

Advanced Quantum Mechanics

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Abstract

Quantum mechanics is very impressive. But an inner voice tells me that it is not yet the real thing. The theory produces a good deal but hardly brings us closer to the secret of the Old One.

Without wishing to overstate the case, the discovery of quantum mechanics is the single greatest achievement in the history of human civilisation.

Quantum mechanics is an outrageous departure from our classical, comforting, common sense view of the world. It is more baffling and disturbing than anything dreamt up by science fiction writers. And yet it is undoubtably the correct description of the universe we inhabit, providing insights into many aspects of the world around us.

Among the many successes of quantum mechanics are answers to old and very basic questions. Like why is matter stable? And why does the sun shine and why is it yellow? And why are all solids either conductors or insulators? But quantum mechanics also opens up vistas that we didn't previously know existed, from novel states of matter where the constituent particles become so entangled that they can be coaxed to perform seemingly impossible tasks, to the subatomic world of fluctuating ethereal fields, to a revised understanding of the meaning of information and what one can achieve with it.

Although quantum mechanics gives the right answers to all questions, it does so at a price. The answers are always statistical in nature. There are few certainties in the quantum world. Of course, there are few certainties in the classical world too, but we can always strive to eliminate them. In classical physics, knowledge is power: the more you know, the better off and less uncertain you are. This is because classical probabilities are always about our ignorance and any classical system that appears random does so because it is somehow difficult, but never impossible, for us to know what's going on inside.

This is not the way of the quantum world. The randomness is real, the unpredictability inherent. There is no way to game the system or gain some illicit knowledge of underlying quantum properties that would reduce the uncertainty. If, for example, a particle has probability $1/2$ to be in one place and probability $1/2$ to be elsewhere, this may well be because the particle really is in both places at the same time. Any attempt to eliminate the quantum certainty will simply shift it, like a bubble in wallpaper, elsewhere. As we will see, quantum particles are fragile objects and the very act of looking changes them, disturbing many of the other delicate properties that they possess.

The purpose of these lectures is to begin to get to grips with the quantum world and understand some of the strange behaviour that it exhibits. As should be clear already, this is something of a step into the unknown and our classical intuition will not be a great guide in the quantum realm. Fortunately we have a better guide because, for reasons that we do not fully understand, the quantum world is described astonishingly well by the language of mathematics. Our strategy in these lectures, and later ones, will be to embrace this mathematical description and leverage it to build a new intuition for how the universe really works.

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CHAPTER 1

Wave Mechanics and the Schrödinger Equation

The formulation of a consistent theory of statistical mechanics, electrodynamics and special relativity during the latter half of the 19th century and the early part of the 20th century had been a triumph of “unification”. However, the undoubted success of these theories gave an impression that physics was a mature, complete, and predictive science. Nowhere was confidence expressed more clearly than in the famous quote made at the time by Lord Kelvin: *There is nothing new to be discovered in physics now. All that remains is more and more precise measurement.* However, there were a number of seemingly unrelated and unsettling problems that challenged the prevailing theories.

1.1 Historical Foundations of Quantum Physics

1.1.1 Black-body Radiation

In 1860, Gustav Kirchhoff introduced the concept of a “black body”, an object that absorbs all electromagnetic radiation that falls upon it – none passes through and none is reflected. Since no light is reflected or transmitted, the object appears black when it is cold. However, above absolute zero, a black body emits thermal radiation with a spectrum that depends on temperature. To determine the spectrum of radiated energy, it is helpful to think of a black body as a thermal cavity at a temperature, T . The energy radiated by the cavity can be estimated by considering the resonant modes. In three-dimensions, the number of modes, per unit frequency per unit volume is given by

$$N(\nu) d\nu = \frac{8\pi\nu^2}{c^3} d\nu, \quad (1.1)$$

where, as usual, c is the speed of light.

The amount of radiation emitted in a given frequency range should be proportional to the number of modes in that range. Within the framework of classical statistical mechanics, each of these modes has an equal chance of being excited, and the average energy in each mode is $k_B T$ (equipartition), where k_B is the Boltzmann constant. The corresponding energy density is therefore given by the Rayleigh-Jeans law,

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} k_B T. \quad (1.2)$$

This result predicts that $\rho(\nu, T)$ increases without bound at high frequencies, ν — the ultraviolet (UV) catastrophe. However, such behaviour stood in contradiction with experiment which revealed that the high-frequency dependence is quite benign. To resolve difficulties presented by the UV catastrophe, Planck hypothesised that, for each mode ν ,

energy is quantised in units of $h\nu$, where h denotes the Planck constant. In this case, the energy of each mode is given by

$$\langle \varepsilon(\nu) \rangle = \frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/k_B T}}{\sum_{n=0}^{\infty} \nu e^{-nh\nu/k_B T}} = \frac{h\nu}{e^{h\nu/k_B T} - 1}, \quad (1.3)$$

leading to the anticipated suppression of high frequency modes. From this result one obtains the celebrated Planck radiation formula,

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} \langle \varepsilon(\nu) \rangle = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/k_B T} - 1}. \quad (1.4)$$

This result conforms with experiment, and converges on the Rayleigh-Jeans law at low frequencies, $h\nu/k_B T \rightarrow 0$. Planck's result suggests that electromagnetic energy is quantised: light of wavelength $\lambda = c/\nu$ is made up of quanta each of which has energy $h\nu$. The equipartition law fails for oscillation modes with high frequencies, $h\nu \gg k_B T$.

A quantum theory for the specific heat of matter, which takes into account the quantization of lattice vibrational modes, was subsequently given by Debye and Einstein.

1.1.2 Photoelectric Effect

We turn now to the second ground-breaking experiment in the development of quantum theory. When a metallic surface is exposed to electromagnetic radiation, above a certain threshold frequency, the light is absorbed and electrons are emitted (see figure, right). In 1902, Philipp Eduard Anton von Lenard observed that the energy of individual emitted electrons increases with the frequency of the light. This was at odds with Maxwell's wave theory of light, which predicted that the electron energy would be proportional to the intensity of the radiation.

In 1905, Einstein resolved this paradox by describing light as composed of discrete quanta (photons), rather than continuous waves. Based upon Planck's theory of black-body radiation, Einstein theorized that the energy in each quantum of light was proportional to the frequency. A photon above a threshold energy, the "work function" W of the metal, has the required energy to eject a single electron, creating the observed effect. In particular, Einstein's theory was able to predict that the maximum kinetic energy of electrons emitted by the radiation should vary as

$$\text{K.E.}_{\text{max}} = h\nu - W. \quad (1.5)$$

Later, in 1916, Millikan was able to measure the maximum kinetic energy of the emitted electrons using an evacuated glass chamber. The kinetic energy of the photoelectrons was found by measuring the potential energy of the electric field, eV, needed to stop them. As well as confirming the linear dependence of the kinetic energy on frequency, by making use of his estimate for the electron charge, e , established from his oil drop experiment in 1913, he was able to determine Planck's constant to a precision of around 0.5%. This discovery led to the quantum revolution in physics and earned Einstein the Nobel Prize in 1921.

1.1.3 Compton Scattering

In 1923, Compton investigated the scattering of high energy X-rays and γ -ray from electrons in a carbon target. By measuring the spectrum of radiation at different angles relative to the incident beam, he found two scattering peaks. The first peak occurred at a wavelength which matched that of the incident beam, while the second varied with angle. Within the framework of a purely classical theory of the scattering of electromagnetic radiation from a charged particle - Thomson scattering - the wavelength of a low-intensity beam should remain unchanged.

Compton's observation demonstrated that light cannot be explained purely as a classical wave phenomenon. Light must behave as if it consists of particles in order to explain the low-intensity Compton scattering. If one assumes that the radiation is comprised of photons that have a well defined momentum as well as energy, $p = \frac{h\nu}{c} = \frac{h}{\lambda}$, the shift in wavelength can be understood: The interaction between electrons and high energy photons (ca. keV) results in the electron being given part of the energy (making it recoil), and a photon with the remaining energy being emitted in a different direction from the original, so that the overall momentum of the system is conserved. By taking into account both conservation of energy and momentum of the system, the Compton scattering formula describing the shift in the wavelength as function of scattering angle θ can be derived,

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_e c}(1 - \cos \theta). \quad (1.6)$$

The constant of proportionality $h/m_e c = 0.002426$ nm, the Compton wavelength, characterizes the scale of scattering. Moreover, as $h \rightarrow 0$, one finds that $\Delta\lambda \rightarrow 0$ leading to the classical prediction.

