Lecture Synopsis

1. Operators and Commutators
   (a) Postulates of QM
   (b) Linear operators
   (c) Hermitian operators
   (d) The unit operator
   (e) Commutators
   (f) The uncertainty principle
   (g) Constants of the motion

2. The Harmonic Oscillator
   (a) Definitions
   (b) Creation and annihilation operators
   (c) Eigenvalues and eigenstates
   (d) Matrix elements

3. Angular Momentum
   (a) Definitions
   (b) Commutation relations
   (c) Raising and lowering operators
   (d) Eigenvalues and eigenstates
   (e) Coupling of angular momenta

4. Matrix Formulation of QM
   (a) Introduction
   (b) Hermitian matrices
   (c) Hamiltonian matrices
   (d) The variational method
   (e) Secular equations
   (f) Examples

Bibliography

P.W. Atkins, Molecular Quantum Mechanics (OUP).
P.A.M. Dirac, The Principles of Quantum Mechanics (OUP).
Problems

1. Construct quantum mechanical operators in the position representation for the following observables: (a) the kinetic energy of a particle in one and three dimensions, (b) the kinetic energy of two particles in three dimensions, (c) the energy of the helium atom in atomic units, and (d) the electric dipole moment of a molecule with $N$ nuclei and $n$ electrons.

2. Confirm that the operator $\ell_z = -i\hbar(\partial/\partial\phi)$ is Hermitian by considering the integral

$$\int_0^{2\pi} \psi_m(\phi)^* \ell_z \psi_n(\phi) \, d\phi,$$

where both wavefunctions satisfy the periodic boundary condition $\psi(\phi + 2\pi) = \psi(\phi)$.

3. If $A$ and $B$ are Hermitian operators, show that the operators $C_{\pm} = A \pm iB$ are Hermitian conjugates, i.e., that

$$\langle \psi | C_+ | \phi \rangle = \langle \phi | C_- | \psi \rangle^* = \langle (C_- \psi) | \phi \rangle,$$

and use this result to show that $\langle \psi | C_+ C_- | \psi \rangle \geq 0$.

4. Use the unit operator $1 = \sum_n |n\rangle \langle n|$ to show that a Hermitian operator $A$ can be written in terms of its orthonormal eigenstates $|n\rangle$ and real eigenvalues $a_n$ as

$$A = \sum_n |n\rangle a_n \langle n|,$$

and hence deduce by induction that

$$A^k = \sum_n |n\rangle a_n^k \langle n| \quad \text{for } k = 0, 1, 2, \ldots$$

What is the corresponding expression for a general function $f(A)$ of $A$?

5. Evaluate the commutators (a) $[x, y]$, (b) $[p_x, p_y]$, (c) $[x, p]$, (d) $[x^2, p]$, (e) $[x^n, p]$, (f) $[(1/x), p]$, (g) $[(1/x), p^2]$, (h) $[xp_y - yp_x, yp_z - zp_y]$, and (i) $[x^2(\partial^2/\partial y^2), y(\partial/\partial x)]$, where $p$ denotes $p_x$ unless otherwise specified.

6. If $A$ and $B$ are Hermitian operators, show that $C = i[A, B]$ is also Hermitian.

7. Evaluate the commutators $[H, p_x]$ and $[H, x]$, where

$$H = \frac{p_x^2}{2m} + \frac{1}{2} k x^2.$$

Hence use the fact that

$$\frac{d \langle \Omega \rangle}{dt} = \frac{i}{\hbar} \langle [H, \Omega] \rangle$$

to find expressions for the rate of change of the expectation values of position and momentum for a harmonic oscillator. Solve the resulting pair of differential equations and show that the expectation values change with time in the same way as for a classical oscillator.
8. Use the properties of the creation and annihilation operators given in the appendix to construct the first three harmonic oscillator eigenfunctions in the position representation, where \( p_x = -i\hbar(\partial/\partial x) \). (Hint: First solve the first-order differential equation
\[
a\psi_0(x) = 0
\]
for \( \psi_0(x) \), and then use the relation
\[
\psi_n(x) = \left( \frac{1}{n\hbar\omega} \right)^{1/2} a^\dagger \psi_{n-1}(x)
\]
to obtain \( \psi_1(x) \) and \( \psi_2(x) \). In order to normalize \( \psi_0(x) \) you will need to know the standard integral \( \int_{-\infty}^{\infty} \exp(-ax^2) \, dx = \sqrt{\pi/a} \).

