

Revision Lecture 27 April 2020

In black is a simple list of results from the course, the sort thing you should make in a more compact form while revising. Following each item in blue are the sort of comments I would have made in the revision lecture on how this might be examined. These comments are generic and not specifically will be examined in this year's exam. I also reference some relevant example exam questions whose solutions are available on DUO. The exam questions won't ask you to reproduce the proofs of these results from the main notes, but understanding the proofs in detail will be helpful as you may need to apply similar techniques to solve parts of the exam questions.

Remember that like last year all the exam questions are compulsory and the long question is worth 30 marks. (Prior to last year there were two long questions each worth 20 marks in both the QM and EM parts of the paper and you could choose to not do one of the four.)

Wave-particle duality and the wavefunction

Wave-particle duality implies particles are described by a wavefunction $\Psi(x, t)$ with

$$P(x, t)dx = |\Psi(x, t)|^2 dx = \Psi^*(x, t)\Psi(x, t) dx.$$

This implies wavefunctions must be normalized such that $\int \Psi^*(x, t)\Psi(x, t)dx = \langle \Psi | \Psi \rangle = 1$

Given an expression for a wavefunction e.g.

$$\psi = Ax(x - L), \quad 0 < x < L$$

you should be able to work out the normalization constant A and compute the probability of a particle being in any specified range of x (e.g. 2018 1a, 2019 1a).

Operators and expectation values

All measurable quantities have their associated operator

$$\begin{aligned}\hat{x} &= x \\ \hat{p}_x &= -i\hbar \frac{\partial}{\partial x} \\ \hat{H} &= \frac{\hat{p}^2}{2m} + V(x) = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \\ \hat{E} &= i\hbar \frac{\partial}{\partial t}.\end{aligned}$$

For any such quantity the associated expectation value (ensemble average value) is given by

$$\langle Q \rangle = \int \Psi^* \hat{Q} \Psi dx = \langle \Psi | \hat{Q} | \Psi \rangle.$$

As $\langle Q \rangle$ is real such operators must be **Hermitian**, i.e.

$$\int \Psi^* \hat{Q} \Psi dx = \int \Psi \hat{Q}^* \Psi^* dx, \quad \langle \Psi | \hat{Q} | \Psi \rangle = \langle \hat{Q} \Psi | \Psi \rangle = \langle \Psi | \hat{Q} \Psi \rangle^*$$

for any Ψ . Since this is true for any Ψ being Hermitian also implies

$$\int f^* \hat{Q} g \, dx = \int g \hat{Q}^* f^* \, dx, \quad \langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle = \langle g | \hat{Q} f \rangle^*.$$

For a given wavefunction, ψ , you could be asked to evaluate the expectation value of a given quantity. This means knowing, or looking up, the associated operator and then evaluating the expressions denoted above. (2017 1c, 2017 1d, 2019 1f, 2014 1c)

The Hermitian property is very important. You should be able to use and manipulate it to solve problems. (e.g. 2017 1b)

The Schrödinger equation

Heuristically the energy conservation equation

$$H = E, \quad p^2/2m + V = E$$

implies the **time dependent Schrödinger equation**

$$\hat{H}\Psi = \hat{E}\Psi, \quad \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi = i\hbar \frac{\partial \Psi}{\partial t}.$$

If $V(x)$ does not depend on time we can find separable solutions $\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$, where $\psi(x)$ satisfies the **time independent Schrödinger equation**

$$\frac{-\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x)\psi = E\psi.$$

You should know the form of both the time-independent and time-dependent Schrödinger equations and the relationship between their solutions. I.E. given an eigenfunction of the time-independent Schrödinger equation you should be able to determine its energy and insert the time dependence (e.g. 2019 2b).

Eigenfunctions and superpositions

This is an eigenfunction-eigenvalue equation. It will have multiple solutions, $\psi_n(x)$ labelled by their energy eigenvalue E_n , i.e.

$$\frac{-\hbar^2}{2m} \frac{d^2 \psi_n}{dx^2} + V(x)\psi_n = E_n\psi_n.$$

E.g. for the infinite square well ($V(x) = 0$ for $0 < x < L$ and $V(x) = \infty$ elsewhere)

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right).$$

Eigenfunctions are orthonormal (orthogonal and normalized)

$$\int \psi_m^* \psi_n \, dx = \langle \psi_m | \psi_n \rangle = \delta_{mn}.$$

Such eigenfunctions form a complete set, meaning any function $\phi(x)$ can be expressed as a linear superposition with weights c_n , i.e.

$$\phi(x) = \sum_n c_n \psi_n(x)$$

where orthonormality implies

$$c_n = \langle \psi_n | \phi \rangle = \int \psi_n^* \phi dx.$$

$$\sum_n |c_n|^2 = 1 \quad (\text{proved using } \int \phi^* \phi dx = 1)$$

and the $|c_n|^2$ can be identified as the probability of being in state ψ_n . E.g. if a system is prepared in state $\phi(x) = \sum_n c_n \psi_n(x)$ and the energy is measured, the probability of measuring E_n is $|c_n|^2$.