1.1.4 Atomic Spectra

The discovery by Rutherford that the atom was comprised of a small positively charged nucleus surrounded by a diffuse cloud of electrons led naturally to the consideration of a planetary model of the atom. However, a classical theory of electrodynamics would predict that an accelerating charge would radiate energy leading to the eventual collapse of the electron into the nucleus. Moreover, as the electron spirals inwards, the emission would gradually increase in frequency leading to a broad continuous spectra. Yet, detailed studies of electrical discharges in low-pressure gases revealed that atoms emit light at discrete frequencies. The clue to resolving these puzzling observations lay in the discrete nature of atomic spectra. For the hydrogen atom, light emitted when the atom is thermally excited has a particular pattern: Balmer had discovered in 1885 that the emitted wavelengths follow the empirical law, $\lambda = \lambda_0(1/4 - 1/n^2)$ where $n = 3, 4, 5, \dots$ and $\lambda_0 = 3645.6$ Å. Neils Bohr realized that these discrete values of the wavelength reflected the emission of individual photons having energy equal to the energy difference between two allowed orbits of the electron circling the nucleus (the proton), $E_n - E_m = h\nu$, leading to the conclusion that the allowed energy levels must be quantised and varying as $E_n = -\frac{hcR_H}{n^2}$, where $R_H = 109678 \text{ cm}^{-1}$ denotes the Rydberg constant.

How could the quantum $h\nu$ restricting allowed radiation energies also restrict the allowed electron orbits? In 1913 Bohr proposed that the angular momentum of an electron in one of these orbits is quantised in units of Planck's constant,

$$L = m_e v r = n \hbar, \quad \hbar = \frac{h}{2\pi}. \quad (1.7)$$

But why should only certain angular momenta be allowed for the circling electron? A heuristic explanation was provided by de Broglie: just as the constituents of light waves (photons) are seen through Compton scattering to act like particles (of definite energy and momentum), so particles such as electrons may exhibit wave-like properties. For photons, we have seen that the relationship between wavelength and momentum is $p = h/\lambda$. de Broglie hypothesized that the inverse was true: for particles with a momentum p , the wavelength is

$$\lambda = \frac{h}{p}, \quad \text{i.e. } p = \hbar k \quad (1.8)$$

where k denotes the wavevector of the particle. Applied to the electron in the atom, this result suggested that the allowed circular orbits are standing waves, from which Bohr's angular momentum quantization follows. The de Broglie hypothesis found quantitative support in an experiment by Davisson and Germer, and independently by G. P. Thomson in 1927. Their studies of electron diffraction from a crystalline array of Nickel atoms confirmed that the diffraction angles depend on the incident energy (and therefore momentum).

1.2 Wave Mechanics

de Broglie's doctoral thesis, defended at the end of 1924, created a lot of excitement in European physics circles. Shortly after it was published in the Autumn of 1925, Pieter Debye, a theorist in Zurich, suggested to Erwin Schrödinger that he give a seminar on de Broglie's work. Schrödinger gave a polished presentation, but at the end, Debye remarked that he considered the whole theory rather childish: Why should a wave confine itself to a circle in space? It wasn't as if the circle was a waving circular string; real waves in space diffracted and diffused; in fact they obeyed three-dimensional wave equations, and that was what was needed. This was a direct challenge to Schrödinger, who spent some weeks in the Swiss mountains working on the problem, and constructing his equation.

1.2.1 Maxwell's Wave Equation

For a monochromatic wave in vacuum, with no currents or charges present, Maxwell's wave equation,

$$\nabla^2 \mathbf{E} - \frac{1}{c^2} \ddot{\mathbf{E}} = 0, \quad (1.9)$$

admits the plane wave solution, $\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$, with the linear dispersion relation $\omega = c|\mathbf{k}|$ and c the velocity of light. Here, (and throughout the text) we adopt the convention, $\ddot{\mathbf{E}} = \partial_t^2 \mathbf{E}$. We know from the photoelectric effect and Compton scattering

that the photon energy and momentum are related to the frequency and wavelength of light through the relations $E = h\nu = \hbar\omega$, $p = \frac{h}{\lambda} = \hbar k$. The wave equation tells us that $\omega = c|\mathbf{k}|$ and hence $E = c|\mathbf{p}|$. If we think of $e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$ as describing a particle (photon) it would be more natural to write the plane wave in terms of the energy and momentum of the particle as $E_0 e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$. Then, one may see that the wave equation applied to the plane wave describing particle propagation yields the familiar energy momentum relationship, $E^2 = (c\mathbf{p})^2$ for a massless relativistic particle.

This discussion suggests how one might extend the wave equation from the photon (with zero rest mass) to a particle with rest mass m_0 . We require a wave equation that, when it operates on a plane wave, yields the relativistic energy-momentum invariant, $E^2 = (c\mathbf{p})^2 + (m_0 c^2)^2$. Writing the plane wave function $\phi(\mathbf{r}, t) = A e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$, where A is a constant, we can recover the energy-momentum invariant by adding a constant mass term to the wave operator,

$$\left(\nabla^2 - \frac{\partial_t^2}{c^2} - \frac{m_0^2 c^2}{\hbar^2} \right) e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} = - \frac{((c\mathbf{p})^2 - E^2 + m_0^2 c^4)}{(\hbar c)^2} e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} = 0. \quad (1.10)$$

This wave equation is called the **Klein-Gordon equation** and correctly describes the propagation of relativistic particles of mass m_0 . However, its form is inappropriate for non-relativistic particles, like the electron in hydrogen.

Continuing along the same lines, let us assume that a non-relativistic electron in free space is also described by a plane wave of the form $\Psi(\mathbf{r}, t) = A e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$. We need to construct an operator which, when applied to this wave function, just gives us the ordinary non-relativistic energy-momentum relation, $E = \frac{\mathbf{p}^2}{2m}$. The factor of \mathbf{p}^2 can be recovered from two derivatives with respect to \mathbf{r} , but the only way we can get E is by having a single differentiation with respect to time, i.e.

$$i\hbar \partial_t \Psi(\mathbf{r}, t) = - \frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t). \quad (1.11)$$

This is Schrödinger's equation for a free non-relativistic particle. One remarkable feature of this equation is the factor of i which shows that the wavefunction is complex.

How, then, does the presence of a spatially varying scalar potential affect the propagation of a de Broglie wave? This question was considered by Sommerfeld in an attempt to generalize the rather restrictive conditions in Bohr's model of the atom. Since the electron orbit was established by an inverse square force law, just like the planets around the Sun, Sommerfeld couldn't understand why Bohr's atom had only circular orbits as opposed to Keplerlike elliptical orbits. (Recall that all of the observed spectral lines of hydrogen were accounted for by energy differences between circular orbits.

de Broglie's analysis of the allowed circular orbits can be formulated by assuming that, at some instant, the spatial variation of the wavefunction on going around the orbit includes a phase term of the form $e^{ipq/\hbar}$, where here the parameter q measures the spatial distance around the orbit. Now, for an acceptable wavefunction, the total phase change on going around the orbit must be $2\pi n$, where n is integer. For the usual Bohr circular

orbit, where $p = |\mathbf{p}|$ is constant, this leads to quantization of the angular momentum $L = pr = n\hbar$.

Sommerfeld considered a general Keplerian elliptical orbit. Assuming that the de Broglie relation $p = h/\lambda$ still holds, the wavelength must vary as the particle moves around the orbit, being shortest where the particle travels fastest, at its closest approach to the nucleus. Nevertheless, the phase change on moving a short distance Δq should still be $p\Delta q/\hbar$. Requiring the wavefunction to link up smoothly on going once around the orbit gives the **Bohr-Sommerfeld quantisation condition**

$$\oint p \, dq = nh, \quad (1.12)$$

where \oint denotes the line integral around a closed orbit. Thus only certain *elliptical* orbits are allowed. The mathematics is non-trivial, but it turns out that every allowed elliptical orbit has the same energy as one of the allowed circular orbits. That is why Bohr's theory gave the correct energy levels. This analysis suggests that, in a varying potential, the wavelength changes in concert with the momentum.

