Part IB Quantum Mechanics, Michaelmas 2019

Tuesday and Thursday, 11.05 a.m. to 11.55 a.m., Mill Lane lecture room 3

Prof. Adrian Kent (apak@damtp.cam.ac.uk)

I am very grateful to previous lecturers of this course, and in particular to Jonathan Evans and Eugene Lim, who very generously shared their lecture notes and thoughts on the material. These notes have been influenced by their presentations of many of the course topics, and sometimes draw directly on their discussions. I am also grateful to past students of the course, whose feedback and corrections have been very helpful. More feedback – whether noting typos or other errors or more general comments – would be very welcome!

The completed lecture notes are intended to be a reasonably complete summary of the course. However, material not covered in the printed notes will be added during lectures, for instance in answer to questions (which are encouraged!) or whenever there is time for further discussion that could be helpful. Non-examinable sections of the lecture notes are marked by asterisks at the start and the end. Some footnotes also contain references to results proved in textbooks or other references but not in the notes: these proofs too are, obviously, non-examinable.

Further course material will be added from time to time on the course web page, which is linked from www.qi.damtp.cam.ac.uk (follow the link to Undergraduate and Masters Lecture Courses on the left menu).

If you wish to make additional notes during lectures you will probably find it simplest to make them on separate sheets of paper, with footnote numbers to refer them to the appropriate place in the printed notes.

Highlights of this course:

- Historical development of quantum mechanics
- The one-dimensional Schrödinger equation; solution for particles in various potentials; probabilistic interpretation; beam scattering and tunneling.
- The basic formalism of quantum mechanics – states, operators, observables, measurement, the uncertainty principle: a new way of treating familiar dynamical quantities (position, momentum, energy, angular momentum).
- Quantum mechanics in three dimensions: the 3D Schrödinger equation, angular momentum, the hydrogen atom and other solutions of the 3D SE.

Version dated 27.08.19. Any updated versions will be placed on the course web page linked from www.qi.damtp.cam.ac.uk.

Recommended books

(*) R. Feynman, R. Leighton and M. Sands, *Feynman lectures on physics*, volume 3, chapters 1-3 (Addison-Wesley, 1989).

A beautifully written and profoundly thoughtful introduction to some of the basic ideas of quantum theory. Feynman was one of the twentieth century's most creative physicists. As these chapters illustrate, he also thought very deeply and carefully about fundamental questions in physics and about the scientific process itself. I really recommend these chapters very strongly as background reading for the course.

(*) A. Rae and J. Napolitano, *Quantum Mechanics*, chapters 1-5 (IOP Publishing, 2002).

A very good textbook which covers a range of elementary and more advanced topics in quantum theory, including a short discussion of the conceptual problems of quantum mechanics. The first five chapters form a good course text for IB QM.

(*) S. Gasiorowicz, *Quantum Physics* (Wiley 2003).

A very nicely and clearly written book, with good illustrations, which covers most of the course material well.

P. Landshoff, A. Metherell and G. Rees, *Essential Quantum Physics* (Cambridge University Press, 2001).

Another nicely and concisely written textbook, which also covers most of the course material for IB QM well.

P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, 1967; reprinted 2003).

A more advanced treatment. Despite its age it is still a valuable exposition of the insights and perspectives of one of the pioneers of quantum theory. You may want to consider looking at this if you intend to go beyond this course and pursue Part II and Part III courses in quantum physics.

S. Brandt and H.D. Dahmen, *The Picture Book of Quantum Mechanics* (4th edition; Springer, 2012). An excellent book with accompanying plots and simulations. These give visual explanations that nicely illuminate the mathematics of solutions of the Schrödinger equation, tunnelling, reflection from barriers, atomic electron states, and other quantum phenomena.

(*) Particularly recommended.

Contents

1 Quantum Mechanics, science and technology

1.1 Quantum Mechanics and fundamental science

Quantum mechanics is the non-relativistic version of relativistic quantum field theory. Collectively, we refer to these theories as "quantum theory". Most physicists would agree quantum theory is the most remarkable, interesting and surprising physical theory we have discovered.[1] Although ultimately only a non-relativistic part of a larger theory, quantum mechanics already teaches us that our universe follows laws that involve beautiful and intricate mathematics, and whose form we could not possibly have imagined had they not been illuminated by experiment.

Among other things, quantum mechanics explains the essential features of the following:

- the structure of atoms and molecules and their chemical interactions; i.e. chemistry, and biochemistry and so, in principle, biology. We will begin to discuss this towards the end of the course, when we consider quantum mechanical descriptions of the hydrogen atom and, more qualitatively, other atoms. This description is made more precise and taken further in Part II Principles of Quantum Mechanics.

- the structure and properties of solids (and so, in principle, much of classical mechanics). Conductivity (some basic theory of which is introduced in Part II Applications of Quantum Mechanics) and superconductivity.

- the thermodynamics of light and other electromagnetic radiation and also how electromagnetic radiation interacts with matter. To describe this properly requires relativistic quantum field theory, which isn't covered until Part III.

- the physics of subatomic particles, radioactivity, nuclear fission and fusion. Again, we need relativistic quantum field theory to describe these phenomena in full detail. But, as we'll see later, even elementary quantum mechanics gives us some useful insights into the physics of nuclear fission and fusion. For example, we can understand the random nature of these processes, and the way fusion and fission rates depend on relevant potentials, as a consequence of quantum tunnelling.

Modern cosmological models are also based on quantum theory. Since we do not have a quantum theory of gravity, and do not know for sure whether there is one, these cosmological models are at best incomplete. Nonetheless they give a good qualitative fit to observational data. Many physicists hope that this project can be completed, so that we can describe the entire universe and its evolution by quantum theory.[2] These topics are covered in detail in the Part II and Part III Cosmology courses.

[1] Einstein's general theory of relativity is the only other contender. It is an extraordinarily beautiful theory that transformed our understanding of space and time and their relationship to matter, and that gave us the tools to understand the cosmos. The two theories are fundamentally incompatible, and it is uncertain precisely which parts of which theory will survive in a future unification. Still, I find quantum theory more intriguing, because of the variety of deep mathematical concepts it combines and because it is so different from and so much stranger than the theories that preceded it.

[2] It is also true that many thoughtful physicists suspect that the project cannot be completed, because we will need something other than a quantum theory of gravity, or because quantum theory will turn out not to hold on large scales. If so, comparing quantum cosmological models to observation should eventually give us insight into new physics.

1.2 Quantum Mechanics and technology

Many of the revolutionary technological developments of the last hundred years rely on quantum mechanics:

- semiconductor physics – transistors, diodes, integrated circuits, and hence the computing and IT industries.
- laser physics
- nuclear power and the as yet unrealised dream of controllable fusion power
- tunnelling electron microscopy and atomic manipulation
- More recent inventions relying on the distinctive properties of *quantum information*. These include quantum cryptography. Its best known application is quantum key distribution, which in principle allows perfectly secure communication, and is now practical with large data transmission rates and over long distances, including between satellite and ground stations. There are many other applications, including quantum authentication, quantum position verification, quantum bit string commitment, quantum multi-party computation and quantum digital signatures. Quantum information allows perfect security for some of these tasks, and security advantages for others.

  Another major development has been the invention of quantum algorithms and various types of quantum computers. We now know that quantum computers are substantially more efficient than classical computers for some important applications, including factorisation (at least compared to the best known classical algorithms) and the simulation of quantum systems. Small scale quantum computers have been built, and many research groups are competing to build a quantum computer large enough to exploit the theoretical advantages. In September 2019, Google claimed the first demonstration of so-called "quantum supremacy", a calculation on a quantum computer that is infeasible on classical computers.[3]

  Other fascinating applications include quantum teleportation – which in principle gives a way of effectively deleting a physical system at A and recreating it at B without sending it along a path from A to B – and other types of quantum communication.

  All of these topics are covered in the Part II Quantum Information and Computation course. Notes for that course, and for Part III courses in this area, along with some information about research work on these topics in DAMTP, can be found on http://www.qi.damtp.cam.ac.uk.

[3] There are nuances of definition here, and the community is still assessing the claim.

