Advanced Quantum Mechanics

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This is the web page for Advanced Quantum Mechanics (PHYS30201) for the session 2012/13.

The notes are not intended to be fully self-contained, but summarise lecture material and give pointers to textbooks.

These notes have been prepared with TEX4ht, and use MathML to render the equations. Try the link to “This course and other resources” to see if your browser is compatible. (In particular there is a problem with square roots of fractions that you should check is OK.) If you are using Internet Explorer, you may need to download “MathPlayer” from here.

Please report errors to Judith McGovern.

This course and other resources.

The books I have relied on most in preparing this course are:

- Shankar, R. Principles of Quantum Mechanics 2nd ed. (Plenum 1994) [preview] [Errata to 13th printing, (2006)]
- Gasiorowicz, S. Quantum Physics 3rd ed. (Wiley 2003) [Supplementary material] [errata]
- Mandl, F. Quantum Mechanics (Wiley 1992)
- Townsend, J.S. A Modern Approach to Quantum Mechanics (McGraw-Hill 1992) [preview]

Throughout these notes, I have provided section references, mostly to the first three of these.

Note that Shankar and Townsend use Gaussian rather than SI units, as do older editions of Gasiorowicz. Notes on translation are given in section A.12.

I have found two sets of extensive on-line quantum mechanics notes that are at the right level for this course. One is by Prof Richard Fitzpatrick, of the University of Texas at Austin. His UG course notes are here and his PG notes here. The UG notes start at the level of our PHYS20101 course, but continue to the end of this course. The PG notes also start from the begining but more in the style of PHYS20602, and continue to the end of this course. They seem very much equivalent (though not quite idential) for the coverage of this course.

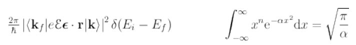
The other is by Prof Jim Branson of the University of California, San Diego, notes available here; these again start at the beginning, but go beyond this course and cover parts of PHYS30202 as well.

Both sets of notes should be useful for revision of background material and as an alternative resource for this course. Both have more details in the derivations than I have given here.

These notes have been prepared with TEX4ht, and use MathML to render the equations. If you are using Internet Explorer, you may need to download "MathPlayer" from here. Once you have done so, the following should look more or less the same:

$$\tfrac{2\pi}{\hbar}\left|\langle \mathbf{k}_f|e\mathcal{E}\boldsymbol{\epsilon}\cdot\mathbf{r}|\mathbf{k}\rangle\right|^2\delta(E_i-E_f) \qquad\qquad \int_{-\infty}^{\infty} x^n \mathrm{e}^{-\alpha x^2}\mathrm{d}x = \sqrt{\frac{\pi}{\alpha}}$$

The first is MathML, the second is an image. Subtle things to look out for are bold-face for vectors **k** etc; not so subtle is whether the square root in the second equation covers both numerator and denominator. If you are using Firefox, you may need to download STIX fonts; see here. Safari (even 5.1) is still a mess, unfortunately.



$$\tfrac{2\pi}{\hbar}\left|\langle \mathbf{k}_f|e\mathcal{E}\boldsymbol{\epsilon}\cdot\mathbf{r}|\mathbf{k}\rangle\right|^2\delta(E_i-E_f) \qquad\qquad \int_{-\infty}^{\infty} x^n \mathrm{e}^{-\alpha x^2}\mathrm{d}x = \sqrt{\frac{\pi}{\alpha}}$$

The advantage of MathML is accessibility (at least in theory), equations that can be magnified if you change the magnification of the page (or that pop out with a click using "MathPlayer"), and much cleaner directories. The disadvantage is that I don't think it looks as nice on average, and I don't know in advance how much trouble might be caused by incompatable browsers. I may revert to using images for equations (as the web notes discussed above do) if there are widespread problems, so let me know.

Operator methods in Quantum Mechanics

1.1 Postulates of Quantum Mechanics

Summary: All of quantum mechanics follows from a small set of assumptions, which cannot themselves be derived.

There is no unique formulation or even number of postulates, but all formulations I've seen have the same basic content. This formulation follows Shankar most closely, though he puts III and IV together. Nothing significant should be read into my separating them (as many other authors do), it just seems easier to explore the consequences bit by bit.

I: The state of a particle is given by a vector $|\psi(t)\rangle$ in a Hilbert space. The state is normalised: $\langle\psi(t)|\psi(t)\rangle = 1$.

This is as opposed to the classical case where the position and momentum can be specified at any given time.

This is a pretty abstract statement, but more informally we can say that the wave function $\psi(x,t)$ contains all possible information about the particle. How we extract that information is the subject of subsequent postulates.

The really major consequence we get from this postulate is *superposition*, which is behind most quantum weirdness such as the two-slit experiment.

II: There is a Hermitian operator corresponding to each observable property of the particle. Those corresponding to position $\hat{\mathbf{x}}$ and momentum $\hat{\mathbf{p}}$ satisfy $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$.

Other examples of observable properties are energy and angular momentum. The choice of these operators may be guided by classical physics (eg $\hat{\mathbf{p}}\cdot\hat{\mathbf{p}}/2m$ for kinetic energy and $\hat{\mathbf{x}}\times\hat{\mathbf{p}}$ for orbital angular momentum), but ultimately is verified by experiment (eg Pauli matrices for spin-$\frac{1}{2}$ particles).

The commutation relation for $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ is a formal expression of Heisenberg's uncertainty principle.

III: Measurement of the observable associated with the operator $\widehat{\Omega}$ will result in one of the eigenvalues ω_i of $\widehat{\Omega}$. Immediately after the measurement the particle will be in the corresponding eigenstate $|\omega_i\rangle$.

This postulate ensures *reproducibility* of measurements. If the particle was not initially in the state $|\omega_i\rangle$ the result of the measurement was not predictable in advance, but for the result of a measurement to be meaningful the result of a subsequent measurement must be predictable. ("Immediately" reflects the fact that subsequent time evolution of the system will change the value of ω unless it is a constant of the motion.)

IV: The probability of obtaining the result ω_i in the above measurement (at time t_0) is $|\langle\omega_i|\psi(t_0)\rangle|^2$.

If a particle (or an ensemble of particles) is repeatedly prepared in the same initial state $|\psi(t_0)\rangle$ and the measurement is performed, the result each time will in general be different (assuming this state is not an eigenstate of $\widehat{\Omega}$; if it is the result will be the corresponding ω_i each time). Only the distribution of results can be predicted. The postulate expressed this way has the same content as saying that the average value of ω is given by $\langle\psi(t_0)|\widehat{\Omega}|\psi(t_0)\rangle$. (Note the distinction between repeated measurements on freshly-prepared particles, and repeated measurements on the same particle which will give the same ω_i each subsequent time.)

V: The time evolution of the state $|\psi(t)\rangle$ is given by $i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = \widehat{H}|\psi(t)\rangle$, where $\widehat{H}$ is the operator corresponding to the classical Hamiltonian.

In most cases the Hamiltonian is just the energy and is expressed as $\hat{\mathbf{p}}\cdot\hat{\mathbf{p}}/2m + V(\hat{\mathbf{x}})$. (They differ in some cases though - see texts on classical mechanics such as Kibble and Berkshire.) In the presence of non-conservative forces such as magnetism the Hamiltonian is still equal to the energy, but its expression in terms of $\hat{\mathbf{p}}$ is more complicated.

VI: The Hilbert space for a system of two or more particles is a product space.

This is true whether the particles interact or not, ie if the states $|\phi_i\rangle$ span the space for one particle, the states $|\phi_i\rangle \otimes |\phi_j\rangle$ will span the space for two particles. If they do interact though, the eigenstates of the Hamiltonian will not just be simple products of that form, but will be linear superpositions of such states.

References

- **Shankar 4**

1.2 Position and Momentum Representations

Summary: The *position-space representation* allows us to make contact with quantum mechanics expressed in terms of wavefunctions

- Working in one dimension for the moment, it is convenient to define the state $|x_0\rangle$ which is an eigenfunction of the position operator: $\hat{x}|x_0\rangle = x_0|x_0\rangle$. Here we have used x_0 to indicate a *specific* value of x – say 3 m right of the origin - but we also write $|x\rangle$ when we want to leave the exact value open. It's like the difference between $|\omega_1\rangle$ and $|\omega_i\rangle$.

- The set $\{|x\rangle\}$ form a complete set as $\hat{x}$ is Hermitian, but now when we expand another state in terms of these, we have to integrate rather than sum, and rather than a discrete set of coefficients $\{a_i\}$ we have a continuous set or function, $|\alpha\rangle = \int \alpha(x')|x'\rangle \mathrm{d}x'$. (Integration limits are $-\infty \to \infty$ unless otherwise specified.)

- We choose the normalisation to be $\langle x|x'\rangle = \delta(x - x')$. Then $\alpha(x) = \langle x|\alpha\rangle$. This is called the *wave function in position space* of the state $|\alpha\rangle$. With this normalisation the identity operator is
$$\int_{-\infty}^{\infty} |x'\rangle\langle x'|\mathrm{d}x'.$$
These states have infinite norm and so don't really belong to our vector space, but we don't need to worry about this! (See PHYS20602 notes for much more detail.)

- Since $|\alpha\rangle = \int \alpha(x')|x'\rangle \mathrm{d}x'$, from the fourth postulate we might expect that $P(x) \equiv |\alpha(x)|^2$ is the probability of finding the particle at position x. But we also need $\int P(x')\mathrm{d}x' = 1$ – the probability of finding the particle at *some* x is unity. The transition from sums to integrals corresponds to the transition from discrete probabilities to *probability distributions*, and so the correct interpretation is that $P(x)\mathrm{d}x$ is the probability of finding the particle in an infinitesimal interval between x and $x + \mathrm{d}x$.

- Since $\langle x|\hat{x}|\alpha\rangle = x\langle x|\alpha\rangle = x\alpha(x)$, we can say that the position operator in the position space representation is simply x, and operating with it is equivalent to multiplying the wave function by x.

- If we make the hypothesis that $\langle x|\hat{p}|\alpha\rangle = -i\hbar \mathrm{d}\alpha(x)/\mathrm{d}x$, we can see that the required commutation relation $[\hat{x}, \hat{p}] = i\hbar$ is satisfied.

- We can equally imagine states of definite momentum, $|p\rangle$, with $\hat{p}|p\rangle = p|p\rangle$. Then $\tilde{\alpha}(p) = \langle p|\alpha\rangle$ is the wave function in *position space*; in this representation $\hat{p}$ is given by p and $\hat{x}$ by $(i\hbar)\mathrm{d}/\mathrm{d}p$.

- Let's write the position-space wave function of $|p\rangle$, $\langle x|p\rangle$, as $\phi_p(x)$. Since $\langle x|\hat{p}|p\rangle$ can be written as either $p\phi_p(x)$ or $-i\hbar \mathrm{d}\phi_p(x)/\mathrm{d}x$, we see that $\phi_p(x) = (1/\sqrt{2\pi\hbar})\, \mathrm{e}^{ipx/\hbar}$. This is just a plane wave, as expected. (The normalisation is determined by $\langle p|p'\rangle = \delta(p - p')$.)

- This implies that $\alpha(x) = (1/\sqrt{2\pi\hbar}) \int \mathrm{e}^{ip'x/\hbar}\tilde{\alpha}(p')\mathrm{d}p'$, that is the position- and momentum-space wave functions are Fourier transforms of each other. (The $1/\sqrt{\hbar}$ is present in the prefactor because we are using p and not $k = p/\hbar$ as the conjugate variable.)

- Strictly speaking we should write the position-space representations of $\hat{x}$ and $\hat{p}$ as $\langle x|\hat{x}|x'\rangle = x'\delta(x - x')$ and $\langle x|\hat{p}|x'\rangle = (i\hbar)\mathrm{d}\delta(x - x')/\mathrm{d}x'$. These only make sense in a larger expression in which integration over x' is about to be performed.

- The extension to three dimensions is trivial, with the representation of the vector operator $\hat{\mathbf{p}}$ in position space being $-i\hbar\nabla$. Since differentiation with respect to one coordinate commutes with multiplication by another, $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$ as required. (We have used $\hat{\mathbf{x}}$ as the position operator. We will however use $\mathbf{r}$ as the position vector. The reason we don't use $\hat{\mathbf{r}}$ is that it is so commonly used to mean a unit vector. Thus $\hat{\mathbf{x}}|\mathbf{r}\rangle = \mathbf{r}|\mathbf{r}\rangle$.)

  The generalisation of $\phi_p(x)$ is $\phi_{\mathbf{p}}(\mathbf{r}) = (1/\sqrt{2\pi\hbar})\, \mathrm{e}^{i\mathbf{p}\cdot\mathbf{r}/\hbar}$, which is a plane wave travelling in the direction of $\mathbf{p}$.

- In the position representation, the Schrödinger equation reads

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

  Note though that position and time are treated quite differently in quantum mechanics. There is no operator corresponding to time, and t is just part of the label of the state: $\psi(\mathbf{r}, t) = \langle \mathbf{r}|\psi(t)\rangle$.

- Together with the probability density, $\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2$, we also have a probability flux $\mathbf{j}(\mathbf{r}) = (-i\hbar/2m)(\psi(\mathbf{r})^*\nabla\psi(\mathbf{r}) - \psi(\mathbf{r})\nabla\psi(\mathbf{r})^*)$. The continuity equation $\nabla \cdot \mathbf{j} = -\partial\rho/\partial t$ which ensures local conservation of probability density follows from the Schrödinger equation.

- A two-particle state has a wave function which is a function of the two positions, $\Phi(\mathbf{r}_1, \mathbf{r}_2)$, and the basis kets are direct product states $|\mathbf{r}_1\rangle \otimes |\mathbf{r}_2\rangle$. For states of non-interacting distinguishable particles where it is possible to say that the first particle is in single-particle state $|\psi\rangle$ and the second in $|\phi\rangle$, the state of the system is $|\psi\rangle \otimes |\phi\rangle$ and the wave function is $\Phi(\mathbf{r}_1, \mathbf{r}_2) = (\langle\mathbf{r}_1| \otimes \langle\mathbf{r}_2|)(|\psi\rangle \otimes |\phi\rangle) = \langle\mathbf{r}_1|\psi\rangle\langle\mathbf{r}_2|\phi\rangle = \psi(\mathbf{r}_1)\phi(\mathbf{r}_2)$.

- From $i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = \widehat{H}|\psi(t)\rangle$ we obtain $|\psi(t + \mathrm{d}t)\rangle = \left(1 - \frac{i}{\hbar}\widehat{H}\mathrm{d}t\right)|\psi(t)\rangle$. Thus

$$|\psi(t)\rangle = \lim_{N\to\infty}\left(1 - \frac{i}{\hbar}\frac{(t-t_0)}{N}\widehat{H}\right)^N |\psi(t_0)\rangle = \mathrm{e}^{-i\widehat{H}(t-t_0)/\hbar}|\psi(t_0)\rangle \equiv U(t, t_0)|\psi(t_0)\rangle$$

  where the exponential of an operator is defined as $\mathrm{e}^{\widehat{\Omega}} = \sum_n \frac{1}{n!}\widehat{\Omega}^n$. If the Hamiltonian depends explicitly on time, we have $U(t, t_0) = T\exp\left(-i\int_{t_0}^{t}\widehat{H}(t')\mathrm{d}t'/\hbar\right)$, where the *time-ordered* exponential denoted by $T\exp$ means that in expanding the exponential, the operators are ordered so that $\widehat{H}(t_1)$ always sits to the right of $\widehat{H}(t_2)$ (so that it acts first) if $t_1 < t_2$. (This will be derived later, and is given here for completeness.)

References

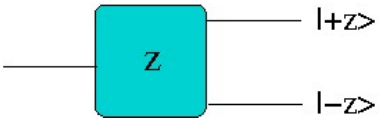
- **Shankar ch 1.10**
- **Mandl ch 12.4**

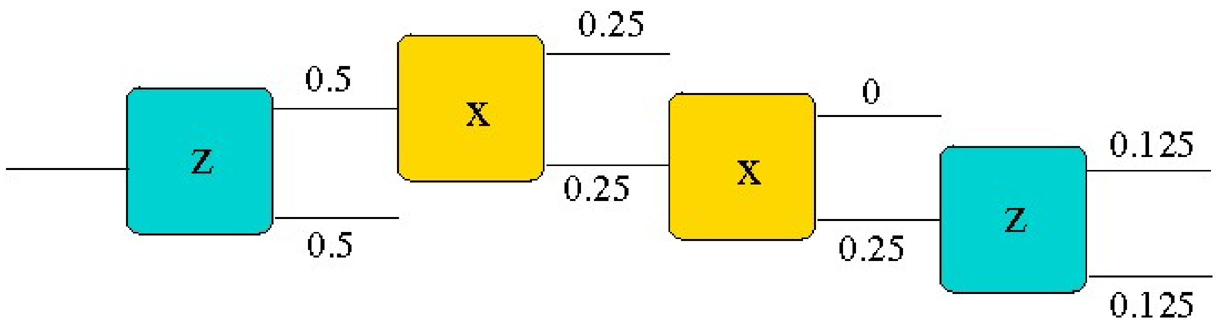
1.3 The Stern-Gerlach experiment

Summary: Simple extensions of the Stern-Gerlach experiment reduce the predictions about quantum measurement to their essence.

The usual reason for considering the Stern-Gerlach experiment is that it shows experimentally that angular momentum is quantised, and that particles can have intrinsic angular momentum which is an integer multiple of $\frac{1}{2}\hbar$. An inhomogeneous magnetic field deflects particles by an amount proportional to the component of their magnetic moment parallel to the field; when a beam of atoms passes through they follow only a few discrete paths ($2j+1$ where j is their total angular momentum quantum number) rather than, as classically predicted, a continuum of paths (corresponding to a magnetic moment which can be at any angle relative to the field).

For our purposes though a Stern-Gerlach device is a quick and easily-visualised way of making measurements of quantities (spin components) for which the corresponding operators do not commute, and thereby testing the postulates concerned with measurement. We restrict ourselves to spin-$\frac{1}{2}$; all we need to know is that if we write $|+\mathbf{n}\rangle$ to indicate a particle with its spin up along the direction $\mathbf{n}$, and $|-\mathbf{n}\rangle$ for spin down, then the two orthogonal states $\{|\pm\mathbf{n}\rangle\}$ span the space for any $\mathbf{n}$, and $|\langle\pm\mathbf{n}|\pm\mathbf{n}'\rangle|^2 = \frac{1}{2}$ if $\mathbf{n}$ and $\mathbf{n}'$ are perpendicular.





In the figure above we see an unpolarised beam entering a Stern-Gerlach device with its field oriented in the z-direction. If we intercept only the upper or lower exiting beam, we have a pure spin-up or spin-down state.

Here we see a sequence of Stern-Gerlach devices with their fields oriented in either the x- or z-direction. The numbers give the fraction of the original unpolarised beam which reaches this point. The sequence of two x-devices in a row illustrates reproducibility. The final z-device is the really crucial one. Do you understand why half of the particles end up spin-down, even though we initially picked the $|+\mathbf{z}\rangle$ beam?

- **Townsend ch 1.4**

1.4 Ehrenfest's Theorem and the Classical Limit

Summary: The form of classical mechanics which inspired Heisenberg's formulation of Classical Mechanics allows us to see when particles should behave classically.

Using $i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = \widehat{H}|\psi(t)\rangle$ and hence $-i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi(t)| = \langle\psi(t)|\widehat{H}$, and writing $\langle\widehat{\Omega}\rangle \equiv \langle\psi(t)|\Omega|\psi(t)\rangle$, we have Ehrenfest's Theorem

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\widehat{\Omega}\rangle = \frac{1}{i\hbar}\langle[\widehat{\Omega},\widehat{H}]\rangle + \langle\frac{\partial\widehat{\Omega}}{\partial t}\rangle$$

The second term disappears if $\widehat{\Omega}$ is a time-independent operator (like momentum, spin...). Note we are distinguishing between *intrinsic* time-dependence of an operator, and the time-dependence of its expectation value in a given state.

This is very reminiscent of a result which follows from Hamilton's equations in classical mechanics, for a function of position, momentum (and possibly time explicitly) $\Omega(p,x,t)$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\Omega(p,x,t) &= \frac{\partial\Omega}{\partial x}\frac{\mathrm{d}x}{\mathrm{d}t} + \frac{\partial\Omega}{\partial p}\frac{\mathrm{d}p}{\mathrm{d}t} + \frac{\partial\Omega}{\partial t}\\ &= \frac{\partial\Omega}{\partial x}\frac{\partial H}{\partial p} - \frac{\partial\Omega}{\partial p}\frac{\partial H}{\partial x} + \frac{\partial\Omega}{\partial t}\\ &\equiv \{\Omega,H\} + \frac{\partial\Omega}{\partial t}\end{aligned}$$

where the notation $\{\Omega,H\}$ is called the *Poisson bracket* of Ω and H, and is simply defined in terms of the expression on the line above which it replaced. (For $\Omega = x$ and $\Omega = p$ we can in fact recover Hamilton's equations for $\dot{p}$ and $\dot{x}$ from this more general expression.)

In fact for $\widehat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$, we can further show that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{x} \rangle = \langle \frac{\hat{p}}{m} \rangle \qquad \text{and} \qquad \frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{p} \rangle = -\langle \frac{\mathrm{d}V(\hat{x})}{\mathrm{d}\hat{x}} \rangle$$

which looks very close to Newton's laws. Note though that $\langle \mathrm{d}V(\hat{x})/\mathrm{d}\hat{x} \rangle \neq \mathrm{d}\langle V(\hat{x}) \rangle / \mathrm{d}\langle \hat{x} \rangle$ in general.

This correspondence is not just a coincidence, in the sense that Heisenberg was influenced by it in coming up with his formulation of quantum mechanics. It confirms that it is the expectation value of an operator, rather than the operator itself, which is closer to the classical concept of the time evolution of some quantity as a particle moves along a trajectory.

Similarity of formalism is not the same as identity of concepts though. Ehrenfest's Theorem does not say that the expectation value of a quantity follows a classical trajectory in general. What it does ensure is that if the uncertainty in the quantity is sufficiently small, in other words if Δx and Δp are both small (in relative terms) then the quantum motion will aproximate the classical path. Of course because of the uncertainty principle, if Δx is small then Δp is large, and it can only be *relatively* small if p itself is really large—ie if the particle's mass is macroscopic. More specifically, we can say that we will be in the classical regime if the de Broglie wavelength is much less that the (experimental) uncertainty in x. (In the Stern-Gerlach experiment the atoms are heavy enough that (for a given component of their magnetic moment) they follow approximately classical trajectories through the inhomogeneous magnetic field.)

- **Shankar ch 2.7, ch 6**
- **Mandl ch 3.2**

Approximate methods I: variational method and WKB

It is often (almost always!) the case that we cannot solve real problems analytically. Only a very few potentials have analytic solutions, by which I mean one can write down the energy levels and wave functions in closed form, as for the harmonic oscillator and Coulomb potential. In fact those are really the only useful ones (along with square wells)... In the last century, a number of approximate methods have been developed to obtain information about systems which can't be solved exactly.

These days, this might not seem very relevant. Computers can solve differential equations very efficiently. But:

- It is always useful to have a check on numerical methods
- Even supercomputers can't solve the equations for many interacting particle exactly in a reasonable time (where "many" may be as low as four, depending on the complexity of the interaction) — ask a nuclear physicist or quantum chemist.
- Quantum field theories are systems with infinitely many degrees of freedom. All approaches to QFT must be approximate.
- If the system we are interested in is close to a soluble one, we might obtain more insight from approximate methods than from numerical ones. This is the realm of perturbation theory. The most accurate prediction ever made, for the anomalous magnetic moment of the electron, which is good to one part in 10^{12}, is a 4th order perturbative calculation.

2.1 Variational methods: ground state

Summary: Whatever potential we are considering, we can always obtain an *upper bound* on the ground-state energy.

Suppose we know the Hamiltonian of a bound system but don't have any idea what the energy of the ground state is, or the wave function. The variational principle states that if we simply guess the wave function, the expectation value of the Hamiltonian in that wave function will be greater than the true ground-state energy:

$$\frac{\langle\Psi|\widehat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_0$$

This initially surprising result is more obvious if we consider expanding the (normalised) $|\Psi\rangle$ in the true energy eigenstates $|n\rangle$, which gives $\langle\widehat{H}\rangle = \sum_n P_n E_n$. Since all the probabilities

P_n are non-negative, and all the E_n greater than or equal to E_0, this is obviously not less than E_0.

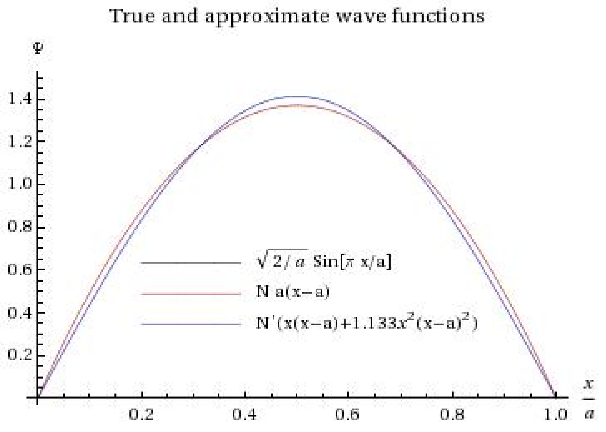
It is also clear that the better the guess (in the sense of maximising the overlap with the true ground state) the lower the energy bound, till successively better guesses converge on the true result.

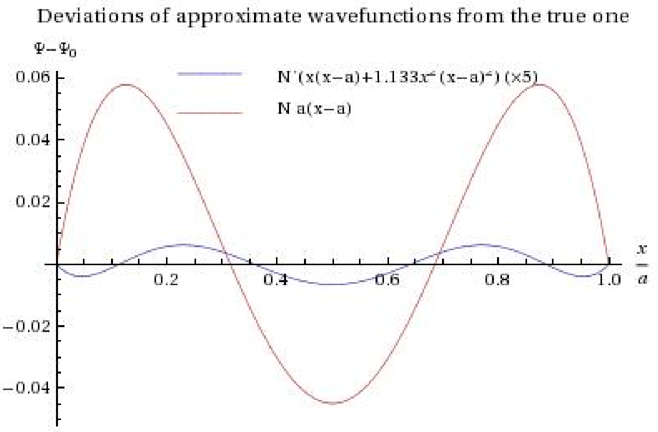
As a very simple example, consider the infinite square well with $V = 0$, $0 < x < a$ and $V = \infty$ otherwise. As a trial function, we use $\Psi(x) = x(a-x)$, $0 < x < a$ and $\Psi(x) = 0$ otherwise. Then

$$\frac{\langle\Psi|\widehat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{10\,\hbar^2}{2ma^2} = 1.013\frac{\pi^2\,\hbar^2}{2ma^2}$$

This is spectacularly good! Obviously it helped that our trial wave function looked a lot like what we'd expect of the true solution - symmetric about the midpoint, obeying the boundary conditions, no nodes....

In general, we will do better if we have an adjustable parameter, because then we can find the value which minimises our upper bound. So we could try $\Psi(x) = x(a-x) + bx^2(a-x)^2$ (with our previous guess corresponding to $b = 0$). Letting Mathematica do the dirty work, we get an energy bound which is a function of b, which takes its minimum value of $1.00001E_0$ at $b = 1.133/a^2$. Not much room for further improvement here!





Above we have plotted, on the left, the true and approximate wave functions (except that the true one is hidden under the second approximation, given in blue) and on the right, the deviations of the approximate wave functions from the true one (except that for the second approximation the deviation has been multiplied by 5 to render it visible!) This illustrates a general principle though: the wave function does have deviations from the true one on the part-per-mil scale, while the energy is good to 1 part in 10^5. This is because the error in the energy is proportional to the coefficients squared of the admixture of "wrong" states, whereas the error in the wave function is linear in them.

Another example, for which the analytic solution is not known, is the quartic potential, $V(x) = \beta x^4$. Here a Gaussian trial wave function $\Psi(x) = \mathrm{e}^{-ax^2/2}$ gives an upper bound for the ground energy state of $\frac{3}{8}6^{1/3} = 0.68$ in units of $(\hbar^4\beta/m^2)^{1/3}$. (The value obtained from numerical solution of the equation is 0.668).

- **Gasiorowicz ch 14.4**
- **Mandl ch 8.1**

- **Shankar ch 16.1**

2.2 Variational methods: excited states

Summary: Symmetry considerations may allow us to extend the variational method to certain excited states.

Looking again at the expression $\langle\widehat{H}\rangle = \sum_n P_n E_n$, and recalling that the P_n are the squares of the overlap between the trial function and the actual eigenstates of the system, we see that we can only find bounds on excited states if we can arrange for the overlap of the trial wave function with all lower states to be zero. Usually this is not possible.