1.2.2 Schrödinger's Equation

Following Sommerfeld's considerations, let us then consider a particle moving in one spatial dimension subject to a "roller coaster-like" potential. How do we expect the wavefunction to behave? As discussed above, we would expect the wavelength to be shortest where the potential is lowest, in the minima, because that's where the particle is going the fastest. Our task then is to construct a wave equation which leads naturally to the relation following from (classical) energy conservation, $E = \frac{p^2}{2m} + V(x)$. In contrast to the free particle case discussed above, the relevant wavefunction here will no longer be a simple plane wave, since the wavelength (determined through the momentum via the de Broglie relation) varies with the potential. However, at a given position x , the momentum is determined by the "local wavelength". The appropriate wave equation is the one-dimensional Schrödinger equation,

$$i\hbar\partial_t\Psi(x,t) = -\frac{\hbar^2\partial_x^2}{2m}\Psi(x,t) + V(x)\Psi(x,t), \quad (1.13)$$

with the generalization to three-dimensions leading to the Laplacian operator ∇^2 in place of ∂_x^2 (cf. Maxwell's equation).

So far, the validity of this equation rests on plausibility arguments and hand-waving. Why should anyone believe that it really describes an electron wave? Schrödinger's test of his equation was the hydrogen atom. He looked for Bohr's "stationary states": states in which the electron was localized somewhere near the proton, and having a definite energy. The time dependence would be the same as for a plane wave of definite energy, $e^{-Et/\hbar}$; the spatial dependence would be a time-independent function decreasing rapidly at large distances from the proton. From the solution of the stationary wave equation for the Coulomb potential, he was able to deduce the allowed values of energy and momentum. These values were exactly the same as those obtained by Bohr (except that the lowest allowed state in the "new" theory had zero angular momentum): impressive evidence that the new theory was correct.

1.3 Postulates of Quantum Theory

Since there remains no “first principles” derivation of the quantum mechanical equations of motion, the theory is underpinned by a set of “postulates” whose validity rest on experimental verification. Needless to say, quantum mechanics remains perhaps the most successful theory in physics.

- **Postulate 1.** The state of a quantum mechanical system is completely specified by a function $\Psi(\mathbf{r}, t)$ that depends upon the coordinates of the particle(s) and on time. This function, called the wavefunction or state function, has the important property that $|\Psi(\mathbf{r}, t)|^2 d\mathbf{r}$ represents the probability that the particle lies in the volume element $d\mathbf{r} \equiv d^d\mathbf{r}$ located at position \mathbf{r} at time t .

The wavefunction must satisfy certain mathematical conditions because of this probabilistic interpretation. For the case of a single particle, the net probability of finding it at some point in space must be unity leading to the normalization condition, $\int_{-\infty}^{\infty} |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = 1$. It is customary to also normalize many-particle wavefunctions to unity. The wavefunction must also be single-valued, continuous, and finite.

- **Postulate 2.** To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics.

If we require that the expectation value of an operator \hat{A} is real, then it follows that \hat{A} must be a Hermitian operator. If the result of a measurement of an operator \hat{A} is the number a , then a must be one of the eigenvalues, $\hat{A}\Psi = a\Psi$, where Ψ is the corresponding eigenfunction. This postulate captures a central point of quantum mechanics – the values of dynamical variables can be quantized (although it is still possible to have a continuum of eigenvalues in the case of unbound states).

- **Postulate 3.** If a system is in a state described by a normalized wavefunction Ψ , then the average value of the observable corresponding to \hat{A} is given by

$$\langle \hat{A} \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\mathbf{r}. \quad (1.14)$$

If the system is in an eigenstate of \hat{A} with eigenvalue a , then any measurement of the quantity A will yield a . Although measurements must always yield an eigenvalue, the state does not have to be an eigenstate of \hat{A} initially. An arbitrary state can be expanded in the complete set of eigenvectors of \hat{A} ($\hat{A}\Psi_i = a_i\Psi_i$) as $\Psi = \sum_i^n c_i\Psi_i$, where n may go to infinity. In this case, the probability of obtaining the result a_i from the measurement of \hat{A} is given by $P(a_i) = |\langle \Psi_i | \Psi \rangle|^2 = |c_i|^2$. The expectation value of \hat{A} for the state Ψ is the sum over all possible values of the measurement and given by

$$\langle \hat{A} \rangle = \sum_i a_i |\langle \Psi_i | \Psi \rangle|^2 = \sum_i |c_i|^2 a_i. \quad (1.15)$$

Finally, a measurement of Ψ which leads to the eigenvalue a_i , causes the wavefunction to “collapse” into the corresponding eigenstate Ψ_i . (In the case that a_i is degenerate, then Ψ becomes the projection of Ψ onto the degenerate subspace). Thus, measurement affects the state of the system.

- **Postulate 4.** The wavefunction or state function of a system evolves in time according to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi(\mathbf{r}, t), \quad (1.16)$$

where \hat{H} is the Hamiltonian of the system. If Ψ is an eigenstate of \hat{H} , it follows that $\Psi(\mathbf{r}, t) = \Psi(\mathbf{r}, 0)e^{-iEt/\hbar}$.

CHAPTER 2

Quantum Mechanics in One Dimension

Following the rules of quantum mechanics, we have seen that the state of a quantum particle, subject to a scalar potential $V(\mathbf{r}, t)$, is described by the time-dependent Schrödinger equation,

$$i\hbar\partial_t\Psi(\mathbf{r}, t) = -\frac{\hbar^2\nabla^2}{2m}\Psi(\mathbf{r}, t) + V(\mathbf{r}, t)\Psi(\mathbf{r}, t). \quad (2.1)$$

As with all second order linear differential equations, if the potential $V(\mathbf{r}, t)$ is time-independent, the time-dependence of the wavefunction can be separated from the spatial dependence. Setting $\Psi(\mathbf{r}, t) = T(t)\psi(\mathbf{r})$, and separating the variables, the Schrödinger equation takes the form,

$$\frac{\left(-\frac{\hbar^2\nabla^2}{2m}\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r})\right)}{\psi(\mathbf{r})} = \frac{i\hbar\partial_t T(t)}{T(t)} = \text{const.} = E. \quad (2.2)$$

Since we have a function of only \mathbf{r} set equal to a function of only t , they both must equal a constant. In the equation above, we call the constant E (with some knowledge of the outcome). We now have an equation in t set equal to a constant, $i\hbar\partial_t T(t) = ET(t)$, which has a simple general solution, $T(t) = Ce^{-iEt/\hbar}$, where C is some constant. The corresponding equation in \mathbf{r} is then given by the stationary, or **time-independent Schrödinger equation**,

$$-\frac{\hbar^2\nabla^2}{2m}\psi(x) + V(x)\psi(x) = E\psi(x). \quad (2.3)$$

The full time-dependent solution is given by $\Psi(\mathbf{r}, t) = e^{-iEt/\hbar}\psi(\mathbf{r})$ with definite energy, E . Their probability density $|\Psi(\mathbf{r}, t)|^2 = |\psi(\mathbf{r})|^2$ is constant in time – hence they are called stationary states! The operator

$$\hat{H} = -\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r}) \quad (2.4)$$

defines the **Hamiltonian** and the stationary wave equation can be written as the eigenfunction equation, $\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$, i.e. $\psi(\mathbf{r})$ is an eigenstate of \hat{H} with eigenvalue E .

To explore its properties, we will first review some simple and, hopefully, familiar applications of the equation to one-dimensional systems. In addressing the one-dimensional geometry, we will divide our consideration between potentials, $V(x)$, which leave the particle free (i.e. unbound), and those that bind the particle to some region of space.

2.1 Wave Mechanics of Unbound Particles

2.1.1 Particle Flux and conservation of probability

In analogy to the Poynting vector for the electromagnetic field, we may want to know the probability current. For example, for a free particle system, the probability density is uniform over all space, but there is a net flow along the direction of momentum. We can derive an equation showing conservation of probability by differentiating the probability density, $P(x, t) = |\Psi(x, t)|^2$, and using the Schrödinger equation, $\partial_t P(x, t) + \partial_x j(x, t) = 0$. This translates to the usual conservation equation if $j(x, t)$ is identified as the probability current,

$$j(x, t) = -\frac{i\hbar}{2m}[\Psi^* \partial_x \Psi - \Psi \partial_x \Psi^*]. \quad (2.5)$$

If we integrate over some interval in x , $\int_a^b \partial_t P(x, t) dx = -\int_a^b \partial_x j(x, t) dx$ it follows that $\partial_t \int_a^b P(x, t) dx = j(x = a, t) - j(x = b, t)$, i.e. the rate of change of probability is equal to the net flux entering the interval.