9. Use the fact that \( x \) and \( p_x \) can be written in terms of the creation and annihilation operators \( a^\dagger \) and \( a \) to show that the ground state of the harmonic oscillator has minimum uncertainty, i.e., that
\[
\Delta x \Delta p_x = \frac{1}{2} \hbar,
\]
where
\[
\Delta x = \left[ \langle 0 | x^2 | 0 \rangle - \langle 0 | x | 0 \rangle^2 \right]^{1/2},
\]
and
\[
\Delta p_x = \left[ \langle 0 | p_x^2 | 0 \rangle - \langle 0 | p_x | 0 \rangle^2 \right]^{1/2}.
\]
Do the excited states also have minimum uncertainty?

10. Use the definitions of the orbital angular momentum operators given in the appendix to evaluate the following commutators: (a) \([\ell_x, \ell_y]\), (b) \([\ell_y^2, \ell_x]\), (c) \([\ell^2, \ell_x]\), (d) \([\ell_z, \ell_\pm]\), (e) \([\ell^2, \ell_\pm]\), and (f) \([\ell_+, \ell_-]\).

11. Evaluate the following matrix elements, where the notation is \( \langle \ell', m' \| A \| \ell, m \rangle \): (a) \( \langle 0, 0 | \ell_z | 0, 0 \rangle \), (b) \( \langle 1, 1 | \ell_+ | 0, 0 \rangle \), (c) \( \langle 2, 1 | \ell_+ | 2, 0 \rangle \), (d) \( \langle 2, 2 | \ell_z^2 | 2, 0 \rangle \), (e) \( \langle 2, 0 | \ell_+ \ell_- | 2, 0 \rangle \), (f) \( \langle 2, 0 | \ell_- \ell_+ | 2, 0 \rangle \), and (g) \( \langle 2, 0 | \ell_z^2 \ell_+^2 | 2, 0 \rangle \).

12. Show that, if the state \( |\gamma\rangle \) is real, then the expectation value of each component of the angular momentum in the state is zero. Does this imply that the angular momentum is zero? (Hint: Consider the integral \( \langle \gamma | \ell_x | \gamma \rangle \), and use the Hermicity of \( \ell_x \) to write \( \langle \gamma | \ell_x | \gamma \rangle = \langle \gamma | \ell_x | \gamma \rangle^* = \langle \gamma | \ell_x^* | \gamma \rangle \).

13. Demonstrate that, if \( \langle j_1 q, j_2 q' \rangle = 0 \) for all \( q \) and \( q' \), then \( j_1 \wedge j_2 = -j_2 \wedge j_1 \). Go on to show that if \( j_1 \wedge j_1 = i\hbar j_1 \) and \( j_2 \wedge j_2 = i\hbar j_2 \), then \( j \wedge j = i\hbar j \) where \( j = j_1 + j_2 \). Confirm that \( j_1 - j_2 \) is not an angular momentum.