However an exception occurs where the states of the system can be separated into sets with different symmetry properties or other quantum numbers. Examples include parity and (in 3 dimensions) angular momentum. For example the lowest state with odd parity will automatically have zero overlap with the (even-parity) ground state, and so an upper bound can be found for it as well.

For the square well, the relevant symmetry is reflection about the midpoint of the well. If we choose a trial function which is antisymmetric about the midpoint, it must have zero overlap with the true ground state. So we can get a good bound on the first excited state, since $\langle\widehat{H}\rangle = \sum_{n>0} P_n E_n > E_1$. Using $\Psi_1(x) = x(a-x)(2x-a)$, $0 < x < a$ we get $E_1 \leq 42\,\hbar^2/2ma^2 = 1.064E_1$.

If we wanted a bound on E_2, we'd need a wave function which was orthogonal to both the ground state and the first excited state. The latter is easy by symmetry, but as we don't know the exact ground state (or so we are pretending!) we can't ensure the first. We can instead form a trial wave function which is orthogonal to the best *trial* ground state, but we will no longer have a strict upper bound on the energy E_2, just a guess as to its value.

In this case we can choose $\Psi(x) = x(a-x) + bx^2(a-x)^2$ with a new value of b which gives orthogonality to the previous state, and then we get $E_2 \sim 10.3E_0$ (as opposed to 9 for the actual value).

- **Mandl ch 8.3**
- **Shankar ch 16.1**

2.3 Variational methods: the helium atom

Summary: The most famous example of the variational principle is the ground state of the two-electron helium atom.

If we could switch off the interactions between the electrons, we would know what the ground state of the helium atom would be: $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{100}^{Z=2}(\mathbf{r}_1)\phi_{100}^{Z=2}(\mathbf{r}_2)$, where ϕ_{nlm}^{Z} is a single-particle wave function of the hydrogenic atom with nuclear charge Z. For the ground state $n = 1$ and $l = m = 0$ (spherical symmetry). The energy of the two electrons would be $2Z^2 E_{\rm Ry} = -108.8$ eV. But the experimental energy is only -78.6 eV (ie it takes 78.6 eV to fully ionise neutral helium). The difference is obviously due to the fact that the electrons repel one another.

The full Hamiltonian (ignoring the motion of the proton - a good approximation for the accuracy to which we will be working) is

$$-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2) - 2\,\hbar c\alpha\left(\frac{1}{|\mathbf{r}_1|}+\frac{1}{|\mathbf{r}_2|}\right)+\hbar c\alpha\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}$$

where ∇_1^2 involves differentiation with respect to the components of $\mathbf{r}_1$, and $\alpha = e^2/(4\pi\epsilon_0\,\hbar c) \approx 1/137$. (See here for a note on units in EM.)

A really simple guess at a trial wave function for this problem would just be $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ as written above. The expectation value of the repulsive interaction term is $(5Z/4)E_{\rm Ry}$ giving a total energy of -74.8 eV. (Gasiorowicz demonstrates the integral, as do Fitzpatrick and Branson.)

It turns out we can do even better if we use the atomic number Z *in the wave function* Ψ as a variational parameter (that in the Hamiltonian, of course, must be left at 2). The best value turns out to be $Z = 27/16$ and that gives a better upper bound of -77.5 eV – just slightly higher than the experimental value. (Watch the sign – we get an lower bound for the ionization energy.) This effective nuclear charge of less than 2 presumably reflects the fact that to some extent each electron screens the nuclear charge from the other.

- **Gasiorowicz ch 14.2, 14.4 (most complete)**
- **Mandl ch 7.2, 8.8.2 (clearest)**
- **Shankar ch 16.1 (not very clear; misprints in early printings)**

2.4 WKB approximation

Summary: The WKB approximation works for potentials which are slowly-varying on the scale of the wavelength of the particle and is particularly useful for describing tunnelling.

The WKB approximation is named for G. Wentzel, H.A. Kramers, and L. Brillouin, who independently developed the method in 1926. There are pre-quantum antecedents due to Jeffreys and Raleigh, though.

We can always write the one-dimensional Schrödinger equation as

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = -k(x)^2\phi(x)$$

where $k(x) \equiv \sqrt{2m(E-V(x))}/\hbar$. We could think of the quantity $k(x)$ as a spatially-varying wavenumber ($k = 2\pi/\lambda$), though we anticipate that this can only make sense if it doesn't change too quickly with position - else we can't identify a wavelength at all.

Let's see under what conditions a solution of the form

$$\psi(x) = A\exp\left(\pm i\int^x k(x')\mathrm{d}x'\right)$$

might be a good approximate solution. Plugging this into the SE above, the LHS reads $-(k^2 \mp ik')\psi$. (Here and hereafter, primes denote differentiation wrt x — except when they indicate an integration variable.) So provided $|k'/k| \ll |k|$, or $|\lambda'| \ll 1$, this is indeed a good solution as the second term can be ignored. And $|\lambda'| \ll 1$ does indeed mean that the wavelength is slowly varying. (One sometimes reads that what is needed is that the potential is slowly varying. But that is not a well defined statement, because $\mathrm{d}V/\mathrm{d}x$ is not dimensionless. For any smooth potential, at high-enough energy we will have $|\lambda'| \ll 1$. What is required is that the *lengthscale* of variation of λ, or k, or V (the scales are all approximately equal) is large compared with the de Broglie wavelength of the particle.

An obvious problem with this form is that the current isn't constant: if we calculate it we get $|A|^2 \hbar k(x)/m$. A better approximation is

$$\psi(x) = \frac{A}{\sqrt{k(x)}} \exp\left(\pm i \int^x k(x')\mathrm{d}x'\right)$$

which gives a constant flux. (Classically, the probability of finding a particle in a small region is inversely proportional to the speed with which it passes through that region.) Furthermore one can show that if the error in the first approximation is $\mathcal{O}\,|\lambda'|$, the residual error with the second approximation is $\mathcal{O}\,|\lambda'|^2$. At first glance there is a problem with the second form when $k(x) = 0$, ie when $E = V(x)$. But near these points - the classical turning points - the whole approximation scheme is invalid, because $\lambda \to \infty$ and so the potential cannot be "slowly varying" on the scale of λ.

For a region of constant potential, of course, there is no difference between the two approximations and both reduce to a plain wave, since $\int^x k(x')\mathrm{d}x' = kx$.

For regions where $E < V(x)$, $k(x)$ will be imaginary and there is no wavelength as such. But defining $\lambda = 2\pi/k$ still, the WKB approximation will continue to be valid if $|\lambda'| \ll 1$.

Tunnelling and bound-state problems inevitably include regions where $E \approx V(x)$ and the WKB approximation isn't valid. This would seem to be a major problem. However if such regions are short the requirement that the wave function and its derivative be continuous can help us to "bridge the gap".

- **Gasiorowicz Supplement 4 A**
- **Shankar ch 16.2**

2.4.1 WKB approximation for bound states

In a bound state problem with potential $V(x)$, for a given energy E, we can divide space into classically allowed regions, for which $E > V(x)$, and classically forbidden regions for which $E < V(x)$. For simplicity we will assume that there are only three regions in total, classically forbidden for $x < a$ and $x > b$, and classically allowed for $a < x < b$.

In the classically allowed region $a < x < b$ the wave function will be oscillating and we can write it either as a superposition of right- and left-moving complex exponentials or as

$$\psi(x) = \frac{A}{\sqrt{k(x)}} \cos\left(\int^x k(x')\mathrm{d}x' + \phi\right)$$

For the particular case of a well with infinite sides the solution must vanish at the boundaries, so (taking the lower limit of integration as a for definiteness; any other choice just shifts ϕ) $\phi = (n' + \frac{1}{2})\pi$ and $\int_a^b k(x')\mathrm{d}x' + \phi = (n'' + \frac{1}{2})\pi$; in other words $\int_a^b k(x')\mathrm{d}x' = (n+1)\pi$, with integer $n \geq 0$. Of course for constant k this gives $k = n\pi/(b-a)$, which is exact.

For a more general potential, outside the classically allowed region we will have decaying exponentials. In the vicinity of the turning points these solutions will not be valid, but if we approximate the potential as linear we can solve the Schrödinger equation exactly (in terms of Airy functions). Matching these to our WKB solutions in the vicinity of $x = a$ and $x = b$ gives the surprisingly simple result that inside the well

$$\psi(x) = \frac{A}{\sqrt{k(x)}} \cos\left(\int_a^x k(x')\mathrm{d}x' - \pi/4\right) \qquad \text{and} \qquad \psi(x) = \frac{A'}{\sqrt{k(x)}} \cos\left(\int_b^x k(x')\mathrm{d}x' + \pi/4\right)$$

which can only be satisfied if $A' = \pm A$ and $\int_a^b k(x')\mathrm{d}x' = (n+\frac{1}{2})\pi$. This latter is the quantisation condition for a finite well; it is different from the infinite well because the solution can leak into the forbidden region. (For a semi-infinite well, the condition is that the integral equal $(n + \frac{3}{4})\pi$. This is the appropriate form for the $l = 0$ solutions of a spherically symmetric well.) Unfortunately we can't check this against the finite square well though, because there the potential is definitely not slowly varying at the edges, nor can it be approximated as linear. But we can try the harmonic oscillator, for which the integral gives $E\pi/\hbar\omega$ and hence the quantisation condition gives $E = (n + \frac{1}{2})\,\hbar\omega$! The approximation was only valid for large n (small wavelength) but in fact we've obtained the exact answer for all levels.

Details of the matching process are given in section 2.4.1.1, since I've not found them in full detail in any textbook. They are not examinable.

- **Gasiorowicz Supplement 4 A**
- **Shankar ch 16.2**

2.4.1.1 Matching with Airy Functions

This section is not examinable. More about Airy functions can be found in section A.7.

If we can treat the potential as linear over a wide-enough region around the turning points that, at the edges of the region, the WKB approximation is valid, then we can match the WKB and exact solutions.

Consider a linear potential $V = \beta x$ as an approximation to the potential near the right-hand turning point b. We will scale $x = (\hbar^2/(2m\beta))^{1/3} z$ and $E = (\hbar^2\beta^2/2m)^{1/3}\mu$, so the turning point is at $z = \mu$. Then the differential equation is $y''(z) - zy(z) + \mu y(z) = 0$ and the solution which decays as $z \to \infty$ is $y(z) = A\mathrm{Ai}(z - \mu)$. This has to be matched, for z not too close to μ, to the WKB solution. In these units, $k(x) = (\mu - z)$ and $\int_b^x k(x')\mathrm{d}x' = \int_\mu^z (\mu - z')\mathrm{d}z' = -(2/3)(\mu - z)^{3/2}$, so

$$\psi^{\mathrm{WKB}}_{x<b}(z) = \frac{B}{(\mu - z)^{1/4}} \cos\left(-\tfrac{2}{3}(\mu - z)^{3/2} + \phi\right) \quad \text{and} \quad \psi^{\mathrm{WKB}}_{x>b}(z) = \frac{C}{(z - \mu)^{1/4}} \exp\left(-\tfrac{2}{3}(z - \mu)^{3/2}\right).$$

(We chose the lower limit of integration to be μ in order that the constant of integration vanished; any other choice would just shift ϕ.) Now the asymptotic forms of the Airy function are known:

$$\mathrm{Ai}(z) \overset{z\to-\infty}{\longrightarrow} \frac{\cos\left(\frac{2}{3}|z|^{3/2} - \frac{\pi}{4}\right)}{\sqrt{\pi}\,|z|^{1/4}} \qquad \text{and} \qquad \mathrm{Ai}(z) \overset{z\to\infty}{\longrightarrow} \frac{\mathrm{e}^{-\frac{2}{3}z^{3/2}}}{2\sqrt{\pi}z^{1/4}}$$

so

$$\mathrm{Ai}(z - \mu) \overset{z\to-\infty}{\longrightarrow} \frac{\cos\left(\frac{2}{3}(\mu - z)^{3/2} - \frac{\pi}{4}\right)}{\sqrt{\pi}(\mu - z)^{1/4}} \qquad \text{and} \qquad \mathrm{Ai}(z - \mu) \overset{z\to\infty}{\longrightarrow} \frac{\mathrm{e}^{-\frac{2}{3}(z-\mu)^{3/2}}}{2\sqrt{\pi}(z - \mu)^{1/4}}$$

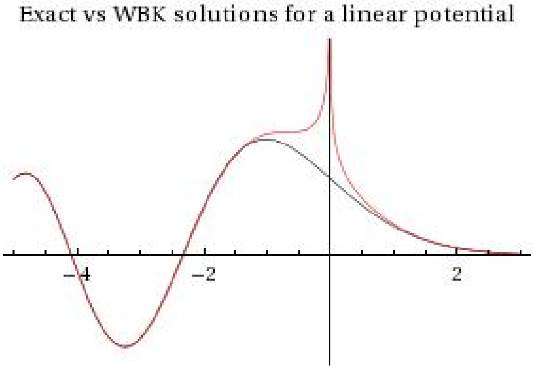
and these will match the WKB expressions exactly provided $C = 2B$ and $\phi = \pi/4$.

At the left-hand turning point a, the potential is $V = -\beta x$ (with a different β in general) and the solution $y(z) = A\mathrm{Ai}(-z-\mu)$. On the other hand the WKB integral is $\int_a^x k(x')\mathrm{d}x' = \int_\mu^z (\mu + z')\mathrm{d}z' = 2/3(\mu + z)^{3/2}$. So in the classically allowed region we are comparing

$$\mathrm{Ai}(-z-\mu) \overset{z\to\infty}{\longrightarrow} \frac{\cos\left(\frac{2}{3}(z+\mu)^{3/2} - \frac{\pi}{4}\right)}{\sqrt{\pi}(z+\mu)^{1/4}} \qquad \text{with} \qquad \psi_{x>a}^{\text{WKB}}(z) = \frac{D}{(\mu+z)^{1/4}}\cos\left(\tfrac{2}{3}(\mu+z)^{3/2} + \phi\right)$$

which requires $\phi = -\pi/4$. (Note that ϕ is different in each case because we have taken the integral from a different place.)

It is worth stressing that though the exact (Airy function) and WKB solutions match "far away" from the turning point, they do not do so close in. The $(z-\mu)^{-1/4}$ terms in the latter mean that they blow up, but the former are perfectly smooth. They are shown (for $\mu = 0$) below, in red for the WKB and black for the exact functions. We can see they match very well so long as $|z - \mu| > 1$; in fact $z \to \infty$ is overkill!



So now we can be more precise about the conditions under which the matching is possible: we need the potential to be linear over the region $\Delta x \sim (\hbar^2/(2m\beta))^{1/3}$ where $\beta = \mathrm{d}V/\mathrm{d}x$. Linearity means that $\Delta V/\Delta x \approx \mathrm{d}V/\mathrm{d}x$ at the turning point, or $\left|\mathrm{d}^2V/\mathrm{d}x^2\right|\Delta x \ll \mathrm{d}V/\mathrm{d}x$ (assuming the curvature is the dominant non-linearity, as is likely if V is smooth). For the harmonic oscillator, $\left|\mathrm{d}^2V/\mathrm{d}x^2\right|\Delta x/(\mathrm{d}V/\mathrm{d}x) = 2(\hbar\omega/E)^{2/3}$ which is only much less than 1 for very large n, making the exact result even more surprising!

2.4.2 WKB approximation for tunnelling

For the WKB approximation to be applicable to tunnelling through a barrier, we need as always $|\lambda'| \ll 1$. In practice that means that the barrier function is reasonably smooth and that $E \ll V(x)$. Now it would of course be possible to do a careful calculation, writing down the WKB wave function in the three regions (left of the barrier, under the barrier and right of the barrier), linearising in the vicinity of the turning points in order to match the wave function and its derivatives at both sides. This however is a tiresomely lengthy task, and we will not attempt it. Instead, recall the result for a high, wide square barrier; the transmission coefficient in the limit $\mathrm{e}^{-2\kappa\Delta L} \ll 1$ is given by

$$T = \frac{16k_1k_2\kappa^2}{(\kappa^2 + k_1^2)(\kappa^2 + k_2^2)}\mathrm{e}^{-2\kappa L}$$

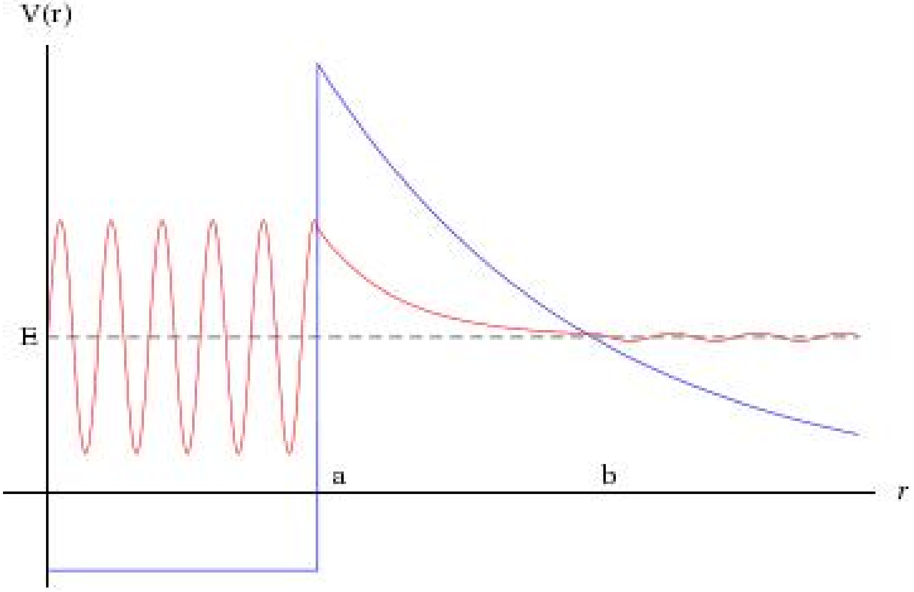
where k_1 and k_2 are the wavenumbers on either side of the barrier (width L, height V) and $\kappa = \sqrt{2m(V-E)}$. (See the notes for PHYS20101, where however $k_1 = k_2$.) All the prefactors are not negligible, but they are weakly energy-dependent, whereas the $\mathrm{e}^{-2\kappa L}$ term is very strongly energy dependent. If we plot $\log T$ against energy, the form will be essentially const $-\,2\kappa(E)L$, and so we can still make predictions without worrying about the constant.

For a barrier which is not constant, the WKB approximation will yield a similar expression for the tunnelling probability:

$$T = [\text{prefactor}] \times \exp(-2\int_a^b \kappa(x')\mathrm{d}x')$$

where $\kappa(x) \equiv \sqrt{2m(V(x)-E)}/\hbar$. The WKB approximation is like treating a non-square barrier like a succession of square barriers of different heights. The need for $V(x)$ to be slowly varying is then due to the fact that we are slicing the barrier sufficiently thickly that $\mathrm{e}^{-2\kappa\Delta L} \ll 1$ for each slice.

The classic application of the WKB approach to tunnelling is alpha decay. The potential here is a combination of an attractive short-range nuclear force and the repulsive Coulomb interaction between the alpha particle and the daughter nucleus. Unstable states have energies greater than zero, but they are long-lived because they are classically confined by the barrier. (It takes some thought to see that a repulsive force can cause quasi-bound states to exist!) The semi-classical model is of a pre-formed alpha particle bouncing back and forth many times (f) per second, with a probability of escape each time given by the tunnelling probability, so the decay rate is given by $1/\tau = fT$. Since we can't calculate f with any reliability we would be silly to worry about the prefactor in T, but the primary dependence of the decay rate on the energy of the emitted particle will come from the easily-calculated exponential.



In the figure above the value of a is roughly the nuclear radius R, and b is given by $V_C(b) = E$, with the Coulomb potential $V_C(r) = zZ\,\hbar c\alpha/r$. ($Z$ is the atomic number of the daughter nucleus and $z = 2$ that of the alpha.) The integral in the exponent can be done (see Gasiorowicz Supplement 4 B for details; the substitution $r = b\cos^2\theta$ is used), giving in the limit $b \gg a$

$$2\int_a^b \kappa(x')\mathrm{d}x' = 2\pi zZ\alpha\sqrt{\frac{mc^2}{2E}} = 39\frac{Z}{\sqrt{E(\mathrm{MeV})}} \Rightarrow \log_{10}\frac{1}{\tau} = \text{const} - 1.72\frac{Z}{\sqrt{E(\mathrm{MeV})}}$$

Data for the lifetimes of long-lived isotopes (those with low-energy alphas) fit such a functional form well, but with 1.61 rather than 1.72. In view of the fairly crude approximations made, this is a pretty good result. Note it is independent of the nuclear radius because we used $b \gg a$; we could have kept the first correction, proportional to $\sqrt{b/a}$, to improve the result.

- **Gasiorowicz Supplement 4 B**
- **Shankar ch 16.2**

Approximate methods II: Time-independent perturbation theory

3.1 Formalism

Summary: Perturbation theory is the most widely used approximate method. "Time-independent perturbation theory" deals with bound states eg the spectrum of the real hydrogen atom and its response to external fields.

Perturbation theory is applicable when the Hamiltonian $\widehat{H}$ can be split into two parts, with the first part being exactly solvable and the second part being small in comparison. The first part is always written $\widehat{H}^{(0)}$, and we will denote its eigenstates by $|n^{(0)}\rangle$ and energies by $E_n^{(0)}$ (with wave functions $\phi_n^{(0)}$). These we know. The eigenstates and energies of the full Hamiltonian are denoted $|n\rangle$ and E_n, and the aim is to find successively better approximations to these. The zeroth-order approximation is simply $|n\rangle = |n^{(0)}\rangle$ and $E_n = E_n^{(0)}$, which is just another way of saying that the perturbation is small.

Nomenclature for the perturbing Hamiltonian $\widehat{H} - \widehat{H}^{(0)}$ varies. δV, $\widehat{H}^{(1)}$ and $\lambda\widehat{H}^{(1)}$ are all common. It usually is a perturbing potential but we won't assume so here, so we won't use the first. The second and third differ in that the third has explicitly identified a small, dimensionless parameter (eg α in EM), so that the residual $\widehat{H}^{(1)}$ isn't itself small. With the last choice, our expressions for the eigenstates and energies of the full Hamiltonian will be explicitly power series in λ, so $E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$ etc. With the second choice the small factor is hidden in $\widehat{H}^{(1)}$, and is implicit in the expansion which then reads $E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \ldots$. In this case one has to remember that anything with a superscript (1) is first order in this implicit small factor, or more generally the superscript (m) denotes something which is mth order. For the derivation of the equations we will retain an explicit λ, but thereafter we will set it equal to one to revert to the other formulation. We will take λ to be real so that $\widehat{H}_1$ is Hermitian.

We start with the master equation

$$(\widehat{H}^{(0)} + \lambda\widehat{H}^{(1)})|n\rangle = E_n|n\rangle.$$

Then we substitute in $E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$ and $|n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \ldots$ and expand. Then since λ is a free parameter, we have to match terms on each side with the same powers of λ, to get

$$\begin{aligned}
\widehat{H}^{(0)}|n^{(0)}\rangle &= E_n^{(0)}|n^{(0)}\rangle \\
\widehat{H}^{(0)}|n^{(1)}\rangle + \widehat{H}^{(1)}|n^{(0)}\rangle &= E_n^{(0)}|n^{(1)}\rangle + E_n^{(1)}|n^{(0)}\rangle \\
\widehat{H}^{(0)}|n^{(2)}\rangle + \widehat{H}^{(1)}|n^{(1)}\rangle &= E_n^{(0)}|n^{(2)}\rangle + E_n^{(1)}|n^{(1)}\rangle + E_n^{(2)}|n^{(0)}\rangle
\end{aligned}$$

We have to solve these sequentially. The first we assume we have already done. The second will yield $E_n^{(1)}$ and $|n^{(1)}\rangle$. Once we know these, we can use the third equation to yield $E_n^{(2)}$ and $|n^{(2)}\rangle$, and so on.

In each case, to solve for the energy we take the inner product with $\langle n^{(0)}|$ (ie the same state) whereas for the wave function, we use $\langle m^{(0)}|$ (another state). We use, of course, $\langle m^{(0)}|\widehat{H}^{(0)} = E_m^{(0)}\langle m^{(0)}|$ and $\langle m^{(0)}|n^{(0)}\rangle = \delta_{mn}$.

At first order we get

$$E_n^{(1)} = \langle n^{(0)}|\widehat{H}^{(1)}|n^{(0)}\rangle \qquad \text{and} \qquad \langle m^{(0)}|n^{(1)}\rangle = \frac{\langle m^{(0)}|\widehat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} \quad \forall m \neq n$$

The second equation tells us the overlap of $|n^{(1)}\rangle$ with all the other $|m^{(0)}\rangle$, but not with $|n^{(0)}\rangle$. This is obviously not constrained, because we can add any amount of $|n^{(0)}\rangle$ and the equations will still be satisfied. However we need the state to continue to be normalised, and when we expand $\langle n|n\rangle = 1$ in powers of λ we find that $\langle n^{(0)}|n^{(1)}\rangle$ is required to be imaginary. Since this is just like a phase rotation of the original state and we can ignore it. Hence

$$|n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle m^{(0)}|\widehat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}|m^{(0)}\rangle$$

If the spectrum of $\widehat{H}^{(0)}$ is degenerate, there is a potential problem with this expression because the denominator can be infinite. In that case we have to diagonalise $\widehat{H}^{(1)}$ in the subspace of degenerate states exactly. This is called "degenerate perturbation theory".

Then at second order

$$E_n^{(2)} = \langle n^{(0)}|\widehat{H}^{(1)}|n^{(1)}\rangle = \sum_{m\neq n} \frac{\left|\langle m^{(0)}|\widehat{H}^{(1)}|n^{(0)}\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}}$$

The expression for the second-order shift in the wave function $|n^{(2)}\rangle$ can also be found but it is tedious. The main reason we wanted $|n^{(1)}\rangle$ was to find $E_n^{(2)}$ anyway, and we're not planning to find $E_n^{(3)}$! Note that though the expression for $E_n^{(1)}$ is generally applicable, those for $|n^{(1)}\rangle$ and $E_n^{(2)}$ would need some modification if the Hamiltonian had continuum eigenstates as well as bound states (eg hydrogen atom). Provided the state $|n\rangle$ is bound, that is just a matter of integrating rather than summing. This restriction to bound states is why Mandl calls chapter 7 "bound-state perturbation theory". The perturbation of continuum states (eg scattering states) is usually dealt with separately.

Note that the equations above hold whether we have identified an explicit small parameter λ or not. So from now on we will set λ to one, and $E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \ldots$.

Connection to variational approach:
For the ground state (which is always non-degenerate) $E_0^{(0)} + E_0^{(1)}$ is a variational upper bound on the exact energy E_0, since it is obtained by using the unperturbed ground state as a trial wavefunction for the full Hamiltonian. It follows that the sum of all higher corrections $E_0^{(2)} + \ldots$ must be negative. We can see indeed that $E_0^{(2)}$ will always be negative, since for every term in the sum the numerator is positive and the denominator negative.

- **Gasiorowicz ch 11.1**
- **Mandl ch 7.1,3**
- **Shankar ch 17.1**
- **Townsend ch 11.1-3**

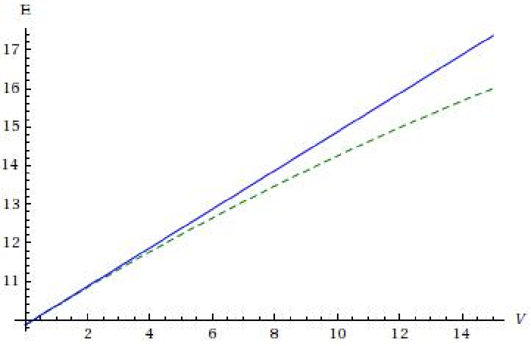
3.1.1 Simple examples of perturbation theory

Probably the simplest example we can think of is an infinite square well with a low step half way across, so that $V(x) = 0$ for $0 < x < a/2$, V_0 for $a/2 < x < a$ and infinite elsewhere. We treat this as a perturbation on the flat-bottomed well, so $H^{(1)} = V_0$ for $a/2 < x < a$ and zero elsewhere.