To extending this analysis to three space dimensions, we use the general form of the continuity equation, $\partial_t P(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0$, from which follows the particle flux,

$$\mathbf{j}(\mathbf{r}, t) = -\frac{i\hbar}{2m}[\Psi^*(\mathbf{r}, t) \nabla \Psi(\mathbf{r}, t) - \Psi(\mathbf{r}, t) \nabla \Psi^*(\mathbf{r}, t)]. \quad (2.6)$$

For completeness, the proof of Eq. (2.6) is provided in the Appendix [A.1.2](#).

2.1.2 Free Particle

In the absence of an external potential, the time-dependent Schrödinger equation (2.1) describes the propagation of travelling waves. In one dimension, the corresponding complex wavefunction has the form

$$\Psi(x, t) = Ae^{i(kx - \omega t)}, \quad (2.7)$$

where A is the amplitude, and $E(k) = \hbar\omega(k) = \frac{\hbar^2 k^2}{2m}$ represents the free particle energy dispersion for a non-relativistic particle of mass, m , and wavevector $k = 2\pi/\lambda$ with λ the wavelength. Each wavefunction describes a plane wave in which the particle has definite energy $E(k)$ and, in accordance with the de Broglie relation, momentum $p = \hbar/k = h/\lambda$. The energy spectrum of a freely-moving particle is therefore continuous, extending from zero to infinity and, apart from the spatially constant state $k = 0$, has a two-fold degeneracy corresponding to right and left moving particles.

For an infinite system, it makes no sense to fix the amplitude A by the normalization of the total probability. Instead, it is useful to fix the flux associated with the wavefunction. Making use of (2.5) for the particle current, the plane wave is associated with a constant (time-independent) flux,

$$j(x, t) = -\frac{i\hbar}{2m}[\Psi^* \partial_x \Psi - \Psi \partial_x \Psi^*] = |A|^2 \frac{\hbar k}{m} = |A|^2 \frac{p}{m}. \quad (2.8)$$

For a given value of the flux j , the amplitude is given, up to an arbitrary constant phase, by $A = \sqrt{mj/\hbar k}$.

To prepare a **wave packet** which is localized to a region of space, we must superpose components of different wave number. In an open system, this may be achieved using a Fourier expansion. For any function,¹ $\psi(x)$, we have the Fourier decomposition,

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(k) e^{ikx} dk, \quad (2.9)$$

where the coefficients are defined by the inverse transform,

$$\psi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} dx. \quad (2.10)$$

The normalization of $\psi(k)$ follows automatically from the normalization of $\psi(x)$, $\int_{-\infty}^{\infty} \psi^*(k) \psi(k) dk = \int_{-\infty}^{\infty} \psi^*(x) \psi(x) dx$, and both can represent probability amplitudes. Applied to a wavefunction, $\psi(x)$ can be understood as a wave packet made up of contributions involving definite momentum states, e^{ikx} , with amplitude set by the Fourier coefficient $\psi(k)$. The probability for a particle to be found in a region of width dx around some value of x is given by $|\psi(x)|^2 dx$. Similarly, the probability for a particle to have wave number k in a region of width dk around some value of k is given by $|\psi(k)|^2 dk$. (Remember that $p = \hbar k$ so the momentum distribution is very closely related. Here, for economy of notation, we work with k .)

The Fourier transform of a normalized Gaussian wave packet, $\psi(k) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha(k-k_0)^2}$ is also a Gaussian,

$$\psi(x) = \left(\frac{1}{2\pi\alpha}\right)^{1/4} e^{ik_0 x} e^{-\frac{x^2}{4\alpha}} \quad (2.11)$$

From these representations, we can see that it is possible to represent a *single* particle, localized in real space as a superposition of plane wave states localized in Fourier space. But note that, while we have achieved our goal of finding localized wave packets, this has been at the expense of having some non-zero width in x and in k .

For the Gaussian wave packet, we can straightforwardly obtain the width (as measured by the root mean square – RMS) of the probability distribution, $\Delta x = (\langle (x - \langle x \rangle)^2 \rangle)^{1/2} = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} = \sqrt{\alpha}$, and $\Delta k = \frac{1}{\sqrt{4\alpha}}$. We can again see that, as we vary the width in k -space, the width in x -space varies to keep the following product constant, $\Delta x \Delta k = \frac{1}{2}$. If we translate from the wavevector into momentum $p = \hbar k$, then $\Delta p = \hbar \Delta k$ and

$$\Delta x \Delta p = \frac{\hbar}{2}. \quad (2.12)$$

¹More precisely, we can make such an expansion providing we meet some rather weak conditions of smoothness and differentiability of $\psi(x)$ – conditions met naturally by problems which derive from physical systems!

If we consider the width of the distribution as a measure of the "uncertainty", we will prove in section 3.1.3 that the Gaussian wave packet provides the minimum uncertainty. This result shows that we cannot know the position of a particle and its momentum at the same time. If we try to localise a particle to a very small region of space, its momentum becomes uncertain. If we try to make a particle with a definite momentum, its probability distribution spreads out over space.

With this introduction, we now turn to consider the interaction of a particle with a non-uniform potential background. For non-confining potentials, such systems fall into the class of **scattering problems**: For a beam of particles incident on a non-uniform potential, what fraction of the particles are transmitted and what fraction are reflected? In the one-dimensional system, the classical counterpart of this problem is trivial: For particle energies which exceed the maximum potential, all particles are eventually transmitted, while for energies which are lower, all particles are reflected. In quantum mechanics, the situation is richer: For a generic potential of finite extent and height, some particles are always reflected and some are always transmitted. Later in the course we will consider the general problem of scattering from a localised potential in arbitrary dimension. But for now, we will focus on the one-dimensional system, where many of the key concepts can be formulated.

2.1.3 Potential Step

As we have seen, for a time-independent potential, the wavefunction can be factorised as $\Psi(x, t) = e^{-iEt/\hbar}\psi(x)$, where $\psi(x)$ is obtained from the stationary form of the Schrödinger equation,

$$\left[-\frac{\hbar^2 \partial_x^2}{2m} + V(x) \right] \psi(x) = E\psi(x), \quad (2.13)$$

and E denotes the energy of the particle. As $|\Psi(x, t)|^2$ represents a probability density, it must be everywhere finite. As a result, we can deduce that the wavefunction, $\psi(x)$, is also finite. Moreover, since E and $V(x)$ are presumed finite, so must be $\partial_x^2 \psi(x)$. The latter condition implies that

- both $\psi(x)$ and $\partial_x \psi(x)$ must be continuous functions of x , even if V has a discontinuity.

Consider then the influence of a potential step on the propagation of a beam of particles. Specifically, let us assume that a beam of particles with kinetic energy, E , moving from left to right are incident upon a potential step of height V_0 at position $x = 0$. If the beam has unit amplitude, the reflected and transmitted (complex) amplitudes are set by r and t . The corresponding wavefunction is given by

$$\begin{aligned} \psi_-(x) &= e^{ik_-x} + r e^{-ik_-x} & x < 0, \\ \psi_+(x) &= t e^{ik_+x} & x > 0, \end{aligned} \quad (2.14)$$

where $k_- = \frac{\sqrt{2mE}}{\hbar}$ and $k_+ = \frac{\sqrt{2m(E-V_0)}}{\hbar}$. Applying the continuity conditions on $\psi(x)$ and $\partial_x \psi(x)$ at the step ($x = 0$), one obtains the relations $1 + r = t$ and $ik_-(1 - r) = ik_+t$

leading to the reflection and transmission amplitudes,

$$r = \frac{k_- - k_+}{k_- + k_+}, \quad t = \frac{2k_-}{k_- + k_+} \quad (2.15)$$

The reflectivity, R , and transmittivity, T , are defined by the ratios,

$$R = \frac{\text{reflected flux}}{\text{incident flux}}, \quad T = \frac{\text{transmitted flux}}{\text{incident flux}}. \quad (2.16)$$

With the incident, reflected, and transmitted fluxes given by $|A|^2 \frac{\hbar k_-}{m}$, $|Ar|^2 \frac{\hbar k_-}{m}$, and $|At|^2 \frac{\hbar k_+}{m}$ respectively, one obtains

$$R = \left| \frac{k_- - k_+}{k_- + k_+} \right|^2 = |r|^2, \quad T = \left| \frac{2k_-}{k_- + k_+} \right|^2 \frac{k_+}{k_-} = |t|^2 \frac{k_+}{k_-} = \frac{4k_- k_+}{(k_- + k_+)^2}. \quad (2.17)$$

From these results one can confirm that the total flux is, as expected, conserved in the scattering process, i.e. $R + T = 1$.