Given a wavefunction describing a system that is in superposition of eigenstates you could be asked to relate the coefficients of those eigenstates to the probabilities they represent. You might also be asked to normalize such a wavefunction by making use of the fact that these probabilities must sum to unity. You should also understand that measuring a quantity **collapses the wavefunction** such that subsequent measurements of the same quantity will yield the same value. (e.g. 2017 1d, 2018 1c, 2019 1g, 2014 1e)

Alternatively you might be given the composite wavefunction and be asked to decompose it into its component eigenfunctions. Questions asking you to do this graphically include: 2018 1b, 2019 1b

A problem that explores most of the above analysis is 2014 2.

Square wells and other potentials

For other potentials, e.g. the finite square or harmonic oscillator $P(x) = \psi^*(x)\psi(x)$ will penetrate into the classically forbidden region.

If $V(x)$ is continuous $\psi(x)$, $d\psi/dx$ and $d^2\psi/dx^2$ must all be continuous. (So that all terms in the Schrödinger equation are continuous). If $V(x)$ has finite discontinuities this still requires $\psi(x)$ and $d\psi/dx$ to be continuous. These properties can be used to sketch wavefunctions, e.g. for the finite square well.

Using these properties you should be able to sketch the wavefunctions for simple unseen potentials. Your sketches should have the right number of extrema for ground state, first excited state etc and go to zero or have continuous gradients as is appropriate for the potential. (e.g. 2017 1a, 2018 1e, 2019 1d)

Ladder operators

E.g. for the harmonic oscillator if $H\psi_n = E_n\psi_n$ then $Ha_+\psi_n = (E_n + \hbar\omega)a_+\psi_n$ and similarly $Ha_-\psi_n = (E_n - \hbar\omega)a_-\psi_n$ where the a_{\pm} are *ladder operators*.

Just need one solution to get started and then we can find all the rest by moving up and down the ladder in energies! I.E. $\psi_{n+1} \propto a_+\psi_n$ and for ground state $a_-\psi_0 = 0$

Also useful for angular momentum states, if $L_z\psi = m\hbar\psi$ then $L_zL_+\psi = (m+1)\hbar L_+\psi$.

You could get asked to make use of given ladder operators either to find the ground state ψ_0 or given a state ψ_n find either ψ_{n-1} or ψ_{n+1} . Remember the ladder operators don't give you

a function that is automatically normalized. Parts of 2014 3 tests the manipulation of ladder operators.

Commutators and uncertainty

The commutator of two operators \hat{A} and \hat{B} is $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$.

If \hat{A} and \hat{B} commute $[\hat{A}, \hat{B}] = 0$, then they have a common set of eigenfunctions

$$\hat{A}f_n = a_n f_n \quad \text{and} \quad \hat{B}f_n = b_n f_n.$$

This means the values of A and B can both be known simultaneously. If for A you measure a_n this implies the system has wavefunction f_n and so if you measure B you will get b_n .

If \hat{A} and \hat{B} do not commute $[\hat{A}, \hat{B}] \neq 0$, then they do not have a common set of eigenfunctions. We instead have

$$\hat{A}f_n = a_n f_n \quad \text{and} \quad \hat{B}g_n = b_n g_n,$$

where because the g_n are a complete set we can expand

$$f_n = \sum c_n g_n$$

and the probability that for B we measure b_n is $|c_n|^2$. I.E. knowing A does not determine the value of B (only probabilities) and measuring B (e.g. finding b_m) collapses the wavefunction from being the superposition $\sum c_n g_n$ to just g_m and so then the system is no longer in an eigenfunction of \hat{A} . If A is measured again its value may change. I.E. non-zero commutators imply an uncertainty principle.

E.g.

$$[x, \hat{p}] = i\hbar \quad \Rightarrow \quad \sigma_x \sigma_p \geq \hbar/2.$$

Note in 3D this extends to

$$[x, \hat{p}_x] = [y, \hat{p}_y] = [z, \hat{p}_z] = i\hbar,$$

but along differing directions the operators commute

$$[x, \hat{p}_y] = [y, \hat{p}_z] = [z, \hat{p}_x] = \text{etc} = 0$$

To check you understand the commutation of operators you might be given examples of operators and asked which do and don't commute. Remember if they involve different variables e.g. x and $\partial/\partial z$ they do not interact and must commute. Other combinations you should be able to reduce to terms involving the fundamental commutator $[x, \hat{p}] = i\hbar$ and other related or trivial terms.