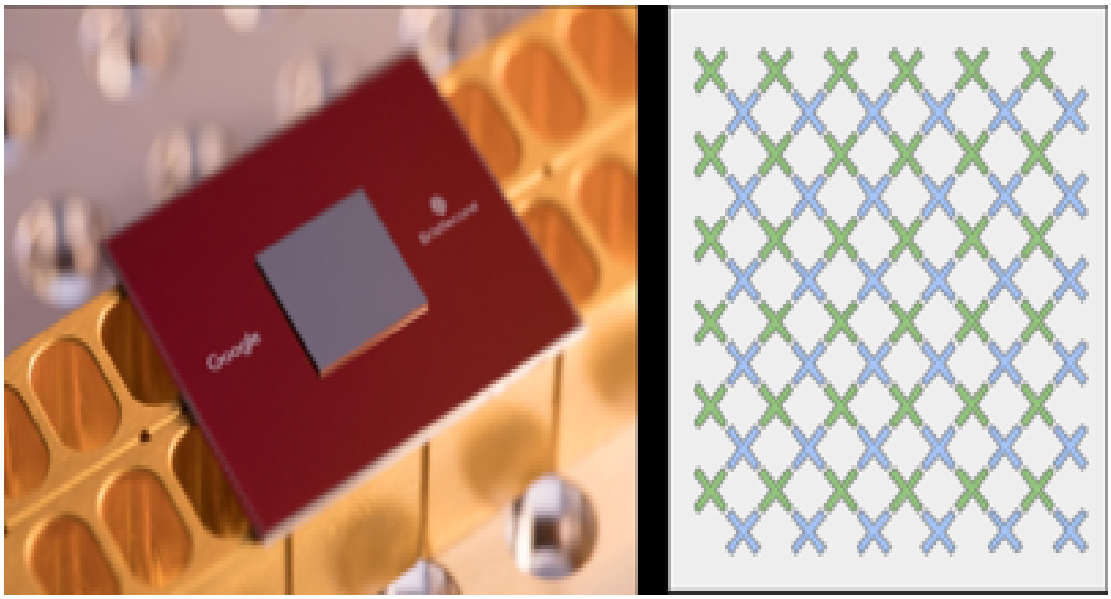

Figure 1: Google's Bristlecone quantum processor. Image on left, map of qubit connections on right.

2 Historical development of quantum mechanics

2.1 Planck's quantum hypothesis (1900)

One of the great puzzles in late 19th century physics was the inability of classical thermodynamics and electromagnetism to predict the correct spectrum — or indeed *any* sensible spectrum — for the frequency distribution of radiation from an idealized black body. Classical thermodynamics predicted an emission spectrum which suggested that the flux of emitted radiation tends to infinity as the frequency tends to infinity, and hence that an infinite amount of energy is emitted per unit time. In 1900, Max Planck showed that one could predict the experimentally observed spectrum by postulating that, because of some (at that point) unknown physics, matter can emit or absorb light of frequency ν only in discrete *quanta* which have energy

$$E = h\nu = \hbar\omega\,. \tag{2.1}$$

Here $\omega = 2\pi\nu$ is the light's *angular frequency* (the number of radians of oscillation per second), and

$$\hbar = \frac{h}{2\pi} \approx 1.055 \times 10^{-34} \text{ Joule sec}\,. \tag{2.2}$$

The constant h is a new constant of nature (Planck's constant). For most purposes it turns out to be notationally more convenient to use $\hbar$ rather than h, and we will generally do so.

2.2 Einstein's explanation of the photoelectric effect (1905)

Experiment shows that light hitting a metal surface in a vacuum can cause electrons to be ejected with a range of energies. To emit any electrons, the incident light needs to have angular frequency ω satisfying $\omega \geq \omega_{\min}$, where $\omega_{\min}$ is a constant depending on the particular metal. When $\omega \geq \omega_{\min}$, one finds that the maximum energy of the emitted electrons, $E_{\max}$, obeys

$$E_{\max} = \hbar\omega - \hbar\omega_{\min} \equiv \hbar\omega - \phi\,, \tag{2.3}$$

where ϕ is the so-called *work function* of the metal. The average rate of electron emission is found to be proportional to the intensity of the incident light, but individual electrons appear to be emitted at random (and so in particular, measured over small enough time intervals, the emission rate fluctuates).

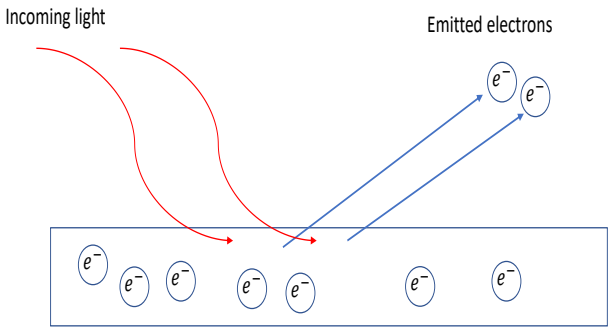

Figure 2: Schematic illustration of the photoelectric effect.

Although light had been understood as an electromagnetic wave, it was hard to explain these effects in terms of a wave model of light. If we think of an incident wave transmitting energy to the electrons and knocking them out of the metal, we would expect the rate of electron emission to be constant (i.e. we would not expect random fluctuations), and we would also expect that light of any frequency would eventually transmit enough energy to electrons to cause some of them to be emitted.

To explain the photoelectric effect, Albert Einstein (in 1905) was led to postulate instead that light is *quantised* in small packets called *photons*, and that a photon of angular frequency ω has energy $\hbar\omega$. He reasoned that two photons are very unlikely to hit the same electron in a short enough time interval that their combined effect would knock the electron out of the metal: the energy an electron acquires from being hit by a photon is very likely to have dissipated by the time it is hit again.

Thus, one can explain the photoelectric effect as the result of single photons hitting electrons near the metal surface, if one assumes that an electron needs to acquire kinetic energy $\geq \phi$ to overcome the binding energy of the metal. An electron which acquires energy $\hbar\omega$ thus carries away energy $\leq \hbar\omega - \phi = E_{\max}$. One can also explain the emission rate observations: the *average* rate of photon arrival is proportional to the intensity of the light, and the rate of emission of electrons is proportional to the rate of photon arrival. However, individual photons arrive, and hit electrons so as to knock them out of the metal, at random – hence the randomly distributed emissions of electrons.

2.3 Diffraction of single photons (1909)

In Cambridge in 1909, J.J. Thomson suggested to G.I. Taylor (who had asked for a research project) that he investigate the interference of light waves of very low intensity. Taylor carried out an experiment in which a light source was successively filtered so that the energy flux was equivalent to the flux of a source sending no more than one photon at a time through the apparatus. He then observed the photographic image built up by diffraction of this feeble light around a needle. The characteristic diffraction pattern – the same pattern seen for strong light sources – was still observed.