2.1.4 Potential Barrier

Having dealt with the potential step, we now turn to consider the problem of a beam of particles incident upon a square potential barrier of height V_0 (presumed positive for now) and width a . As mentioned above, this geometry is particularly important as it includes the simplest example of a scattering phenomenon in which a beam of particles is “deflected” by a local potential. Moreover, this one-dimensional geometry also provides a platform to explore a phenomenon peculiar to quantum mechanics – **quantum tunneling**. For these reasons, we will treat this problem fully and with some care.

Since the barrier is localised to a region of size a , the incident and transmitted wavefunctions have the same functional form, $e^{ik_1 x}$, where $k_1 = \frac{\sqrt{2mE}}{\hbar}$, and differ only in their complex amplitude, i.e. after the encounter with the barrier, the transmitted wavefunction undergoes only a change of amplitude (some particles are reflected from the barrier, even when the energy of the incident beam, E , is in excess of V_0) and a phase shift. To determine the relative change in amplitude and phase, we can parameterise the wavefunction as

$$\begin{aligned} \psi_1(x) &= e^{ik_1 x} + r e^{-ik_1 x} & x \leq 0 \\ \psi_2(x) &= A e^{ik_2 x} + B e^{-ik_2 x} & 0 \leq x \leq a \\ \psi_3(x) &= t e^{ik_1 x} & a \leq x \end{aligned} \quad (2.18)$$

where $k_2 = \frac{\sqrt{2m(E-V_0)}}{\hbar}$. Here, as with the step, r denotes the reflected amplitude and t the transmitted.

Applying the continuity conditions on the wavefunction, ψ , and its derivative, $\partial_x \psi$, at the barrier interfaces at $x = 0$ and $x = a$, one obtains

$$\begin{cases} 1 + r = A + B \\ A e^{ik_2 a} + B e^{-ik_2 a} = t e^{ik_1 a} \end{cases}, \quad \begin{cases} k_1(1 - r) = k_2(A - B) \\ k_2(A e^{ik_2 a} - B e^{-ik_2 a}) = k_1 t e^{ik_1 a} \end{cases}. \quad (2.19)$$

Together, these four equations specify the four unknowns, r , t , A and B . Solving, one obtains

$$t = \frac{2k_1 k_2 e^{-ik_1 a}}{2k_1 k_2 \cos(k_2 a) - i(k_1^2 + k_2^2) \sin(k_2 a)}, \quad (2.20)$$

translating to a transmissivity of

$$T = |t|^2 = \frac{1}{1 + \frac{1}{4} \left(\frac{k_1}{k_2} - \frac{k_2}{k_1} \right)^2 \sin^2(k_2 a)}, \quad (2.21)$$

and the reflectivity, $R = 1 - T$. As a consistency check, we can see that, when $V_0 = 0$, $k_2 = k_1$ and $t = 1$, as expected. Moreover, T is restricted to the interval from 0 to 1 as required. So, for barrier heights in the range $E > V_0 > 0$, the transmittivity T shows an oscillatory behaviour with k_2 reaching unity when $k_2 a = n\pi$ with n integer. At these values, there is a conspiracy of interference effects which eliminate altogether the reflected component of the wave leading to perfect transmission. Such a situation arises when the width of the barrier is perfectly matched to an integer or half-integer number of wavelengths inside the barrier.

When the energy of the incident particles falls below the energy of the barrier, $0 < E < V_0$, a classical beam would be completely reflected. However, in the quantum system, particles are able to tunnel through the barrier region and escape leading to a non-zero transmission coefficient. In this regime, $k_2 = i\kappa_2$ becomes pure imaginary leading to an evanescent decay of the wavefunction under the barrier and a suppression, but not extinction, of transmission probability,

$$T = |t|^2 = \frac{1}{1 + \frac{1}{4} \left(\frac{k_1}{\kappa_2} - \frac{\kappa_2}{k_1} \right)^2 \sinh^2(\kappa_2 a)}. \quad (2.22)$$

For $\kappa_2 a \gg 1$ (the weak tunneling limit), the transmittivity takes the form

$$T \simeq \frac{16k_1^2 \kappa_2^2}{(k_1^2 + \kappa_2^2)^2} e^{-2\kappa_2 a}. \quad (2.23)$$

Finally, on a cautionary note, while the phenomenon of quantum mechanical tunneling is well-established, it is difficult to access in a convincing experimental manner. Although a classical particle with energy $E < V_0$ is unable to penetrate the barrier region, in a physical setting, one is usually concerned with a thermal distribution of particles. In such cases, thermal activation may lead to transmission *over* a barrier. Such processes often overwhelm any contribution from true quantum mechanical tunneling.

2.1.5 The Rectangular Potential Well

Finally, if we consider scattering from a potential well (i.e. with $V_0 < 0$), while $E > 0$, we can apply the results of the previous section to find a continuum of unbound states with the corresponding **resonance** behaviour. However, in addition to these unbound states, for $E < 0$ we have the opportunity to find bound states of the potential. It is to this general problem that we now turn.

2.2 Wave Mechanics of Bound Particles

In the case of unbound particles, we have seen that the spectrum of states is continuous. However, for bound particles, the wavefunctions satisfying the Schrödinger equation have only particular quantised energies. In the one-dimensional system, we will find that all binding potentials are capable of hosting a bound state, a feature particular to the low dimensional system.

2.2.1 The Rectangular Potential Well (Continued)

As a starting point, let us consider a rectangular potential well similar to that discussed above. To make use of symmetry considerations, it is helpful to reposition the potential setting

$$V(x) = \begin{cases} 0 & x \leq -a \\ -V_0 & -a \leq x \leq a \\ 0 & a \leq x \end{cases}, \quad (2.24)$$

where the potential depth V_0 is assumed positive. In this case, we will look for bound state solutions with energies lying in the range $-V_0 < E < 0$. Since the Hamiltonian is invariant under **parity transformation**, $[\hat{H}, \hat{P}] = 0$ (where $\hat{P}\psi(x) = \psi(-x)$), the eigenstates of the Hamiltonian \hat{H} must also be eigenstates of parity, i.e. we expect the eigenfunctions to separate into those symmetric and those antisymmetric under parity.

For $E < 0$ (bound states), the wavefunction outside the well region must have the form

$$\psi(x < -a) = Ce^{\kappa x}, \quad \psi(x > a) = De^{-\kappa x}, \quad (2.25)$$

with $\kappa = \frac{\sqrt{-2mE}}{\hbar}$ while in the central well region, the general solution is of the form

$$\psi(-a < x < a) = A \cos(kx) + B \sin(kx), \quad (2.26)$$

where $k = \frac{\sqrt{2m(E+V_0)}}{\hbar}$. Once again we have four equations in four unknowns. The calculation shows that either A or B must be zero for a solution. This means that the states separate into solutions with even or odd parity.

For the even states, the solution of the equations leads to the quantisation condition, $\kappa = \tan ka$, while for the odd states, we find $\kappa = -\cot ka$. These are transcendental equations, and must be solved numerically. Figure ?? compares $\kappa a = \left(\frac{2mV_0 a^2}{\hbar^2} - (ka)^2 \right)^{1/2}$ with $ka \tan ka$ for the even states and to $-ka \cot ka$ for the odd states. Where the curves intersect, we have an allowed energy. From the structure of these equations, it is evident that an even state solution can always be found for arbitrarily small values of the binding potential V_0 while, for odd states, bound states appear only at a critical value of the coupling strength. The wider and deeper the well, the more solutions are generated.