14. Show that \( \langle j^2, j_1^2 \rangle = 0 \) and \( \langle j^2, j_2^2 \rangle = 0 \) when \( j = j_1 + j_2 \), but that if the magnitudes and projections of \( j_1 \) and \( j_2 \) are specified then the magnitude of \( j \) cannot be specified too. Evaluate \( j^2 | j_1 m_1 j_2 m_2 \rangle \) to confirm your conclusion. (Hint: The first commutator is easily evaluated by writing
\[
j^2 = (j_1 + j_2) \cdot (j_1 + j_2) = j_1^2 + j_2^2 + 2j_1 \cdot j_2,
\]
where
\[ \mathbf{J}_1 \cdot \mathbf{J}_2 = j_{1x}j_{2x} + j_{1y}j_{2y} + j_{1z}j_{2z}, \]
and then calculating the individual commutators from the basic rules. In order to answer the second part of the question, evaluate \([j^2, j_{1z}]\) and \([j^2, j_{2z}]\). The third part can be answered by expanding \(j^2\) as above, noting that
\[ j_{1x}j_{2x} + j_{1y}j_{2y} = \frac{1}{2} (j_{1+}j_{2-} + j_{1-}j_{2+}), \]
and applying \(j^2\) in this form to \(|j_1m_1j_2m_2\rangle\).

15. Use the properties of the spin operators and spin eigenstates of a single electron that are given in the appendix to confirm that the triplet and singlet spin eigenstates \(|S, M_S\rangle\) of a system of two electrons are given by
\[
|1, +1\rangle = \alpha_1\alpha_2, \\
|1, 0\rangle = \sqrt{1/2} (\alpha_1\beta_2 + \beta_1\alpha_2), \\
|1, -1\rangle = \beta_1\beta_2
\]
and
\[
|0, 0\rangle = \sqrt{1/2} (\alpha_1\beta_2 - \beta_1\alpha_2),
\]
respectively. (Hint: The total spin operators of the two-electron system can be written in terms of the spin operators of the individual electrons as \(S_z = s_{1z} + s_{2z}, S_\pm = s_{1\pm} + s_{2\pm}, \) and \(S^2 = s_1^2 + s_2^2 + 2s_1 \cdot s_2\).)

16. Confirm that the Pauli matrices
\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]
satisfy the angular momentum commutation relations when we write \(s_x = \frac{1}{2}\hbar\sigma_x\), etc., and hence provide a matrix representation of angular momentum. Why does the representation correspond to \(s = \frac{1}{2}\)?

17. Using the Pauli matrix representation, reduce the operators \(s_x s_y, s_x s_y s_z^2, \) and \(s_x^2 s_y s_z^2\) to a single spin operator. (Hint: on writing \(s_x s_y = \frac{1}{2}\hbar^2 \sigma_x \sigma_y\) and evaluating the matrix product it turns out that \(s_x s_y \propto s_z\), etc.)

18. Chemical shift and spin-spin coupling effects in \(^1H\) nmr are incorporated in the two-spin Hamiltonian
\[
H = (\nu_1/\hbar) I_{1z} + (\nu_2/\hbar) I_{2z} + (J/\hbar^2) \mathbf{I}_1 \cdot \mathbf{I}_2,
\]
where \(\mathbf{I}_1\) and \(\mathbf{I}_2\) are nuclear spin operators. Show that the matrix of this Hamiltonian in the basis \(|\alpha_1\alpha_2\rangle, |\alpha_1\beta_2\rangle, |\beta_1\alpha_2\rangle, |\beta_1\beta_2\rangle\) is
\[
H = \begin{pmatrix} \frac{1}{2}(\nu_1 + \nu_2) + \frac{1}{4}J & 0 & 0 & 0 \\ 0 & \frac{1}{2}(\nu_1 - \nu_2) - \frac{1}{4}J & \frac{1}{2}J & 0 \\ 0 & \frac{1}{2}J & -\frac{1}{2}(\nu_1 - \nu_2) - \frac{1}{4}J & 0 \\ 0 & 0 & 0 & \frac{1}{2}(\nu_1 + \nu_2) + \frac{1}{4}J \end{pmatrix},
\]
and hence that the eigenstates and eigenvalues of the two-spin system are