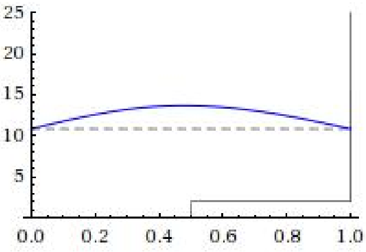
The ground-state unperturbed wavefunction is $\psi_0^{(0)} = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$, with unperturbed energy $E_0^{(0)} = \pi^2\hbar^2/(2ma^2)$. A "low" step will mean $V_0 \ll E_0^{(0)}$. Then we have

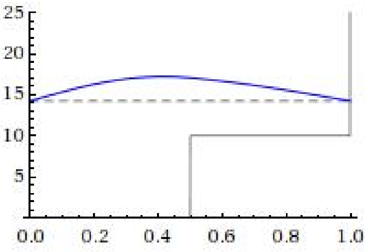
$$E_0^{(1)} = \langle \psi_0^{(0)} | H^{(1)} | \psi_0^{(0)} \rangle = \frac{2}{a} \int_{a/2}^{a} V_0 \sin^2 \frac{\pi x}{a} \mathrm{d}x = \frac{V_0}{2}$$

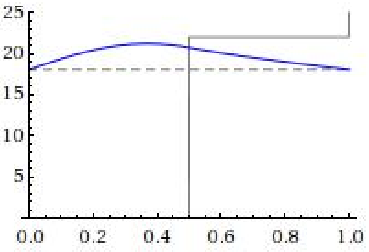
This problem can be solved semi-analytically; in both regions the solutions are sinusoids, but with wavenumbers $k = \sqrt{2mE}/\hbar$ and $k' = \sqrt{2m(E - V_0)}/\hbar$ respectively; satisfying the boundary conditions and matching the wavefunctions and derivatives at $x = a/2$ gives the condition $k \cot(ka/2) = k' \cot(k'a/2)$ which can be solved numerically for E. (You ought to try this, it will be good practice for later sections of the course.) Below the exact solution (green, dotted) and $E_0^{(0)} + E_0^{(1)}$ (blue) are plotted; we can see that they start to diverge when $V_0 = 5$ (everything is in units of $\hbar^2/(2ma^2)$).



We can also plot the exact wavefunctions for different step size, and see that for $V_0 = 10$ (the middle picture, well beyond the validity of first-order perturbation theory) it is significantly different from a simple sinusoid.







Another example is the harmonic oscillator, with a perturbing potential $H^{(1)} = \lambda x^2$. The states of the unperturbed oscillator are denoted $|n^{(0)}\rangle$ with energies $E_0^{(0)} = (n + \frac{1}{2})\hbar\omega$.

Recalling that in terms of creation and annihilation operators (see section A.4), $\hat{x} = \sqrt{\hbar/(2m\omega)}(\hat{a} + \hat{a}^\dagger)$, with $[\hat{a}, \hat{a}^\dagger] = 1$, and so

$$E_n^{(1)} = \langle n^{(0)} | H^{(1)} | n^{(0)} \rangle = \frac{\hbar\lambda}{2m\omega} \langle n^{(0)} | (\hat{a}^\dagger)^2 + \hat{a}^2 + 2\hat{a}^\dagger\hat{a} + 1 | n^{(0)} \rangle = \frac{\lambda}{m\omega^2} \hbar\omega (n + \tfrac{1}{2})$$

The first-order change in the wavefunction is also easy to compute, as $\langle m^{(0)}|H^{(1)}|n^{(0)}\rangle = 0$ unless $m = n \pm 2$. Thus

$$\begin{aligned} |n^{(1)}\rangle &= \sum_{m\neq n} \frac{\langle m^{(0)}|\widehat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}|m^{(0)}\rangle \\ &= \frac{\hbar\lambda}{2m\omega}\left(\frac{\sqrt{(n+1)(n+2)}}{-2\hbar\omega}|(n+2)^{(0)}\rangle + \frac{\sqrt{n(n-1)}}{2\hbar\omega}|(n-2)^{(0)}\rangle\right) \\ \text{and} \qquad E_n^{(2)} &= \langle n^{(0)}|\widehat{H}^{(1)}|n^{(1)}\rangle = \sum_{m\neq n} \frac{\left|\langle m^{(0)}|\widehat{H}^{(1)}|n^{(0)}\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}} \\ &= \left(\frac{\hbar\lambda}{2m\omega}\right)^2\left(\frac{(n+1)(n+2)}{-2\hbar\omega} + \frac{n(n-1)}{2\hbar\omega}\right) = -\tfrac{1}{2}\left(\frac{\lambda}{m\omega^2}\right)^2\hbar\omega(n+\tfrac{1}{2}) \end{aligned}$$

We can see a pattern emerging, and of course this is actually a soluble problem, as all that the perturbation has done is change the frequency. Defining $\omega' = \omega\sqrt{1 + 2\lambda/(m\omega^2)}$, we see that the exact solution is

$$E_n = (n+\tfrac{1}{2})\hbar\omega' = (n+\tfrac{1}{2})\hbar\omega\left(1 + \frac{\lambda}{m\omega^2} - \frac{1}{2}\left(\frac{\lambda}{m\omega^2}\right)^2 + \ldots\right)$$

in agreement with the perturbative calculation.

3.2 Example of degenerate perturbation theory

Suppose we have a three state basis and an $\widehat{H}^{(0)}$ whose eigenstates, $|1^{(0)}\rangle$, $|2^{(0)}\rangle$ and $|3^{(0)}\rangle$, have energies $E_1^{(0)}$, $E_2^{(0)}$ and $E_3^{(0)}$ (all initially assumed to be different). A representation of this system is

$$|1^{(0)}\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \qquad |2^{(0)}\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \qquad |3^{(0)}\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \qquad \widehat{H}^{(0)} = \begin{pmatrix} E_1^{(0)} & 0 & 0 \\ 0 & E_2^{(0)} & 0 \\ 0 & 0 & E_3^{(0)} \end{pmatrix}.$$

Now let's consider the perturbation

$$\widehat{H}^{(1)} = a\begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Then we can show that, to first order in a

$$E_1^{(1)} = E_2^{(1)} = E_3^{(1)} = a, \qquad |1^{(1)}\rangle = \frac{a}{E_1^{(0)} - E_2^{(0)}}|2^{(0)}\rangle, \qquad |2^{(1)}\rangle = \frac{a}{E_2^{(0)} - E_1^{(0)}}|1^{(0)}\rangle, \qquad |3^{(1)}\rangle = 0$$

And hence also

$$E_1^{(2)} = -E_2^{(2)} = \frac{a^2}{E_1^{(0)} - E_2^{(0)}}, \qquad E_3^{(2)} = 0$$

We note that because $\widehat{H}^{(1)}$ is already diagonal in the $|3^{(0)}\rangle$ space, the first-order shift in energy is exact and there is no change to that eigenvector. In this case it is straightforward to obtain the eigenvalues of $\widehat{H}^{(0)} + \widehat{H}^{(1)}$ exactly:

$$E_1 = \tfrac{1}{2}\left(2a + E_1^{(0)} + E_2^{(0)} - \sqrt{4a^2 + (E_2^{(0)} - E_1^{(0)})^2}\right), \quad E_2 = \tfrac{1}{2}\left(2a + E_1^{(0)} + E_2^{(0)} + \sqrt{4a^2 + (E_2^{(0)} - E_1^{(0)})^2}\right)$$

and $E_3 = E_3^{(0)} + a$, and so we can check the expansion to order a^2.

Now consider the case where $E_2^{(0)} = E_1^{(0)}$. We note that $|1^{(0)}\rangle$ and $|2^{(0)}\rangle$ are just two of an infinite set of eigenstates with the same energy $E_1^{(0)}$, since any linear combination of them is another eigenstate. Our results for the third state are unchanged, but none of those obtained for the first two still hold. Instead we have to work in a new basis, $|1'^{(0)}\rangle$ and $|2'^{(0)}\rangle$ which diagonalises $\widehat{H}^{(1)}$. By inspection we see that this is

$$|1'^{(0)}\rangle = \frac{1}{\sqrt{2}}(|1^{(0)}\rangle + |2^{(0)}\rangle) \qquad \text{and} \qquad |2'^{(0)}\rangle = \frac{1}{\sqrt{2}}(|1^{(0)}\rangle - |2^{(0)}\rangle).$$

Then $\widehat{H}^{(1)}|1'^{(0)}\rangle = 2a|1'^{(0)}\rangle$ and $\widehat{H}^{(1)}|2'^{(0)}\rangle = 0$. Hence

$$E_{1'}^{(1)} = 2a, \qquad E_{2'}^{(1)} = 0, \qquad |1'^{(1)}\rangle = |2'^{(1)}\rangle = 0, \qquad E_{1'}^{(2)} = E_{2'}^{(2)} = 0$$

In this case because $\widehat{H}^{(1)}$ doesn't mix states 1 & 2 with 3, diagonalising it in the subspace is actually equivalent to solving the problem exactly. We can check our results against the exact eigenvalues for $E_2^{(0)} = E_1^{(0)}$ and see that they are correct, except that we made the "wrong" choice for our labelling of $|1'^{(0)}\rangle$ and $|2'^{(0)}\rangle$.

3.3 The fine structure of hydrogen

Although the Schrödinger equation with a Coulomb potential reproduces the Bohr model and gives an excellent approximation to the energy levels of hydrogen, the true spectrum was known to be more complicated right from the start. The small deviations are termed "fine structure" and they are of order 10^{-4} compared with the ground-state energy (though the equivalent terms for many-electron atoms can be sizable). Hence perturbation theory is an excellent framework in which to consider them.

There are two effects to be considered. One arises from the use of the non-relativistic expression $p^2/2m$ for the kinetic energy, which is only the first term in an expansion of $\sqrt{(mc^2)^2 + (pc)^2} - mc^2$. The first correction term is $-p^4/(8m^3c^2)$, and its matrix elements are most easily calculated using the trick of writing it as $-1/(2mc^2)(\widehat{H}^{(0)} - V_C(r))^2$, where $\widehat{H}^{(0)}$ is the usual Hamiltonian with a Coulomb potential. Now in principle we need to be careful here, because $\widehat{H}^{(0)}$ is highly degenerate (energies depend only on n and not on l or m). However we have $\langle nl'm'|(\widehat{H}^{(0)} - V_C(r))^2|nlm\rangle = \langle nl'm'|(E_n^{(0)} - V_C(r))^2|nlm\rangle$, and since in this form the operator is spherically symmetric, it can't link states of different l or m. So the basis $\{|nlm\rangle\}$ already diagonalises $\widehat{H}^{(0)}$ in each subspace of states with the same n, and we have no extra work to do here. (We are omitting the superscript $^{(0)}$ on the hydrogenic states, here and below.)

The final result for the kinetic energy effect is

$$\langle nlm|\widehat{H}_{\text{KE}}^{(1)}|nlm\rangle = -\frac{\alpha^2\,|E_n^{(0)}|}{n}\left(\frac{2}{2l+1} - \frac{3}{4n}\right)$$

In calculating this the expressions $E_n^{(0)} = \frac{1}{2n^2}\alpha^2 mc^2$ and $a_0 = \hbar/(mc\alpha)$ are useful. Tricks for doing the the radial integrals are explained in Shankar qu. 17.3.4; they are tabulated in section A.3. Details of the algebra for this and the following calculation are given here.

The second correction is the spin-orbit interaction:

$$\widehat{H}_{\text{SO}}^{(1)} = \frac{1}{2m^2c^2r}\frac{\mathrm{d}V_C}{\mathrm{d}r}\widehat{\mathbf{L}}\cdot\widehat{\mathbf{S}}$$

In this expression $\widehat{\mathbf{L}}$ and $\widehat{\mathbf{S}}$ are the vector operators for orbital and spin angular momentum respectively. The usual (somewhat hand-waving) derivation talks of the electron seeing a magnetic field from the proton which appears to orbit it; the magnetic moment of the electron then prefers to be aligned with this field. This gives an expression which is too large by a factor of 2; an exact derivation requires the Dirac equation.

This time we will run into trouble with the degeneracy of $\widehat{H}^{(0)}$ unless we do some work first. The usual trick of writing $2\widehat{\mathbf{L}}\cdot\widehat{\mathbf{S}} = \widehat{\mathbf{J}}^2 - \widehat{\mathbf{L}}^2 - \widehat{\mathbf{S}}^2$ where $\widehat{\mathbf{J}} = \widehat{\mathbf{L}} + \widehat{\mathbf{S}}$ tells us that rather than working with eigenstates of $\widehat{\mathbf{L}}^2$, $\hat{L}_z$, $\widehat{\mathbf{S}}^2$ and $\hat{S}_z$, which would be the basis we'd get with the minimal direct product of the spatial state $|nlm_l\rangle$ and a spinor $|sm_s\rangle$, we want to use eigenstates of $\widehat{\mathbf{L}}^2$, $\widehat{\mathbf{S}}^2$ $\widehat{\mathbf{J}}^2$ and $\hat{J}_z$, $|nljm_j\rangle$, instead. (Since $S = \frac{1}{2}$ for an electron we suppress it in the labelling of the state.) An example of such a state is $|n1\frac{1}{2}\frac{1}{2}\rangle = \sqrt{\frac{2}{3}}|n11\rangle \otimes |\frac{1}{2} - \frac{1}{2}\rangle - \sqrt{\frac{1}{3}}|n10\rangle \otimes |\frac{1}{2}\frac{1}{2}\rangle$.

Then

$$\langle nljm_j|\widehat{H}^{(1)}_{\rm SO}|nljm_j\rangle = \frac{\alpha^2\,|E^{(0)}_n|}{n}\left(\frac{2}{2l+1} - \frac{2}{2j+1}\right)$$

(This expression is only correct for $l \neq 0$. However there is another separate effect, the Darwin term, which only affects s-waves and whose expectation value is just the same as above (with $l = 0$ and $j = \frac{1}{2}$), so we can use this for all l. The Darwin term can only be understood in the context of the Dirac equation.)

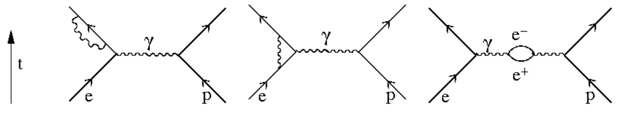
So finally

$$E^{(1)}_{nj} = \frac{\alpha^2\,|E^{(0)}_n|}{n}\left(\frac{3}{4n} - \frac{2}{2j+1}\right).$$

The degeneracy of all states with the same n has been broken. States of $l = j \pm \frac{1}{2}$ are still degenerate, a result that persists to all orders in the Dirac equation (where in any case orbital angular momentum is no longer a good quantum number.) So the eight $n = 2$ states are split by 4.5×10^{-5} eV, with the ${}^2p_{3/2}$ state lying higher that the degerate ${}^2p_{1/2}$ and ${}^2s_{1/2}$ states.

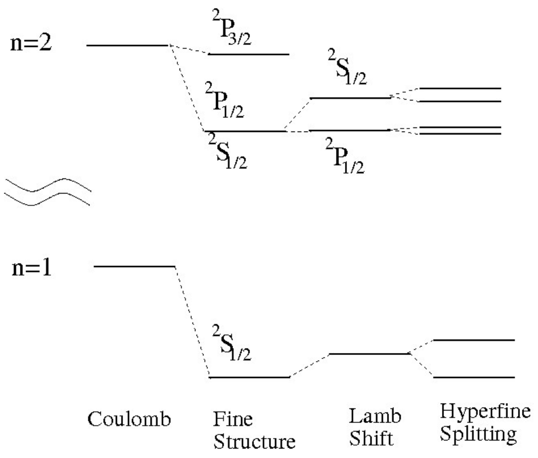
Two other effects should be mentioned here. One is the *hyperfine splitting*. The proton has a magnetic moment, and the energy of the atom depends on whether the electon spin is aligned with it or not— more precisely, whether the total spin of the electon and proton is 0 or 1. The anti-aligned case has lower energy (since the charges are opposite), and the splitting for the 1s state is 5.9×10^{-6} eV. (It is around a factor of 10 smaller for any of the $n = 2$ states.) Transitions between the two hyperfine states of 1s hydrogen give rise to the 21 cm microwave radiation which is a signal of cold hydrogen gas in the galaxy and beyond.

The final effect is called the *Lamb shift*. It cannot be accounted for in quantum mechanics, but only in quantum field theory.



The diagrams above show corrections to the simple Coulomb force which would be represented by the exchange of a single photon between the proton and the electron. The most notable effect on the spectrum of hydrogen is to lift the remaining degeneracy between the ${}^2p_{1/2}$ and ${}^2s_{1/2}$ states, so that the latter is higher by 4.4×10^{-6} eV.

Below the various corrections to the energy levels of hydrogen are shown schematically. The gap between the $n = 1$ and $n = 2$ shells is supressed, and the Lamb and hyperfine shifts are exaggerated in comparison with the fine-structure. The effect of the last two on the ${}^2p_{3/2}$ level is not shown.



- **Gasiorowicz ch 12.1,2,4**
- **Mandl ch 7.4**
- **Shankar ch 17.3**
- **Townsend ch 11.6,7**

3.4 The Zeeman effect: hydrogen in an external magnetic field

(Since we will not ignore spin, this whole section is about the so-called anomalous Zeeman effect. The so-called normal Zeeman effect cannot occur for hydrogen, but is the special case for certain multi-electron atoms for which the total spin is zero.)

With an external magnetic field along the z-axis, the perturbing Hamiltonian is $\widehat{H}^{(1)} = -\boldsymbol{\mu}\cdot\mathbf{B} = (eB/2m)(\widehat{L}_Z + 2\widehat{S}_z)$. The factor of 2 multiplying the spin is of course the famous g-factor for spin, as predicted by the Dirac equation. Clearly this is diagonalised in the $\{|nlm_lm_s\rangle\}$ basis ($s=\frac{1}{2}$ suppressed in the labelling as usual.) Then $E^{(1)}_{nlm_lm_s} = -(eB\hbar/2m)(m_l + 2m_s)$. If, for example, $l=2$ there are 7 possible values of $m_l + 2m_s$ between -3 and 3, with -1, 0 and 1 being degenerate ($5\times 2 = 10$ states in all).

This is fine if the magnetic field is strong enough that we can ignore the fine structure discussed in the last section. But typically it is not. For a weak field the fine structure effects will be stronger, so we will consider them part of $\widehat{H}^{(0)}$ for the Zeeman problem; our basis is then $\{|nljm_j\rangle\}$ and states of the same j but different l are degenerate. This degeneracy however is not a problem, because the operator $(\widehat{L}_z + 2\widehat{S}_z)$ does not connect states of different l. So we can use non-degenerate perturbation theory, with

$$E^{(1)}_{nljmj} = \frac{eB}{2m}\langle nljm_j|\widehat{L}_z + 2\widehat{S}_z|nljm_j\rangle.$$

If $\widehat{J}_z$ is conserved but $\widehat{L}_z$ and $\widehat{S}_z$ are not, the expectation values of the latter two might be expected to be proportional to the first, modified by the average degree of alignment: $\langle\widehat{S}_z\rangle = \hbar m_j\langle\widehat{\mathbf{S}}\cdot\widehat{\mathbf{J}}\rangle/\langle\widehat{\mathbf{J}}\rangle^2$ and similarly for L_z. (This falls short of a proof but is in fact correct; see

Mandl 7.5.3 for details.) Using $2\widehat{\mathbf{S}}\cdot\widehat{\mathbf{J}} = \widehat{\mathbf{S}}^2 + \widehat{\mathbf{J}}^2 - \widehat{\mathbf{L}}^2$ and the equivalent with $\widehat{\mathbf{S}} \leftrightarrow \widehat{\mathbf{L}}$ gives

$$E^{(1)}_{nljmj} = \frac{eB\hbar m_j}{2m}\left(1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}\right) = \frac{eB\hbar m_j}{2m} g_{jls}.$$

Of course for hydrogen $s(s+1) = \frac{3}{4}$, but the expression above, which defines the *Landé g factor*, is actually more general and hence I've left it with an explicit s. For hydrogen, $j = l \pm \frac{1}{2}$ and so $g = (1 \pm \frac{1}{2l+1})$.

Thus states of a given j (already no longer degenerate due to fine-structure effects) are further split into $(2j+1)$ equally-spaced levels. Since spectroscopy involves observing transitions between two states, both split but by different amounts, the number of spectral lines can be quite large.

- **Gasiorowicz ch 12.3**
- **Mandl ch 7.5**
- **(Shankar ch 14.5)**
- **Townsend ch 11.8**

3.5 The Stark effect: hydrogen in an external electric field

With an external electric field along the z-axis, the perturbing Hamiltonian is $\widehat{H}^{(1)} = -e\mathcal{E}z$ (we use $\mathcal{E}$ for the electric field strength to distinguish it from the energy.) Now it is immediately obvious that $\langle nlm|z|nlm\rangle = 0$ for any state: The probability density is symmetric on reflection in the xy-plane, but z is antisymmetric. So for the ground state, the first order energy shift vanishes. (We will return to excited states, but think now about why we can't conclude the same for them.) This is not surprising, because an atom of hydrogen in its ground state has no electric dipole moment: there is no $\mathbf{p}\cdot\mathbf{E}$ term to match the $\boldsymbol{\mu}\cdot\mathbf{B}$ one.

To calculate the second-order energy shift we need $\langle n'l'm'|z|100\rangle$. We can write z as $r\cos\theta$ or $\sqrt{4\pi/3}rY_{10}(\theta,\phi)$. The lack of dependence on ϕ means that m can't change, and in addition l can only change by one unit, so $\langle n'l'm'|z|100\rangle = \delta_{l'1}\delta m'0\langle n'10|z|100\rangle$. However this isn't the whole story: there are also states in the continuum, which we will denote $|\mathbf{k}\rangle$ (though these are not plane waves, since they see the Coulomb potential). So we have

$$E^{(2)}_{100} = (e\mathcal{E})^2 \sum_{n>1} \frac{|\langle n10|z|100\rangle|^2}{E^{(0)}_1 - E^{(0)}_n} + (e\mathcal{E})^2 \int \mathrm{d}^3k \frac{|\langle \mathbf{k}|z|100\rangle|^2}{E^{(0)}_1 - E^{(0)}_k}$$

(We use E_1 for E_{100}). This is a compact expression, but it would be very hard to evaluate directly. We can get a crude estimate of the size of the effect by simply replacing all the denominators by $E^{(0)}_1 - E^{(0)}_2$; this overestimates the magnitude of every term but the first, for which it is exact, so it will give an upper bound on the magnitude of the shift. Then

$$\begin{aligned} E^{(2)}_1 &> \frac{(e\mathcal{E})^2}{E^{(0)}_1 - E^{(0)}_2}\left(\sum_{n\geq 1}\sum_{lm}\langle 100|z|nlm\rangle\langle nlm|z|100\rangle + \int \mathrm{d}^3k\langle 100|z|\mathbf{k}\rangle\langle \mathbf{k}|z|100\rangle\right) \\ &= \frac{(e\mathcal{E})^2}{E^{(0)}_1 - E^{(0)}_2}\langle 100|z^2|100\rangle = -\frac{8(e\mathcal{E})^2 a_0^3}{3\hbar c\alpha} \end{aligned}$$

where we have included $n = 1$ and other values of l and m in the sum because the matrix elements vanish anyway, and then used the completeness relation involving all the states, bound and unbound, of the hydrogen atom.

There is a trick for evaluating the exact result, which gives 9/4 rather than 8/3 as the constant (See Shankar.) So our estimate of the magnitude is fairly good. (For comparison with other ways of writing the shift, note that $(e\mathcal{E})^2/\hbar c\alpha = 4\pi\epsilon_0\mathcal{E}^2$—or in Gaussian units, just $\mathcal{E}^2$.)

Having argued above that the hydrogen atom has no electric dipole, how come we are getting a finite effect at all? The answer of course is that the field polarises the atom, and the induced dipole can then interact with the field.

Now for the first excited state. We can't conclude that the first-order shift vanishes here, of course, because of degeneracy: there are four states and $\widehat{H}^{(1)}$ is not diagonal in the usual basis $|2lm\rangle$. In fact as we argued above it only connects $|200\rangle$ and $|210\rangle$, so the states $|21 \pm 1\rangle$ decouple and their first order shifts do vanish. Using $\langle 210|z|200\rangle = -3a_0$, we have in this subspace (with $\langle 200| = (1, 0)$ and $\langle 210| = (0, 1)$)

$$\widehat{H}^{(0)} = -3a_0 e\mathcal{E} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},$$

and the eigenstates are $\sqrt{1/2}(|200\rangle \pm |210\rangle)$ with eigenvalues $\mp 3a_0 e\mathcal{E}$. So the degenerate quartet is split into a triplet of levels (with the unshifted one doubly degenerate).

In reality the degeneracy of the $n = 2$ states is lifted by the fine-structure splitting; are these results then actually relevant? They will be approximately true if the field is large; at an intermediate strength both fine-structure and Stark effects should be treated together as a perturbation on the pure Coulomb states. For very weak fields degenerate perturbation theory holds in the space of $j = \frac{1}{2}$ states, which are split by $\mp\sqrt{3}a_0 e\mathcal{E}$.

- **Gasiorowicz ch 11.3**
- **Shankar ch 17.2,3**
- **Townsend ch 11.4**

Approximate methods III: Time-dependent perturbation theory

4.1 Formalism

Summary: Time-dependent perturbation theory applies to cases where the perturbing field changes with time, but also to processes such as absorption and emission of photons, and to scattering.

In time-dependent perturbation theory, we typically consider a situation where, at the beginning and end, the only Hamiltonian acting is the time-independent $\widehat{H}^{(0)}$, but for some time in between another, possibly time-dependent, effect acts so that for this period $\widehat{H} = \widehat{H}^{(0)} + \widehat{H}^{(1)}(t)$. If a system starts off in an eigenstate of $\widehat{H}^{(0)}$ it will have a certain probability of ending up in another, and that transition probability is generally what we are interested in.

There are many similarities in approach to the time-independent case, but it is worth noting that our interest in the states $|n^{(0)}\rangle$ is slightly different. In the time-independent case these were only approximations to the true eigenstates of the system. In the time-dependent case they remain the actual eigenstates of the system asymptotically (a phrase that means away from the influence of the perturbation, either in space or, as here, in time). Furthermore while the time-dependent perturbation is acting the familiar connection between the TISE and TDSE breaks down, so the eigenstates of the Hamiltonian, while instantaneously definable, are not of any real significance anyway. For that reason we will drop the label $^{(0)}$ on the states, since we won't be defining any other set of states, and similarly we will refer to their unperturbed energies just as E_n.

Because the states $|n\rangle$ are a complete set, at any instant we can decompose the state of the system

$$|\psi(t)\rangle = \sum_n c_n(t)|n\rangle \equiv \sum_n d_n(t)\mathrm{e}^{-iE_nt/\hbar}|n\rangle$$

In defining the $d_n(t)$ we have pulled out the time variation due to $\widehat{H}^{(0)}$. So in the absence of the perturbation, the d_n would be constant and equal to their initial values. Conversely, it is the time evolution of the d_n which tells us about the effect of the perturbation. Typically we start with all the d_n except one equal to zero, and look for non-zero values of the others subsequently.

$$\begin{aligned}\left(\widehat{H}^{(0)} + \widehat{H}^{(1)}(t)\right)|\psi(t)\rangle &= i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle \\ \Rightarrow i\hbar\dot{d}_n &= \sum_m d_m(t)\mathrm{e}^{i\omega_{nm}t}\langle n|\widehat{H}^{(1)}(t)|m\rangle\end{aligned}$$

where we used m as the dummy index in the summation and took the inner product with $\mathrm{e}^{iE_nt/\hbar}\langle n|$, and we have defined $\omega_{nm} \equiv (E_n - E_m)/\hbar$ (and $\dot{d}_n$ represents the time derivative of d_n.)

So far this is *exact*, but usually impossible to solve, consisting of an infinite set of coupled differential equations! Which is where perturbation theory comes in. If we start with $d_i(t_0) = 1$ and all others zero (i for initial), and if the effect of $\widehat{H}^{(1)}$ is small, then d_i will always be much bigger than all the others and, to first order, we can replace the sum overall states by just the contribution of the ith state. Furthermore to this order d_i barely changes, so we can take it out of the time integral to get

$$d_n(t) = -\tfrac{i}{\hbar}\int_{t_0}^{t} \mathrm{e}^{i\omega_{ni}t}\langle n|\widehat{H}^{(1)}(t)|i\rangle \mathrm{d}t$$

Having obtained a first-order expression for the d_n, we could substitute it back in to get a better, second-order, approximation and so on.

- **Gasiorowicz ch 15.1**
- **Mandl ch 9.1-3**
- **(Shankar ch 18.2)**
- **Townsend ch 14.6**

4.1.1 Perturbation which is switched on slowly

Let $\widehat{H}^{(1)}(t) = \widehat{H}^{(1)}\mathrm{e}^{t/\tau}$ start acting at time $t = -\infty$ so that it reaches full strength at $t = 0$. Then

$$\begin{aligned} d_n(0) &= -\tfrac{i}{\hbar}\langle n|\widehat{H}^{(1)}|i\rangle \int_{-\infty}^{0} \mathrm{e}^{t/\tau}\mathrm{e}^{i\omega_{ni}t}\mathrm{d}t \\ &= -\frac{i}{(1/\tau + i\omega_{ni})\hbar}\langle n|\widehat{H}^{(1)}|i\rangle \end{aligned}$$

In the limit $\tau \gg 1/\omega_{ni}$ we simply recover the expression for the first-order shifts of the eigenkets in time-independent perturbation theory. With an adiabatic (exceedingly slow) perturbation the system evolves smoothly from the state $|i^{(0)}\rangle$ to the state $|i\rangle$.