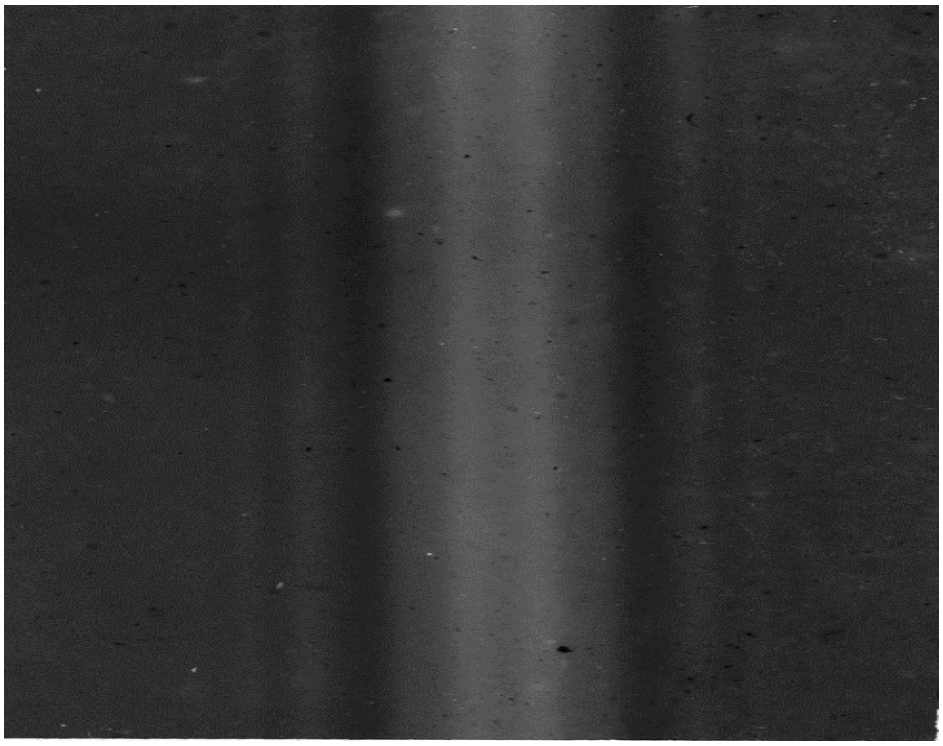

Figure 3: Photograph of diffraction bands caused by a thin wire in feeble light. See: Taylor, Proc. Camb. Phil. Soc., 15, 114, 1909. The exposure was 400 hours. Source: Cavendish Laboratory. Licensed under Creative Commons.

This seems to suggest that single photons propagate through the apparatus and nonetheless "self-interfere" in such a way that the diffraction pattern is cumulatively built up. This is indeed how Taylor's results were interpreted for several decades after the development of quantum mechanics in 1926. Problems were later noticed

with this interpretation of this particular experiment: having the average energy flux of a single photon does not always imply that a source is emitting single photons. However, the experiment was subsequently repeated with genuine single photon sources, still showing the same diffraction pattern. Qualitatively similar patterns are seen in diffraction experiments for single electrons and other types of matter (see below).

2.4 The Rutherford atom (1911)

After discovering the electron in 1897, J.J. Thomson proposed a model of the atom as a sort of "plum pudding" with Z pointlike electrons of charge $-e$ embedded in a sphere of positive charge $+Ze$.

Geiger and Marsden's famous experiment, carried out at Rutherford's suggestion, tested for large angle scattering of a beam of α-particles directed at gold foil. One would not expect significant scattering from a loosely distributed low charge density "plum pudding" atom, and Rutherford thought it unlikely anything interesting would be observed. But, in fact, some α-particles *were* observed to be scattered through angles of up to 180°. In Rutherford's famous phrase,

> "It was as if you fired a 15-inch shell at tissue paper and it came back and hit you."

The scattering suggests a high density positive charge within the atom. Rutherford thus postulated a new model of the atom, with a heavy nearly pointlike nucleus, of charge $+Ze$, surrounded by Z electrons in orbit.

(A short popular account can be found at
http://physicsopenlab.org/2017/04/11/the-rutherford-geiger-marsden-experiment/
.)

2.5 The Bohr atom (1913)

Although the Rutherford atom was more compatible with the Geiger-Marsden scattering data than was the "plum pudding" model, it had a number of theoretical defects.

First, according to Maxwell's electrodynamics, electrons in orbit around a nucleus would radiate, since they are continually undergoing acceleration. This would cause them to lose energy and fall in towards the nucleus. Stationary electrons would also fall into the nucleus because of electrostatic attraction. This would suggest that atoms must be unstable, which they generally are not.

Second, the model fails to explain why atoms have characteristic line spectra corresponding to discrete frequencies at which they absorb or emit light. For example, hydrogen has frequencies given by the *Rydberg formula* (Rydberg, 1890):

$$\omega_{mn} = 2\pi c R_0 \left(\frac{1}{n^2} - \frac{1}{m^2}\right) \qquad \text{for } m > n\,, \tag{2.4}$$

where the *Rydberg constant*

$$R_0 \approx 1.097 \times 10^7\ \mathrm{m}^{-1}\,. \tag{2.5}$$

Third, it fails to explain why atoms belong to a finite number of chemical species, with all members of the same species behaving identically. For instance, if a hydrogen atom can have an electron in any type of orbit around its nucleus, one would expect infinitely many different types of hydrogen atom, corresponding to the infinitely many different possible orbits, and one would expect the atoms to have different physical and chemical properties, depending on the details of the orbit.

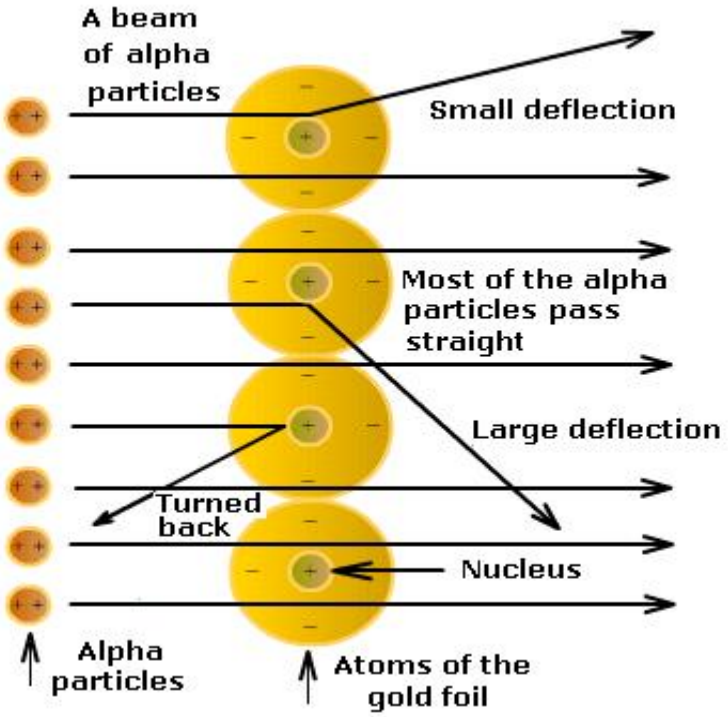

Figure 4: Schematic illustration of the Geiger-Marsden experiment, from the web page cited above.

Niels Bohr, in 1913, observed that these problems could be resolved in a way consistent with Planck's and Einstein's earlier postulates, if we suppose that the electron orbits of hydrogen atoms are *quantised* so that the orbital angular momentum takes one of a discrete set of values

$$L = n\hbar\,, \tag{2.6}$$

where n is a positive integer.

Thus, if we take an electron e moving with velocity v in a circular orbit of radius r about a proton p, $F = m_e a$ gives us that the Coulomb force

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{m_e v^2}{r}\,. \tag{2.7}$$

If we also have

$$L = m_e v r = n\hbar \tag{2.8}$$

then

$$\frac{n^2\hbar^2}{r^3 m_e} = \frac{e^2}{4\pi\epsilon_0 r^2} \tag{2.9}$$

and hence

$$r = n^2\left(\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2}\right) = n^2 a_0\,, \tag{2.10}$$