<table>
<thead>
<tr>
<th>Eigenstate</th>
<th>Eigenvalue</th>
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<tbody>
<tr>
<td>$</td>
<td>\alpha_1 \alpha_2\rangle$</td>
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<tr>
<td>$</td>
<td>\alpha_1 \beta_2\rangle \cos \theta +</td>
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<tr>
<td>$-</td>
<td>\alpha_1 \beta_2\rangle \sin \theta +</td>
</tr>
<tr>
<td>$</td>
<td>\beta_1 \beta_2\rangle$</td>
</tr>
</tbody>
</table>

where $\tan 2\theta = J/(\nu_1 - \nu_2)$ if $\nu_1 > \nu_2$. (Hint: In order to calculate the required matrix elements of the $I_1 \cdot I_2$ term, use the final expression for $j_1 \cdot j_2$ that is given in problem 14).

19. Verify that if we take $\psi = e^{-\zeta r}$ as a trial wavefunction for the ground state of the hydrogen atom, where $\zeta$ is an arbitrary positive parameter, and we use atomic units then

$$E = \frac{1}{2}\zeta^2 - \zeta.$$ 

Hence show that the “best” wavefunction of this kind has $\zeta = 1$. What is the best value of $\zeta$ for the Li$^{++}$ ion? (Hint: Since $\psi$ is independent of $\theta$ and $\phi$, you can use

$$H = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

with

$$\nabla^2 \psi = \frac{d^2\psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr}$$

and $d\tau = 4\pi r^2 dr$.)

20. The Hamiltonian for a He-like atom with nuclear charge $Z$ can be written in atomic units as

$$H = -\frac{1}{2}\nabla^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}.$$

Assuming the normalized trial wavefunction

$$\Psi(r_1, r_2) = \psi(r_1)\psi(r_2) = \frac{\zeta^3}{\pi} e^{-\zeta(r_1 + r_2)},$$

use the variational method to determine the optimum value of $\zeta$ for He, Li$^+$, and Be$^{++}$, and hence variational upper bounds on the true ground state energies of these atoms. The basic integrals required are

$$\langle \Psi | -\frac{1}{2}\nabla^2 | \Psi \rangle = \frac{1}{2}\zeta^2, \quad \langle \Psi | -\frac{Z}{r_i} | \Psi \rangle = -Z\zeta \quad \text{and} \quad \langle \Psi | \frac{1}{r_{12}} | \Psi \rangle = \frac{5}{8}\zeta,$$

and the experimental ground state energies are $-2.85$, $-7.22$ and $-13.60$ a.u.
21. Consider a two-state system with orthonormal basis states $|1\rangle$ and $|2\rangle$ defined by

$$H^{(0)} |1\rangle = E_1^0 |1\rangle \quad \text{and} \quad H^{(0)} |2\rangle = E_2^0 |2\rangle,$$

where $E_1^0 < E_2^0$. If the total Hamiltonian is

$$H = H^{(0)} + H^{(1)},$$

where $H^{(1)}$ only has real off-diagonal matrix elements $\langle 1 | H^{(1)} | 2 \rangle = \langle 2 | H^{(1)} | 1 \rangle = \beta$, use the variational method with trial wavefunction $|\psi\rangle = c_1 |1\rangle + c_2 |2\rangle$ to calculate the ground state energy of the system.

22. The application of a small external electric field (Stark effect) introduces a small term $H^{(1)} = \epsilon r \cos \theta$ into the Hamiltonian of an atom. Show, by symmetry, that the only non-zero matrix element of this perturbation between $s$ and $p$ atomic orbitals is $\langle s | H^{(1)} | p_z \rangle = \beta$, say. Prove, by expressing the problem in matrix form, that the energy levels arising from the combination of $s$ and $p_z$ vary linearly with $\epsilon$ for the H atom ($E_s = E_p$) but quadratically with $\epsilon$ (in the limit of small $\epsilon$) for alkali metals ($E_s \neq E_p$).