4.1.2 Sudden perturbation

Consider a constant perturbation $\widehat{H}^{(1)}$ which is switched on at $t = -\epsilon/2$ and off at $t = \epsilon/2$.

$$\begin{aligned} d_n(\infty) &= -\tfrac{i}{\hbar}\langle n|\widehat{H}^{(1)}|i\rangle \int_{-\epsilon/2}^{\epsilon/2} \mathrm{e}^{i\omega_{ni}t}\mathrm{d}\,t \\ &= -\langle n|\widehat{H}^{(1)}|i\rangle \frac{2i}{\hbar\omega_{ni}}\sin(\epsilon\omega_{ni}/2) \xrightarrow{\epsilon\to 0} -i\frac{\epsilon}{\hbar}\langle n|\widehat{H}^{(1)}|i\rangle \to 0. \end{aligned}$$

So sudden changes to a system leave the state unchanged.

Actually we didn't need to switch off at $t = \epsilon/2$, we can instead regard the expression above as $d_n(\epsilon/2)$, ie the coefficient immediately after turning on the perturbation. The conclusion is the same: a change in the system which is sudden (compared with $1/\omega_{ni}$) doesn't change the state of the system. We can use this to conclude, for instance, that the electronic configuration is unchanged when a tritium nucleus beta-decays to helium-3. Of course this configuration is not an eigenstate of the new Hamiltonian, but we can take it as an initial state for the subsequent time evolution.

4.2 Oscillatory perturbation and Fermi's golden rule

Summary: Fermi's golden rule is the most important result of this chapter

Without specifying anything more about the system or perturbation, let us consider the case $\widehat{H}^{(1)}(t) = \widehat{H}^{(1)}\mathrm{e}^{-i\omega t}$. (Note ω is not now anything to do with the harmonic oscillator, and indeed if we wanted to apply this to that system we'd need to use labels to distinguish the oscillator frequency from the applied frequency).

At the outset we should note that with this problem we are heading towards the interaction of atoms with a radiation field.

For definiteness, let the perturbation apply from $-t/2$ to $t/2$. Then

$$\begin{aligned}
d_n(t) &= -\tfrac{i}{\hbar}\langle n|\widehat{H}^{(1)}|i\rangle \int_{-t/2}^{t/2} \mathrm{e}^{i(\omega_{ni}-\omega)t'}\mathrm{d}t' \\
&= -\frac{2i}{\hbar(\omega_{ni}-\omega)}\langle n|\widehat{H}^{(1)}|i\rangle \sin\left(\tfrac{1}{2}(\omega_{ni}-\omega)t\right) \\
\Rightarrow P_{i\to n} &= \frac{4}{\hbar^2(\omega_{ni}-\omega)^2}\left|\langle n|\widehat{H}^{(1)}|i\rangle\right|^2 \sin^2\left(\tfrac{1}{2}(\omega_{ni}-\omega)t\right) \\
&= \frac{t^2}{\hbar^2}\left|\langle n|\widehat{H}^{(1)}|i\rangle\right|^2 \mathrm{sinc}^2\left(\tfrac{1}{2}(\omega_{ni}-\omega)t\right)
\end{aligned}$$

where $\mathrm{sinc}(x) \equiv \sin(x)/x$.

This expression is unproblematic provided $\hbar\omega$ doesn't coincide with any excitation energy of the system. In that case, the transition probability just oscillates with time and remains very small.

The more interesting case is where we lift that restriction, but the expression then requires rather careful handling! The standard exposition goes as follows: as t becomes very large, $t\,\mathrm{sinc}^2(\frac{1}{2}(\omega_{ni}-\omega)t)$ is a sharper and sharper – and taller and taller – function of $\omega_{ni}-\omega$, and in fact tends to $2\pi\delta(\omega_{ni}-\omega)$. (The normalisation comes from comparing the integrals of each side with respect to ω: $\int_{-\infty}^{\infty}\mathrm{sinc}^2 x\mathrm{d}x = \pi$. See section A.8 for more on δ-functions.) Then we have

$$P_{i\to n} = \tfrac{2\pi t}{\hbar^2}\left|\langle n|\widehat{H}^{(1)}|i\rangle\right|^2 \delta(\omega_{ni}-\omega).$$

The need to take the average over a long time period to obtain the frequency-matching delta function is easily understood if we remember that any wave train only approaches monochromaticity in the limit that it is very long; any truncation induces a spread of frequencies.

So the probability increases linearly with time, which accords with our expectation if the perturbation has a certain chance of inducing the transition in any given time interval. Finally then, we write for the *transition rate* (probability per unit time):

$$R_{i\to n} = \tfrac{1}{t}P_{i\to n} = \tfrac{2\pi}{\hbar}\left|\langle n|\widehat{H}^{(1)}|i\rangle\right|^2 \delta(E_{ni}-\hbar\omega)$$

This result is commonly known as "Fermi's golden rule", and it is the main result of this section. We have written $\hbar\omega = E$ to highlight the δ-function as enforcing conservation of energy in the transition: the energy difference between the final and initial state must be supplied by the perturbation. Although we have assumed nothing about radiation in the derivation, we have ended up with the prediction that only the correct frequency of perturbation can induce a transition, a result reminiscent of the photoelectric effect which demonstrates empirically that energy is absorbed from fields in quanta of energy $\hbar\omega$.

Taking on trust its importance though, how are we to interpret it? Taken literally, it says that if $E \neq E_{ni}$ nothing happens, which is dull, and if $E = E_{ni}$ the transition rate is infinite and first-order perturbation theory would appear to have broken down! The resolution is that for actual applications, we do not have perfectly monochromatic radiation inducing transitions to single, absolutely sharp energy levels. Such a perfect resonance would indeed give infinite transition rates, but is unphysical. In practice there is always an integration over energy, with a weighting function $\rho(E)$ which is a distribution function smearing the strength over a range of energies. Authors who don't like playing with δ functions leave the $t^2\mathrm{sinc}^2(\ldots)$ form in place till this is evident, but the bottom line is the same (see eg Mandl).

Had we started from $\widehat{H}^{(1)}\mathrm{e}^{i\omega t}$ we would have ended up with $\delta(E_{ni} + E)$ In this case, energy must be given up to the perturbing field: this is emission rather than absorption. With a real field $\cos(\omega t) = \frac{1}{2}(\mathrm{e}^{i\omega t} + \mathrm{e}^{-i\omega t})$, both processes can occur.

Finally we must point out that though we've derived Fermi's golden rule for oscillatory perturbations, the expression holds equally in the $\omega \to 0$ limit i.e. for a *constant* perturbation acting from time $-t/2 \to t/2$. It should be easy to see that exactly the same result is obtained, except that the energy-conservation δ-function is simply δE_{ni}. This form is more appropriate if, instead of considering an external field which can supply or absorb energy, one thinks in terms of photons and defines $|n\rangle$ and $|i\rangle$ to include not only the atomic state, but also any incoming or out-going photon. Viewed in that way the energies of the initial and final state must be the same. Both derivations are valid but the one given here is more appropriate for our purposes given that we are not going to quantise the radiation field. (Wait till next year for that!) However the constant perturbation form will be used in scattering in the next chapter.

- **Gasiorowicz ch 15.2**
- **(Mandl ch 9.4)**
- **Shankar ch 18.2**
- **(Townsend ch 14.7)**

4.3 Emission and absorption of radiation

Summary: Classical physics allows us to calculate rates of absorption and stimulated emission of radiation. It cannot handle spontaneous emission, but a clever argument about transition rates in thermal equilibrium allows us to predict that too.

Consider an oscillating electric field $\mathcal{E}\boldsymbol{\epsilon}\cos(\omega t)$. (The unit vector $\boldsymbol{\epsilon}$ indicates the direction of the field.) This corresponds to a perturbation

$$\widehat{H}^{(1)}(t) = -e\mathcal{E}\cos(\omega t)\boldsymbol{\epsilon}\cdot\mathbf{r}$$

which has the form we considered when deriving Fermi's golden rule.

We note that a field of this form is a long-wavelength-approximation to the electric field of an electromagnetic wave. Electric effects are much stronger than magnetic in this limit, so we are justified in ignoring the magnetic field in writing $\widehat{H}^{(1)}$. This is called the *electric dipole approximation* because $\widehat{H}^{(1)} \propto e\mathbf{r}\cdot\boldsymbol{\epsilon} = \mathbf{d}\cdot\boldsymbol{\epsilon}$ where $\mathbf{d}$ is the electric dipole moment (we don't use $\mathbf{p}$ for obvious reasons!). (Most textbooks more correctly start from the vector potential $\mathbf{A}$ to derive the same perturbing Hamiltonian, see section 4.6. We follow Mandl here.)

To avoid unphysically sharp resonance as discussed above we actually need to consider a field with a range of frequencies, each being incoherent (so we add probabilities not amplitudes). The energy per unit volume in a frequency range $\omega \to \omega + \mathrm{d}\omega$ is denoted $\rho(\omega)\mathrm{d}\omega$, and $\frac{1}{2}\epsilon_0\mathcal{E}^2 = \rho(\omega)$. (This expression allows for a factor of 2 from including the magnetic field energy, but also a factor of $\frac{1}{2}$ from the time average $\langle\cos^2\omega t\rangle$). Then we have

$$\begin{aligned} R_{i\to f} &= \frac{2\pi}{\hbar^2}\int\left(\tfrac{1}{2}e\mathcal{E}(\omega)\right)^2 |\langle f|\boldsymbol{\epsilon}\cdot\mathbf{r}|i\rangle|^2\left(\delta(\omega_{fi}-\omega)+\delta(\omega_{fi}+\omega)\right)\mathrm{d}\omega \\ &= \frac{\pi e^2}{\epsilon_0\hbar^2}\rho(|\omega_{fi}|)\,|\langle f|\boldsymbol{\epsilon}\cdot\mathbf{r}|i\rangle|^2 \end{aligned}$$

where the result applies equally to absorption (with $E_f > E_i$) or emission (with $E_f < E_i$). We note that as promised we now have a well-behaved result with no infinities around!

This is as far as we can go without being more specific about the system, except for one thing. The symmetry between emission and absorption is rather odd. Of course absorption needs a field to supply energy—or in quantum terms, to absorb a photon—a source of photons is needed. But why should the same be true for emission? What we have calculated here is *stimulated emission*, and it certainly does occur; it is behind the workings of a laser. Though our calculation is classical, stimulated emission can be thought of as due to the bosonic nature of photons - they "like to be in the same state", so emission is more likely the more photons of the right energy are already present. But surely an excited atom in a vacuum at zero temperature can still decay! There must be *spontaneous emission* too, and the classical calculation can't predict it.

There is however a very clever argument due to Einstein which connects the rates for stimulated and spontaneous emission, which says that if we regard the the energy density $\rho(\omega)$ as proportional to the number of photons in a mode of this frequency, $n(\omega)$, then to allow for spontaneous emission we simply need to replace $n(\omega)$ with $n(\omega)+1$. (Since classical fields correspond to huge numbers of photons, the difference between n and $n+1$ is utterly negligible.)

- **(Gasiorowicz ch 15.3)**
- **Mandl ch 9.5**
- **(Shankar ch 18.5)**
- **(Townsend ch 14.7)**

4.3.1 Einstein's A and B coefficients

Consider for simplicity a gas of "atoms" which can either be in their ground state or an excited state (excitation energy E), and let the numbers in each be n_0 and n_1. The atoms will interact with the black-body radiation field, emitting and absorbing quanta of energy, to reach thermal equilibrium. We will need Planck's law for the energy density of the black-body radiation field at a given frequency:

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\hbar\omega/k_BT} - 1} = f(\omega)n(\omega, T)$$

where the temperature-independent prefactor $f(\omega)$ arises from the density of states, and $n(\omega, T)$ is the Bose-Einstein expression for the average number of quanta of energy in a given mode. See section A.10 for more details about the Bose-Einstein distribution.

The rates of absorption and stimulated emission are proportional to the energy density in the field at $\omega = E/\hbar$, and the coefficients are denoted B_{01} and B_{10}, while the rate of spontaneous emission is just A_{10}. (We have seen that $B_{01} = B_{10}$, but we won't assume that here.) Then the rate of change of n_0 and n_1 is

$$\dot{n}_0 = -n_0 B_{01}\rho(\omega) + n_1 A_{10} + n_1 B_{10}\rho(\omega) \qquad \text{and} \qquad \dot{n}_1 = -\dot{n}_0.$$

At thermal equilibrium, $\dot{n}_0 = \dot{n}_1 = 0$ and $n_1/n_0 = e^{-E/k_BT}$. Using the Planck law for $\rho(E/\hbar)$, with some rearrangement we get

$$A_{10}(e^{E/k_BT} - 1) + B_{10}f(\omega) - e^{E/k_BT}B_{01}f(\omega) = 0$$

Now this has to be true for any temperature, so we can equate coefficients of e^{E/k_BT} to give $A_{10} = B_{01}f(\omega)$ and $A_{10} = B_{10}f(\omega)$. So we recover $B_{01} = B_{10}$, which we already knew, but we also get a prediction for A_{10}. Thus we have

$$\dot{n}_1 = B_{10}f(\omega)\Big(-n_1\big(n(\omega, T) + 1\big) + n_0 n(\omega, T)\Big)$$

We see that the total emission probability corresponds to replacing $n(\omega, T)$ with $n(\omega, T)+1$. This result is confirmed by a full calculation with quantised radiation fields, where the factor arises from the fact that the creation operator for quanta in a mode of the EM field has the usual normalisation $a^\dagger_\omega|n_\omega\rangle = \sqrt{n_\omega + 1}\,|n_\omega + 1\rangle$.

- **Gasiorowicz Supplement 1**

4.4 Radiative decay of $2p$ state of hydrogen

Summary: This is the classic test-case of the theory we've developed so far. It passes with flying colours!

We wish to calculate the total decay rate of the $2p$ state of hydrogen. We start with the expression for spontaneous decay deduced from the preceding arguments:

$$R_{i\to f} = \frac{\pi e^2}{\epsilon_0\hbar^2}\hbar\omega D(\omega\hat{\mathbf{k}})\,|\langle f|\boldsymbol{\epsilon}\cdot\mathbf{r}|i\rangle|^2$$

where $\omega \equiv \omega_{fi}$ is taken as read. The expression $D(\omega\hat{\mathbf{k}})$ is the density of states factor for photons with a particular direction of propagation $\hat{\mathbf{k}}$ (which must be perpendicular to $\boldsymbol{\epsilon}$): $D(\omega\hat{\mathbf{k}}) = \omega^2/(2\pi c)^3$. It is just $D(\mathbf{k})$ written in terms of ω so that $\int D(\omega\hat{\mathbf{k}})d\omega = \int D(\mathbf{k})dk$. See section A.10 for more details.

Now we don't care about the direction in which the final photon is emitted, nor about its polarisation, and so we need to integrate and sum the decay rate to a particular photon mode, as written above, over these. ($\boldsymbol{\epsilon}$ is the polarisation vector.) We can pick any of the $2p$ states (with $m = 0, \pm 1$) since the decay rate can't depend on the direction the angular momentum is pointing, so we will choose $m = 0$. Then $\langle 100|\boldsymbol{\epsilon}\cdot\mathbf{r}|210\rangle = \langle 100|\epsilon_z z|210\rangle$ as we can see by writing $\boldsymbol{\epsilon}\cdot\mathbf{r}$ in terms of the $l = 1$ spherical harmonics (see A.2). There are two polarisation states and both are perpendicular to $\mathbf{k}$; if we use spherical polar coordinates in k-space, (k, θ_k, ϕ_k), we can take the two polarisation vectors to be $\boldsymbol{\epsilon}^{(1)} = \boldsymbol{\theta}_k$ and $\boldsymbol{\epsilon}^{(2)} = \boldsymbol{\phi}_k$. Only the first contributes since $\epsilon_z^{(1)} = -\sin\theta_k$ but $\epsilon_z^{(2)} = 0$.

We will need to integrate over all directions of the emitted photon. Hence the decay rate is

$$\begin{aligned}
R_{i\to f} &= \frac{\pi e^2}{\epsilon_0 \hbar^2}\hbar\omega\frac{\omega^2}{8\pi^3 c^3}\int \sin^2\theta_k\,|\langle 100|z|210\rangle|^2 \sin\theta_k \mathrm{d}\theta_k \mathrm{d}\phi_k \\
&= \frac{e^2\omega^3}{8\pi^2 c^3\hbar\epsilon_0}\frac{8\pi}{3}\,|\langle 100|z|210\rangle|^2 \\
&= \frac{4\alpha\omega^3}{3c^2}\frac{2^{15}a_0^2}{3^{10}} \qquad \text{where } \hbar\omega = (3/4)E_{\mathrm{Ry}} \\
&= \left(\frac{2}{3}\right)^8 \frac{\alpha^5 mc^2}{\hbar} = 6.265\times 10^8\ \mathrm{s}^{-1}
\end{aligned}$$

This matches the experimental value of the $2^2p_{1/2}$ state to better than one part in 10^{-5}, at which point the effects of fine structure enter. The fact that this rate is very much smaller than the frequency of the emitted photon (2.5×10^{15} Hz) justifies the use of the long-time approximation which led to Fermi's golden rule.

- **Gasiorowicz ch 17.2,4**
- **Shankar ch 18.5**
- **Townsend ch 14.8**

4.5 Finite width of excited state

Summary: A full treatment of the effect on states of coupling to radiation is beyond the scope of the course. But we can motivate the fact that a finite lifetime leads to broadening of the state.

In first-order perturbation theory, changes in the initial state are ignored. But in fact we have often been told that a state which can decay with a lifetime τ has an uncertainty in its energy of the order $\Delta E = \hbar/\tau$. How does this arise?

At second order in perturbation theory the first-order expressions for the coefficients d_n ($n \neq i$) give a non-vanishing expression for the rate of change of the initial state d_i. The mathematical treatment required to do this properly is too subtle to be worth giving here, but the bottom line is (taking $t = 0$ as the starting time for simplicity)

$$P_{i\to i} = \mathrm{e}^{-\Gamma_i t/\hbar} \qquad \text{where} \quad \Gamma_i = \hbar\sum_n R_{i\to n}$$

which is exactly as one would expect. Γ, which has units of energy, is called the *line width*; $\hbar/\Gamma$ is the total lifetime of the state.

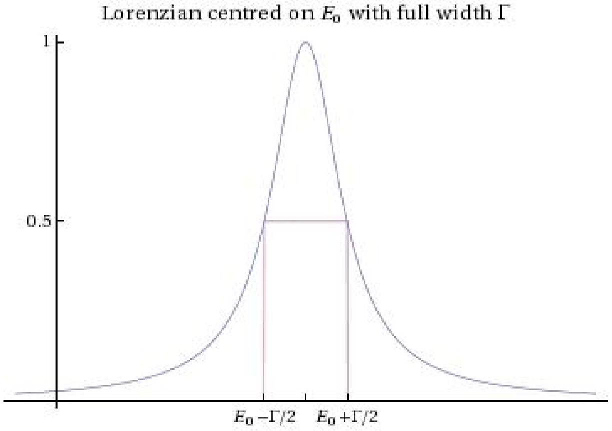
Furthermore if one returns to the derivation of the d_n and allows for the fact that d_i is decaying exponentially (rather than constant as assumed at that order of perturbation theory) we find the integral

$$\frac{i}{\hbar}\int_0^t \mathrm{e}^{i(\omega_{ni}-\omega)t'-\Gamma t'/(2\hbar)}\mathrm{d}t' \quad \rightarrow \quad \frac{1}{\hbar(\omega_{ni}-\omega)+\frac{i}{2}\Gamma}$$

The modulus is

$$\frac{1}{(E_{ni}-\hbar\omega)^2+\frac{1}{4}\Gamma^2}$$

This is a *Lorentzian*; Γ is the full width at half maximum and its presence tames the energy δ-function we found originally. (Hence sensible results can be found even if there is not a continuum of photon states.) The upshot is that we no longer need exact energy matching for a transition to occur; the energy of an unstable state is not precise, but has an uncertainty: $\Delta E \approx \Gamma = \hbar/\tau$.



- **Gasiorowicz ch 15.3 (and Supplement 15-A)**
- **Mandl ch 9.5.3**

4.6 Selection rules

Summary: In atomic physics, almost all observed transitions are of the electric dipole form we have been studying. Only certain transitions are allowed.

The heart of all our expressions for interaction with the electromagnetic field was the matrix element $e\mathcal{E}\langle f|\boldsymbol{\epsilon}\cdot\mathbf{r}|i\rangle$, obtained from a spatially invariant electric field which we argued was the long-wavelength limit of an electromagnetic wave. Since the wavelength of light generated from atomic transitions if of the order of $10^{-7}-10^{-8}$ m, while atomic sizes are of order 10^{-10} m, this should be a good approximation.

For completeness we note that the expression $\mathbf{E}=-\nabla\phi(\mathbf{r})$ is no longer actually valid for time-dependent fields; the correct expression is $\mathbf{E}=-\nabla\phi(\mathbf{r})-\mathrm{d}\mathbf{A}/\mathrm{d}t$ where $\mathbf{A}$ is the vector potential; furthermore a very convenient gauge for radiation is $\phi = 0, \mathbf{A} = A_0\boldsymbol{\epsilon}\mathrm{e}^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$ with $\mathbf{k}\cdot\boldsymbol{\epsilon} = 0$ and $A_0 = \mathcal{E}/\omega$. Anticipating results from PHYS30202 we have the Hamiltonian

$$\widehat{H} = \frac{(\mathbf{p}-e\mathbf{A})\cdot(\mathbf{p}-e\mathbf{A})}{2m} - e\phi(\mathbf{r}) + \frac{e}{m}(\mathbf{B}\cdot\widehat{\mathbf{S}})$$

and so in this gauge (ignoring the spin term) $\widehat{H}^{(1)} = -e\mathbf{A}\cdot\mathbf{p}/m$ and the matrix element is proportional to $\langle f|\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}\boldsymbol{\epsilon}\cdot\mathbf{p}|i\rangle$. Now if $\lambda \gg a_0$, then the phase $\mathbf{k}\cdot\mathbf{r}$ will scarcely vary as $\mathbf{r}$ is integrated over the extent of the atom. The long-wavelength (electric dipole) limit is equivalent to setting $\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i\mathbf{k}\cdot\mathbf{r} + \ldots$ and discarding all terms except the first, as well as ignoring the spin term in the Hamiltonian. The final step then comes in noting that $\hat{\mathbf{p}} = \frac{m}{i\hbar}[\widehat{\mathbf{r}}, \widehat{H}_0]$ and $\langle f|[\widehat{\mathbf{r}}, \widehat{H}]|i\rangle = \hbar\omega_{fi}\langle f|\widehat{\mathbf{r}}|i\rangle$. Putting everything together we recover $e\mathcal{E}\langle f|\boldsymbol{\epsilon}\cdot\mathbf{r}|i\rangle$ as assumed previously, provided $\omega = \omega_{fi}$. As argued above this is a good approximation, unless the leading term vanishes. In other words if a transition cannot take place because the electric dipole matrix element vanishes, we cannot conclude that it cannot take place at all. It will however be much slower, and if a different transition is allowed by the electric dipole selection rules it will be hard to see the "forbidden" transition. Transitions which take place via the neglected terms are successively called magnetic dipole, electric quadruple, magnetic quadruple, electric octupole.... These transitions are important in nuclear physics, but rarely in atomic physics.

So what conditions must a pair of states satisfy for electric dipole transitions to be allowed? We need the matrix element $\langle n'l's'; j'm_j'|\mathbf{r}|nls; jm_j\rangle$ to be non-vanishing; for hydrogen of course $s = s' = \frac{1}{2}$. It is useful to write $\mathbf{r}(= x\,\mathbf{e}_1 + y\,\mathbf{e}_2 + z\,\mathbf{e}_3)$ as

$$\mathbf{r} = \sqrt{4\pi}\,r\left(Y_1^1\mathbf{e}_- + Y_1^0\mathbf{e}_0 + Y_1^{-1}\mathbf{e}_+\right) \qquad \text{where} \qquad \mathbf{e}_\pm = \pm\sqrt{\tfrac{1}{2}}(\mathbf{e}_1 \pm i\mathbf{e}_2), \quad \mathbf{e}_0 = \mathbf{e}_3.$$

The components of $\mathbf{r}$ in this spherical basis are referred to as r_q, rather than the cartesian r_i.

Since the spherical components of $\mathbf{r}$ are just the $l = 1$ spherical harmonics, we see that acting on a state with a component of $\mathbf{r}$ is like coupling in another $l = 1$ system. So the usual rules of addition of angular momentum apply, and we see that the electric dipole operator can only cause transitions between systems whose total angular momentum differs by at most one unit. (This is an example of a general theorem that vector operators transfer one unit of angular momentum—the Wigner-Eckhart theorem: see section A.2.) Similarly, the z-component of angular momentum can't change by more than one unit. Hence we have our the selection rules $\Delta j = 0, \pm 1$ and $\Delta m_j = 0, \pm 1$

However the electric dipole operator is independent of spin. If we look at matrix elements of the form $\langle j'l'm_j'|r_q|jlm_j\rangle$, we see that it reduces to terms of the form $\langle l'm_l'|r_q|lm_l\rangle$ which will vanish unless $l + 1 \geq l' \geq |l - 1|$. However there is an extra consideration. The spherical harmonics have *good parity*: under reflection in the origin they are either odd (for odd l) or even (for even l). $\mathbf{r}$ is odd. Now the integral of an odd-parity function over all angles is clearly zero, so if l is odd (even), $\mathbf{r}|lm_l\rangle$ is even (odd) and so $|l'm_l'\rangle$ must be even (odd) if the angular integral is not to vanish. Therefore we see that $l = l'$, while allowed by the rules of addition of angular momentum (if $l \neq 0$), is not allowed by parity conservation. (The rule for the integral of a product of three spherical harmonics is given in section A.2.)

So finally, for hydrogen, we have the following selection rules:

$$\Delta j = 0, \pm 1, \quad \Delta m_j = 0, \pm 1 \quad \text{and} \quad \Delta l = \pm 1$$

We saw from the example of the decay of the $2p$ state that the rate was proportional to the energy difference cubed. In general states will decay fastest to the lowest state they are allowed to, so states np will decay mostly to $1s$, nd to $2p$ etc. But what about the $2s$ states?

In this course we are not generally concerned with multi-electron atoms, but at this point we should say something about selection rules more generally. First note that as every electron feels the electric field, the dipole operator is $e\mathcal{E}\boldsymbol{\epsilon}\cdot\mathbf{R}$ where $\mathbf{R} = \sum_i \mathbf{r}_i$, the sum of the individual position vectors. Second we note that while strictly the only good quantum number of an atom is J, associated with the total angular momentum $\widehat{\mathbf{J}} = \sum_i(\widehat{\mathbf{L}}_i + \widehat{\mathbf{S}}_i)$, for reasonably light atoms L and S, corresponding to $\widehat{\mathbf{L}} = \sum_i \widehat{\mathbf{L}}_i$ and $\widehat{\mathbf{S}} = \sum_i \widehat{\mathbf{S}}_i$, are also "reasonably good" quantum numbers (in the sense that states so constructed are a good zeroth-order approximation to the states of the full Hamiltonian). We are assuming this when we use spectroscopic notation ${}^{(2S+1)}L_J$ for the atomic states. This is called "LS coupling". In that case we can again say that since the dipole operator is spin-independent spin won't change ($\Delta S = 0$), and coupling a vector operator again means that $L + 1 \geq L' \geq |L - 1|$. This time $\Delta L = 0$ is not excluded though, because L isn't connected to the parity of the atomic state. So for light atoms we have, along with a parity change,

$$\Delta J = 0,\ \pm 1, \quad \Delta M_J = 0,\ \pm 1, \quad \Delta S = 0 \quad \text{and} \quad \Delta L = 0, \pm 1 \quad \text{but no } L = 0 \to L = 0 \text{ transitions}$$

Examples of such allowed transitions are shown in this diagram of the energy levels of helium: All of these levels have one excited electron and so have the configuration $1snl$. Note that in helium the states of the same n are no longer degenerate as the higher the value of l, the more the nuclear charge is screened by the $1s$ electron. Also, triplet states (orthohelium) lie lower than singlet (parahelium), because the latter, having antisymmetric spin wave functions, must have symmetric spatial wavefunctions which bring the electrons closer together and hence increase the Coulomb repulsion. Note that the diagram above doesn't specify J values.