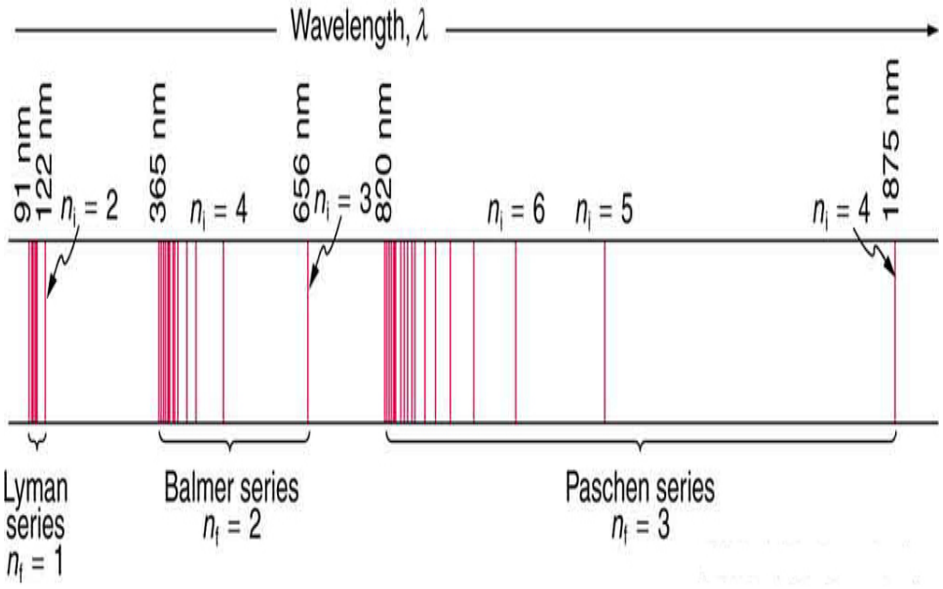

Figure 5: Spectra for the hydrogen atom. The figure shows three horizontal lines at small distances from each other. Between the two lower lines, the Lyman series, with four vertical red bands in compact form, is shown. This has $n_f = 1$ and $n_i \geq 2$, and wavelengths in the range $91 - 100$ nanometers. The Balmer series is shown to the right side of this series. This has $n_f = 2$ and $n_i \geq 3$, and wavelengths in the range $365 - 656$ nanometers. At the right side of this, the Paschen series bands are shown. This has $n_f = 3$ and $n_i \geq 4$, and wavelengths in the range $820 - 1875$ nanometers. The Rydberg formula is obtained by taking $n_f = n$, $n_i = m$.
Source for figure and caption: https://opentextbc.ca/physicstestbook2
Image licenced under Creative Commons.

where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.53 \times 10^{-10} \text{ m} \tag{2.11}$$

is the *Bohr radius*.

We can then obtain the energy of the n-th Bohr orbit from (2.7) and the Coulomb potential:

$$E_n = \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{8\pi\epsilon_0 r} = -\frac{e^2}{8\pi\epsilon_0 n^2 a_0} = -\frac{e^4 m_e}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} = \frac{E_1}{n^2}\,, \tag{2.12}$$

where

$$E_1 = -\frac{e^4 m_e}{32\pi^2\epsilon_0^2\hbar^2} \approx -13.6 \text{ eV}\,. \tag{2.13}$$

Thus we have $n = 1$ with energy $E = E_1$ defining the lowest possible energy state, or *ground state*, of the Bohr atom. The higher energy *excited states*, so called because they can be created by "exciting" the ground state atom with radiation, correspond to $n > 1$. These can decay to the ground state: the ground state has no lower energy state to decay to, and so is stable. (The Bohr model does not allow a state with zero orbital angular momentum, which would correspond to $n = 0$, $r = 0$ and $E = -\infty$.)

The energy emitted for a transition from the m-th to the n-th Bohr orbital is $E_{mn} = E_m - E_n$. Using $E_{mn} = \hbar\omega_{mn}$, where ω_{mn} is the angular frequency of the emitted photon, we have

$$\omega_{mn} = 2\pi R_0 c(\frac{1}{n^2} - \frac{1}{m^2}) \,, \tag{2.14}$$

where

$$R_0 = \frac{m_e c}{2\hbar}(\frac{e^2}{4\pi\epsilon_0\hbar c})^2 \,, \tag{2.15}$$

which agrees well with the experimentally determined value of the Rydberg constant.

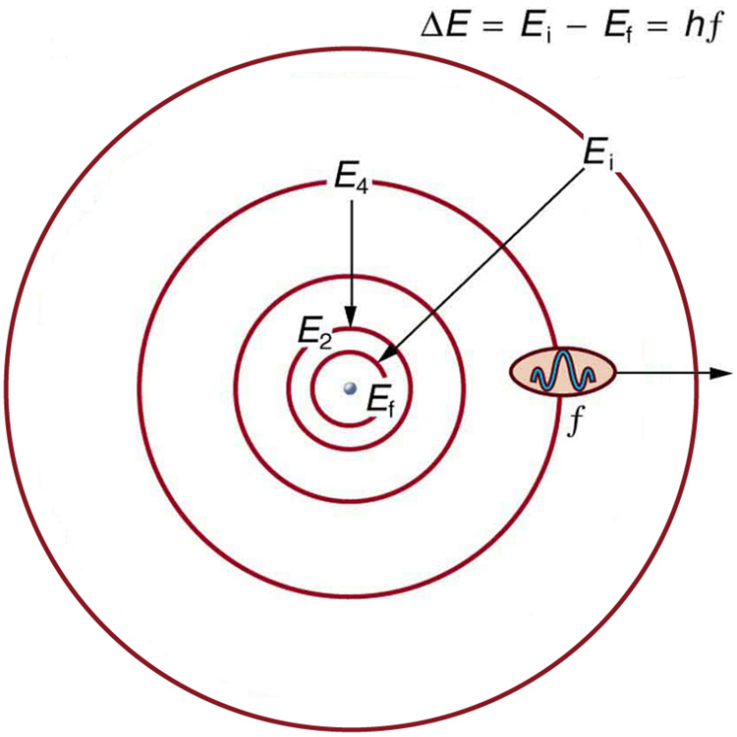

Figure 6: The orbits of Bohr's planetary model of an atom; five concentric circles are shown. The radii of the circles increase from innermost to outermost circles. On the circles, labels E_1, E_2, up to E_i are marked. Source for figure and caption: https://opentextbc.ca/physicstestbook2
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Bohr's model of the atom was rather more successful than its predecessors. It predicts the energy levels of the hydrogen atom and the spectrum of photons emitted and absorbed. It also accounted for spectroscopic data for ionised helium (He^+) and for some emission and absorption spectra for other atoms. (We now understand that these are the spectra produced by the innermost electrons, which can be modelled in a way qualitatively similar to the electron in the hydrogen atom.)

However, as Bohr himself stressed, the model offered no *explanation* of atomic physics. For example, as Rutherford commented, it's quite mysterious that an electron which jumps from the m-th to the n-th orbit seems to know in advance what frequency to radiate at during the transition. Moreover, the Bohr model is quite

wrong about the details of electron orbits, even for the hydrogen atom. Nonetheless, it was an important stepping stone on the path to quantum mechanics, suggesting some link between Planck's constant, atomic spectra and atomic structure, and the quantisation of angular momentum and other dynamical quantities.

2.6 Compton scattering (1923)

In 1923, Arthur Holly Compton observed the scattering of X-rays by electrons associated with atoms in a crystal. Because the X-ray energies were much larger than the electron binding energies, the electrons can effectively be modelled by free electrons. Indeed, we also directly observe that if an electron beam and an X-ray beam converge, some electrons and some X-rays are deflected. This is very difficult to reconcile with a pure wave model of electromagnetic radiation, because the energy and momentum transfer for individual scatterings does not depend on the intensity of the X-ray beam.

A simple alternative explanation is that the scattering results from collisions between a single photon in one beam and a single electron in the other, in which energy and momentum are transferred between the photon and the electron. (A relativistic treatment of this scattering process was given in the IA Dynamics and Relativity course.) This explanation is consistent with the observed scattering data and with conservation of (relativistic) energy and momentum, provided we assume that a photon of angular frequency ω has a definite momentum

$$\underline{p} = \hbar \underline{k} \,, \tag{2.16}$$

where $\underline{k}$ is the wave vector of the corresponding electromagnetic wave, so that

$$|\underline{p}| = \frac{\hbar\omega}{c} = \hbar |\underline{k}| \,. \tag{2.17}$$

2.7 Wave and particle models of electromagnetic radiation

We thus see the emergence of two different models of light and other electromagnetic radiation.

Sometimes (classical electromagnetism, diffraction experiments with a strong light source, ...) it is useful to model light in terms of waves:

$$e^{i(\underline{k}.\underline{x}-\omega t)}\,, \tag{2.18}$$

where $\underline{k}$ is the wave vector, ω the angular frequency, $c = \frac{\omega}{|\underline{k}|}$ the speed of light in a vacuum, and the wavelength $\lambda = \frac{2\pi c}{\omega} = \frac{2\pi}{|\underline{k}|}$.