Ehrenfest and virial theorems

We showed that for any operator Q ,

$$\frac{d\langle Q \rangle}{dt} = \frac{i}{\hbar} \langle [H, Q] \rangle + \left\langle \frac{\partial Q}{\partial t} \right\rangle.$$

One useful example of this is the **virial theorem**

$$\left\langle \frac{p^2}{m} \right\rangle = \left\langle x \frac{dV}{dx} \right\rangle \quad \text{or} \quad \langle T \rangle = \frac{1}{2} \left\langle x \frac{dV}{dx} \right\rangle$$

This is useful as often the potential V is known and this then gives an easy way of computing the kinetic energy T .

In time available for a short exam question I wouldn't ask you to prove these relations, but I might give you one such relation and ask you to make use of it. E.g. 2018 1d requires you to relate $\langle T \rangle$ to $\langle V \rangle$ when $V \propto 1/r$ and then make use of this to compute $\langle T \rangle$ given the value of the total energy, $\langle T \rangle + \langle V \rangle$.

3D wavefunctions, angular momentum and Spherical Harmonics

In 3D, solutions of Schrödinger's equation can be found by seeking solutions that are separable. If the potential is separable in Cartesian coordinates $V(x, y, z) = V_x(x) + V_y(y) + V_z(z)$ then $\psi(x, y, z) = \psi_x(x)\psi_y(y)\psi_z(z)$. Only the infinite square well and harmonic oscillator $V = (k_x x^2 + k_y y^2 + k_z z^2)/2$ separate in this way.

3D wavefunctions have 3 independent quantum numbers. Symmetric potentials will have energy levels that are degenerate, i.e. distinct wavefunctions with different sets of quantum numbers that have the same energy.

If a potential is spherically symmetric $V(r)$, then Schrödinger's equation is separable in spherical polar coordinates, r, θ, ϕ and has the form

$$\frac{-\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + V(r)\psi + \frac{\hat{L}^2 \psi}{2mr^2} = E\psi, \quad \text{where } \psi = R(r)Y(\theta, \phi).$$

Here all the angular dependence is in the total angular momentum operator \hat{L}^2 . The eigenfunction of \hat{L}^2 are the spherical harmonics $Y_{lm}(\theta, \phi)$ which satisfy

$$\hat{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm} \quad \text{and} \quad \hat{L}_z Y_{lm} = m\hbar Y_{lm} \quad \text{with} \quad -l < m < l.$$

We choose to normalise them such that

$$\int_{\text{sphere}} Y_{lm} Y_{lm}^* d\Omega = \int_{\theta=-\pi/2}^{\pi/2} \int_{\phi=0}^{2\pi} Y_{lm} Y_{lm}^* \sin \theta d\theta d\phi = 1.$$

The angular equation does not depend on the form of $V(r)$ and the solutions have the form

$$\psi(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi).$$

Remembering that the volume element in spherical polars $dV = r^2 \sin \theta d\theta d\phi dr$ the radial probability distribution

$$P(r)dr = r^2 R_{nl}^* R_{nl} dr.$$

For the Coulomb potential the energy level depend only on the principal quantum number, n , e.g. for hydrogen

$$E = -\frac{13.6 \text{ eV}}{n^2}.$$

In decays between atomic electronic states the change in energy is taken away by the emitted photon

$$hf = hc/\lambda = \Delta E.$$

To test you understand that the r^2 factor must be included when calculating the probability of being at a given radius you might, for a given wavefunction, be asked to compute where the probability peaks or the probability of being in a particular range of r (e.g. 2018 1g, 2014 1b)

It is important to know that the Y_{lm} are the eigenfunctions of L^2 and L_z and to know their eigenvalues. You may be asked to state the degeneracies of states for which it is important to know what range of m you can have for a given l . This is best remembered using the vector model.

Other questions require you to be able the energy of the transition between two states to the wavelength of the photon that would be absorbed or emitted.

Non-degenerate perturbation theory

If we perturb a system whose unperturbed Hamiltonian, eigenfunctions and energy levels satisfy

$$H_0 \psi_n^0 = E_n^0 \psi_n^0,$$

such that the perturbed Hamiltonian is $H = H_0 + H'$ then corresponding perturbations to the energy levels are

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle.$$

To make sure you understand how to work out these energy perturbations you might be asked to apply this expression for a particular example wavefunction and perturbation (e.g. 2018 1h, 2018 2, 2019 1e, 2014 1g).