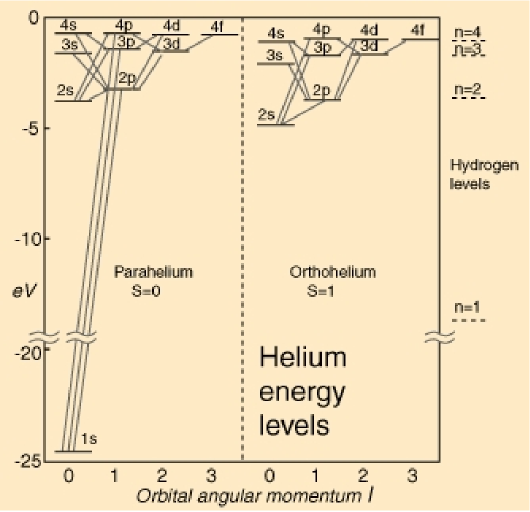


Figure 4.1: ©Hyperphysics at Georgia State University

If L and S are not good quantum numbers, there is still one thing we can say: since $\mathbf{R}$ is a vector operator, we must have $J + 1 \geq J' \geq |J - 1|$:

$$\Delta M_J = 0,\ \pm 1, \qquad \Delta J = 0, \pm 1 \quad \text{but no } J = 0 \to J = 0 \text{ transitions}$$

In helium violations of LS coupling will be very small (giving rise to very weak transitions) and will be of similar size to those due to terms ignored in making the dipole approximation. An example is the first excited state of orthohelium, in which one electron is in the $2p$ state and $S = 1$, with total $J = 1$. According the the electric dipole selection rules in LS coupling it cannot decay to the ground state (which has $S = 0$), but the fact that the spin-orbit interaction mixes the $S = 0$ and $S = 1$ states allows a very weak electric-dipole decay which has only recently been observed.

Violations of the electric dipole selection rules—“forbidden” transitions—must be due to higher-order operators (quadrupole and higher). These allow successively greater changes in J. But all orders, $J = 0 \rightarrow J = 0$ transitions are excluded. So for example the ground state of orthohelium (one electron in the $2s$ state and $S = 1$) is forbidden from decaying via an electric dipole transition by the parity selection rule. Even magnetic dipole transitions are only allowed through violations of LS coupling , and as a result its lifetime is 10^4 s. The single-photon decay of the $2s_{1/2}$ state of hydrogen is a similarly “forbidden” magnetic dipole transition, but in fact the two-photon decay dominates with a lifetime of about 0.1 sec.

An example of an absolutely forbidden process is the single-photon decay of the first excited state of parahelium (one electron in the $2s$ state and $S = 0$, hence $J = 0$). In fact it decays by emitting two photons with a lifetime of 19.7 ms.

- **Gasiorowicz ch 14.3, 17.3**
- **Mandl ch 6.2– most complete**
- **Shankar ch 17.2**
- **(Townsend ch 14.8)**

4.7 Heisenberg vs Schrödinger pictures

When at the start we, for convenience, absorbed the time dependence due to $\widehat{H}^{(0)}$ into the definition of the coefficients (switching from $c_n(t)$ to $d_n(t) = \mathrm{e}^{iE_n^{(0)}t/\hbar}c_n(t)$), we did something which has a rather fancy name: we switched to the *interaction picture*.

The *Schrödinger picture* is the one we are used to. Our basis kets $|n\rangle$ (eigenkets of the Hamiltonian $\widehat{H}$) are time-independent but quantum states are built from them with time-dependent coefficients: $|\psi_S(t)\rangle = \sum_n c_n(t)|n\rangle$. These satisfy the Schrödinger equation $i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi_S(t)\rangle = \widehat{H}|\psi_S(t)\rangle$ which implies $|\psi_S(t)\rangle = U(t,t_0)|\psi_S(t_0)\rangle$ where $U(t,t_0) = T\exp\{-(i/\hbar)\int_{t_0}^{t}\widehat{H}(t')\mathrm{d}\,t'\}$. In this picture the Hamiltonian itself is not usually time-dependent (in the absence of external forcing) nor are the other operators such as $\hat{x}$, $\hat{p}$. The expectation value of operators can change though of course - as we’ve seen $\mathrm{d}\langle\hat{\Omega}\rangle/\mathrm{d}t = \langle[\hat{\Omega},\widehat{H}]\rangle$

One can also however work in an alternative picture, the *Heisenberg picture*, in which the quantum states are time-independent: $|\psi_H\rangle = U^{\dagger}(t,t_0)|\psi_S(t)\rangle = |\psi_S(t_0)\rangle$. The rational for this is that nothing really changes fundamentally in such a state, in particular the chance of obtaining energy E_n is constant. Clearly this state does *not* obey the TDSE or any equation giving evolution in time. However the results for the time-dependence of observables must be the same as before, so in the Heisenberg picture *operators* all carry time-dependence: $\Omega_H(t) = U^{\dagger}(t,t_0)\Omega_S U(t,t_0)$. Thus it is the time-dependence of the operator itself that is given by the commutator with $\widehat{H}$, ie $\frac{\mathrm{d}}{\mathrm{d}t}\hat{\Omega}_H = [\hat{\Omega}_H,\widehat{H}]$. (Note $\widehat{H}$ itself is clearly the same in both pictures, and only time-dependent if there are external forcing terms.)

The *interaction picture* is somewhere in between. As we have done throughout this section, we split the Hamiltonian into two parts, typically the “free” Hamiltonian $\widehat{H}^{(0)}$ which will be time-independent, and a (possibly time-dependent) “interaction” Hamiltonian $\widehat{H}^{(1)}$. We then work in a picture which would be Heisenberg's if $\widehat{H}^{(1)}$ vanished, but use the Schrödinger picture to include the effects of $\widehat{H}^{(1)}$. Thus

$$|\psi_I(t)\rangle = U^{(0)\dagger}(t,t_0)|\psi_S(t)\rangle = \sum_n d_n(t)|n\rangle \qquad \text{and} \qquad \Omega_I(t) = U^{(0)\dagger}(t,t_0)\Omega_S U^{(0)}(t,t_0)$$

with

$$i\hbar\tfrac{\mathrm{d}}{\mathrm{d}t}|\psi_I(t)\rangle = \widehat{H}_I^{(1)}|\psi_I(t)\rangle \qquad \text{and} \qquad \tfrac{\mathrm{d}}{\mathrm{d}t}\hat{\Omega}_I = [\hat{\Omega}_I, \widehat{H}_I^{(0)}]$$

Note that now we do have to specify $\widehat{H}_I^{(1)}(t) = U^{(0)\dagger}(t,t_0)H_S^{(1)}(t_0)U^{(0)}(t,t_0)$ because in general $[\widehat{H}^{(0)}, \widehat{H}_S^{(1)}] \neq 0$.

Concentrating on the time evolution of the state, we *define* $U_I(t,t_0)$ such that $|\psi_I(t)\rangle = U_I(t,t_0)|\psi_I(t_0)\rangle$. It is clear that this satisfies

$$i\hbar\tfrac{\mathrm{d}}{\mathrm{d}t}U_I(t,t_0) = \widehat{H}_I^{(1)}(t)U_I(t,t_0)$$

which is formally solved by

$$U_I(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} \widehat{H}_I^{(1)}(t')U_I(t',t_0)\mathrm{d}\,t'$$

(just differentiate both sides by t; the 1 comes from the initial condition that $U_I(t_0,t_0) = 1$.)

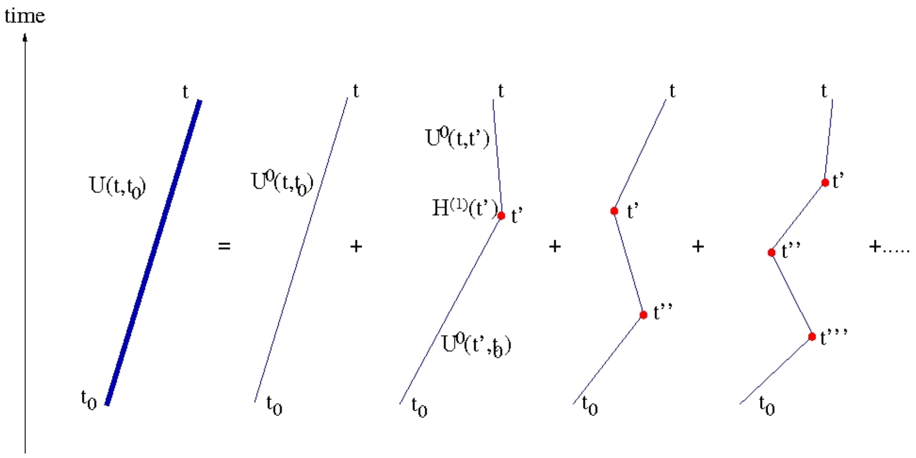
The utility of this comes if $H_I^{(1)}(t')$ is small, since we can then develop a perturbative sequence for U_I, the zeroth approximation being just 1, the first correction coming from substituting 1 for U_I in the integral, the second approximation from substituting the first approximation for U_I in the integral and so on:

$$\begin{aligned} U_I(t,t_0) &= 1 - \frac{i}{\hbar}\int_{t_0}^{t}\widehat{H}_I^{(1)}(t')\mathrm{d}\,t' - \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t'}\widehat{H}_I^{(1)}(t')\widehat{H}_I^{(1)}(t'')\mathrm{d}\,t'\mathrm{d}\,t'' \\ &\quad + \frac{i}{\hbar^3}\int_{t_0}^{t}\int_{t_0}^{t'}\int_{t_0}^{t''}\widehat{H}_I^{(1)}(t')\widehat{H}_I^{(1)}(t'')\widehat{H}_I^{(1)}(t''')\mathrm{d}\,t'\mathrm{d}\,t''\mathrm{d}\,t''' + \ldots \end{aligned}$$

Reverting to the Schrödinger picture, this reads

$$\begin{aligned} U(t,t_0) &= U^{(0)}(t,t_0)U_I(t,t_0) \\ &= U^{(0)}(t,t_0) - \frac{i}{\hbar}\int_{t_0}^{t}U^{(0)}(t,t')\widehat{H}_S^{(1)}(t')U^{(0)}(t',t_0)\mathrm{d}\,t' \\ &\quad - \frac{1}{\hbar^2}\int_{t_0}^{t}\int_{t_0}^{t'}U^{(0)}(t,t')\widehat{H}_S^{(1)}(t')U^{(0)}(t',t'')\widehat{H}_S^{(1)}(t'')U^{(0)}(t'',t_0)\mathrm{d}\,t'\mathrm{d}\,t'' \\ &\quad + \frac{i}{\hbar^3}\int_{t_0}^{t}\int_{t_0}^{t'}\int_{t_0}^{t''}U^{(0)}(t,t')\widehat{H}_S^{(1)}(t')U^{(0)}(t',t'')\widehat{H}_S^{(1)}(t'')U^{(0)}(t'',t''')\widehat{H}_S^{(1)}(t''')U^{(0)}(t''',t_0)\mathrm{d}\,t'\mathrm{d}\,t''\mathrm{d}\,t''' + .. \end{aligned}$$

where we have used the combination property of the unitary time-evolution operators, $U^{(0)}(t,t_0)U^{(0)\dagger}(t',t_0) = U^{(0)}(t,t')$ if t' is between t and t_0. We see that we have a picture where the free Hamiltonian $\widehat{H}^{(0)}$ governs the time evolution for most of the time, interrupted by interactions ($\widehat{H}^{(1)}$) on occasions, with multiple interactions being less progressively less likely. This is illustrated below. Note that eigenstates of $H_S^{(0)}$ remain so under the action of $U^{(0)}(t',t'')$: $U^{(0)}(t',t'')|n^{(0)}\rangle = \mathrm{e}^{-i(t'-t'')E_n^{(0)}/\hbar}|n^{(0)}\rangle$. So if the system starts off in a particular state $|i^{(0)}\rangle$ it will remain in it till it reaches the first interaction. At that point it can undergo a transition into any other state



$|n^{(0)}\rangle$ for which $\langle n^{(0)}|H^{(1)}|i^{(0)}\rangle \neq 0$. If we are looking for the probability that the system ends up in state $|f^{(0)}\rangle$ then in the first term in the expansion we need $i = f$, in the second we need them to be linked by $\langle f^{(0)}|H^{(1)}|i^{(0)}\rangle$, but in the third and subsequent terms the transition from $|i^{(0)}\rangle$ to $|f^{(0)}\rangle$ can be via one or more *intermediate states.* Energy does not have to be conserved in these intermediate steps, only in the overall transition: the system can "borrow" energy from the field for a short time, as reflected in the expression $\Delta E \Delta t \sim \hbar$. Exactly the same idea is behind the picture of elementary particles interacting via virtual particles, as depicted in Feynman diagrams.

This is a good opportunity to introduce the time-ordered exponential. If we introduce the *time-ordering* operator, such that $T\hat{A}(t)\hat{B}(t') = \hat{A}(t)\hat{B}(t')$ if $t' < t$ and $\hat{B}(t')\hat{A}(t)$ if $t' > t$ (and assuming they commute if $t' = t$), then we can write

$$\int_{t_0}^{t}\int_{t_0}^{t'} \widehat{H}(t')\widehat{H}(t'')\mathrm{d}\,t'\mathrm{d}\,t'' = \frac{1}{2}T\int_{t_0}^{t}\int_{t_0}^{t} \widehat{H}(t')\widehat{H}(t'')\mathrm{d}\,t'\mathrm{d}\,t'';$$

extending the t'' integral from t' to t generates terms in which the two Hamiltonians are in the wrong order but the T operator switches them so the net effect is that we over-count by a factor of two. Similarly with three factors we can extend the integrals to t but over count by 3!, and so on. Hence we can write

$$\begin{aligned} U_I(t,t_0) &= 1 - \frac{i}{\hbar}T\int_{t_0}^{t}\widehat{H}_I^{(1)}(t')\mathrm{d}\,t' - \frac{1}{2!}\frac{1}{\hbar^2}T\int_{t_0}^{t}\int_{t_0}^{t}\widehat{H}_I^{(1)}(t')\widehat{H}_I^{(1)}(t'')\mathrm{d}\,t'\mathrm{d}\,t'' \\ &\quad + \frac{1}{3!}\frac{i}{\hbar^3}T\int_{t_0}^{t}\int_{t_0}^{t}\int_{t_0}^{t}\widehat{H}_I^{(1)}(t')\widehat{H}_I^{(1)}(t'')\widehat{H}_I^{(1)}(t''')\mathrm{d}\,t'\mathrm{d}\,t''\mathrm{d}\,t''' + \ldots \\ &= T\exp\left(\frac{i}{\hbar}\int_{t_0}^{t}\widehat{H}_I^{(1)}(t')\mathrm{d}\,t'\right). \end{aligned}$$

Identical algebra is used in writing the full evolution operator as $U(t,t_0) = T\exp\left(\frac{i}{\hbar}\int_{t_0}^{t}\widehat{H}(t')\mathrm{d}\,t'\right)$ as was asserted in section 1.2.

- **(Gasiorowicz ch 16.3)**
- **Shankar ch 18.3**
- **Townsend ch 14.5**

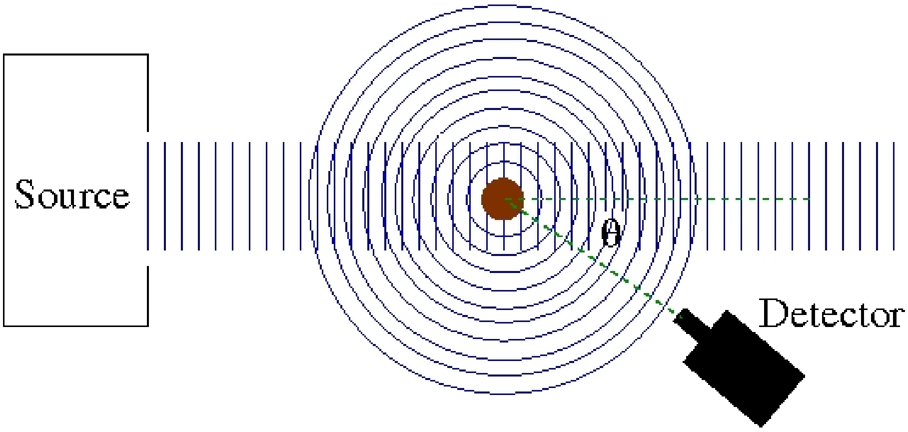
Approximate methods IV: Scattering theory

5.1 Preliminaries

Summary: Scattering experiments provide us with almost all the information we have about the nature of sub-atomic matter. Here we will only consider elastic scattering.

All we know about the structure of sub-atomic matter comes from scattering experiments, starting with Rutherford's discovery of the nucleus right up to the Tevatron and LHC. In this course we will introduce the main ideas, but largely confine ourselves to elastic scattering of particles from a fixed, localised potential $V(\mathbf{r})$; this is the limit of two-body scattering where one particle (the projectile) is much lighter than the other (the stationary target). We will be looking for the probability that the particle is scattered away from its original direction.

A careful approach would involve a wavepacket for the projectile, and the problem would involve a fully time-dependent approach as the wavepacket aproached the scattering centre, interacted with it and then moved away out of its influence. An easier approach is to use an incident plane wave to represent a coherent beam of particles of fixed momentum; the wavepacket aproach must give the same results in the limit that the momentum spread in the packet is small. The lateral spread of the wavefronts will be large compared to the range of $V(\mathbf{r})$ but small compared to the perpendicular distance from the beam to the detector, so that unless we put the detector directly in the line of the beam, we will only detect scattered particles.



We define the scattering *cross section* as the rate of particles scattered from the field divided by the incoming flux. Since the units of flux are particles per second per metre^2, the cross section has units of area. This has an obvious geometric interpretation. (The non-SI units of cross-section used in particle physics are barns, where 1 barn is 10^{-28} m^2 - that's as in "barn door", something you can't miss!) We are often interested in angular distributions too – they are rarely isotropic as depicted above – so then we are interested in the scattering rate into a given solid angle. Conventionally θ measures the angle from the beam direction, as shown above, and ϕ the angle in a plane perpendicular to the beam direction.

An infinitesimal solid angle, spanned by infinitesimal range of θ and ϕ, is $\mathrm{d}\Omega = \sin\theta \mathrm{d}\theta \mathrm{d}\phi$. If we have a detector at distance r with a (small) opening of area $\mathrm{d}S$ facing the scattering source it subtends a solid angle $\mathrm{d}\Omega = \mathrm{d}S/r^2$. If the scattering rate into this detector divided by the initial flux is denoted $\mathrm{d}\sigma$, the *differential cross section* is $\mathrm{d}\sigma/\mathrm{d}\Omega$. Obviously $\int(\mathrm{d}\sigma/\mathrm{d}\Omega)\mathrm{d}\Omega = \sigma$ if the integral is taken over all angles.

Outside the range of $V(\mathbf{r})$ the scattered particles are free and have the same energy as initially (elastic scattering). The wavefunction must satisy Schrödinger's equation which can be written $(\nabla^2 + k^2)\psi_{\rm sc} = 0$ (with $\hbar^2k^2/2m = E$). Now we know that $\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}$ is a plane wave solution of this, but we are looking for outgoing waves emanating from the centre. These are spherical harmonics times *spherical Bessel functions*, and have the asymptotic form (as $r \to \infty$)

$$\psi_{\rm sc} \to \sum_{lm} A_{lm}(k) Y_l^m(\theta,\phi)\frac{\mathrm{e}^{ikr}}{r} = f(k,\theta,\phi)\frac{\mathrm{e}^{ikr}}{r}$$

The function $f(k,\theta,\phi)$ is called the scattering amplitude - note it has dimensions of length. (The fact that as $r \to \infty$ the radial wavefunction doesn't depend on l can be seen from the fact that $\nabla^2 \to \mathrm{d}^2/\mathrm{d}r^2$; the angular part falls off as $1/r^2$.)

The flux in this wave is

$$\frac{\hbar}{2im}(\psi^*_{\rm sc}\nabla\psi_{\rm sc} - \psi_{\rm sc}\nabla\psi^*_{\rm sc}) \overset{r\to\infty}{\longrightarrow} |f(k,\theta,\phi)|^2 \frac{\hbar k}{mr^2}\hat{\mathbf{r}}$$

which is indeed outgoing (had we chosen e^{-ikr} it would have been ingoing). If we have a detector with a (small) opening of area $r^2\mathrm{d}\Omega$ facing the scattering source the rate of particles hitting it is $|f(\theta,\phi)|^2(\hbar k/m)\mathrm{d}\Omega$. Since the flux in the beam wave $\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}$ is $\frac{\hbar k}{m}$, we have

$$\mathrm{d}\sigma = |f(k,\theta,\phi)|^2 \mathrm{d}\Omega \qquad \text{and} \qquad \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f(k,\theta,\phi)|^2$$

So the scattering amplitude squared is the differential cross section. Now all we have to do is calculate it!

- **Gasiorowicz ch 19.1,**
- **Mandl ch 11.1**
- **Shankar ch 19.1,2**
- **Townsend ch 13.1**

5.2 The Born approximation

Summary: If the potential is weak, we can use first order perturbation theory to calculate cross sections.

If the scattering potential $V(\mathbf{r})$ is weak, we can ignore multiple interactions and use first-order perturbation theory. In this context, this is called the *Born approximation.*

First order time-dependent perturbation theory means using Fermi's golden rule. $V(\mathbf{r})$ is constant, not oscillatory, so the energy-conservation δ-function links incoming and scattering states with the same energy, hence we are dealing with elastic scattering (as already assumed). Our goal is to calculate $\mathrm{d}\sigma/\mathrm{d}\Omega$, so we are interested in all the out-going momentum states which fall within $\mathrm{d}\Omega$ at a given scattering angle $\{\theta, \phi\}$:

$$\begin{aligned}
R_{\mathbf{k}_i\to\mathrm{d}\Omega} &= \sum_{\mathbf{k}_f\in\mathrm{d}\Omega} \tfrac{2\pi}{\hbar} \left|\langle\mathbf{k}_f|V(\mathbf{r})|\mathbf{k}_i\rangle\right|^2 \delta(E_i - E_f) \\
&= \frac{2\pi}{\hbar}\int_0^\infty \left|\langle\mathbf{k}_f|V(\mathbf{r})|\mathbf{k}_i\rangle\right|^2 \delta\left(\frac{\hbar^2}{2m}(k_f^2 - k_i^2)\right) D(\mathbf{k}_f) d\Omega \mathrm{d}k_f \\
&= \frac{mV}{4\pi^2\hbar^3} k_f \left|\langle\mathbf{k}_f|V(\mathbf{r})|\mathbf{k}_i\rangle\right|^2 \mathrm{d}\Omega \\
\Rightarrow \mathrm{d}\sigma &= \frac{m^2V^2}{4\pi^2\hbar^4} \left|\langle\mathbf{k}_f|V(\mathbf{r})|\mathbf{k}_i\rangle\right|^2 \mathrm{d}\Omega \\
\Rightarrow |f(k,\theta,\phi)| &= \frac{m}{2\pi\hbar^2}\int \mathrm{e}^{i(\mathbf{k}_i-\mathbf{k}_f)\cdot\mathbf{r}} V(\mathbf{r})\mathrm{d}^3r
\end{aligned}$$

(Since the density of states is for single particles, we adjusted the normalisation of the incoming beam to also contain one particle in volume V; hence V drops out. For the density of states, see A.10. For transforming the argument of delta functions, see A.8.)

Writing $\mathbf{k}_i - \mathbf{k}_f = \mathbf{q}$, the momentum transfered from the initial to the final state, we have the very general result that $f(k, \theta, \phi)$ is just proportional to $\tilde{V}(\mathbf{q})$, the Fourier transform of $V(\mathbf{r})$.

The classic application is Rutherford scattering, but we will start with a Yukawa potential $V(r) = -\lambda\mathrm{e}^{-\mu r}/r$; the Coulomb potential is the $\mu \to 0$ limit. Taking the z-axis along q for the spatial integration (this is quite independent of the angles used in defining the scattering direction) and noting that $q = 2k\sin(\theta/2)$, we get

$$\begin{aligned}
|f(k,\theta,\phi)| &= \frac{m}{2\pi\hbar^2}\int \mathrm{e}^{iqr'\cos\theta'}\lambda\mathrm{e}^{-\mu r'} r' \sin\theta' \mathrm{d}\theta' \mathrm{d}\phi' \mathrm{d}r' \\
&= \frac{2m\lambda}{\hbar^2(\mu^2+q^2)} \\
\Rightarrow \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} &= \frac{4m^2\lambda^2}{\hbar^4(\mu^2+4k^2\sin^2(\theta/2))^2} \\
\Rightarrow \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}_{\mathrm{Coulomb}} &= \frac{\hbar^2c^2\alpha^2}{16E^2\sin^4(\theta/2)}
\end{aligned}$$

We note that the independence of ϕ is quite general for a spherical potential.

This result, though derived at first-order, is in fact correct to all orders and agrees with the classical expression, which is called the Rutherford cross section. (Just as well for Rutherford!) (The apearance of $\hbar$ is only because we have written e^2 in terms of α.) The reason we took the limit of a Yukawa is that our formalism doesn't apply to a Coulomb potential, because there is no asymptotic region - the potential is infinite ranged. The cross section blows up at $\theta = 0$, the forward direction, but obviously we can't put a detector there as it would be swamped by the beam.

- **Gasiorowicz ch 19.3**

- (**Mandl ch 11.3**)
- **Shankar ch 19.3**
- (**Townsend ch 13.2**)

(The references in brackets do not use the FGR to obtain the Born cross section.)

5.3 Phase Shifts

Summary: Scattering experiements in the real world yield complicated differential cross sections. If the behaviour for (imagined) incoming particles of definite angular momentum can be deduced from the angular dependence, it is easier to recognise what the results are telling us about the potential.

An important concept in scattering is that of *phase shifts*. The basic idea is that since angular momentum is conserved by a spherically symmetric potential $V(r)$, if the incoming wave were an eigenfunction of angular momentum, so would the outgoing wave. This would be the case independently of the potential, and the only influence of the potential would be on the relative phase of the outgoing wave compared to the incoming wave. Since this is a set-up which cannot be experimentally realised it might seem a pointless observation, until you recognise that a plane wave must be expressible as a sum of such angular momentum eigenstates which are called *partial waves*. In practice it is often the case, for a short-ranged potential, and an incoming wave which is not too high energy, that only the lowest partial waves are significantly scattered. Classically, for a particle with momentum p, the closest approach is $d = L/p$. If a is the range of the potential, then only particles with $L \lesssim pa$ (or $l \lesssim ka$) will be scattered. Thus the first few phase shifts can be an efficient way of describing low-energy scattering data.

Let us recall that for a free particle in spherical coordinates the seperable solutions are $\psi = R_l(r)Y_{lm}(\theta, \phi)$, where the radial wavefunction satisfies

$$\frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2} rR_l(r) - \frac{l(l+1)}{r^2}R_l(r) + k^2 R_l(r) = 0$$

whose solutions are spherical Bessel functions, the regular ones $j_l(kr)$ and the irregular ones $n_l(kr)$; the latter blow up at the orgin. For example $j_0(z) = \sin z/z$, $n_0(z) = -\cos z/z$ and $j_1 = \sin z/z^2 - \cos z/z$. Note that all tend to either $\pm \sin z/z$ or $\pm \cos z/z$ at large z. Specifically,

$$j_l(z) \xrightarrow{z\to\infty} \frac{\sin(z - \pi l/2)}{z} \qquad n_l(z) \xrightarrow{z\to\infty} -\frac{\cos(z - \pi l/2)}{z}$$

It can be shown that the expansion of a plane wave in spherical coordinates is

$$\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} = \mathrm{e}^{ikr\cos\theta} = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr) P_l(\cos\theta) \xrightarrow{r\to\infty} \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)\left(\frac{\mathrm{e}^{ikr}}{r} - (-1)^l \frac{\mathrm{e}^{-ikr}}{r}\right) P_l(\cos\theta)$$

where the $P_l(\cos\theta)$ are Legendre polynomials (proportional to Y_l^0). Fairly obviously, for each partial wave the plane wave consists of both outgoing and incoming waves with equal and opposite flux. (Further notes on this expression and on spherical Bessel functions can be found in A.6; see also Gasiorowicz Supplement 8-B.)

Now consider the case in the presence of the potential. Close to the centre, the wave is not free and can't be described by spherical Bessel functions. But beyond the range of the potential, it can. Furthermore $n_l(kr)$ can enter since the origin isn't included in the region for which this description can hold. The general form will be

$$\begin{aligned}\psi_k(r,\theta) &= \sum_{l=0}^{\infty} \left(C_l j_l(kr) + D_l n_l(kr)\right) P_l(\cos\theta) = \sum_{l=0}^{\infty} A_l \left(\cos\delta_l j_l(kr) - \sin\delta_l n_l(kr)\right) P_l(\cos\theta) \\ &\xrightarrow{r\to\infty} \sum_{l=0}^{\infty} A_l \frac{\sin(kr - \pi l/2 + \delta_l)}{kr} P_l(\cos\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (-i)^l A_l \left(\frac{\mathrm{e}^{ikr+i\delta_l}}{r} - (-1)^l \frac{\mathrm{e}^{-ikr-i\delta_l}}{r} \right) P_l(\cos\theta).\end{aligned}$$

The coeffients C_l and D_l can be taken to be real (since the wave equation is real), $A_l = \sqrt{C_l^2 + D_l^2}$ and $\tan\delta_l = -D_l/C_l$. The magnitudes of the incoming and outgoing waves are thus again equal.