2.2.2 The δ -Function Potential Well

Let us now consider perhaps the simplest binding potential, the δ -function, $V(x) = -aV_0\delta(x)$. Here the parameter ‘ a ’ denotes some microscopic length scale introduced to make the product $a\delta(x)$ dimensionless.² For a state to be bound, its energy must be negative. Moreover, the form of the potential demands that the wavefunction is symmetric under parity, $x \rightarrow -x$. (A wavefunction which was antisymmetric must have $\psi(0) = 0$ and so could not be influenced by the δ -function potential.) We therefore look for a solution of the form

$$\psi(x) = A \begin{cases} e^{\kappa x} & x < 0 \\ e^{-\kappa x} & x > 0 \end{cases}, \quad (2.27)$$

where $\kappa = \frac{\sqrt{-2mE}}{\hbar}$. With this choice, the wavefunction remains everywhere continuous including at the potential, $x = 0$. Integrating the stationary form of the Schrödinger equation across an infinitesimal interval that spans the region of the δ -function potential, we find that

$$\partial_x \psi|_{+\epsilon} - \partial_x \psi|_{-\epsilon} = -\frac{2maV_0}{\hbar^2} \psi(0). \quad (2.28)$$

From this result, we obtain that $\kappa = maV_0/\hbar^2$, leading to the bound state energy

$$E = -\frac{ma^2V_0^2}{2\hbar^2}. \quad (2.29)$$

Indeed, the solution is unique. An attractive δ -function potential hosts only one bound state.

2.2.3 The δ -Function Model of a Crystal

Finally, as our last example of a one-dimensional quantum system, let us consider a particle moving in a periodic potential. The **Kronig-Penney model** provides a caricature of a (one-dimensional) crystalline lattice potential. The potential created by the ions is approximated as an infinite array of potential wells defined by a set of repulsive δ -function potentials,

$$V(x) = aV_0 \sum_{n=-\infty}^{\infty} \delta(x - na). \quad (2.30)$$

Since the potential is repulsive, it is evident that all states have energy $E > 0$. This potential has a new symmetry; a translation by the lattice spacing a leaves the potential unchanged, $V(x + a) = V(x)$. The probability density must therefore exhibit the same translational symmetry,

$$|\psi(x + a)|^2 = |\psi(x)|^2 \quad (2.31)$$

which means that, under translation, the wavefunction differs by at most a phase, $\psi(x + a) = e^{i\phi}\psi(x)$. In the region from $(n-1)a < x < na$, the general solution of the Schrödinger equation is plane wave like and can be written in the form,

$$\psi_n(x) = A_n \sin[k(x - na)] + B_n \cos[k(x - na)], \quad (2.32)$$

²Note that the dimensions of $\delta(x)$ are $[\text{Length}]^{-1}$.

where $k = \frac{\sqrt{2mE}}{\hbar}$ and, following the constraint on translational invariance, $A_{n+1} = e^{i\phi} A_n$ and $B_{n+1} = e^{i\phi} B_n$. By applying the boundary conditions, one can derive a constraint on k similar to the quantised energies for bound states considered above.

Consider the boundary conditions at position $x = na$. Continuity of the wavefunction, $\psi_n|_{x=na} = \psi_{n+1}|_{x=na}$, translates to the condition, $B_n = A_{n+1} \sin(-ka) + B_{n+1} \cos(-ka)$ or

$$B_{n+1} = \frac{B_n + A_{n+1} \sin(ka)}{\cos(ka)}. \quad (2.33)$$

Similarly, the discontinuity in the first derivative, $\partial_x \psi_{n+1}|_{x=na} - \partial_x \psi_n|_{x=na} = \frac{2maV_0}{\hbar^2} \psi_n(na)$, leads to the condition $k[A_{n+1} \cos(ka) + B_{n+1} \sin(ka) - A_n] = \frac{2maV_0}{\hbar^2} B_n$. Substituting the expression for B_{n+1} and rearranging, one obtains

$$A_{n+1} = \frac{2maV_0}{\hbar^2 k} B_n \cos(ka) - B_n \sin(ka) + A_n \cos(ka). \quad (2.34)$$

Similarly, replacing the expression for A_{n+1} in that for B_{n+1} , one obtains the parallel equation,

$$B_{n+1} = \frac{2maV_0}{\hbar^2 k} B_n \sin(ka) + B_n \cos(ka) + A_n \sin(ka). \quad (2.35)$$

With these two equations, and the relations $A_{n+1} = e^{i\phi} A_n$ and $B_{n+1} = e^{i\phi} B_n$, we obtain the quantisation condition,³

$$\cos \phi = \cos(ka) + \frac{maV_0}{\hbar^2 k} \sin(ka). \quad (2.37)$$

As $\hbar k = \sqrt{2mE}$, this result relates the allowed values of energy to the real parameter, ϕ . Since $\cos \phi$ can only take values between -1 and 1 , there are a sequence of allowed bands of energy with energy gaps separating these bands.

Such behaviour is characteristic of the spectrum of periodic lattices: In the periodic system, the wavefunctions – known as **Bloch states** – are indexed by a “quasi”-momentum index k , and a band index n where each Bloch band is separated by an energy gap within which there are no allowed states. In a **metal**, electrons (fermions) populate the energy states starting with the lowest energy up to some energy scale known as the **Fermi energy**. For a partially-filled band, low-lying excitations associated with the continuum of states allow electrons to be accelerated by a weak electric field. In a **band insulator**, all states are filled up to an energy gap. In this case, a small electric field is unable to excite electrons across the energy gap – hence the system remains insulating.

2.3 Wentzel, Kramers and Brillouin (WKB) Method

The WKB (or Wentzel, Kramers and Brillouin) approximation describes a “quasi-classical” method for solving the one-dimensional time-independent Schrödinger equation. Note

³Eliminating A_n and B_n from the equations, a sequence of cancellations obtains

$$e^{2i\phi} + e^{i\phi} \left(\frac{2maV_0}{\hbar^2 k} \sin(ka) + 2 \cos(ka) \right) + 1 = 0. \quad (2.36)$$

Then multiplying by $e^{-i\phi}$, we obtain the expression for $\cos \phi$.

that the consideration of one-dimensional systems is less restrictive than it may sound as many symmetrical higher-dimensional problems are rendered effectively one-dimensional (e.g. the radial equation for the hydrogen atom). The WKB method is named after physicists Wentzel, Kramers and Brillouin, who all developed the approach independently in 1926. Earlier, in 1923, the mathematician Harold Jeffreys had developed a general method of approximating the general class of linear, second-order differential equations, which of course includes the Schrödinger equation. But since the Schrödinger equation was developed two years later, and Wentzel, Kramers, and Brillouin were apparently unaware of this earlier work, the contribution of Jeffreys is often neglected.

The WKB method is important both as a practical means of approximating solutions to the Schrödinger equation, and also as a conceptual framework for understanding the classical limit of quantum mechanics. The WKB approximation is valid whenever the wavelength, λ , is small in comparison to other relevant length scales in the problem. This condition is not restricted to quantum mechanics, but rather can be applied to any wave-like system (such as fluids, electromagnetic waves, etc.), where it leads to approximation schemes which are mathematically very similar to the WKB method in quantum mechanics. For example, in optics the approach is called the **eikonal method**, and in general the method is referred to as **short wavelength asymptotics**. Whatever the name, the method is an old one, which predates quantum mechanics – indeed, it was apparently first used by Liouville and Green in the first half of the nineteenth century. In quantum mechanics, λ is interpreted as the de Broglie wavelength, and L is normally the length scale of the potential. Thus, the WKB method is valid if the wavefunction oscillates many times before the potential energy changes significantly

2.3.1 Semi-Classical Approximation to Leading Order

Consider then the propagation of a quantum particle in a slowly-varying one-dimensional potential, $V(x)$. Here, by “slowly-varying” we mean that, in any small region the wavefunction is well-approximated by a plane wave, and that the wavelength only changes over distances that are long compared with the local value of the wavelength. We’re also assuming for the moment that the particle has positive kinetic energy in the region. Under these conditions, we can anticipate that the solution to the time-independent Schrödinger equation

$$-\frac{\hbar^2 \partial_x^2}{2m} \psi(x) + V(x) \psi(x) = E \psi(x), \quad (2.38)$$

will take the form $A(x)e^{\pm ip(x)x}$ where $p(x)$ is the “local” value of the momentum set by the classical value, $p^2/2m + V(x) = E$, and the amplitude, $A(x)$, is slowly-varying compared with the phase factor. Clearly this is a *semi-classical* limit: \hbar has to be sufficiently small that there are many oscillations in the typical distance over which the potential varies.⁴

⁴To avoid any point of confusion, it is of course true that \hbar is a fundamental constant – not easily adjusted! So what do we mean when we say that the semi-classical limit translates to $\hbar \rightarrow 0$? The validity of the semi-classical approximation relies upon $\lambda/L \ll 1$. Following the de Broglie relation, we may write this inequality as $\hbar/pL \ll 1$, where p denotes the particle momentum. Now, in this correspondence, both p and L can be considered as “classical” scales. So, formally, we can think of accessing the semi-classical limit by adjusting \hbar so that it is small enough to fulfil this inequality. Alternatively, at fixed \hbar , we can access the semi-classical regime by reaching to higher and higher energy scales (larger and larger p) so that the inequality becomes valid.