Degenerate perturbation theory

If we have two degenerate states that satisfy

$$H_0 \psi_a^0 = E^0 \psi_a^0 \quad \text{and} \quad H_0 \psi_b^0 = E^0 \psi_b^0$$

then the eigenfunctions of the perturbed Hamiltonian $H = H_0 + H'$ are

$$\psi = \alpha \psi_a + \beta \psi_b,$$

where α , β and the perturbation to the energy level, E^1 , are given by the solution of

$$\begin{pmatrix} W_{aa} - E^1 & W_{ab} \\ W_{ba} & W_{bb} - E^1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix},$$

where $W_{ab} = \langle \psi_a | H' | \psi_b \rangle$ etc.

If $W_{ab} = W_{ba} = 0$, which is true if ψ_a and ψ_b are eigenfunctions of H' , then this reduces to the non-degenerate perturbation theory result.

If the original eigenfunctions are eigenfunctions of the perturbation use non-degenerate perturbation theory.

Full degenerate perturbation theory problems tend to be too long for the exam format but even in short questions we can test your understanding for some steps of the process such as solving the above matrix equation for specific examples of the constants to determine the energy perturbations and corresponding eigenfunctions (e.g. 2019 1h, 2014 1h).

Hydrogen quantum numbers and fine structure

The solutions to the basic Schrödinger equation for hydrogen are highly degenerate.

To fully specify the wave function, ψ_{nlmm_s} , one must define the values of

- n principal quantum number. ($n = 1, 2, 3, \dots$)
- l total orbital angular momentum quantum number $L^2 = l(l+1)\hbar^2$. ($l = 0, \dots, n-1$)
- m magnetic quantum number, component of orbital angular momentum along z -axis $m\hbar$. ($m = -l, \dots, l$)
- m_s component of spin angular momentum along z -axis $m_s\hbar$. ($m_s = \pm 1/2$)

The energy levels only depend on n and so are $2n^2$ fold degenerate.

e.g. $n = 3$ can have $l = 0$ $m = 0$ $m_s = \pm 1/2$, 2 states
 plus $l = 1$ $m = -1, 0, 1$ $m_s = \pm 1/2$, 6 states
 plus $l = 2$ $m = -2, -1, 0, 1, 2$, $m_s = \pm 1/2$ 10 states,

which equals $18 = 2 \times 3^2$

We can use an alternative decomposition of these degenerate states in which we label the wave function ψ_{nljm_j} by

- n principal quantum number. ($n = 1, 2, 3, \dots$)
- l total orbital angular momentum quantum number $L^2 = l(l+1)\hbar^2$. ($l = 0, \dots, n-1$)
- j total angular momentum quantum number $J^2 = j(j+1)\hbar^2$. ($j = 1/2$ for $l = 0$ or otherwise $j = l - 1/2$ or $l + 1/2$ as j must be positive)
- m_j component of the total angular momentum along z -axis $m_j\hbar$. ($m_j = -j, \dots, j$)

e.g. $n = 3$ can have $l = 0$ $j = 1/2$ $m_j = \pm 1/2$, 2 states
 plus $l = 1$ $j = 1/2$, $m = \pm 1/2$ or
 $j = 3/2$, $m = -3/2, -1/2, 1/2, 3/2$ 2 + 4 states
 plus $l = 2$ $j = 3/2$, $m = -3/2, -1/2, 1/2, 3/2$ or
 $j = 5/2$, $m = -5/2, -3/2, -1/2, 1/2, 3/2, 5/2$ 4 + 6 states,

which equals $18 = 2 \times 3^2$

Relativistic corrections to the energy levels can be modelled by treating them as perturbations to the Hamiltonian of the non-relativistic Schrödinger equation. For this we use the second labelling as the perturbations commute with J enabling us to use non-degenerate perturbation theory. These give rise to the **fine structure** of hydrogen and we showed

$$E_{nj} = E_n^0 \left(1 + \frac{\alpha^2}{n^2} \left[\frac{n}{(j+1/2)} - \frac{3}{4} \right] \right),$$

but I don't expect you to remember this or be able to prove it!

While you won't be asked to prove this formula you may be asked to make use of it. For this you need to know what values of j you can have for a given n . Again the vector model describing the addition of angular momentum (orbital and angular) is key to quickly identifying the possibilities.

Parts of 2014 3 test the understanding and manipulation of angular momentum operators.