Sometimes (photoelectric effect, spectroscopy in the Bohr model of the hydrogen atom, Compton scattering, ...) it is useful to adopt a particle model, in which light is made up of photons with energy and momentum

$$E = \hbar\omega\,, \qquad \underline{p} = \hbar\underline{k}\,. \tag{2.19}$$

The word "model" is chosen deliberately here. A model can be useful (as the wave and particle models of light are, in the appropriate contexts) without being completely correct. Indeed, G.I. Taylor's 1909 demonstration of single photon diffraction already gave an example of a single experiment for which neither the wave nor the particle model of light appeared to be adequate. A simple particle model would not predict the observed diffraction pattern, while a simple wave model cannot explain the observation of single photons recorded on the photographic film.[4]

2.8 De Broglie waves (1924)

Louis de Broglie reexamined and extended Einstein's photon hypothesis. If, he argued, Einstein was right that light waves can be considered as composed of particles – photons – might it not equally be the case that objects like electrons, which were thought of as particles, could exhibit wave-like behaviour?

As he pointed out in his 1924 PhD thesis, this would make the Bohr angular momentum quantization condition

$$L = pr = n\hbar \tag{2.20}$$

at least somewhat less mysterious. If we suppose that an electron of momentum p can (somehow) be thought of as a wave with *de Broglie wavelength*

$$\lambda = \frac{2\pi\hbar}{p}\,, \tag{2.21}$$

then the electron in the n-th Bohr orbit would be in a standing wave pattern with n wavelengths:

$$2\pi r = \frac{2\pi n\hbar}{p} = n\lambda\,. \tag{2.22}$$

De Broglie hypothesised that the frequency and wavevectors of the relevant wave were related to the energy and momentum of the particle as for photons: that is, we have $E = \hbar\omega$, $\underline{p} = \hbar\underline{k}$ even for particles with nonzero mass. (In fact, he speculated – incorrectly, according to our current understanding – that photons might also have a small nonzero mass.)

Einstein wrote, on learning of de Broglie's hypothesis, that

[4] See earlier comment: to justify this fully we need to consider versions of the experiment with a guaranteed single photon source.

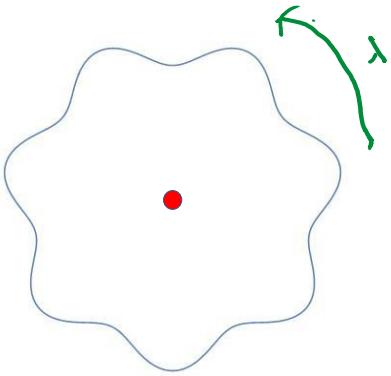

Figure 7: Schematic illustration of the de Broglie model of electron orbits in an atom.

> "I believe it is the first feeble ray of light on this worst of our physics enigmas."

It was.

2.9 Matter wave diffraction (1923-7)

We know that the wave model of light predicts, correctly, that light should form interference and diffraction patterns. De Broglie's hypothesis suggests the same should be true of electrons and other massive particles. This was first confirmed in experiments carried out (from 1923-7) by Davisson and Germer and (independently in 1927) by G.P. Thomson, who observed diffractive scattering of electrons from metallic crystals, with diffraction patterns consistent with the de Broglie wavelength $\lambda = \frac{2\pi\hbar}{p}$.

G.P. Thomson was the son of J.J. Thomson, who in 1897 discovered the electron, in experiments in which it behaves as (and so was then understood to be) a particle. It is a pleasing historical quirk that G.P. Thomson was the co-discoverer of the wave-like behaviour of electrons in diffraction experiments.

Many diffraction experiments with electrons, neutrons and other particles have since been carried out, all confirming de Broglie's prediction.

2.10 Discussion of the double slit experiment

(Cf Feynman volume III chapters I-III)

A nice version of the double slit experiment with electrons was carried out by Akira Tonomura. It is described at
http://www.hitachi.com/rd/portal/highlight/quantum/doubleslit/index.html

Like the other diffraction experiments mentioned above, this shows that electrons and other massive particles can produce interference patterns in the same sort of way as light and water waves. At the same time, it gives very vivid evidence of electrons being detected as individual particles. We stress again that *both* the wave description *and* the particle description are just models that are sometimes useful but, as this experiment again illustrates, not fundamentally correct. To analyse this

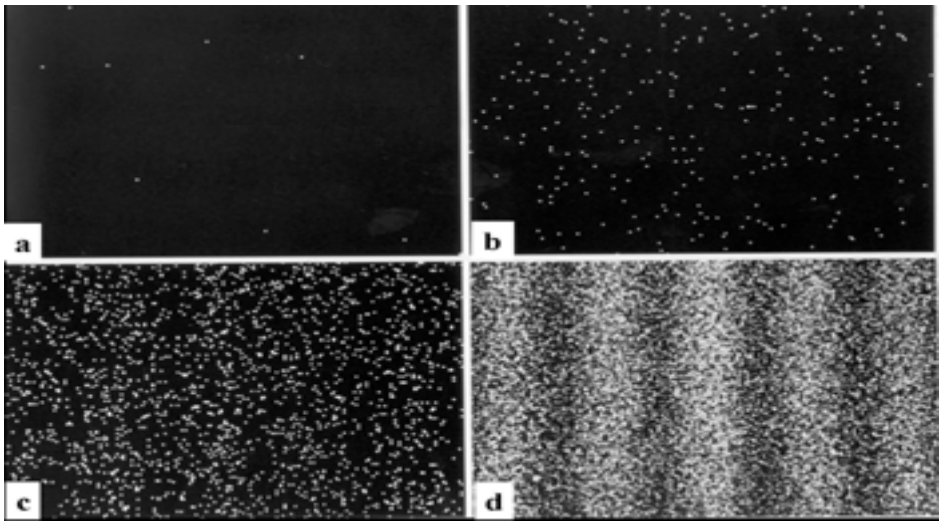

Figure 8: Single electron detection events building up an interference pattern in Tonomura's experiment. Copyright in these documents published on Hitachi World-Wide Web Server is owned by Hitachi, Ltd.

conclusion in more detail, let's follow Feynman in considering an idealised version of the double slit experiment, in which we assume we have perfect detectors that can register the passage of an electron without affecting it.

The observed interference pattern in a double slit experiment agrees with that predicted by a wave model (and disagrees with that predicted by a particle model). *But* the electrons arrive individually at the detector, which registers each time one arrives — as a particle model (but not a wave model) would suggest. The same is true of other massive particles, and also of photons. Even if we reduce the intensity of the source so that *only one* electron on average is between the source and the screen at any given time, we *still* see individual electrons detected in a pattern that cumulatively reproduces the distribution predicted by the wave model.

It's tempting to think that, when electrons leave the source, they behave like bullets from a gun – i.e. like particles coming from a well-defined small region. Certainly if we place a detector near the source this is what the detections suggest (although if we do this the electrons don't continue into the rest of the apparatus). It's also tempting to think that, since the electrons (etc.) arrive at the detector and are detected there as particles, with a definite or nearly definite position, they must have behaved like classical particles throughout, following some definite path from the source, through one hole or the other, to the detector. But, tempting though this last intuition may be, it's hard to reconcile with the observed interference pattern. If the electrons behaved like bullets throughout, we'd expect something like a superposition of two Gaussian distributions from the two slits, instead of the pattern of minima and maxima we observe.

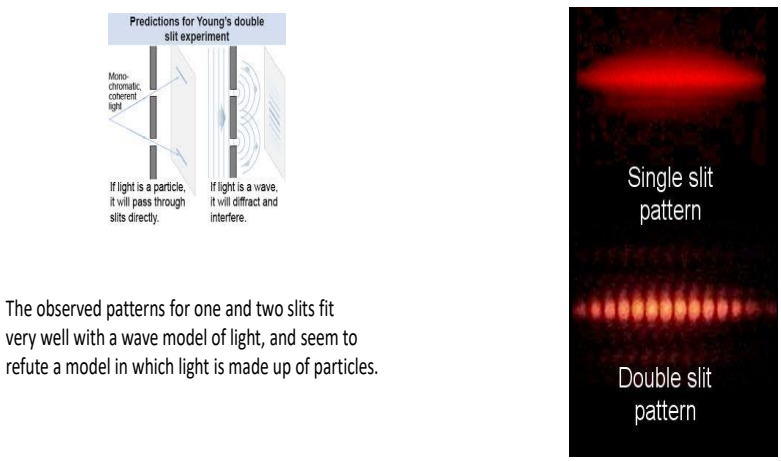

Figure 9: The double slit experiment.

