical experiment

$\text{Up} = 0$

$\text{Down} = 1$

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>N-1</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td></td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

$n$ up arrangements

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>result</th>
<th>probability</th>
<th>$w_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$p_0$</td>
<td>$w_0 = 0$</td>
</tr>
<tr>
<td>$N$</td>
<td>$p_1$</td>
<td>$w_1 = 1$</td>
</tr>
<tr>
<td>$(N-1)(N-2)/2$</td>
<td>$p_2$</td>
<td>$w_2 = 2$</td>
</tr>
<tr>
<td>$N!/n!(N-n)!$</td>
<td>$p_n$</td>
<td>$w_n = n$</td>
</tr>
<tr>
<td>$N$</td>
<td>$p_{N-1}$</td>
<td>$w_{N-1} = N-1$</td>
</tr>
<tr>
<td>1</td>
<td>$p_N$</td>
<td>$w_N = N$</td>
</tr>
</tbody>
</table>

**Average of number of up**

$$\langle w \rangle = \sum_{n=0}^{N} p_n w_n \quad \rightarrow \quad \frac{N}{2}$$
All possible arrangements

\[
\sum_{n=0}^{N} \frac{N!}{n!(N-n)!} = 2^N
\]

\[
(1+x)^N = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} x^n
\]

Probability of \( n \) up

\[
p_n = \frac{N!}{n!(N-n)!} \left(\frac{1}{2}\right)^N
\]

\[
N(1+x)^{N-1} = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} nx^{n-1}
\]

Number of up in average

\[
\langle w \rangle = \sum_{n=0}^{N} p_n w_n = \frac{1}{2^N} \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} = \frac{N}{2}
\]
When \( n \) is discrete integers

\[
\langle w \rangle = \sum_{n=0}^{N} p_n w_n
\]

When \( n \) is continuous variable \( u \)

\[
\langle w \rangle = \int p(u)w(u)\,du
\]

Probability that \( w(u) \) lies in between \( u \) and \( u+du \)  

\[
\int p(u)\,du = 1 \iff \sum_{n=0}^{N} p_n = 1
\]

\( p(u) \) is called probability density

Special case \( w(u) = u \) \((w_n = n)\)
**Interpretation of wave function**

\[
\langle A \rangle = \frac{\int \psi(x)^* \hat{A}(x) \psi(x) dx}{\int \psi(x)^* \psi(x) dx}
\]

**Normalization of wave function**

\[
\int \psi(x)^* \psi(x) dx = 1
\]

\[p(x) = \psi^*(x)\psi(x)\]  \hspace{1cm} \text{\(p(x)\) is probability density} \hspace{1cm} \int p(x) dx = 1

Probability that \(A(x)\) lies in between \(x\) and \(x+dx\) = \(p(x)dx\)

\[
\langle A(t) \rangle = \int \psi(x,t)^* \hat{A}(x) \psi(x,t) dx
\]

At time \(t\)
1D

\[ \langle x \rangle = \int \psi(x)^* \hat{x} \psi(x) \, dx \]

Probability that \( x \) lies in between \( x \) and \( x + dx \) = \( \psi^*(x) \psi(x) \, dx \)

2D

\[ \langle x \rangle = \int \psi(x, y)^* \hat{x} \psi(x, y) \, dx \, dy \]

Probability that \( x \) lies in area from \( x, y \) to \( x + dx \) and \( y + dy \) = \( \psi^*(x, y) \psi(x, y) \, dx \, dy \)

3D

\[ \langle x \rangle = \int \psi(x, y, z)^* \hat{x} \psi(x, y, z) \, dx \, dy \, dz \]

Probability that \( x \) lies in volume = \( \psi^*(x, y, z) \psi(x, y, z) \, dx \, dy \, dz \)
\[ \langle A \rangle = \int \psi(x)^* \hat{A}(x) \psi(x) dx \]