Now we need to match the incoming waves with the plane waves, since that's the bit we control; hence $(-i)^l A_l \mathrm{e}^{-i\delta_l} = (2l+1)$. So finally

$$\begin{aligned}\psi_k(r,\theta) &\xrightarrow{r\to\infty} \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) \left(\mathrm{e}^{2i\delta_l} \frac{\mathrm{e}^{ikr}}{r} - (-1)^l \frac{\mathrm{e}^{-ikr}}{r} \right) P_l(\cos\theta) \\ &= \mathrm{e}^{ikr\cos\theta} + \sum_{l=0}^{\infty} (2l+1) \left(\mathrm{e}^{2i\delta_l} \frac{\mathrm{e}^{ikr}}{r} + \frac{\mathrm{e}^{ikr}}{r} \right) P_l(\cos\theta) \\ \Rightarrow f(k,\theta) &= \sum_{l=0}^{\infty} (2l+1) \frac{\mathrm{e}^{i\delta_l} \sin\delta_l}{k} P_l(\cos\theta)\end{aligned}$$

Because of the orthogonality of the $P_l(\cos\theta)$, the cross section can also be written as a sum over partial cross sections

$$\sigma = \int |f(k,\theta)|^2 \mathrm{d}\Omega = \sum_{l=0}^{\infty} \sigma_l = \sum_{l=0}^{\infty} \frac{4\pi}{k^2} (2l+1) \sin^2\delta_l$$

As argued at the start, this depends only on the phase shifts δ_l.

The significance of δ_l can be appreciated if we compare the asymptotic form of the radial wavefunction in the presence and absence of the potential; without we have $\sin(kr - l\pi l/2)/r$ but with the potential we have $\sin(kr - \pi l/2 + \delta_l)/r$. So δ_l is just the phase by which the potential shifts the wave compared with the free case.

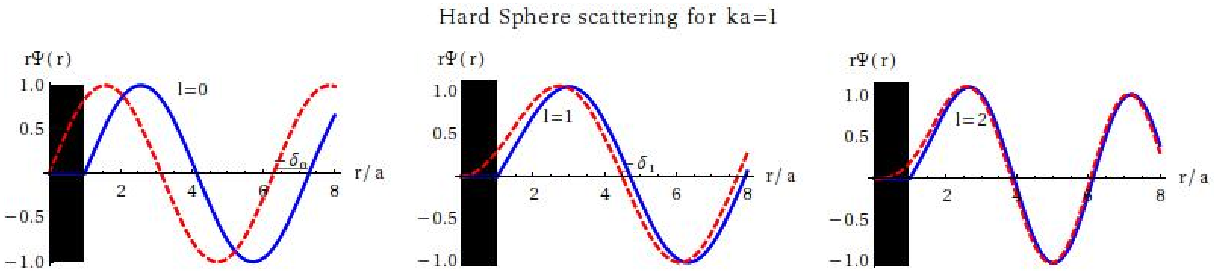
- **Gasiorowicz ch 19.2**
- **Mandl ch 11.5**
- **Shankar ch 19.5**
- **Townsend ch 13.4,5**

5.3.1 Hard sphere scattering

For hard sphere scattering, the potential is infinite for $r < a$ and zero for $r > a$. The free form of the wavefuntion therefore holds for all $r > a$, and the wavefunction must vanish at the surface ($r = a$). Since the partial waves are all independent, this means each partial wave must vanish at $r = a$, ie $C_l j_l(ka) + D_l n_l(ka) = 0$. Thus

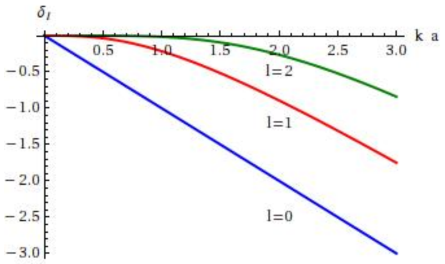
$$\delta_l \equiv \arctan\left(-\frac{D_l}{C_l}\right) = \arctan\left(\frac{j_l(ka)}{n_l(ka)}\right)$$

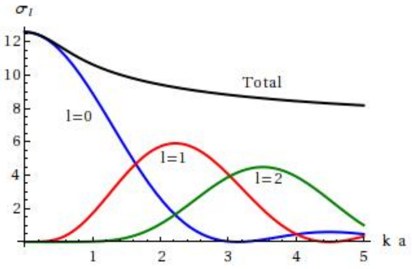
For $l = 0$ this is very simple: $\delta_0 = -ka$. For higher l it has to be solved numerically.



In this figure above we see the corresponding wave functions, blue with the potential and red (dashed) in its absence. The phase shifts δ_l are the displacements between the two.

The graph below shows the phase-shifts and cross sections for this case.





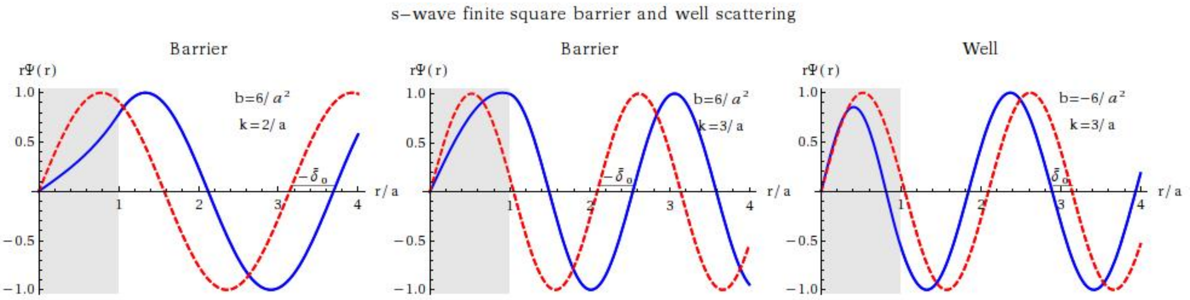
The fact that the phase-shifts are negative indicates a repulsive potential. The fact that the phase-shifts and cross sections don't tend to zero as $k \to \infty$ is atypical, and comes from the potential being infinite - we can't use the Born approximation here either.

Since as $z \to 0$, $j_l(z)/n_l(z) \sim z^{2l+1}$, in the low-energy limit $ka \ll 1$ all higher phase shifts are negligible. Then $\sigma \approx \sigma_0 = 4\pi a^2 \mathrm{sinc}^2(ka)$ which tends to 4 times the classical limit of πa^2. In the high-energy limit $ka \gg 1$, all phase shifts up to $l \sim ka$ will be significant, and if there are enough of them the average value of $\sin^2 \delta_l$ will just be $\frac{1}{2}$. Then we have $\sigma = \frac{2\pi a^2}{(ka)^2} \sum_{l=0}^{ka}(2l+1) \to 2\pi a^2$. We might have expected πa^2 in this, the classical, limit, but wave optics actually predicts the factor of 2, a phenomenon related to Poisson's spot.

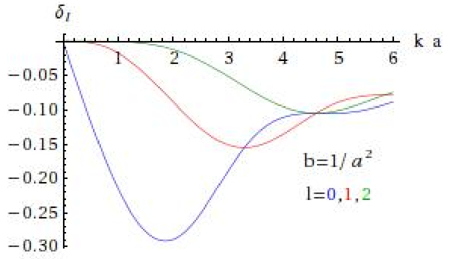
5.3.2 Scattering from a finite square barrier or well

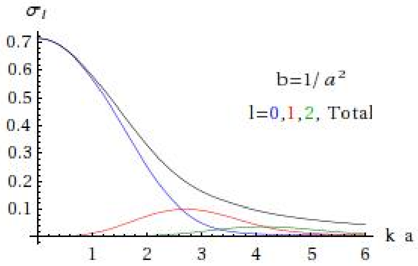
Here we are dealing with $V(r) = 0$ for $r > a$, and $V(r) = V_0$ for $r < a$, where V_0 can be greater than zero (a barrier, repulsive) or less (a well, attractive). It will be useful to define the quantity $b = 2mV_0/\hbar^2$, which has dimesions of inverse length squared. Note that as we are working in 3D the wells and barriers are all spherical.

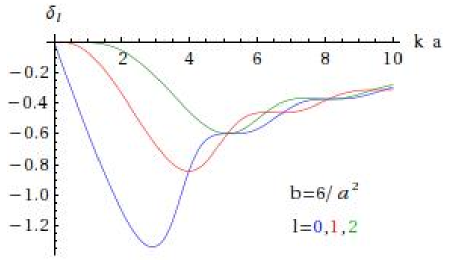
In this case the wave function will again be $C_l j_l(kr) + D_l n_l(kr)$ for $r > a$, and again $\delta_l = \arctan(-D_l/C_l)$. However this time the wave function for $r < a$ doesn't vanish, but has the form $A_l j_l(k'r)$ where $k' = \sqrt{k^2 - b}$ and we find D_l/C_l by matching the wave function and its derivative at $r = a$. Examples of the resulting wavefunctions are shown below, first for a barrier with $k < \sqrt{b}$, then a barrier with $k > \sqrt{b}$, then a well. As before blue indicates the wavefuntion in the presence of the potential and red (dashed) in its absence. In the first two cases the repulsive barrier "pushes the wave outwards" and the phase-shift is negative, in the third the well "draws the wave inwards" and the phase-shift is positive. (Note: what is marked as "δ" on the plots is actually δ/ka — a given distance on the graph will represent a larger phase shift if λ is small.)

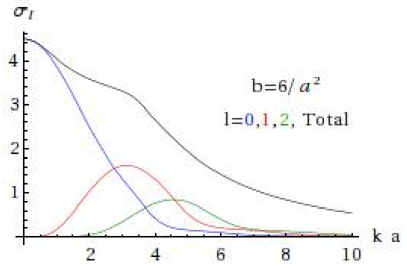


The next two pictures show phase-shifts and cross sections for repulsive potentials (barriers), with the lower one being stronger that the upper one. As expected the phase-shifts start at zero and are negative; as in the hard-sphere case the magnitudes grow initially, but as k increases the barrier gradually becomes less and less significant and the phase-shifts and cross sections fall off to zero.

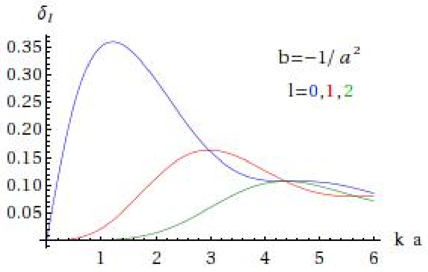


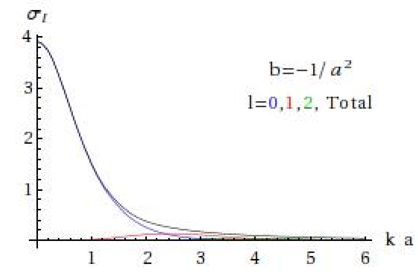


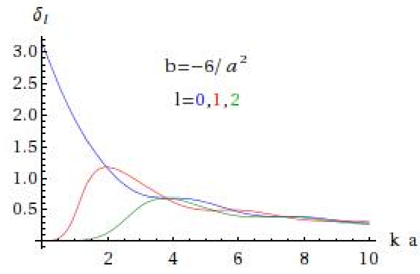


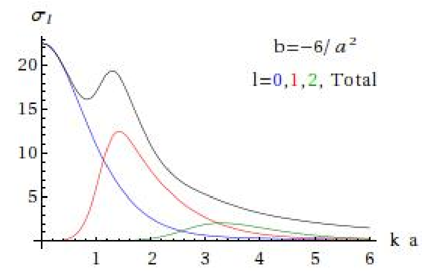


The next two pictures show attractive potentials, and as expected the phase shifts are positive and they and the cross sections fall to zero as $k \to \infty$. For the weaker well (top) the

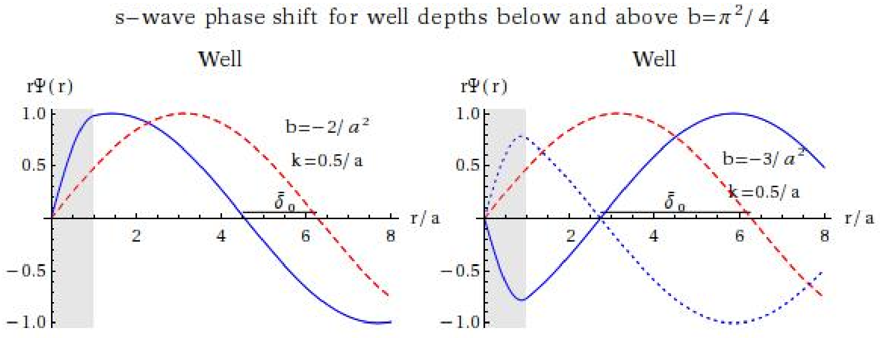




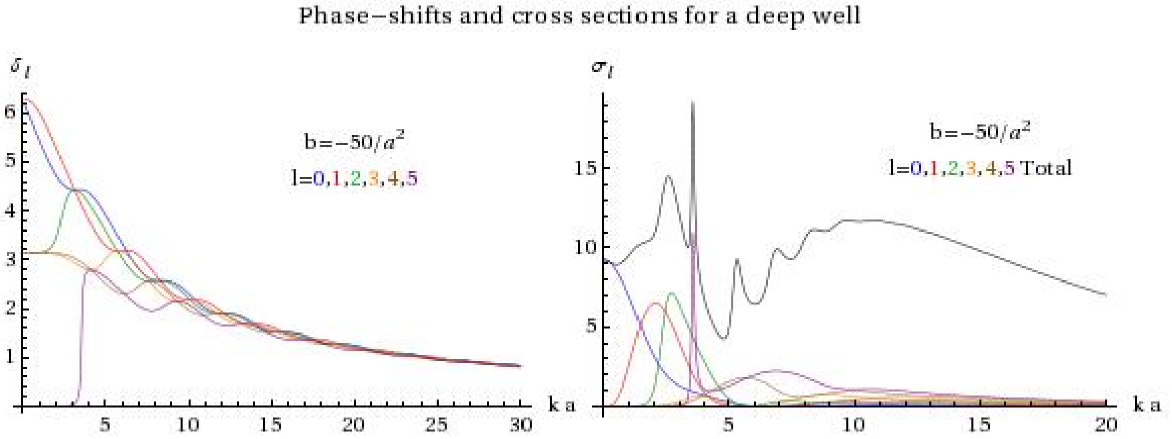




phase shifts start at zero at $k = 0$ as expected, but for the stronger well the s-wave phase-shift has jumped to π. Why is this? First, we should remember that since we determined δ via an arctangent, it was ambiguous up to a multiple of π. (Another way of seeing that is to recognise that the wave function itself is only defined up to an overall sign.) The correct value can be determined by examining pictures of wavefunctions (if we know the exact solutions as here), or by requiring δ to be a continuous function of k, falling to zero as $k \to \infty$. Below the wave functions are shown for low k and well depths either side of the critical value; in the second $-\psi$ is shown by the blue dotted line, and it is this which when compared with the red dashed line gives a positive phase shift of more than $\pi/2$ (rather than a smaller negative shift of $\delta - \pi$). What determines the critical value? A finite square well in 3D has an s-wave

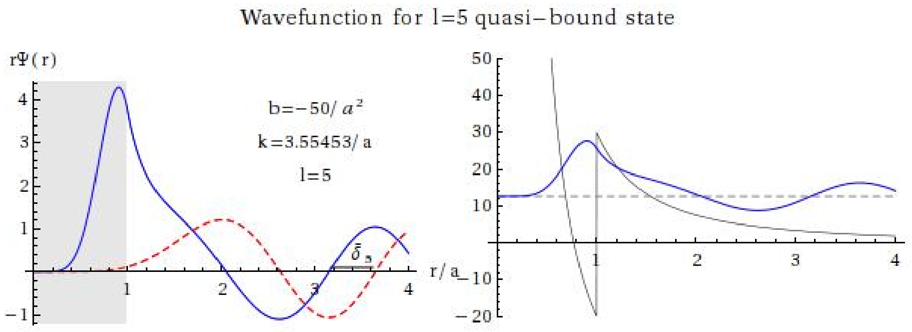


zero-energy bound-state (i.e. states that would be bound if the well were infinitesimally deeper) if $\sqrt{b} = (2n + 1)\pi/2a$, $n = 0, 1, 2 \ldots$. The lowest of these is $b = 2.467/a^2$, and that is the value at which the phase shift at $k = 0$ jumps from 0 to π. This is an example of Levinson's theorem, which says that for well-behaved finite-range potentials the value of the phase-shift δ_l at the origin is $n\pi$ where n is the number of bound states of the potential with angular momentum l. This is an example of how we can obtain information about the potential from scattering. This plot shows a much deeper well. From this we can deduce that for $b = -50/a^2$ there are two bound states with $l = 0$, two with $l = 1$, one each with $l = 2$, 3 and 4, but none with $l = 5$



(or higher). We can also see that for k greater than around $5/a$ the partial wave description becomes too cumbersome - dozens of partial waves have to be included to reproduce the cross section - far more than could realistically be deduced from experiment.

The plot above also suggests that something interesting is happening around $k = 3.5/a$, where there is a very sharp peak in the cross section. It comes from the $l = 5$ partial wave, where the phase-shift rises very rapidly from around 0 to nearly π. Since the cross section is proportional to $\sin^2 \delta_l$ we see that it will rise and fall rapidly over the region in k, peaking at $\delta_l = \pi/2$. What is happening here is suggested by the next plot, of the $l = 5$ wave function: We can see that for $l > 0$, the combination of the square well and the centrifugal barrier allows for quasi-bound states to form with energies greater than zero — very similar to the situation with radioactive decay, in which α particles were trapped for a time by the Coulomb repulsion (see 2.4.2). When we send in a beam of particles, they will tend to get trapped and the wave function within the well will be large. This is called a *resonance*. We can't see the wavefunction, of course, but the clue is in the phase shift, which rises rapidly through $\pi/2$ as we scan the energy across the peak. As a function of k, the phase shift and cross section will have the form

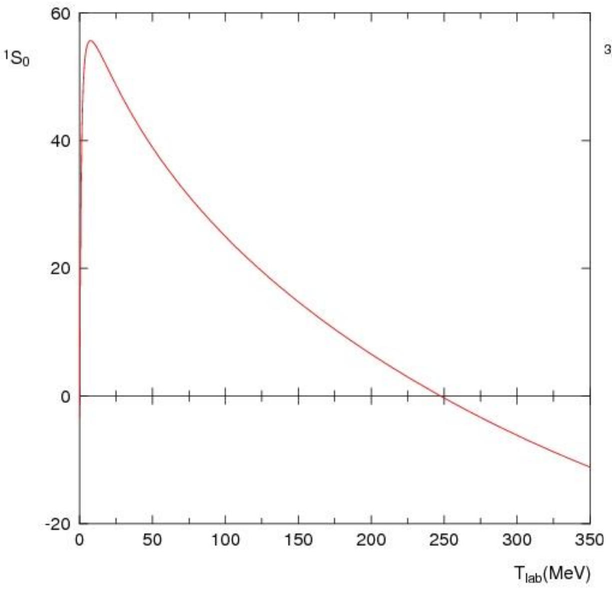


$$\delta_l = \delta_b + \arctan\left(\frac{\Gamma/2}{E_r - E}\right) \qquad \sigma_l = \frac{4\pi}{k^2}\frac{\Gamma^2/4}{(E-E_r)^2 + \Gamma^2/4}$$

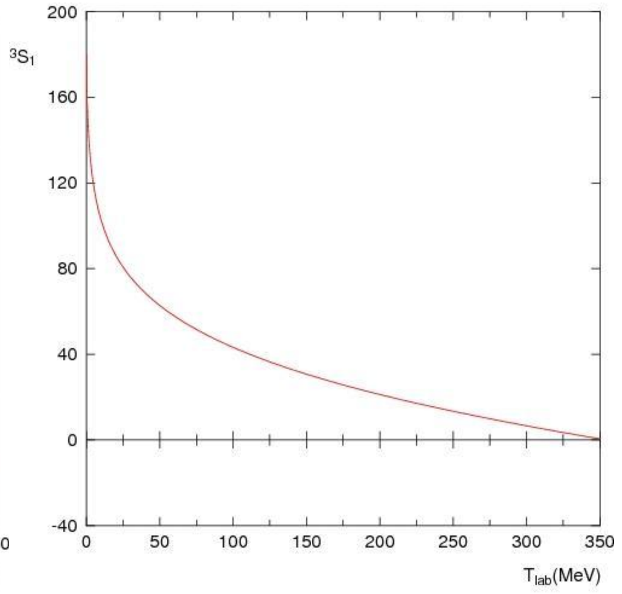
This is a Lorentzian (ignoring the relatively slowly varying factor of k^{-2}) and in the context of scattering it is termed a *Breit-Wigner* curve. The width Γ gives the lifetime of the quasi-bound state.

The phase shift is very useful for distinguishing random bumps in the cross section from true resonances. For instance when b is just too low for there to be a zero-energy s-wave bound state there will be a significant bump in the cross section, but it is not a resonance: there is no centrifugal barrier to trap the particles. (Many text-books fudge this issue, since $l > 0$ is hard to deal with analytically. The correct term for a not-quite-bound state is a virtual state.) In the plot for $b = -50$, we can see a number of bumps; the one at $ka \approx 2.5$ might be a d-wave virtual state, but only the really sharp peak at $ka \approx 3.5$ is a resonance. Examples of resonances in particle physics are the Δ, a sort of excited proton, which shows up very strongly in p-wave πN scattering, and the Z-boson which was seen in e^+e^- scattering at LEP.

Low-energy nucleon-nucleon scattering shows nice examples of both resonances and virtual states: The phase shift is given in degrees. (Note the potential is more complicated than a square well!). In the proton-proton channel there is a virtual state, but no resonance or bound state. If the nuclear force were a little stronger perhaps di-protons could exist. In the neutron-proton channel though the phase shift starts at π (180°) indicating the presence of a bound state — the deuteron. (Plots are from the Nijmegen phase shift analysis of nucleon-nucleon scattering.) The fact that the phase shift starts to go negative at high-enough energy suggests that there is a repulsive hard core to the interaction (as indeed we know from the size of nuclei that there must be).

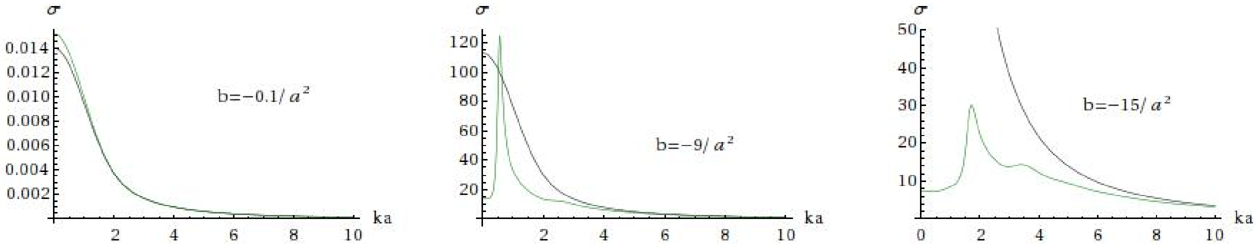


pp phaseshift $^1S_0$



np phaseshift $^3S_1$

It can be shown (see examples) that the Born approximation is good for high-enough energy scattering ($k \gg ba$), and the shallower the well the greater its domain of validity till if $ba^2 \ll 1$ it will be good everywhere. In the latter case the potential will not have any bound states or resonances. Where the Born approximation breaks down, it is clear that multiple interactions must be important (see 4.7).


Exact vs Born cross sections

Quantum Measurement

6.1 The Einstein-Poldosky-Rosen "paradox" and Bell's inequalities

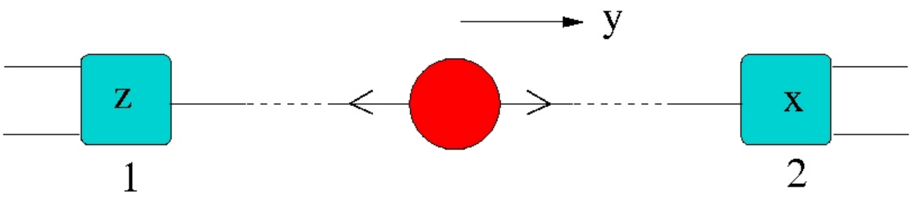
Summary: This section is about nothing less important than "the nature of reality"!

In 1935 Einstein, along with Boris Poldosky and Nathan Rosen, published a paper entitled "Can quantum-mechanical description of physical reality be considered complete?" By this stage Einstein had accepted that the uncertainty principle did place fundamental restrictions on what one could discover about a particle through measurements conducted on it. The question however was whether the measuring process actually somehow brought the properties into being, or whether they existed all along but without our being able to determine what they were. If the latter was the case there would be "hidden variables" (hidden from the experimenter) and the quantum description—the wave function—would not be a complete description of reality. Till the EPR paper came out many people dismissed the question as undecidable, but the EPR paper put it into much sharper focus. Then in 1964 John Bell presented an analysis of a variant of the EPR paper which showed that the question actually was decidable. Many experiments have been done subsequently, and they have come down firmly in favour of a positive answer to the question posed in EPR's title.

The original EPR paper used position and momentum as the two properties which couldn't be simultaneously known (but might still have hidden definite values), but subsequent discussions have used components of spin instead, and we will do the same. But I will be quite lax about continuing to refer to "the EPR experiment".

There is nothing counter-intuitive or unclassical about the fact that we can produce a pair of particles whose total spin is zero, so that if we find one to be spin-up along some axis, the other must be spin down. All the variants of the experiment to which we will refer can be considered like this: such a pair of electrons is created travelling back-to-back at one point, and travel to distant measuring stations where each passes through a Stern-Gerlach apparatus (an "SG") of a certain orientation in the plane perpendicular to the electrons' momentum.

As I say there is nothing odd about the fact that when the two SGs have the same orientation the two sequences recorded at the two stations are perfectly anti-correlated (up to measurement errors). But consider the case where they are orientated at 90° with respect to each other as below: Suppose for a particular pair of electrons, we measure number 1 to be spin up in the z-direction and number 2 to be spin down in the x-direction. Now let's think about what *would have happened* if we had instead measured the spin in the x-direction of particle 1. Surely, say EPR, we know the answer. Since particle 2 is spin down in the x-direction, particle 1 would have been spin up. So now we know that before it reached the detector, particle 1 was spin up



in the z-direction (because that's what we got when we measured it) and also spin up in the x-direction (because it is anti-correlated with particle 2 which was spin down). We have beaten the uncertainty principle, if only retrospectively.

But of course we know we can't construct a wave function with these properties. So is there more to reality than the wave function? Bell's contribution was to show that the assumption that the electron really has definite values for different spin components—if you like, it has an instruction set which tells it which way to go through any conceivable SG that it might encounter—leads to testable predictions.

For Bell's purposes, we imagine that the two measuring stations have agreed that they will set their SG to one of 3 possible settings. Setting A is along the z-direction, setting C is along the x direction, and setting B is at 45° to both. In the ideal set-up, the setting is chosen just before the electron arrives, sufficiently late that no possible causal influence (travelling at not more than the speed of light) can reach the other lab before the measurements are made. The labs record their results for a stream of electrons, and then get together to classify each pair as, for instance, $(A\uparrow, B\downarrow)$ or $(A\uparrow, C\uparrow)$ or $(B\uparrow, B\downarrow)$ (the state of electron 1 being given first). Then they look at the number of pairs with three particular classifications: $(A\uparrow, B\uparrow)$, $(B\uparrow, C\uparrow)$ and $(A\uparrow, C\uparrow)$. Bell's inequality says that, if the way the electrons will go through any given orientation is set in advance,

$$N(A\uparrow, B\uparrow) + N(B\uparrow, C\uparrow) \geq N(A\uparrow, C\uparrow)$$

where $N(A\uparrow, B\uparrow)$ is the number of $(A\uparrow, B\uparrow)$ pairs etc.

Now let's prove that.