23. The application of an external magnetic field (Zeeman effect) introduces a perturbation $H^{(1)} = \mu_0 \mathbf{B} \cdot \mathbf{L}$ into the Hamiltonian of an atom. Investigate the consequences of this effect for the $2^1 P_1$ state of the He atom when the field is applied in (a) the $z$ direction and (b) the $x$ direction. (Hint: The unperturbed $^1 P_1$ level is three-fold degenerate, and you will need to diagonalize a $3 \times 3$ matrix if the field is in the $x$ direction.)
Appendix

1. The harmonic oscillator

The harmonic oscillator problem consists of finding the eigenvalues and eigenstates of the Hamiltonian

\[ H = \frac{p_x^2}{2m} + \frac{1}{2} kx^2, \]  

(1)

where

\[ [x,p_x] = i\hbar. \]  

(2)

The solution proceeds by defining the Hermitian conjugate creation and annihilation operators

\[ a^\dagger = \sqrt{\frac{k}{2}x - i\sqrt{\frac{1}{2m}}p_x}, \]  

(3a)

\[ a = \sqrt{\frac{k}{2}x + i\sqrt{\frac{1}{2m}}p_x}, \]  

(3b)

and observing that the Hamiltonian \( H \) can be factorized as

\[ H = a^\dagger a + \frac{1}{2} \hbar \omega, \]  

(4a)

\[ H = a a^\dagger - \frac{1}{2} \hbar \omega, \]  

(4b)

where \( \omega = \sqrt{k/m} \). It follows from these factorizations that if \( H |n\rangle = E_n |n\rangle \) then

\[ Ha^\dagger |n\rangle = (E_n + \hbar \omega)a^\dagger |n\rangle, \]  

(5a)

\[ Ha |n\rangle = (E_n - \hbar \omega)a |n\rangle, \]  

(5b)

and hence (after some further analysis – see lectures) that

\[ a^\dagger |n\rangle = \sqrt{(n + 1)\hbar \omega} |n + 1\rangle, \]  

(6a)

\[ a |n\rangle = \sqrt{n\hbar \omega} |n - 1\rangle, \]  

(6b)

and

\[ H |n\rangle = \left( n + \frac{1}{2} \right) \hbar \omega |n\rangle, \]  

(7)

for \( n = 0,1,2,\ldots \). Note also that the harmonic oscillator eigenstates are orthonormal \( \langle n'|n\rangle = \delta_{n'n} \), that Eqs. (3a) and (3b) can be inverted to give \( x \) and \( p_x \) in terms of \( a^\dagger \) and \( a \), and that Eqs. (6a) and (6b) can be used to solve for the harmonic oscillator eigenfunctions \( \psi_n(x) \) in the position representation (if they are required – they hardly ever are) as described in problem 8.
2. Angular momentum

The angular momentum problem consists of finding the simultaneous eigenvalues and eigenstates of $j^2$ and $j_z$, where

$$j^2 = j_x^2 + j_y^2 + j_z^2,$$

and

$$[j_x, j_y] = i\hbar j_z, \quad [j_y, j_z] = i\hbar j_x, \quad [j_z, j_x] = i\hbar j_y,$$

and (therefore)

$$[j^2, j_x] = [j^2, j_y] = [j^2, j_z] = 0.$$  

The solution proceeds by defining the Hermitian conjugate raising and lowering operators

$$j_\pm = j_x \pm ij_y,$$

which satisfy the commutation relations

$$[j^2, j_\pm] = 0, \quad [j_z, j_\pm] = \pm i\hbar j_\pm, \quad [j_+, j_-] = 2\hbar j_z,$$

and allow $j^2$ to be factorized as

$$j^2 = j_+ j_- - \hbar j_z + j_z^2,$$

$$j^2 = j_- j_+ + \hbar j_z + j_z^2.$$  

It follows from the commutation relations in Eq. (12) that if $j^2 |j, m\rangle = \hbar^2 f(j, m) |j, m\rangle$ and $j_z |j, m\rangle = \hbar m |j, m\rangle$ then