There seems, in any case, a simple way to investigate more closely. Suppose that we have ideal detectors, which register that an electron has passed through a region, but don't obstruct its path. We can set up a double slit experiment with one of these ideal detectors adjacent to each slit (for definiteness, let us say they are on the far side, between the slit and the screen). Now we don't need to speculate: we can *observe* which slit the electron goes through. **But** when we do this, the interference pattern *changes*: we see a superposition of two Gaussians, as predicted by a particle model, rather than the pattern of maxima and minima predicted by the wave model and observed in the previous experiment.

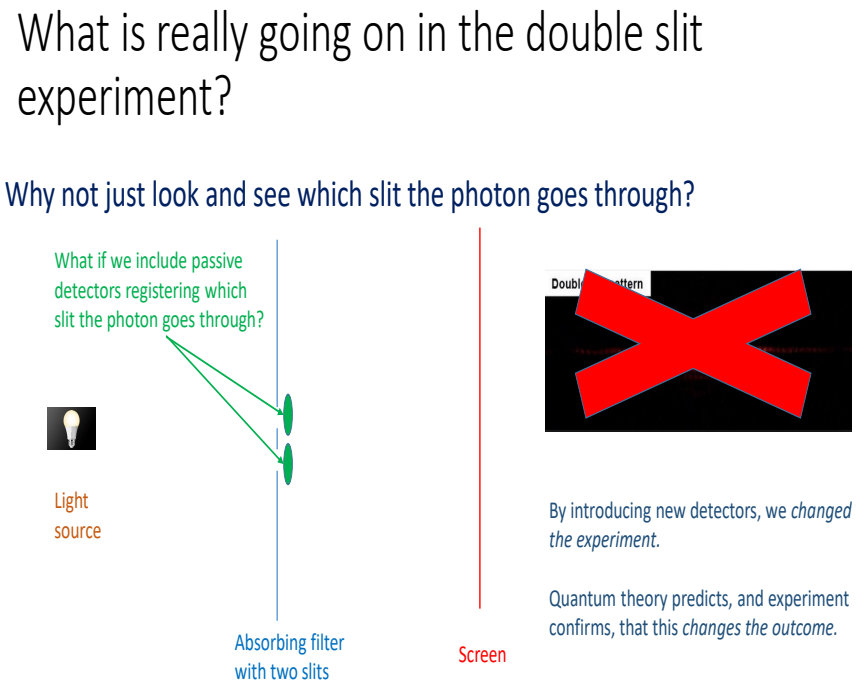

Figure 10: Observing which slit the electron goes through in the double slit experiment.

2.10.1 What can we conclude from double slit experiments?

1. As we already stressed, the wave model and the particle model are just that — models. *Neither* of them is adequate to explain the behaviour of electrons, photons, or other objects. Each of them can sometimes give a partial explanation of our observations, but that explanation *is not consistent with all the data*.

2. In particular, the type of reasoning about electron paths that would apply within a particle model does not generally apply in Nature. We can't assume that the electron follows a definite path through one slit or the other, and we can't assume (as we could with a classical particle) that observing which slit it goes through makes no difference to the interference pattern.

3. Some textbooks summarize the state of affairs described in point 1 by saying that electrons (photons, etc.) exhibit something called "wave-particle duality". This term can mislead, if it is interpreted as a sort of explanation of what is going on rather than just a catchy name for it.

The fact is that our classical wave and particle models are *fundamentally inadequate* descriptions. It isn't correct to say that an electron (or photon, etc.) is both a wave and a particle in the classical senses of either of those words. The electron is something different again, though it has some features in common with both. To go further, we need a *new* physical model: quantum mechanics.

4. We saw that the electron interference pattern builds up over time, yet the points at which individual electrons hit the screen do not appear to be precisely predictable: they seem to arrive at random. It might seem natural to speculate that this apparent randomness might be explained by the fact that we don't have complete data about the experiment. Perhaps, for example, the electrons leave the

source in slightly different directions, or perhaps they have some sort of internal structure that we haven't yet discussed (and perhaps hasn't yet been discovered), and perhaps *this* determines precisely where they hit the screen.

As we'll see, according to quantum mechanics this is not the case. Quantum mechanics, unlike classical mechanics, is an *intrinsically probabilistic* theory, and it tells us that there is simply no way to predict precisely where the electron will hit the screen, *even if* we have a precise and complete description of its physical state when it leaves the source.

Now, of course, quantum mechanics might not be the final theory of nature. It's possible that some as yet unknown and more complete theory could underlie quantum mechanics, and it's logically possible that this theory (if there is one) could be deterministic. However, there are very strong reasons to doubt that any theory underlying quantum mechanics can be deterministic. In particular, it can be proved (given a few very natural assumptions) that any such theory would be inconsistent with special relativity. This follows from Bell's theorem and experimental tests thereof: it is discussed further in the Part II course "Principles of Quantum Mechanics" and in Part III courses.)

2.11 *Ongoing tests of quantum theory

Although later developments are beyond the scope of this course, it would be wrong to leave the impression that the historical development of quantum mechanics ended in the first part of last century. Indeed, the basic principles of quantum mechanics are still being questioned and tested by some theorists and experimentalists today. Quantum theory is very well confirmed as a theory of microscopic physics. However, the case for believing that it applies universally to physics on all scales is much weaker.

There is a good scientific motivation for testing any scientific theory in new domains, which is that theories developed to explain phenomena in one domain may not necessarily apply in other domains. For example, quantum theory itself shows us the limits of validity of Newtonian mechanics and of classical electrodynamics. Similarly, Einstein's general theory of relativity shows us the limits of validity of Newton's theory of gravity.

There is also a specific motivation for wanting to test quantum theory for macroscopic systems. This is that the problems in making sense of quantum theory as an *explanation* of natural phenomena seem to stem from the fact that the classical physics we see on macroscopic scales appears to emerge from quantum theory in a way that, despite many attempts, remains hard to pin down. Many theorists believe it remains fundamentally unexplained. Many others believe it is explained or explainable, but there is no real consensus among them about the right explanation.

Interestingly, we know there are consistent (non-relativistic) theories that agree very precisely with quantum mechanical predictions for microscopic (small mass) particles, but disagree for macroscopic (large mass) ones.

In the past few years, experimental technology has advanced far enough to demonstrate diffraction of quite complex molecules. (Some descriptions of these experiments can be found at
https://vcq.quantum.at/; see in particular the work of the Arndt and Aspelmayer research groups.) Attempts continue to demonstrate interferometry for larger and larger objects, motivated not only by the technological challenge but also by the possibility of testing the validity of quantum mechanics in new domains. In October 2019, Fein et al. reported interference experiments for molecules of weight larger than 25kDa (See https://www.nature.com/articles/s41567-019-0663-9 and the rather amusing Q and A summary
https://www.quantumnano.at/detailview-news/news/facts-fiction-in-reports-on-high-mass-interference/).