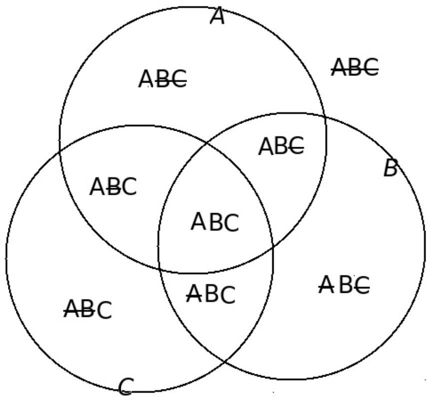
Imagine any set of objects (or people!) with three distinct binary properties a, b and c—say blue or brown eyes, right or left handed, and male or female (ignoring messy reality in which there are some people not so easily classified). In each case, let us denote the two possible values as A and $\overline{A}$ etc ($\overline{A}$ being "not A" in the sense it is used in logic). Then every object is classified by its values for the three properties as, for instance, ABC or $A\overline{BC}$ or $\overline{A}BC\ldots$. The various possibilities are shown on a Venn diagram below (sorry that the bars are through rather than over the letters...) In any given collection of objects, there will be no fewer than zero objects in each subset, obviously. All the Ns are greater than or equal to zero. Now we want to prove that the number of objects which are $A\overline{B}$ (irrespective of c) plus those that are $B\overline{C}$ (irrespective of a) is greater than or equal to the number which are $A\overline{C}$ (irrespective of b):

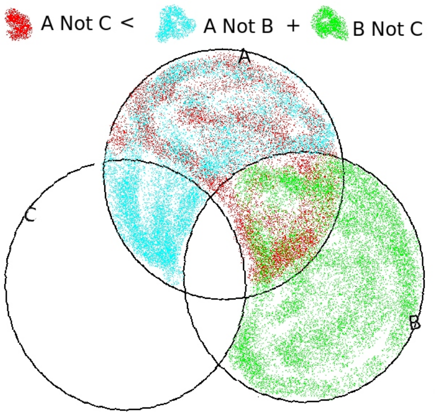
$$N(A\overline{B}) + N(B\overline{C}) \geq N(A\overline{C})$$

This is obvious from the diagram below, in which the union of the blue and green sets fully contains the red set.

A logical proof is as follows:

$$\begin{aligned} N(A\overline{B}) + N(B\overline{C}) &= N(A\overline{B}C) + N(A\overline{BC}) + N(AB\overline{C}) + N(\overline{A}B\overline{C}) \\ &= N(A\overline{B}C) + N(A\overline{C}) + N(\overline{A}B\overline{C}) \geq N(A\overline{C}) \end{aligned}$$





To apply to the spins we started with, we identify A with $A\uparrow$ and $\overline{A}$ with $A\downarrow$. Now if an electron is $A\uparrow B\downarrow$ (whatever C might be) then its partner must be $A\downarrow B\uparrow$, and so the result of a measurement A on the first and B on the second will be $(A\uparrow, B\uparrow)$. Hence the inequality for the spin case is a special case of the general one. We have proved Bell's inequality assuming, remember, that the electrons really do have these three defined properties even if, for a single electron, we can only measure one of them.

Now let's consider what quantum mechanics would say. We first remind ourselves of the relation between the spin-up and spin-down states for two directions:

$$\begin{aligned} |\theta,\uparrow\rangle &= \cos\tfrac{\theta}{2}|0,\uparrow\rangle + \sin\tfrac{\theta}{2}|0,\downarrow\rangle & \qquad |0,\uparrow\rangle &= \cos\tfrac{\theta}{2}|\theta,\uparrow\rangle - \sin\tfrac{\theta}{2}|\theta,\downarrow\rangle \\ |\theta,\downarrow\rangle &= -\sin\tfrac{\theta}{2}|0,\uparrow\rangle + \cos\tfrac{\theta}{2}|0,\downarrow\rangle & \qquad |0,\downarrow\rangle &= \sin\tfrac{\theta}{2}|\theta,\uparrow\rangle + \cos\tfrac{\theta}{2}|\theta,\downarrow\rangle \end{aligned}$$

where θ is the angle between the orientation of the two axes. For A and B or for B and C $\theta = 45°$; for A and C it is $90°$.

Consider randomly oriented spin-zero pairs and settings A, B and C equally likely. If the first SG is set to A and the second to B (which happens 1 time in 9), there is a probability of 1/2 of getting $A\uparrow$ at the first station. But then we know that the state of the second electron is $|A\downarrow\rangle$ and the probability that we will measure spin in the B direction to be up is $\sin^2 22.5°$. Thus the fraction of pairs which are $(A\uparrow, B\uparrow)$ is $\frac{1}{2}\sin^2 22.5° = 0.073$, and similarly for $(B\uparrow, C\uparrow)$. But the fraction which are $(A\uparrow, C\uparrow)$ is $\frac{1}{2}\sin^2 45° = 0.25$. So the prediction of quantum mechanics for $9N_0$ measurements is

$$N(A\overline{B}) + N(B\overline{C}) = 0.146N_0 < N(A\overline{C}) = 0.25N_0$$

So Bell's inequality does not hold. The experiment has been done many times, starting with the pioneering work of Alain Aspect, and every time the predictions of quantum mechanics are upheld and Bell's inequality is violated. (Photons rather than electrons are used. Early experiments fell short of the ideal in many ways, but as loopholes have been successively closed the result has become more and more robust.)

It seems pretty inescapable that the electrons have not "decided in advance" how they will pass through any given SG. Do we therefore have to conclude that the measurement made at station 1 is responsible for collapsing the wave function at station 2, even if there is no time for light to pass between the two? It is worth noting that no-one has shown any way to use this set-up to send signals between the stations; on their own they both see a totally random succession of results. It is only in the statistical correlation that the weirdness shows up...

In writing this section I found this document by David Harrison of the University of Toronto very useful.

- **(Gasiorowicz ch 20.3,4)**
- **Mandl ch 6.3**
- **Townsend ch 5.4,5**

Further discussions can be found in N. David Mermin's book *Boojums all the way through* (CUP 1990) and in John S. Bell's *Speakable and unspeakable in quantum mechanics* (CUP 1987).

Mathematical background and revision

Most of the material presented here is expected to be revision. Some however (eg Airy functions) is not, but is useful background material for one or more sections of the course. There are references to contour integrals which can be ignored by students who have not taken a course on the subject.

A.1 Vector Spaces

Basic results are presented here without explanation. See your PHYS20602 notes for more details. The first five points are definitions (except for the Schwarz inequality in the 4th point); the rest can be proved.

- We will consider a complex vector space, with vectors (kets) written $|\alpha\rangle$. (What we write inside is just a label; it might (anticipating) be the corresponding wave function, or an eigenvalue, or just a number if we have some natural ordering principle.)
- For complex scalars a and b, the ket $|a\alpha+b\beta\rangle = a|\alpha\rangle + b|\beta\rangle$ is also in the space. The null vector is written 0 (not $|0\rangle$): $0|\alpha\rangle = 0$.
- The corresponding bras $\langle\alpha|$ are taken from the dual space. $\langle a\alpha + b\beta| = a^*\langle\alpha| + b^*\langle\beta|$. (We use the same labels for bras and kets.)
- There is a finite inner product $\langle\alpha|\beta\rangle$; $\langle\alpha|\alpha\rangle(\equiv |\alpha|^2)$ is real and positive (unless $\langle\alpha|\alpha\rangle = 0$ which implies $|\alpha\rangle = 0$). $\langle\beta|\alpha\rangle = \langle\alpha|\beta\rangle^*$. For normalised states, $\langle\alpha|\alpha\rangle = 1$ and $|\langle\alpha|\beta\rangle| \leq 1$ (with equality only for $|\beta\rangle = |\alpha\rangle$.)
- Operators transform one ket into another: $\widehat{\Omega}|\alpha\rangle = |\widehat{\Omega}\alpha\rangle$. (It may be necessary to specify a domain of validity.) The adjoint operator $\widehat{\Omega}^\dagger$ is defined by $\langle\alpha|\widehat{\Omega}^\dagger = \langle\widehat{\Omega}\alpha|$. If $\widehat{\Omega}^\dagger = \widehat{\Omega}$ the operator is self-adjoint or *Hermitian.*
- The eigenvalues ω_i of the Hermitian operator $\widehat{\Omega}$ are real. The corresponding normalised eigenfunctions $|\omega_i\rangle$ are orthogonal $\langle\omega_i|\omega_j\rangle = \delta_{ij}$ and form a complete set: $|\alpha\rangle = \sum_i a_i|\omega_i\rangle$ for any $|\alpha\rangle$, where $a_i = \langle\omega_i|\alpha\rangle$. (If some of the ω_i are degenerate the orthogonalisation within the corresponding set of eigenkets will need to be done by hand, but it can be done.) If $|\beta\rangle = \sum_i b_i|\omega_i\rangle$, then $\langle\beta|\alpha\rangle = \sum_i b_i^* a_i$.
- If $\widehat{\Omega}$ is Hermitian, the matrix element can be formed with $\widehat{\Omega}$ "acting either way": $\langle\beta|\widehat{\Omega}|\alpha\rangle = \langle\beta|\widehat{\Omega}\alpha\rangle = \langle\widehat{\Omega}\beta|\alpha\rangle (= \sum_i \omega_i b_i^* a_i)$.
- The object $|\beta\rangle\langle\alpha|$ is an operator, since acting on a ket it gives another ket: $(|\beta\rangle\langle\alpha|)|\phi\rangle = (\langle\alpha|\phi\rangle)|\beta\rangle$; the adjoint operator is $|\alpha\rangle\langle\beta|$. By completeness, $\sum_i |\omega_i\rangle\langle\omega_i| = \widehat{I}$ (the identity operator).

- In the basis $\{|\omega_i\rangle\}$, an operator $\widehat{\Theta}$ is characterised by its matrix elements $\theta_{ij} \equiv \langle\omega_i|\widehat{\Theta}|\omega_j\rangle$, and we have

$$\langle\beta|\widehat{\Theta}|\alpha\rangle = \sum_i \sum_j b_i^* \theta_{ij} a_j = (b_1^*, b_2^*, b_3^*, \ldots) \begin{pmatrix} \theta_{11} & \theta_{12} & \theta_{13} & . & . \\ \theta_{21} & \theta_{22} & \theta_{23} & . & . \\ \theta_{31} & \theta_{32} & \theta_{33} & . & . \\ . & . & . & . & . \\ . & . & . & . & . \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ . \\ . \end{pmatrix}$$

  The matrix elements of $\widehat{\Theta}^\dagger$ are $\langle\omega_i|\widehat{\Theta}^\dagger|\omega_j\rangle = \theta_{ji}^*$. (Thus the matrix of coefficients is transposed as well as complex conjugated.) If $\widehat{\Gamma}$ is another operator with matrix elements in this basis γ_{ij}, the matrix elements of $\widehat{\Theta}\widehat{\Gamma}$ are $\sum_k \theta_{ik}\gamma_{kj}$. Also, $\widehat{\Theta} \equiv \sum_{ij} |\omega_i\rangle\theta_{ij}\langle\omega_j|$.

See section 1.2 for the aplication to quantum mechanics, including states such as $|x\rangle$ and $|p\rangle$.

References

- **Shankar 1.1-6**

A.1.1 Direct Products

We can form a new vector space by taking the *direct product* of two vector spaces. In quantum mechanics, this arises for instance if we have two particles, or if we have two sources of angular momentum for a single particle. Taking two particles as an example, if the first (say a proton) is in the state $|\phi\rangle$ and the second (say a neutron) is in the state $|\alpha\rangle$, the state of the whole system is given by $|\phi\rangle \otimes |\alpha\rangle$, where we specify at the start that we will write the proton state first, and the symbol "$\otimes$" is really just a separator. All states of this form are in the new vector space, but not all states of the new vector space are of this separable form. As a simple example, $|\phi\rangle \otimes |\alpha\rangle + |\psi\rangle \otimes |\beta\rangle$ is a possible state of the system in which neither the proton nor the neutron is in a definite state, but the two are entangled, such that if we find the proton in state $|\phi\rangle$ we know the neutron is in state $|\alpha\rangle$, but if the proton is in state $|\psi\rangle$ the neutron must be in state $|\beta\rangle$.

Operators can be of three forms: they can act only on one particle, they can act on both particles but independently on each, or they can be more complicated. If $\widehat{A}$ acts only on the proton, and $\widehat{B}$ only on the neutron, then in the two particle space we have to write the former as $\widehat{A} \otimes \widehat{I}_n$ where $\widehat{I}_n$ is the identity operator for neutron states, and the latter as $\widehat{I}_p \otimes \widehat{B}$. Again, the "$\otimes$" acts to separate "proton" from "neutron". In each case one of the two particles' states is unchanged. On the other hand $\widehat{A} \otimes \widehat{B}$ changes the states of both particles, and $\widehat{A} \otimes \widehat{B} + \widehat{C} \otimes \widehat{D}$ does too, but in a more complicated way. (The latter expression is only valid if $\widehat{C}$ and $\widehat{D}$ are proton and neutron operators respectively.) Some examples:

$$\begin{aligned}
\Big(\langle\phi| \otimes \langle\alpha|\Big)\Big(|\psi\rangle \otimes |\beta\rangle\Big) &= \langle\phi|\psi\rangle\langle\alpha|\beta\rangle \\
\Big(\widehat{A} \otimes \widehat{I}_n\Big)\Big(|\phi\rangle \otimes |\alpha\rangle\Big) &= \Big(\widehat{A}|\phi\rangle\Big) \otimes |\alpha\rangle \\
\Big(\widehat{A} \otimes \widehat{I}_n + \widehat{I}_p \otimes \widehat{B}\Big)\Big(|\phi\rangle \otimes |\alpha\rangle\Big) &= \Big(\widehat{A}|\phi\rangle\Big) \otimes |\alpha\rangle + |\phi\rangle \otimes \Big(\widehat{B}|\alpha\rangle\Big) \\
\Big(\widehat{A} \otimes \widehat{B} + \widehat{C} \otimes \widehat{D}\Big)\Big(|\phi\rangle \otimes |\alpha\rangle + |\psi\rangle \otimes |\beta\rangle\Big) &= \Big(\widehat{A}|\phi\rangle\Big) \otimes \Big(\widehat{B}|\alpha\rangle\Big) + \Big(\widehat{A}|\psi\rangle\Big) \otimes \Big(\widehat{B}|\beta\rangle\Big) \\
&\quad + \Big(\widehat{C}|\phi\rangle\Big) \otimes \Big(\widehat{D}|\alpha\rangle\Big) + \Big(\widehat{C}|\psi\rangle\Big) \otimes \Big(\widehat{D}|\beta\rangle\Big)
\end{aligned}$$

If $|\phi\rangle$ is the spatial state of a particle and $|\alpha\rangle$ its spin state, the common notation $\phi(x)|\alpha\rangle$ actually stands for $\big(\langle x|\otimes I_S\big)\big(|\phi\rangle\otimes|\alpha\rangle\big)$.

The direct product notation is clumsy, and shorthands are often used. If we indicate via a label which space an operator acts on, eg by writing $\widehat{A}_p$ and $\widehat{B}_n$, or if it is otherwise obvious, we often drop the explict identity operators in the other space and hence just write the operator in the third equation above as $\widehat{A}_p+\widehat{B}_n$. Even more succinctly, we may use a single ket with two labels to stand for the state of the combined system, for example $|\phi,\alpha\rangle$. An example of this would be the two-dimensional harmonic oscillator described in section A.4. Such a labelling though implies that we want to use basis states that are direct products of the sub-space basis states, and that might not be convenient. In the case of addition of angular momentum (section A.2), we are more likely to want to use eigenstates of the total angular momentum of the system as our basis states, and they are not seperable.

References

- **Shankar 10.1**

A.2 Angular Momentum

We omit hats on operators, and don't always distinguish between operators and their position-space representation.

Orbital angular momentum

$$\mathbf{L}=\mathbf{r}\times\mathbf{p}\Rightarrow L_z=-i\hbar(x\tfrac{\partial}{\partial y}-y\tfrac{\partial}{\partial x})\quad\text{etc}$$

$$\mathbf{L}^2=-\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right);\qquad L_z=-i\hbar\frac{\partial}{\partial\phi}$$

$$\nabla^2=\nabla_r^2-\frac{1}{\hbar^2r^2}\mathbf{L}^2;\qquad\nabla_r^2\psi\equiv\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)=\frac{1}{r}\frac{\partial^2}{\partial r^2}r\psi$$

Eigenfunctions of $\mathbf{L}^2$ and L_z are spherical harmonics $Y_l^m(\theta,\phi)$ with eigenvalues $\hbar^2l(l+1)$ and $\hbar m$ respectively; l and m are integers and must satisfy $l\geq 0$ and $m=-l,-l+1,\ldots l$. In Dirac notation, the eigenstates are $|lm\rangle$ and $Y_l^m=\langle\mathbf{r}|lm\rangle$.

$$Y_0^0(\theta,\phi)=\sqrt{\frac{1}{4\pi}}\qquad\qquad Y_1^{\pm1}(\theta,\phi)=\mp\sqrt{\frac{3}{8\pi}}\,\sin\theta\,\mathrm{e}^{\pm i\phi}$$

$$Y_1^0(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\,\cos\theta\qquad\qquad Y_2^{\pm2}(\theta,\phi)=\sqrt{\frac{15}{32\pi}}\,\sin^2\theta\,\mathrm{e}^{\pm2i\phi}$$

$$Y_2^{\pm1}(\theta,\phi)=\mp\sqrt{\frac{15}{8\pi}}\,\sin\theta\,\cos\theta\,\mathrm{e}^{\pm i\phi}\qquad\qquad Y_2^0(\theta,\phi)=\sqrt{\frac{5}{16\pi}}\,(3\cos^2\theta-1)$$

The Mathematica function to obtain them is `SphericalHarmonicY`[l,m,θ,ϕ]. These are normalised and orthogonal:

$$\int(Y_{l'}^{m'})^*Y_l^m\mathrm{d}\Omega=\delta_{ll'}\delta_{mm'}\qquad\text{where}\qquad\mathrm{d}\Omega=\sin\theta\mathrm{d}\theta\mathrm{d}\phi$$

Rules obeyed by any angular momentum (eg $\mathbf{J}$ can be replaced by $\mathbf{L}$ or $\mathbf{S}$):

$$[J_x,J_y]=i\hbar J_z\quad\text{etc};\qquad[\mathbf{J}^2,J_i]=0;\qquad J_\pm\equiv J_x\pm iJ_y;\qquad[J_+,J_-]=2\hbar J_z;\qquad[J_z,J_\pm]=\pm\hbar J_\mp$$

$$\mathbf{J}^2=J_x^2+J_y^2+J_z^2=\tfrac{1}{2}(J_+J_-+J_-J_+)+J_z^2=J_+J_-+J_z^2-2\hbar J_z$$

$$\mathbf{J}^2|j,m\rangle=\hbar^2j(j+1)|j,m\rangle;\quad J_z|j,m\rangle=\hbar m|j,m\rangle;\quad J_\pm|j,m\rangle=\hbar\sqrt{(j\mp m)(j\pm m+1)}|j,m\pm1\rangle$$

In the last line j and m must be integer or half-integer, and $m = -j, -j+1, \dots j$.

For the special case of a *spin-*$\frac{1}{2}$ particle (such as a proton, neutron or electron), the eigenstates of $\mathbf{S}^2$ and S_z are $|\frac{1}{2}, \frac{1}{2}\rangle$ and $|\frac{1}{2}, -\frac{1}{2}\rangle$, often simply written $|\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ or even $|\uparrow\rangle$ and $|\downarrow\rangle$; then $\mathbf{S}^2|\pm\frac{1}{2}\rangle = \frac{3}{4}\hbar^2$ and $S_z|\pm\frac{1}{2}\rangle = \pm\frac{1}{2}\hbar|\pm\frac{1}{2}\rangle$. In this basis, with $|\frac{1}{2}\rangle \equiv \binom{1}{0}$ and $|-\frac{1}{2}\rangle \equiv \binom{0}{1}$, the components of the spin operator are given by $\widehat{S}_i = \frac{1}{2}\hbar\sigma_i$, where σ_i are the *Pauli matrices*

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

If a sytem has two contributions to its angular momentum, with operators $\mathbf{J}_1$ and $\mathbf{J}_2$ and eigenstates $|j_1\ m_1\rangle$ and $|j_2\ m_2\rangle$, the total angular momentum operator is $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$. The quantum number j of the combined system satisfies $j_1 + j_2 \geq j \geq |j_1 - j_2|$, and $m = m_1 + m_2$. Since enumerating states by $\{m_1, m_2\}$ gives $(2j_1+1)(2j_2+1)$ possible states, the number must be unchanged in the $\{j, m\}$ basis, which is verified as follows: labelling such that $j_2 > j_1$ we have

$$\sum_{j=j_2-j_1}^{j_2+j_1} 2j+1 = \Big((j_2+j_1)(j_2+j_1+1)-(j_2-j_1)(j_2-j_1-1)\Big)+(j_2+j_1)-(j_2-j_1)+1 = (2j_1+1)(2j_2+1)$$

Depending on basis, we write the states either as $|j_1\ m_1\rangle \otimes |j_2\ m_2\rangle$ or $|j_1, j_2; j\ m\rangle$, and they must be linear combinations of each other as both span the space:

$$|j_1, j_2; j\ m\rangle = \sum_{m_1 m_2} \langle j_1\ m_1; j_2\ m_2|j\ m\rangle \Big(|j_1\ m_1\rangle \otimes |j_2\ m_2\rangle\Big) \qquad \text{and}$$

$$|j_1\ m_1\rangle \otimes |j_2\ m_2\rangle = \sum_{jm} \langle j_1\ m_1; j_2\ m_2|j\ m\rangle\, |j_1, j_2; j\ m\rangle$$

where the numbers denoted by $\langle j_1\ m_1; j_2\ m_2|j\ m\rangle$ are called Clebsch-Gordan coefficients; they vanish unless $j_1 + j_2 \geq j \geq |j_1 - j_2|$, and $m = m_1 + m_2$. These are tabulated in various places including the Particle Data Group site (see here for examples of how to use them); the Mathematica function to obtain them is `ClebschGordan`$[\{j_1, m_1\}, \{j_2, m_2\}, \{j, m\}]$. There is also an on-line calculator at Wolfram Alpha which is simple to use if you only have a few to calculate. We use the "Condon-Shortley" phase convention, which is the most common; in this convention they are real which is why we have not written $\langle j_1\ m_1; j_2\ m_2|j\ m\rangle^*$ in the second line above.

As an example we list the states arising from coupling angular momenta 1 and $\frac{1}{2}$ (as in p-wave states of the hydrogen atom):

$$\begin{aligned}
|1, \tfrac{1}{2}; \tfrac{1}{2}\ \tfrac{1}{2}\rangle &= \sqrt{\tfrac{2}{3}}|1\ 1\rangle \otimes |\tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle - \sqrt{\tfrac{1}{3}}|1\ 0\rangle \otimes |\tfrac{1}{2}\ \tfrac{1}{2}\rangle \\
|1, \tfrac{1}{2}; \tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle &= \sqrt{\tfrac{1}{3}}|1\ 0\rangle \otimes |\tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle - \sqrt{\tfrac{2}{3}}|1\ {-1}\rangle \otimes |\tfrac{1}{2}\ \tfrac{1}{2}\rangle \\
|1, \tfrac{1}{2}; \tfrac{3}{2}\ \tfrac{3}{2}\rangle &= |1\ 1\rangle \otimes |\tfrac{1}{2}\ \tfrac{1}{2}\rangle \\
|1, \tfrac{1}{2}; \tfrac{3}{2}\ \tfrac{1}{2}\rangle &= \sqrt{\tfrac{1}{3}}|1\ 1\rangle \otimes |\tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle + \sqrt{\tfrac{2}{3}}|1, 0\rangle \otimes |\tfrac{1}{2}\ \tfrac{1}{2}\rangle \\
|1, \tfrac{1}{2}; \tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle &= \sqrt{\tfrac{2}{3}}|1\ 0\rangle \otimes |\tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle + \sqrt{\tfrac{1}{3}}|1\ {-1}\rangle \otimes |\tfrac{1}{2}\ \tfrac{1}{2}\rangle \\
|1, \tfrac{1}{2}; \tfrac{3}{2}\ {-\tfrac{3}{2}}\rangle &= |1\ {-1}\rangle \otimes |\tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle
\end{aligned}$$

Somewhat more generally, the coupling of l and $\frac{1}{2}$ to give $j = l \pm \frac{1}{2}$ is

$$|l, \tfrac{1}{2}; l{\pm}\tfrac{1}{2}\; m\rangle = \sqrt{\frac{l \mp m + \frac{1}{2}}{2l+1}}|l\; m{+}\tfrac{1}{2}\rangle \otimes |\tfrac{1}{2}\; {-}\tfrac{1}{2}\rangle \pm \sqrt{\frac{l \pm m + \frac{1}{2}}{2l+1}}|l\; m{-}\tfrac{1}{2}\rangle \otimes |\tfrac{1}{2}\; \tfrac{1}{2}\rangle.$$

(*The following material is not revision, but is asserted without proof. See Shankar 15.3 for a partial proof.*)
Similarly we can write expressions for products of spherical harmonics:

$$Y_k^q\, Y_l^m = \sum_{l'm'} f(k,l,l')\langle k\; q; l\; m|l'\; m'\rangle Y_{l'}^{m'} \qquad \Rightarrow \int (Y_{l'}^{m'})^* Y_k^q\, Y_l^m \mathrm{d}\Omega = f(k,l,l')\langle k\; q; l\; m|l', m'\rangle$$

where $f(k,l,l') = \sqrt{1/4\pi}\sqrt{(2l+1)(2k+1)/(2l'+1)}\langle k\; 0; l\; 0|l'\; 0\rangle$. The factor $\langle k\; 0; l\; 0|l'\; 0\rangle$ is the one which vanishes unless parity is conserved, ie unless $k+l$ and l' are both odd or both even.

If an operator Ω is a scalar, $[J_i, \Omega] = 0$. If $\mathbf{V}$ is a triplet of operators which form a vector, then

$$\begin{aligned} &[J_x, V_y] = i\hbar V_z; \qquad \Rightarrow [J_z, V_m] = m\hbar V_m, \qquad [J_\pm, V_m] = \hbar\sqrt{(1 \mp m)(2 \pm m)}V_{m\pm 1} \\ &\text{where} \qquad V_{\pm 1} = \mp\sqrt{\tfrac{1}{2}}(V_x \pm V_y), \qquad V_0 \equiv V_z \end{aligned}$$

The operator $\mathbf{r}$ is a vector operator which obeys these rules. Its components in the spherical basis are $\sqrt{4\pi}\, r\, Y_1^m$.

The following rules are obeyed by the matrix elements of a vector operator, by the *Wigner-Eckart theorem*

$$\langle j'\; m'|V_q|j\; m\rangle = \langle j'\, \|\mathbf{V}\|\, j\rangle\langle j'\; m'; 1\; q|j\; m\rangle$$

where $\langle j'\, \|\mathbf{V}\|\, j\rangle$ is called the *reduced matrix element* and is independent of the m, m' and q. The Clebsch-Gordan coefficient will vanish unless $j+1 \geq j' \geq |j-1|$, in other words operating with a vector operator is like adding one unit of angular momentum to the system. This is the origin of electric dipole selection rules for angular momentum. (In the rule for combining spherical harmonics the factor $f(k,l,l')$ is a reduced matrix element.)

A.3 Hydrogen wave functions

The solutions of the Schrödinger equation for the Coulomb potential $V(r) = -\hbar c\alpha/r$ have energy $E_n = -\frac{1}{n^2}E_{\mathrm{Ry}}$, where $E_{\mathrm{Ry}} = \frac{1}{2}\alpha^2 mc^2 = 13.6$ eV (with m the reduced mass of the electron-proton system). (Recall $\alpha = e^2/(4\pi\epsilon_0\hbar c) \approx 1/137$.) The spatial wavefunctions are $\psi_{nlm}(\mathbf{r}) = R_{n,l}(r)Y_l^m(\theta, \phi)$.

The radial wavefunctions are as follows, where $a_0 = \hbar c/(mc^2\alpha)$:

$$
\begin{aligned}
R_{1,0}(r) &= \frac{2}{a_0^{3/2}} \exp\left(-\frac{r}{a_0}\right), \\
R_{2,0}(r) &= \frac{2}{(2\,a_0)^{3/2}} \left(1-\frac{r}{2\,a_0}\right) \exp\left(-\frac{r}{2\,a_0}\right), \\
R_{2,1}(r) &= \frac{1}{\sqrt{3}\,(2\,a_0)^{3/2}} \frac{r}{a_0} \exp\left(-\frac{r}{2\,a_0}\right), \\
R_{3,0}(r) &= \frac{2}{(3\,a_0)^{3/2}} \left(1-\frac{2\,r}{3\,a_0}+\frac{2\,r^2}{27\,a_0^2}\right) \exp\left(-\frac{r}{3\,a_0}\right), \\
R_{3,1}(r) &= \frac{4\sqrt{2}}{9\,(3\,a_0)^{3/2}} \frac{r}{a_0} \left(1-\frac{r}{6\,a_0}\right) \exp\left(-\frac{r}{3\,a_0}\right), \\
R_{3,2}(r) &= \frac{2\sqrt{2}}{27\sqrt{5}\,(3\,a_0)^{3/2}} \left(\frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{3\,a_0}\right).
\end{aligned}
$$

They are normalised, so $\int_0^\infty (R_{n,l}(r))^2 r^2 \mathrm{d}r = 1$. Radial wavefuntions of the same l but different n are orthogonal (the spherical harmonics take care of orthogonality for different ls).