To develop this idea more rigorously, and to emphasize the rapid *phase* variation in the semi-classical limit, we can parameterise the wavefunction as

$$\phi(x) = e^{i\sigma(x)/\hbar}. \quad (2.39)$$

Here the complex function $\sigma(x)$ encompasses both the amplitude and phase. Then, with $-\hbar^2 \partial_x^2 \psi(x) = -i\hbar e^{i\sigma(x)/\hbar} \partial_x^2 \sigma(x) + e^{i\sigma(x)/\hbar} (\partial_x \sigma)^2$, the Schrödinger equation may be rewritten in terms of the phase function as

$$-i\hbar \partial_x^2 \sigma(x) + (\partial_x \sigma)^2 = p^2(x). \quad (2.40)$$

Now, since we're assuming the system is semi-classical, it makes sense to expand $\sigma(x)$ as a power series in \hbar , setting

$$\sigma = \sigma_0 + (\hbar/i)\sigma_1 + (\hbar/i)^2\sigma_2 + \dots. \quad (2.41)$$

At the leading (zeroth) order of the expansion, we can drop the first term in (2.40), leading to $(\partial_x \sigma_0)^2 = p^2(x)$. Defining $p(x) = +\sqrt{2m(E - V(x))}$, this equation permits the two solutions $\partial_x \sigma_0 = \pm p(x)$, from which we conclude

$$\sigma_0(x) = \pm \int^x p(x') dx'. \quad (2.42)$$

From the form of the Schrödinger equation (2.40), it is evident that this approximate solution is only valid if we can ignore the first term. More precisely, we must have

$$\left| \frac{\hbar \partial_x^2 \sigma(x)}{(\partial_x \sigma(x))^2} \right| \equiv |\partial_x (\hbar/\partial_x \sigma)| \ll 1. \quad (2.43)$$

But, in the leading approximation, $\partial_x \sigma(x) \simeq p(x)$ and $p(x) = 2\pi\hbar/\lambda(x)$, so the condition translates to the relation

$$\frac{1}{2\pi} |\partial_x \lambda(x)| \ll 1. \quad (2.44)$$

This means that the change in wavelength over a distance of one wavelength must be small. This condition can not always be met: In particular, if the particle is confined by an attractive potential, at the edge of the classically allowed region, where $E = V(x)$, $p(x)$ must be zero and the corresponding wavelength infinite. The approximation is only valid well away from these **classical turning points**, a matter to which we will return shortly.

2.3.2 Next to Leading Order Correction

Let us now turn to the next term in the expansion in \hbar . Retaining terms from Eq. (2.40) which are of order \hbar , we have

$$-i\hbar \partial_x^2 \sigma_0(x) + 2\partial_x \sigma_0 (\hbar/i) \partial_x \sigma_1 = 0. \quad (2.45)$$

Rearranging this equation, and integrating, we find

$$\partial_x \sigma_1 = -\frac{\partial_x^2 \sigma_0}{2\partial_x \sigma_0} = -\frac{\partial_x p}{2p}, \quad \sigma_1(x) = -\frac{1}{2} \ln p(x) + \text{const.} \quad (2.46)$$

So, to this order of approximation, the wavefunction takes the form,

$$\psi(x) = \frac{C_1}{\sqrt{p(x)}} e^{(i/\hbar) \int^x p dx'} + \frac{C_2}{\sqrt{p(x)}} e^{(-i/\hbar) \int^x p dx'}, \quad (2.47)$$

where C_1 and C_2 denote constants of integration.

To interpret the factors of $\sqrt{p(x)}$, consider the first term: a wave moving to the right. Since $p(x)$ is real (remember we are currently considering the classically allowed region where $E > V(x)$), the exponential has modulus unity, and the local probability density is proportional to $1/p(x)$, i.e. to $1/v(x)$, where $v(x)$ denotes the velocity of the particle. This dependence has a simple physical interpretation: The probability of finding the particle in any given small interval is proportional to the time it spends there. Hence it is inversely proportional to its speed.

We turn now to consider the wavefunction in the classically forbidden region where

$$\frac{p^2}{2m} = E - V(x) < 0. \quad (2.48)$$

Here $p(x)$ is of course pure imaginary, but the same formal phase solution of the Schrödinger equation applies provided, again, that the particle is remote from the classical turning points where $E = V(x)$. In this region, the wavefunction takes the general form,

$$\psi(x) = \frac{C'_1}{\sqrt{|p(x)|}} e^{-(i/\hbar) \int^x |p| dx'} + \frac{C'_2}{\sqrt{|p(x)|}} e^{(i/\hbar) \int^x |p| dx'}. \quad (2.49)$$

This completes our study of the wavefunction in the regions in which the semiclassical approach can be formally justified. However, to make use of this approximation, we have to understand how to deal with the regions close to the classical turning points. Remember that in our treatment of the Schrödinger equation the energy quantization derived from the implementation of boundary conditions.

2.3.3 Connection Formulae, Boundary Conditions and Quantisation Rules

Let us assume that we are dealing with a one-dimensional confining potential where the classically allowed region is unique and spans the interval $b \leq x \leq a$. Clearly, in the classically forbidden region to the right, $x > a$, only the first term in Eq. (2.49) remains convergent and can contribute, while for $x < b$ it is only the second term that contributes. Moreover, in the classically allowed region, $b \leq x \leq a$, the wavefunction has the oscillating form (2.47).

But how do we connect the three regions together? To answer this question, it is necessary to make the assumption that the potential varies sufficiently smoothly that it is a good approximation to take it to be linear in the vicinity of the classical turning points. That is to say, we assume that a linear potential is a sufficiently good approximation out to the point where the short wavelength (or decay length for tunneling regions) description is adequate. Therefore, near the classical turning at $x = a$, we take the potential to be

$$E - V(x) \simeq F_0(x - a), \quad (2.50)$$

where F_0 denotes the (constant) force. For a strictly linear potential, the wavefunction can be determined analytically, and takes the form of an Airy function. In particular, it is known that the Airy function to the right of the classical turning point has the asymptotic form

$$\lim_{x \gg a} \psi(x) = \frac{C}{2\sqrt{|p(x)|}} e^{-(i/\hbar) \int^x |p| dx'}, \quad (2.51)$$

translating to a decay into the classically forbidden region while, to the left, it has the asymptotic oscillatory solution,

$$\lim_{b \ll x < a} \psi(x) = \frac{C}{2\sqrt{|p(x)|}} \cos \left[\frac{1}{\hbar} \int_x^a p dx' - \frac{\pi}{4} \right] \equiv \frac{C}{2\sqrt{|p(x)|}} \cos \left[\frac{\pi}{4} - \frac{1}{\hbar} \int_x^a p dx' \right]. \quad (2.52)$$

At the second classical turning point at $x = b$, the same argument gives

$$\lim_{b < x \ll a} \psi(x) = \frac{C'}{2\sqrt{|p(x)|}} \cos \left[\frac{1}{\hbar} \int_b^x p dx' - \frac{\pi}{4} \right]. \quad (2.53)$$

For these two expressions to be consistent, we must have $C' = \pm C$ and

$$\left(\frac{1}{\hbar} \int_b^x p(x') dx' - \frac{\pi}{4} \right) - \left(\frac{\pi}{4} - \frac{1}{\hbar} \int_x^a p(x') dx' \right) = n\pi, \quad (2.54)$$

where, for n even, $C' = C$ and for n odd, $C' = -C$. Therefore, we have the condition $\frac{1}{\hbar} \int_b^a p(x) dx = (n + 1/2)\pi$, or when cast in terms of a complete periodic cycle of the classical motion,

$$\oint p(x) dx = 2\pi\hbar(n + 1/2). \quad (2.55)$$

This is just the **Bohr-Sommerfeld quantisation condition**, and n can be interpreted as the number of nodes of the wavefunction.