It should be stressed that there is to date (October 2019) *no* experimental evidence for any deviation from quantum mechanics, which has been confirmed in an impressive array of experiments investigating many different physical regimes. *

2.12 Closing comments

1. As we've seen, the photon hypothesis played a key role in the development of quantum mechanics. We've also seen that photons (which are massless) and massive particles (such as electrons) produce qualitatively similar interference and diffraction patterns. However, we won't have much more to say about photons in this course. It turns out that we can develop quantum mechanics for the electron and other massive particles using relatively simple equations. We can build up a good intuition about how quantum systems behave in experiments and in nature from these equations. A fully satisfactory quantum treatment of photons or other massless particles requires a relativistic quantum theory of fields, which requires more sophisticated concepts (and is much harder to make mathematically rigorous). Quantum electrodynamics, which is a relativistic quantum field theory incorporating photons, is discussed in

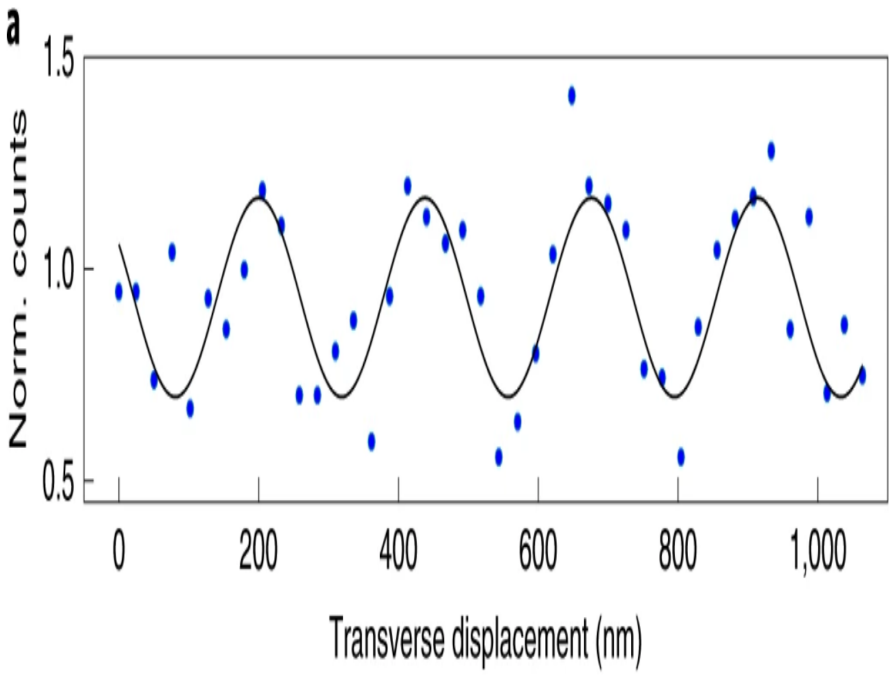

Figure 11: Interference of molecules larger than 25KDa, from the Fein et al. paper cited above.

Part III theoretical physics courses, along with other relevant quantum field theories.

2. Although we've already seen the classical particle model is inadequate, we still need some collective name for electrons, protons, neutrons and so on. Perhaps physicists should have invented another term, but we still call these "particles". We will follow this tradition, so that we might say that the electron is an elementary particle, talk about quantum mechanics applied to an abstract particle of mass m, and so forth — *always keeping in mind that the classical particle model does not actually apply.*

3 The one-dimensional Schrödinger equation

3.1 The 1D Schrödinger equation for a free particle

We are first going to develop quantum mechanics in one space (and one time) dimension. We can solve the equations for simple physical models more easily in 1D than in 3D and, happily, it turns out that 1D solutions give a good qualitative feel for a range of interesting 3D physical phenomena.

In 1924, Schrödinger developed de Broglie's ideas further, into what became a standard way of framing the laws of quantum mechanics.[5]

Recall that de Broglie postulated that matter is described by waves, and that the energy and momentum are related to the angular frequency and wave vector by $E = \hbar\omega$ and $\underline{p} = \hbar\underline{k}$, or in one dimension $p = \hbar k$. We can express this by associating to a particle of energy E and momentum p a wave of the form

$$\psi(x,t) = \exp(i(kx - \omega t))\,. \tag{3.1}$$

Now, for a mass m particle, we have $E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$, and so

$$\psi(x,t) = \exp(i(kx - \omega t)) = \exp(\frac{i}{\hbar}(px - \frac{p^2}{2m}t))\,. \tag{3.2}$$

Notice that we have taken $\psi(x,t)$ to be complex. Using complex numbers to represent waves is familiar in classical electromagnetism, where it allows us to combine the electric and magnetic fields in a single equation. In that context, it's mathematically convenient, but the real and imaginary parts each have a simple physical interpretation. We will see that complex-valued solutions to (generalised) wave equations play a more essential role in quantum mechanics.

The simplest wave equation to which the de Broglie wave is the general solution is the *time-dependent 1D Schrödinger equation for a free particle*:

$$\frac{1}{2m}(-i\hbar\frac{\partial}{\partial x})^2\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t)\,. \tag{3.3}$$

(By a *free particle* we mean a particle not subject to external forces, i.e. one moving in a potential $V(x) = 0$.)

[5] There is an equivalent alternative way of describing quantum mechanics, developed by Heisenberg, Born and Jordan. But Schrödinger's formulation is easier to work with and gives a more intuitive physical picture – so we will follow his approach. Note that "more intuitive" here is a relative statement. As we will see, many of the predictions of quantum mechanics are counter-intuitive. Also, some of the intuitions Schrödinger's picture suggests may be helpful to us in some contexts but are not fundamentally justifiable.

3.2 The momentum operator

We define the *momentum operator*

$$\hat{p} = -i\hbar \frac{\partial}{\partial x} \,. \tag{3.4}$$

So, for the de Broglie wave $\psi(x,t) = \exp(\frac{i}{\hbar}(px - \frac{p^2}{2m}t))$, we have $\hat{p}\psi = p\psi$. In other words, acting with the momentum operator on the de Broglie wave is equivalent to multiplying by the wave momentum.[6] We can rewrite (3.3) as

$$\frac{1}{2m}\hat{p}^2\psi = i\hbar \frac{\partial \psi}{\partial t} \,. \tag{3.5}$$

This is our first example of a general feature of quantum mechanics. Physically significant quantities (in this case momentum) are represented by operators. These operators act on functions that represent physical states (in this case the idealized state defining the de Broglie wave).

Formally, we define an *operator* $\hat{O}$ to be a *linear* map from a space of functions[7] to itself, i.e. any map such that

$$\hat{O}(a_1\psi_1 + a_2\psi_2) = a_1\hat{O}\psi_1 + a_2\hat{O}\psi_2 \tag{3.6}$$

for all complex numbers a_1, a_2 and all functions ψ_1, ψ_2 in the relevant space.

[6] This tells us that the de Broglie wave is an *eigenfunction* of the momentum operator with *eigenvalue* p: we will define these terms more generally later.

[7] We will not be too precise about which space of functions we are working with, but will assume that they are suitably "well behaved". For example, and depending on the context, we might want to consider the space of infinitely differentiable functions, $C^\infty(R)$, or the space of "square integrable" functions, i.e. those satisfying Eqn. (3.11).

3.3 The 1D Schrödinger equation for a particle in a potential

We want to consider particles subject to a potential $V(x)$ as well as free particles.

Examples: alpha rays scattering from a nucleus, electrons diffracting from a crystal, buckyballs going through an interferometer, neutrons or larger massive particles moving in a gravitational field.

To do this, we replace the kinetic energy term in (3.5) by an operator corresponding to the *hamiltonian* or *total energy*:

$$H = \frac{p^2}{2m} + V(x)\,, \tag{3.7}$$

namely

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x)\,, \tag{3.8}$$

where the second operator corresponds to multiplication by $V(x)$.

This gives the general form of the *time-dependent 1D Schrödinger equation* for a single particle:

$$\hat{H}\psi(x,t) = i\hbar\frac{\partial\psi}{\partial t}\,. \tag{3.9}$$

Or, more explicitly:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = i\hbar\frac{\partial\psi}{\partial t}\,. \tag{3.10}$$

Note that there is no way to *prove* mathematically that Eqns. (3.9, 3.10) are physically relevant, although we have given some motivation for them in the light of previous physical models and experimental results. As with any new physical theory, the only real test is experiment. Since it is not yet obvious what the complex-valued solutions to (3.9, 3.10) have to do with experimentally observable quantities, we will first need to give rules for interpreting them physically, and then test these predictions.

3.4 The wavefunction

We call a complex valued function $\psi(x,t)$ that is a solution to (3.9) or (3.10) a *wavefunction*. We say the wavefunction $\psi(x,t)$ is *normalisable* (at time t) if

$$0 < \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx < \infty \,. \tag{3.11}$$

Note that for **any** complex valued $\psi(x,t)$ the integral is real and non-negative.