The following radial integrals can be proved:

$$
\begin{aligned}
\langle r^2 \rangle &= \frac{a_0^2\,n^2}{2}\bigl(5\,n^2+1-3l\,(l+1)\bigr), \\
\langle r \rangle &= \frac{a_0}{2}\bigl(3n^2-l\,(l+1)\bigr), \\
\left\langle \frac{1}{r} \right\rangle &= \frac{1}{n^2 a_0}, \\
\left\langle \frac{1}{r^2} \right\rangle &= \frac{1}{(l+1/2)\,n^3\,a_0^2}, \\
\left\langle \frac{1}{r^3} \right\rangle &= \frac{1}{l\,(l+1/2)\,(l+1)\,n^3\,a_0^3}.
\end{aligned}
$$

For hydrogen-like atoms (single-electron ions with nuclear charge $|e|\,Z$) the results are obtained by substituting $\alpha \to Z\alpha$ (and so $a_0 \to a_0/Z$).

A.4 Harmonic oscillators, creation and annihilation operators

For a particle of mass m in a one-dimensional harmonic oscillator potential $\frac{1}{2}kx^2 \equiv \frac{1}{2}m\omega^2x^2$ where ω is the classical frequency of oscillation, the Hamiltonian is

$$
\widehat{H} = \frac{\hat{p}^2}{2m} + \tfrac{1}{2}m\omega^2\hat{x}^2
$$

The energy levels are $E_n = (n+\frac{1}{2})\hbar\omega$, $n \geq 0$, and, defining the length scale $x_0 = \sqrt{\hbar/m\omega}$, the wave functions are

$$
\phi_0(x) = (\pi x_0^2)^{-1/4}\mathrm{e}^{-x^2/2x_0^2} \qquad \phi_n(x) = \frac{1}{\sqrt{2^n n!}} H_n(\tfrac{x}{x_0})\phi_0(x)
$$

where the Hermite polynomials are $H_0(z) = 1$; $H_1(z) = 2z$; $H_2(z) = 4z^2 - 2$; $H_3(z) = 8z^3 - 12z$; $H_4(z) = 16z^4 - 48x^2 + 12$. The Mathematica functions for obtaining them are `HermiteH[n, z]`.

In bra-ket notation, we will represent the state with quantum umber n as $|n\rangle$, with $\phi_n(x) = \langle x|n\rangle$.

If we define the annihilation and creation operators

$$\hat{a} = \frac{1}{\sqrt{2}}\left(\frac{\hat{x}}{x_0} + i\frac{x_0}{\hbar}\hat{p}\right) \qquad \text{and} \qquad \hat{a}^\dagger = \frac{1}{\sqrt{2}}\left(\frac{\hat{x}}{x_0} - i\frac{x_0}{\hbar}\hat{p}\right)$$

which satisfy $[\hat{a}, \hat{a}^\dagger] = 1$, we have

$$\widehat{H} = \hbar\omega(\hat{a}^\dagger\hat{a} + \tfrac{1}{2}) \qquad [\hat{a}, H] = \hbar\omega\,\hat{a} \qquad \text{and} \qquad [\hat{a}^\dagger, H] = -\hbar\omega\,\hat{a}^\dagger$$

from which it follows that

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle \qquad \text{and} \qquad \hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle.$$

This suggests an interpretation of the states of the system in which the quanta of energy are primary, with $\hat{a}^\dagger$ and $\hat{a}$ respectively creating and annihilating a quantum of energy. Further notes on creation and annihilation operators can be found here.

For a particle in a two-dimensional potential $\frac{1}{2}m\omega_x^2x^2 + \frac{1}{2}m\omega_y^2y^2$, we define $x_0 = \sqrt{\hbar/m\omega_x}$ and $y_0 = \sqrt{\hbar/m\omega_y}$, and the wavefunction of the particle will be determined by two quantum numbers n_x and n_y

$$\begin{aligned}\phi_{0,0}(x,y) &= (\pi x_0 y_0)^{-1/2}\mathrm{e}^{-x^2/2x_0^2}\mathrm{e}^{-y^2/2y_0^2}\\ \phi_{n_x,n_y}(x,y) &= \frac{1}{\sqrt{2^{n_x}n_x!}}H_{n_x}(\tfrac{x}{x_0})\frac{1}{\sqrt{2^{n_y}n_y!}}H_{n_y}(\tfrac{y}{y_0})\phi_{0,0}(x,y)\end{aligned}$$

In bra-ket notation, we will represent the state with quantum numbers n_x and n_y as $|n_x, n_y\rangle$

Creation operators $\hat{a}_x$ and $\hat{a}_x^\dagger$ can be constructed from $\hat{x}$ and $\hat{p_x}$ as above, and we can construct a second set of operators $\hat{a}_y$ and $\hat{a}_y^\dagger$ from $\hat{y}$ and $\hat{p_y}$ (using y_0 as the scale factor) in the same way. Then $\hat{a}_x^\dagger$ and $\hat{a}_y^\dagger$ act on $|n_x, n_y\rangle$ to increase n_x and n_y respectively, and $\hat{a}_x$ and $\hat{a}_y$ to decrease them, and both of the latter annihilate the ground state. So for instance

$$\hat{a}_x|n_x, n_y\rangle = \sqrt{n_x}|n_x - 1, ny\rangle \qquad \text{and} \qquad \hat{a}_y^\dagger|n_x, n_y\rangle = \sqrt{n_y+1}|n_x, n_y+1\rangle.$$

A.5 The Helium atom

New section for 2011/12, to be constructed (26/9/11)

A.6 Spherical Bessel functions

Spherical bessel functions are solutions of the following equation:

$$z^2\frac{\mathrm{d}^2f}{\mathrm{d}z^2} + 2z\frac{\mathrm{d}f}{\mathrm{d}z} + \Big(z^2 - l(l+1)\Big)f = 0$$

for integer l.

The regular solution is denoted $j_l(z)$ and the irregular one, $n_l(z)$ (or sometimes $y_l(z)$). The Mathematica functions for obtaining them are `SphericalBesselJ[l, z]` and `SphericalBesselY[l, z]`. For $l = 0$ the equation is $\frac{\mathrm{d}^2 g}{\mathrm{d}z^2} - g = 0$, where $g = zf$, and so the solutions are $j_0 = \sin z/z$ and $n_0 = -\cos z/z$. The general solutions are

$$j_l(z) = z^l \left(-\frac{1}{z}\frac{d}{dz}\right)^l \left(\frac{\sin z}{z}\right) \qquad \text{and} \qquad n_l(z) = -z^l \left(-\frac{1}{z}\frac{d}{dz}\right)^l \left(\frac{\cos z}{z}\right).$$

The asymptotic forms are

$$\begin{aligned} j_l(z) &\overset{z\to\infty}{\longrightarrow} \frac{\sin(z - l\,\pi/2)}{z} \qquad &\text{and}\qquad n_l(z) &\overset{z\to\infty}{\longrightarrow} -\frac{\cos(z - l\,\pi/2)}{z}; \\ j_l(z) &\overset{z\to 0}{\longrightarrow} \frac{z^l}{(2l+1)!!} \qquad &\text{and}\qquad n_l(z) &\overset{z\to 0}{\longrightarrow} -(2l-1)!!z^{-l-1}. \end{aligned}$$

(Note “n!!” is like factorial but only including the odd (even) numbers for odd (even) n, eg $7!! = 7 \times 5 \times 3 \times 1$ and $6!! = 6 \times 4 \times 2$, with $0!! = 0! \equiv 1$.)

In spherical polar coordinates the Schrödinger equation for a particle in free space ($V(r) = 0$) gives the following equation for the radial wavefuntion:

$$\frac{\mathrm{d}^2 R_l}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R_l}{\mathrm{d}r} + \left(k^2 - \frac{l(l+1)}{r^2}\right) R_l = 0$$

where $k^2 = 2mE/\hbar^2$. So the solution is

$$R_l(r) = Aj_l(kr) + Bn_l(kr)$$

where B will equal zero if the solution has to hold at the origin, but not if the origin is excluded (for instance outside a hard sphere).

Poisson’s integral representation of the regular spherical Bessel functions

$$j_n(z) = \frac{z^n}{2^{n+1} n!} \int_{-1}^{1} \cos(zx)(x^2 - 1)^n \mathrm{d}x$$

together with Rodrigues representation of the Legendre polynomials can be used to show that

$$j_n(z) = \tfrac{1}{2}(-i)^n \int_{-1}^{1} \mathrm{e}^{izx} P_n(x) \mathrm{d}x$$

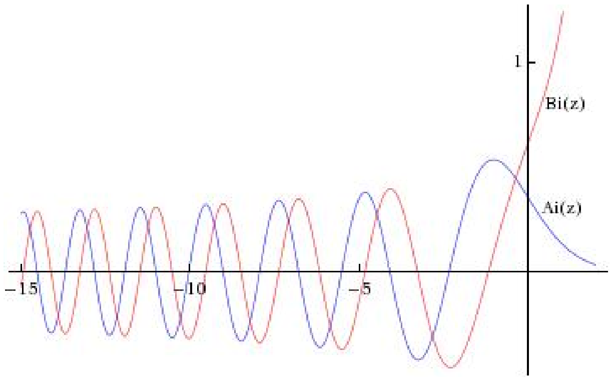
whence follows the expression for the expansion of a plane wave in spherical polars given in section 5.3.

A.7 Airy functions

Airy functions are the solutions of the differential equation:

$$\frac{\mathrm{d}^2 f}{\mathrm{d}z^2} - zf = 0$$

There are two solutions, $\mathrm{Ai}(z)$ and $\mathrm{Bi}(z)$; the first tends to zero as $z \to \infty$, while the second blows up. Both are oscillatory for $z < 0$. The Mathematica functions for obtaining them are



`AiryAi[z]` and `AiryBi[z]`.

The asymptotic forms of the Airy functions are:

$$\mathrm{Ai}(z) \overset{z\to\infty}{\longrightarrow} \frac{\mathrm{e}^{-\frac{2}{3}z^{3/2}}}{2\sqrt{\pi}z^{1/4}} \qquad \text{and} \qquad \mathrm{Ai}(z) \overset{z\to-\infty}{\longrightarrow} \frac{\cos\left(\frac{2}{3}|z|^{3/2}-\frac{\pi}{4}\right)}{\sqrt{\pi}\,|z|^{1/4}}$$

$$\mathrm{Bi}(z) \overset{z\to\infty}{\longrightarrow} \frac{\mathrm{e}^{\frac{2}{3}z^{3/2}}}{\sqrt{\pi}z^{1/4}} \qquad \text{and} \qquad \mathrm{Bi}(z) \overset{z\to-\infty}{\longrightarrow} \frac{\cos\left(\frac{2}{3}|z|^{3/2}+\frac{\pi}{4}\right)}{\sqrt{\pi}\,|z|^{1/4}}$$

The Schrödinger equation for a linear potential $V(x)=\beta x$ in one dimension can be cast in the following form

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+\beta x\psi-E\psi=0$$

Defining $z=x/x_0$, with $x_0=(\hbar^2/(2m\beta))^{1/3}$, and $E=(\hbar^2\beta^2/(2m))^{1/3}\mu$, and with $y(z)\equiv\psi(x)$, this can be written

$$\frac{\mathrm{d}^2y}{\mathrm{d}z^2}-zy+\mu y=0$$

(see section A.11 for more on scaling.) The solution is

$$y(z)=C\,\mathrm{Ai}(z-\mu)+D\,\mathrm{Bi}(z-\mu) \qquad \text{or} \qquad \psi(x)=C\,\mathrm{Ai}\big((\beta x-E)/(\beta x_0)\big)+D\,\mathrm{Bi}\big((\beta x-E)/(\beta x_0)\big)$$

where $D=0$ if the solution has to extend to $x=\infty$. The point $z=\mu$, $x=E/\beta$ is the point at which $E=V$ and the solution changes from oscillatory to decaying / growing.

The equation for a potential with a negative slope is given by substituting $z\to-z$ in the defining equation. Hence the general solution is $\psi(x)=C\,\mathrm{Ai}(-x/x_0-\mu)+D\,\mathrm{Bi}(-x/x_0-\mu)$, with $D=0$ if the solution has to extend to $x=-\infty$.

The first few zeros of the Airy functions are given in Wolfram MathWorld.

A.8 Properties of δ-functions

The δ-function is only defined by its behaviour in integrals:

$$\int_{-a}^{b}\delta(x)\mathrm{d}x=1; \qquad \int_{x_0-a}^{x_0+b}f(x)\delta(x-x_0)\mathrm{d}x=f(x_0)$$

where the limits a and b are positive and as large or small as we want; the integration simply has to span the point on which the δ-function is centred.

The following equivalences may also be proved by changing variables in the corresponding integral (an appropriate integration range is assumed for compactness of notation):

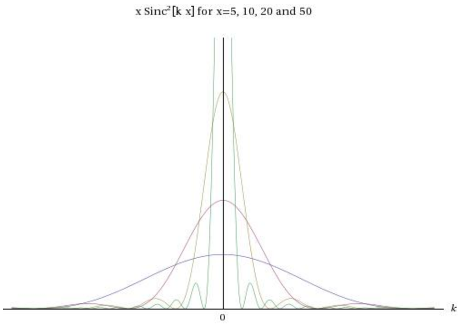
$$\begin{aligned}\delta(ax-b) &= \tfrac{1}{|a|}\delta(x-\tfrac{b}{a}) \qquad \text{since} \quad \int f(x)\delta(ax-b)\mathrm{d}x = \tfrac{1}{a}f(\tfrac{b}{a})\\ \delta(g(x)) &= \sum_i \frac{\delta(x-x_i)}{|g'(x_i)|} \qquad \text{where the } x_i \text{ are the (simple) real roots of } g(x).\end{aligned}$$

Note that the dimensions of a δ-function are the inverse of those of its argument, as should be obvious from the first equation.

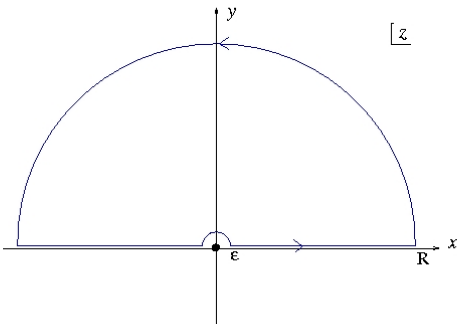
We encounter two functions which tend to δ-functions:

$$\begin{aligned}&\tfrac{1}{2\pi}\int_{-x/2}^{x/2} \mathrm{e}^{i(k-k')x'}\mathrm{d}x' = \tfrac{1}{\pi}\frac{\sin\left(\frac{1}{2}(k-k')x\right)}{k-k'} \xrightarrow{x\to\infty} \delta(k-k')\\ &\tfrac{2}{\pi}\frac{\sin^2\left(\frac{1}{2}(k-k')x\right)}{(k-k')^2 x} \xrightarrow{x\to\infty} \delta(k-k')\end{aligned}$$

In both cases, as $x \to \infty$ the function tends to zero unless $k = k'$, at which point it tends to x, so it looks like an infinite spike at $k = k'$.



That the normalisation (with respect to integration w.r.t k) is correct follows from the following two integrals: $\int_{-\infty}^{\infty}\mathrm{sinc}(t)\mathrm{d}t = \pi$ and $\int_{-\infty}^{\infty}\mathrm{sinc}^2(t)\mathrm{d}t = \pi$. The second of these follows from the first via integration by parts. The integral $\int_{-\infty}^{\infty}\mathrm{sinc}(t)\mathrm{d}t = \Im\int_{-\infty}^{\infty}\mathrm{e}^{it}/t\mathrm{d}t$ may be done via the contour integral below: As no poles are included by the contour, the full contour integral is zero. By Jordan's lemma the integral round the outer circle tends to zero as $R \to 0$ as e^{iz} decays exponentially in the upper half plane. So the integral along the real axis is equal and opposite to the integral over the inner circle, namely $\frac{1}{2}$ of the residue at $x = 0$, $i\pi$. So the imaginary part, the integral of $\mathrm{sinc}(x)$, is π.



A.9 Gaussian integrals

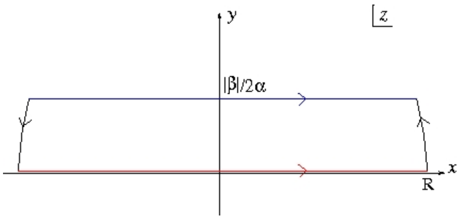
The following integrals will be useful:

$$\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2} \mathrm{d}x = \sqrt{\frac{\pi}{\alpha}} \qquad \text{and} \qquad \int_{-\infty}^{\infty} x^{2n} \mathrm{e}^{-\alpha x^2} \mathrm{d}x = (-1)^n \frac{\mathrm{d}^n}{\mathrm{d}\alpha^n} \left(\sqrt{\frac{\pi}{\alpha}} \right)$$

Often we are faced with a somewhat more complicated integral, which can be cast in Gaussian form by "completing the square" in the exponent and then shifting integration variable $x \to x - \beta/(2\alpha)$:

$$\int_{-\infty}^{\infty} \mathrm{e}^{-\alpha x^2 - \beta x} \mathrm{d}x = \mathrm{e}^{\beta^2/(4\alpha)} \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha(x+\beta/(2\alpha))^2} \mathrm{d}x = \sqrt{\frac{\pi}{\alpha}} \mathrm{e}^{\beta^2/(4\alpha)}$$

This works even if β is imaginary. One way of seeing this is as follows. In the diagram below, as $R \to \infty$ the blue contour is the original one (with β imaginary) and the red one the new contour after shifting; the red and black paths together must equal the blue since there are no poles in the region bounded by the complete contour. However as e^{-z^2} tends to zero faster than $1/R$ as $R \to \infty$ providing $|x| > |y|$, by Jordan's lemma the contribution from the black paths is zero. Hence the two integrals must be the same.



A.10 Density of states, periodic boundary conditions and black-body radiation

In previous thermal and statistical physics courses we have tended to consider a particle in a box (side lengths L_x, L_y L_z), with boundary condition that the wavefunction must vanish at the wall. Then the energy eigenfunctions are of the form

$$\psi_{lmn}(x,y,z) = A \sin\left(\tfrac{\pi l x}{L_x}\right) \sin\left(\tfrac{\pi m y}{L_y}\right) \sin\left(\tfrac{\pi n z}{L_z}\right) = A \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

for positive integers l, m, n, that is, the allowed values of the wavenumber k_i are quantised, though very closely spaced for a macroscopic box. The *density of states* gives the number of states in the vicinity of a given momentum or energy. In momentum space, the number of states with $k(\equiv |\mathbf{k}|)$ in the range $k \to k + \mathrm{d}k$, (where $\mathrm{d}k$ is small, but much bigger than the spacing between states) is

$$D(k)\mathrm{d}k = \frac{Vk^2}{2\pi^2}\mathrm{d}k$$

See here for details of the derivation. Note that as k_x, k_y and k_z all have to be positive, the vector $\mathbf{k}$, which isn't quite a momentum becuase we are dealing with standing waves, has to lie in the positive octant.

In quantum mechanics we prefer not to deal with standing waves, but with momentum eigenstates which are travelling waves. But we still want the advantage of a finite box so that the states remain countable. The solution is to use *periodic boundary conditions* in which, when a particle reaches a wall at, say, (x, y, L_z) it leaves the box and reappears, with the same momentum, at $(x, y, 0)$. This may sound artificial but we get the same expression for $D(k)$; the advantage is that we can usefully talk about $D(\mathbf{k})$ as well.

In this case the boundary condition is $\psi(x, y, L_z) = \psi(x, y, 0)$ and the wavefunction is

$$\psi_{lmn}(x,y,z) = \frac{1}{V}\exp\left(\tfrac{i2\pi lx}{L_x}\right)\exp\left(\tfrac{i2\pi my}{L_y}\right)\exp\left(\tfrac{i2\pi nz}{L_z}\right) = \frac{1}{V}\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}$$

noting now that $k_x = 2\pi l/L_x$ etc since a whole number of wavelengths have to fit into the box. We have fixed the normalisation so that there is one particle in the box; this differs from the δ-function normalisation used elsewhere. We can now talk about the number of states with $\mathbf{k}$ in the range $k_x \to k_x + \mathrm{d}k_x$, $k_y \to k_y + \mathrm{d}k_y$ and $k_z \to k_z + \mathrm{d}k_z$ (where $\mathrm{d}k_i$ is small, but much bigger than the spacing between states)

$$D(\mathbf{k})\mathrm{d}^3k = \frac{\mathrm{d}k_x\mathrm{d}k_y\mathrm{d}k_z}{\frac{2\pi}{L_x}\frac{2\pi}{L_y}\frac{2\pi}{L_z}} = \frac{V}{8\pi^3}\mathrm{d}^3k = \frac{Vk^2}{8\pi^3}\mathrm{d}k\mathrm{d}\Omega_k \quad \Rightarrow D(k)\mathrm{d}k = \frac{Vk^2}{2\pi^2}\mathrm{d}k$$

where $\mathrm{d}\Omega_k = \sin\theta_k\mathrm{d}\theta_k\mathrm{d}\phi_k$. We have obtained the same expression for $D(k)$, as advertised. This time though we integrated over all values of θ_k and ϕ_k, not just the positive octant.

The density of states can be defined with respect to energy, or to frequency, as well. In each case the *number* of states remains the same: $D(k)\mathrm{d}k = D(E)\mathrm{d}E = D(\omega)\mathrm{d}\omega$ so the *density* of states will change by the inverse of the factor which relates k and the new variable: $D(x) = D(k)(\mathrm{d}k/\mathrm{d}x)$.

For non-relativistic particles $k = \sqrt{2mE}/\hbar$, so $D(E) = (Vm\sqrt{2mE})/(2\pi^2\hbar^3)$. For photons though, $k = E/\hbar c$, so $D(E) = (VE^2)/(2\pi^2\hbar^3c^3)$ and $D(\omega) = (V\omega^2)/(2\pi^2c^3)$. In the notes we define $D(\omega\hat{\mathbf{k}})$ which is akin to $D(\mathbf{k})$; the angle integral hasn't yet been done, but the switch to frequency has, bringing in a factor of $1/c^3$.

If a particle has more than one spin state we need to multiply by the degeneracy factor which is 2 for spin-$\frac{1}{2}$ electrons and for photons.

Bose-Einstein statisitics gives the average number of photons $n(\omega, T)$ in a mode of frequency ω at temperature T. Hence we obtain the Planck law for the energy density in space at frequency ω,

$$\rho(\omega) = 2\hbar\omega\tfrac{1}{V}D(\omega)n(\omega,T) = \frac{\hbar\omega^3}{\pi^2c^3}\frac{1}{\mathrm{e}^{\hbar\omega/k_BT}-1}$$

Note the dimesions, which are energy/frequency/length^3. It's "double density" - per unit volume, but also per unit ω. To get the full energy density $U(T)$ we integrate over ω.

A.11 Checking units and scaling

In a general expression, multiply top and bottom by powers of c until, as far as possible, $\hbar$ only occurs as $\hbar c$, m as mc^2 and ω as $\hbar\omega$ or ω/c. Then use the table

$\hbar c$	mc^2	$\hbar\omega$	ω/c	$\hbar$
[Energy][Length]	[Length]	[Energy]	[Length^{-1}]	[Energy][Time]

If the electric charge enters without external fields, write in terms of α. Use the combinations $e\mathbf{E}$ and $\mu_B\mathbf{B}$ (both with dimensions of energy) when external fields enter. (See section A.12 for more on units in EM.)

In calculations use eV or MeV as much as possible (eg instead of using m_e in kg, use $m_e c^2 = 0.511\text{ MeV}$). Remember $\hbar c = 1973\text{ eV Å} = 197.3\text{ MeV fm}$; also useful is $\hbar = 6.582\times 10^{-22}\text{ eV s}^{-1}$.

Often we need to cast the Schrödinger equation in dimensionless units to recognise the solution in terms of special functions. Suppose we have a potential of the form $V(x) = \beta x^n$ for some integer n. Then the dimensions of β are [Energy][Length^{-n}]. The other scales in the problem are $\hbar^2/2m$ which has dimensions [Energy][Length^2] and the particle energy. We proceed by forming a length scale $x_0 = (\hbar^2/(2m\beta))^{1/(n+2)}$ and an energy scale $\mathcal{E} = (\hbar^2\beta^{2/n}/2m)^{n/(n+2)}$. Writing $x = x_0 z$ and $E = \mathcal{E}\mu$, the Schrödinger equation for $y(z) \equiv \psi(x)$ reads

$$f'' - z^n f - \mu f = 0$$

or its 3-d equivalent. For the harmonic oscillator, $n = 2$ and $\beta = \frac{1}{2}m\omega^2$, so $x_0 = (\hbar/m\omega)^{1/2}$ and $\mathcal{E} = \frac{1}{2}\hbar\omega$ as expected. For the hydrogen atom, $n = -1$ and $\beta = \hbar c\alpha$, so $r_0 = \frac{1}{2}a_0$ and $\mathcal{E} = 2mc^2\alpha^2 = 4E_{\text{Ry}}$, which illustrates the fact that we might have to play with numerical factors in the length scale to obtain the standard form.

A.12 Units in EM

There are several systems of units in electromagnetism. We are familiar with SI units, but Gaussian units are still very common and are used, for instance, in Shankar.

In SI units the force between two currents is used to define the unit of current, and hence the unit of charge. (Currents are much easier to calibrate and manipulate in the lab than charges.) The constant μ_0 is *defined* as $4\pi\times 10^{-7}\text{ N A}^{-2}$, with the magnitude chosen so that the Ampère is a "sensible" sort of size. Then Coulomb's law reads

$$\mathbf{F} = \frac{q_1 q_2}{4\pi\epsilon_0\,|\mathbf{r}_1 - \mathbf{r}_2|^2}$$

and ϵ_0 has to be obtained from experiment. (Or, these days, as the speed of light is now has a defined value, ϵ_0 is obtained from $1/(\mu_0 c^2)$.)

However one could in principle equally decide to use Coulomb's law to define charge. This is what is done in Gaussian units, where by definition

$$\mathbf{F} = \frac{q_1 q_2}{|\mathbf{r}_1 - \mathbf{r}_2|^2}$$

Then there is no separate unit of charge; charges are measured in $\text{N}^{1/2}\,\text{m}$ (or the non-SI equivalent): $e = 4.803\times 10^{-10}\text{ g}^{1/2}\,\text{cm}^{3/2}\text{ s}^{-1}$. (You should never need that!) In these units, $\mu_0 = 4\pi/c^2$. Electric and magnetic fields are also measured in different units.

The following translation table can be used:

Gauss	e	$\mathbf{E}$	$\mathbf{B}$
SI	$e/\sqrt{4\pi\epsilon_0}$	$\sqrt{4\pi\epsilon_0}\,\mathbf{E}$	$\sqrt{4\pi/\mu_0}\,\mathbf{B}$

Note that $e\mathbf{E}$ is the same in both systems of units, but $e\mathbf{B}$ in SI units is replaced by $e\mathbf{B}/c$ in Gaussian units. Thus the Bohr magneton μ_B is $e\hbar/2m$ in SI units, but $e\hbar/2mc$ in Gaussian units, and $\mu_B\mathbf{B}$ has dimesions of energy in both systems.

The fine-structure constant α is a dimensionless combination of fundamental units, and as such takes on the same value ($\approx 1/137$) in all systems. In SI it is defined as $\alpha = e^2/(4\pi\epsilon_0\,\hbar c)$, in Gaussian units as $\alpha = e^2/(\,\hbar c)$. In all systems, therefore, Coulomb's law between two particles of charge $z_1 e$ and $z_2 e$ can be written

$$\mathbf{F} = \frac{z_1 z_2\,\hbar c\alpha}{|\mathbf{r}_1 - \mathbf{r}_2|^2}$$

and this is the form I prefer.

Problem Sheets

- Examples 1
- Solutions 1
- Examples 2
- Solutions 2
- Examples 3
- Solutions 3
- Examples 4
- Solutions 4
- Examples 5
- Solutions 5

This formula sheet will be available in the exam. There are other formulae which you are expected to know, of course!

The versions of problem and solutions sheets above have all known errors corrected. A list of errata in the distributed sheets is here.

A list of suitable past exam questions for revision purposes is here.