$$j^2 j_\pm |j, m\rangle = \hbar^2 f(j, m) j_\pm |j, m\rangle,$$

$$j_z j_\pm |j, m\rangle = \hbar (m \pm 1) j_\pm |j, m\rangle,$$

and hence (after some further analysis involving Eq. (13) – see lectures) that

$$j^2 |j, m\rangle = \hbar^2 j(j + 1) |j, m\rangle,$$

$$j_z |j, m\rangle = \hbar m |j, m\rangle,$$

$$j_\pm |j, m\rangle = \hbar \sqrt{j(j + 1) - m(m \pm 1)} |j, m \pm 1\rangle,$$

where $j$ can be a non-negative integer or half-odd integer and $m = -j, -j + 1, \ldots, j - 1, j$. The angular momentum eigenstates $|j, m\rangle$ are also orthonormal, so that $\langle j', m'|j, m\rangle = \delta_{j'j} \delta_{m'm}$, and the matrix elements of the various angular momentum operators follow directly from Eqs. (11) and (15). For example:

$$\langle j, m \pm 1 | j_\pm | j, m\rangle = \hbar \sqrt{j(j + 1) - m(m \pm 1)},$$
\[ \langle j, m + 1 | j_x | j, m \rangle = (j, m + 1 | (j_+ + j_-) / 2 | j, m \rangle = (\hbar / 2) \sqrt{j(j + 1) - m(m + 1)}, \]

(etc.)

All of the above equations, and in particular Eq. (15), apply to a general angular momentum vector operator \( \mathbf{j} \) with components \( j_x, j_y \) and \( j_z \) that satisfy the commutation relations in Eq. (9). Specific examples include:

(i) The orbital angular momentum \( \ell = \mathbf{r} \wedge \mathbf{p} \) of a single electron, the (operator) components of which are defined by

\[
\begin{align*}
\ell_x &= y p_z - z p_y, \\
\ell_y &= z p_x - x p_z, \\
\ell_z &= x p_y - y p_x,
\end{align*}
\]

and the eigenstates \( |\ell, m_\ell\rangle \) of which are restricted to integral values of \( \ell \) and \( m_\ell \) as a result of the periodic boundary condition \( \psi(\phi + 2\pi) = \psi(\phi) \).

(ii) The spin angular momentum \( \mathbf{s} \) (or \( \mathbf{I} \)) of a spin-1/2 particle like an electron (or a proton), the eigenstates of which are usually denoted \( \alpha \equiv |1/2, +1/2\rangle \) and \( \beta \equiv |1/2, -1/2\rangle \) and satisfy Eq. (15) in the form

\[
\begin{align*}
s^2 \alpha &= (3\hbar^2 / 4) \alpha \\
s_+\alpha &= +\langle \hbar / 2 \rangle \alpha \\
s_-\alpha &= 0 \\
s_+\beta &= \hbar \alpha \\
s_-\beta &= 0 \\
s^2 \beta &= (3\hbar^2 / 4) \beta
\end{align*}
\]

with \( \langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \) and \( \langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0 \).

(iii) The composite angular momentum \( \mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2 \) of a system comprising two distinct sources of angular momentum \( \mathbf{j}_1 \) and \( \mathbf{j}_2 \), which may themselves be either orbital or spin angular momenta. Here the allowed values of \( j \) are given by the Clebsch-Gordan series

\[ j = |j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2 - 1, j_1 + j_2, \]

and the angular momentum eigenstates that satisfy Eq. (15) (with \( j^2 = j_1^2 + j_2^2 + 2 \mathbf{j}_1 \cdot \mathbf{j}_2 \), \( j_x = j_{1x} + j_{2x} \) and \( j_\pm = j_{1\pm} + j_{2\pm} \)) are those of the coupled representation \( |j_1, j_2, j, m\rangle \) in which the magnitudes of \( \mathbf{j}_1 \) and \( \mathbf{j}_2 \) are specified along with the magnitude and projection of \( \mathbf{j} \).