We say $\psi(x,t)$ is *normalised* if

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = 1 \,. \tag{3.12}$$

So, given a normalisable $\psi(x,t)$ with $\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = C$, so that $0 < C < \infty$, we can define a normalised wavefunction $C^{-1/2}\psi(x,t)$.

3.4.1 What is the wavefunction?

As we will explain in following lectures, the wavefunction $\psi(x,t)$ of a particle is a mathematical object that allows us to calculate the probability of detecting the particle at any given position if we set up a detector there. More generally, it allows us to calculate the probability of any given outcome for the measurement of any observable quantity (for example, energy or momentum) associated with the particle.

Sometimes in the course of your studies you may suspect that lecturers are temporarily keeping the full truth from you.[8] Sometimes you would be right, but not here. We really don't have a better and more intuitively comprehensible story about the wavefunction.[9]

[8] If charitable, you may also suspect there may be good pedagogical reasons for this.

[9] At least, not one that is generally agreed.

3.4.2 What the wavefunction definitely isn't

Schrödinger initially hoped to interpret the wave function as describing a dispersed cloud of physical material that somehow corresponds to a "smeared-out" particle. This looks a natural interpretation at first sight, but proved untenable and was abandoned.

One problem with this interpretation is that if a charged particle is really a dispersed cloud of charge, we would expect to be able to detect bits of the cloud carrying fractions of the charge of the electron. However, we always find that charged objects carry a charge that is some integer multiple of the electron charge. Classical electrodynamics also suggests that a dispersed charge of cloud should interact repulsively with itself via the Coulomb force, and thus tend to be additionally dispersed, in a way that we do not observe.

Even if these objections could somehow be overcome, another problem remains. No matter how widely the electron's wavefunction is spread out in space, when we look for it by setting up detectors we always find an apparently pointlike particle in a definite location. If the wavefunction really represented a dispersed cloud, this cloud would have to suddenly coalesce into a particle at a single point when we carry out a measurement. This would mean that parts of the cloud would have to travel extremely fast — often much faster than light speed. This is inconsistent with special relativity.

3.5 The superposition principle

Exercises 1. The Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x)\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t)$$

is linear in $\psi(x,t)$: if ψ_1 and ψ_2 are solutions then $a_1\psi_1 + a_2\psi_2$ is a solution too, for any complex a_1, a_2.

2. If ψ_1 and ψ_2 are normalisable and $a_1\psi_1 + a_2\psi_2$ is nonzero [10], then it is also normalisable.

3. Show that it is not generally true that if ψ_1 and ψ_2 are normalised then $a_1\psi_1 + a_2\psi_2$ is, even if $|a_1|^2 + |a_2|^2 = 1$.

The linearity of the Schrödinger equation implies the so-called *superposition principle*: there is a physical solution corresponding to any linear combination of two (or more) physical solutions.

The superposition principle is an essential feature of quantum mechanics, which does not generally apply in classical physics. It makes no sense in Newtonian mechanics to add a linear combination of two orbits of a planet around the Sun: this doesn't define another possible orbit. But in quantum theory, taking sums of physical wavefunctions, for example those of an electron orbiting the nucleus of a hydrogen atom, gives us another wavefunction that has a direct physical meaning.

We will see shortly that we need to normalise a wavefunction to obtain a sensible probability distribution from it and make physical predictions. So to make physical predictions from a superposition, we generally need to normalise the sum $\psi = a_1\psi_1 + a_2\psi_2$. As we've just seen, this is always possible if ψ_1, ψ_2 are normalisable and ψ is nonzero.

[10] I.e. not the zero *function*; it does not vanish everywhere.

3.6 Probabilistic interpretation of the wavefunction: the Born rule

Max Born in 1926 explained the essential connection between the wavefunction and experiment, via the so-called *Born rule*:

If we carry out an experiment to detect the position of a particle described by a normalised wavefunction $\psi(x,t)$, the probability of finding the particle in the interval $[x, x+dx]$ at time t is

$$\int_x^{x+dx} |\psi(y,t)|^2 dy \approx dx|\psi(x,t)|^2 = dx\rho(x,t)\,, \tag{3.13}$$

where we write $\rho(x,t) = |\psi(x,t)|^2$ (see below).

More generally, the probability of finding the particle in any interval $[a,b]$ is

$$\int_a^b |\psi(y,t)|^2 dy\,. \tag{3.14}$$

Intuitively, it may seem that (3.14) should follow from (3.13). Certainly, it would be peculiar if the probability of finding a particle in a given interval depended on how the interval was sub-divided (i.e. on how precise our position measurements were). But we have already seen some apparently peculiar predictions of quantum mechanics, which show it is not safe to rely on intuition. We should rather understand (3.14) as a general postulate from which (3.13) follows as a special case. We will see later (section 6.6) that (3.14) itself is a special case of the general quantum measurement postulates, which apply to measurements of any physical quantity (not only position).

3.6.1 Probability density and probability current

The following mathematical quantities give very useful insights into the behaviour of solutions to the Schrödinger equation:

The *probability density*

$$\rho(x,t) = |\psi(x,t)|^2 \quad . \tag{3.15}$$

We see that the Born rule justifies the interpretation of $\rho(x,t)$ as a probability density. If we measure the position of the particle at time t, the probability of finding the particle in the interval $[x, x+dx]$ is $\rho(x,t)dx$.

The *probability current*

$$J(x,t) = -\frac{i\hbar}{2m}\{\psi^*(x,t)\frac{\partial}{\partial x}\psi(x,t) - (\frac{\partial}{\partial x}\psi^*(x,t))\psi(x,t)\}\,. \tag{3.16}$$

It is easy to verify from (3.10) that

$$\frac{\partial J}{\partial x} + \frac{\partial \rho}{\partial t} = 0\,. \tag{3.17}$$

Thus ρ and J do indeed satisfy a conservation equation, with ρ behaving as a density whose total integral is conserved, and J as a current describing the density flux.

The key point here is that $\frac{\partial \rho}{\partial t}$ can be written as a spatial derivative of some quantity. This means that we can calculate the time derivative of the probability of finding the particle in a region $[a,b]$:

$$\frac{d}{dt}\int_a^b |\psi(x,t)|^2 dx = \int_a^b -\frac{\partial}{\partial x}J(x,t)dx = J(a,t) - J(b,t)\,. \tag{3.18}$$

The last term describes the probability density flux across the endpoints of the interval – the "net flow of probability out of (or in to) the interval".

Now if ψ is normalised, i.e. Eqn (3.12) holds, then $\psi(x) \to 0$ as $x \to \pm\infty$. Thus $J(x) \to 0$ as $x \to \pm\infty$, assuming (as we will here) that $\frac{\partial}{\partial x}\psi(x)$ is bounded as $x \to \infty$. Thus

$$\frac{d}{dt}\int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = \lim_{a\to-\infty} J(a,t) - \lim_{b\to\infty} J(b,t) = 0\,. \tag{3.19}$$

The total probability of finding the particle in $-\infty < x < \infty$ is thus constant over time: $\int_{-\infty}^{\infty} |\psi(y,t)|^2 dy = 1$ for any time t. So, the Born probabilistic interpretation is consistent: whenever we look for the particle, we will definitely find it somewhere, and only in one place.

Notes:

- We will consider measurements of quantities other than position later.
- The Born rule says nothing about where the particle is if we do not measure its position. According to the standard understanding of quantum mechanics, this is a question with no well-defined answer: the particle's position is not defined unless we measure it.

  As we'll see, according to quantum mechanics, we can generally only calculate the probabilities of possible measurement results: we can't predict with certainty which result will occur. Moreover, the theory only allows us to predict probabilities for the possible results of measurements that actually take place in a given experiment. We cannot consistently combine these predictions with those for other measurements that could have been made had we done a different experiment instead.[11]

  We'll see when we discuss the general measurement postulates of quantum mechanics in section 6.6 that measuring the position of a particle generally changes its wavefunction. Recall the earlier discussion of the 2-slit experiment. We found no definite answer to the question "which slit did the particle go through?" – unless we put detectors beside the slits, and this changed the experiment *and changed the interference pattern.*

[11] See again the analysis of the double slit experiment above, and (for example) the relevant chapters of Feynman's lecture notes, for further discussion of this.