(1) If \[ \psi(x) = \psi_n(x) \] where \[ \hat{A} \psi_n(x) = A_n \psi_n(x) \]

\[ \langle A \rangle = \int \psi(x)^* \hat{A}(x) \psi(x) dx = \int \psi_n(x)^* \hat{A}(x) \psi_n(x) dx = A_n \]

\[ \psi(x) = \sum_n c_n \psi_n(x) \]
\[ \int \psi(x)^* \psi(x) dx = 1 \]

\[ 1 = \sum_n c_n^* c_n = \sum_n p_n \]

\[ \langle A \rangle = \int \psi(x)^* \hat{A}(x) \psi(x) dx = \sum_n p_n A_n \]

\[ p_n = c_n^* c_n \] is probability that \( A \) stays in state \( \psi_n(x) \)
Example: Particle in 1D box

Eigenfunctions
\[ \psi_n(x) = B_n \sin \left( \frac{n\pi}{a} x \right) \]
\[ n = 1, 2, \ldots \]

Energy eigenvalues
\[ E_n = \frac{\hbar^2}{8m} \left( \frac{n}{a} \right)^2 \]

Normalization
\[ \int_0^a \psi_n(x) \psi_n(x) dx = (B_n)^2 \int_0^a \sin^2 \left( \frac{n\pi}{a} x \right) dx = (B_n)^2 \frac{a}{2} = 1 \]
\[ B_n = \sqrt{\frac{2}{a}} \]

Probability density
\[ \rho_n(x) = \psi_n(x) \psi_n(x) = \frac{2}{a} \sin^2 \left( \frac{n\pi}{a} x \right) \]

Orthogonal relation
\[ \int_0^a \psi_n(x) \psi_m(x) dx = \frac{2}{a} \int_0^a \sin \left( \frac{n\pi}{a} x \right) \sin \left( \frac{m\pi}{a} x \right) dx = 0 \quad m \neq n \]
$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \left( \frac{n\pi}{a} x \right)$$

$$\rho_n(x) = \psi_n(x) \psi_n(x) = \frac{2}{a} \sin^2 \left( \frac{n\pi}{a} x \right)$$
Position $x$ in average

\[
< x > = \int_0^a \psi_n(x)x\psi_n(x)dx = \frac{2}{a} \int_0^a x \sin^2 \left( \frac{n\pi x}{a} \right) dx = \frac{a}{2}
\]

Momentum $p_x$ in average

\[
< p_x > = \int_0^a \psi_n(x) \frac{\hbar}{i} \frac{d}{dx} \psi_n(x)dx = \frac{n\pi \hbar}{ia^2} \int_0^a \sin \left( \frac{2n\pi x}{a} \right) dx = 0
\]
Calculate

\[ < x^2 >= \int_0^a \psi_n(x)x^2 \psi_n(x)dx = ? \]

\[ < p_x^2 >= \int_0^a \psi_n(x) \left( \frac{\hbar}{i} \frac{d}{dx} \right)^2 \psi_n(x)dx = ? \]

where \[ \psi_n(x) = \sqrt{\frac{2}{a}} \sin \left( \frac{n\pi}{a} x \right) \] (particle in 1D box)
Quantum

\[ \rho_n(x) = \psi_n(x)\psi_n(x) = \frac{2}{a} \sin^2 \left( n\pi \frac{x}{a} \right) \]

with \( n = 20 \)

Classical

\[ \rho(x) \propto \frac{dt}{dx} = \frac{1}{v} = \text{const} \]

\[ \rho(x) = \frac{1}{a} \]
**Probability of finding particle in the region \([x_1 , x_2]\)**

\[
\text{Prob} \left( x_1 \leq x \leq x_2 \right) = \frac{2}{a} \int_{x_1}^{x_2} \sin^2 \left( \frac{n \pi}{a} x \right) dx = \frac{2}{n \pi} \int_{x_1 \pi / a}^{x_2 \pi / a} \sin^2 \left( y \right) dy
\]

\[
= \frac{x_2 - x_1}{a} - \frac{1}{n \pi} \sin \left( n \pi \frac{x_2 - x_1}{a} \right) \cos \left( n \pi \frac{x_2 + x_1}{a} \right)
\]

- When energy is big (i.e., \(n\) is big), the second term is negligible. This is classical limit!!

- The second term is called quantum fluctuation, and it is important in lower energy