Note that the integrated action, $\oint p dx$, represents the area of the classical path in phase space. This shows that each state is associated with an element of phase space $2\pi\hbar$. From this, we can deduce the approximate energy splitting between levels in the semi-classical limit: The change in the integral with energy ΔE corresponding to one level must be $2\pi\hbar$ - one more state and one more node, i.e. $\Delta E \partial_E \oint p dx = 2\pi\hbar$. Now $\partial_p E = v$, so $\oint \partial_E p dx = \oint dx / v = T$, the period of the orbit. Therefore, $\Delta E = 2\pi\hbar/T = \hbar\omega$: In the semi-classical limit, if a particle emits one photon and drops to the next level, the frequency of the photon emitted is just the orbital frequency of the particle.

For a particle strictly confined to one dimension, the connection formulae can be understood within a simple picture: The wavefunction “spills over” into the classically forbidden region, and its twisting there collects an $\pi/4$ of phase change. So, in the lowest state, the total phase change in the classically allowed region need only be $\pi/2$. For the radial equation, assuming that the potential is well behaved at the origin, the wavefunction goes to zero there. A bound state will still spill over beyond the classical turning point at r_0 , say, but clearly there must be a total phase change of $3\pi/4$ in the allowed region for the lowest state, since there can be no spill over to negative r . In this case, the general quantization formula will be

$$\frac{1}{\hbar} \int_r^{r_0} p(r) dr = (n + 3/4)\pi, \quad n = 0, 1, 2, \dots, \quad (2.56)$$

with the series terminating if and when the turning point reaches infinity. In fact, some potentials, including the Coulomb potential and the centrifugal barrier for $\ell \neq 0$, are in fact singular at $r = 0$. These cases require special treatment.

2.3.4 Example: Simple Harmonic Oscillator

For the quantum harmonic oscillator, $H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 = E$, the classical momentum is given by

$$p(x) = \sqrt{2m\left(E - \frac{m\omega^2 x^2}{2}\right)}. \quad (2.57)$$

The classical turning points are set by $E = m\omega^2 x_0^2/2$, i.e. $x_0 = \pm 2E/m\omega^2$. Over a periodic cycle, the classical action is given by

$$\oint p(x) dx = 2 \int_{-x_0}^{x_0} dx \sqrt{2m\left(E - \frac{m\omega^2 x^2}{2}\right)} = 2\pi \frac{E}{\omega}. \quad (2.58)$$

According to the WKB method, the latter must be equated to $2\pi\hbar(n + 1/2)$, with the last term reflecting the two turning points. As a result, we find that the energy levels are as expected specified by $E_n = (n + 1/2)\hbar\omega$.

In the WKB approximation, the corresponding wavefunctions are given by

$$\psi(x) = \frac{C}{\sqrt{p(x)}} \cos\left(\frac{1}{\hbar} \int_{-x_0}^{x_0} p(x') dx' - \frac{\pi}{4}\right) \quad (2.59)$$

$$= \frac{C}{\sqrt{p(x)}} \cos\left(\frac{2\pi}{4}(n + 1/2) \frac{1}{\hbar} \int_0^{x_0} p(x') dx' - \frac{\pi}{4}\right) \quad (2.60)$$

$$= \frac{C}{\sqrt{p(x)}} \cos\left(\frac{n\pi}{2} + \frac{E}{\hbar\omega} \left[\arcsin\left(\frac{x}{x_0}\right) + \frac{x}{x_0} \sqrt{1 - \frac{x^2}{x_0^2}}\right]\right), \quad (2.61)$$

for $0 < x < x_0$ and

$$\psi(x) = \frac{C}{2\sqrt{p(x)}} \exp\left(-\frac{E}{\hbar\omega} \left[\frac{x}{x_0} \sqrt{\frac{x^2}{x_0^2} - 1} - \operatorname{arcosh}\left(\frac{x}{x_0}\right)\right]\right) \quad (2.62)$$

for $x > a$. Note that the failure of the WKB approximation is reflected in the appearance of discontinuities in the wavefunction at the classical turning points. Nevertheless, the wavefunction at high energies provides a strikingly good approximation to the exact wavefunction.

2.3.5 Example: Quantum Tunneling

Consider the problem of quantum tunneling. Suppose that a beam of particles is incident upon a localised potential barrier, $V(x)$. Further, let us assume that, over a single continuous region of space, from b to a , the potential rises above the incident energy of the incoming particles so that, classically, all particles would be reflected. In the quantum system, the some particles incident from the left may tunnel through the barrier and continue propagating to the right. We are interested in finding the transmission probability.

From the WKB solution, to the left of the barrier (region 1), we expect a wavefunction of the form

$$\psi_1(x) = \frac{1}{\sqrt{p}} \exp\left[\frac{i}{\hbar} \int_b^x p dx'\right] + r(E) \frac{1}{\sqrt{p}} \exp\left[-\frac{i}{\hbar} \int_b^x p dx'\right], \quad (2.63)$$

with $p(x) = \sqrt{2m(E - V(x))}$, while, to the right of the barrier (region 3), the wavefunction is given by

$$\psi_3(x) = t(E) \frac{1}{\sqrt{p}} \exp \left[\frac{i}{\hbar} \int_a^x p \, dx' \right]. \quad (2.64)$$

In the barrier region, the wavefunction is given by

$$\psi_2(x) = \frac{C_1}{\sqrt{|p(x)|}} \exp \left[-\frac{i}{\hbar} \int_a^x |p| \, dx' \right] + \frac{C_2}{\sqrt{|p(x)|}} \exp \left[\frac{i}{\hbar} \int_a^x |p| \, dx' \right]. \quad (2.65)$$

Applying the matching conditions on the wavefunction at the classical turning points, one obtains the transmissivity,

$$\boxed{T(E) \simeq \exp \left[-\frac{2}{\hbar} \int_a^b |p| \, dx \right]}. \quad (2.66)$$

Operator Methods in Quantum Mechanics

While the wave mechanical formulation has proved successful in describing the quantum mechanics of bound and unbound particles, some properties can not be represented through a wave-like description. For example, the electron spin degree of freedom does not translate to the action of a gradient operator. It is therefore useful to reformulate quantum mechanics in a framework that involves only operators.

Before discussing properties of operators, it is helpful to introduce a further simplification of notation. One advantage of the operator algebra is that it does not rely upon a particular basis. For example, when one writes $\hat{H} = \frac{\hat{p}^2}{2m}$, where the hat denotes an operator, we can equally represent the momentum operator in the spatial coordinate basis, when it is described by the differential operator, $\hat{p} = -i\hbar\partial_x$, or in the momentum basis, when it is just a number $\hat{p} = p$. Similarly, it would be useful to work with a basis for the wavefunction which is coordinate independent. Such a representation was developed by Dirac early in the formulation of quantum mechanics.

In the parlons of mathematics, square integrable functions (such as wavefunctions) are said form a vector space, much like the familiar three-dimensional vector spaces. In the **Dirac notation**, a state vector or wavefunction, ψ , is represented as a “ket”, $|\psi\rangle$. Just as we can express any three-dimensional vector in terms of the basis vectors, $\mathbf{r} = x\hat{\mathbf{e}}_1 + y\hat{\mathbf{e}}_2 + z\hat{\mathbf{e}}_3$, so we can expand any wavefunction as a superposition of basis state vectors,

$$|\psi\rangle = \lambda_1 |\psi_1\rangle + \lambda_2 |\psi_2\rangle + \cdots . \quad (3.1)$$

Alongside the ket, we can define the “bra”, $\langle\psi|$. Together, the bra and ket define the **scalar product**

$$\langle\phi|\psi\rangle \equiv \int_{-\infty}^{\infty} dx \phi^*(x)\psi(x), \quad (3.2)$$

from which follows the identity, $\langle\phi|\psi\rangle^* = \langle\psi|\phi\rangle$. In this formulation, the real space representation of the wavefunction is recovered from the inner product $\phi(x) = \langle x|\phi\rangle$ while the momentum space wavefunction is obtained from $\phi(p) = \langle p|\phi\rangle$. As with a three-dimensional vector space where $\mathbf{a} \cdot \mathbf{b} \leq |\mathbf{a}||\mathbf{b}|$, the magnitude of the scalar product is limited by the magnitude of the vectors,

$$|\langle\psi|\phi\rangle| \leq \sqrt{\langle\psi|\psi\rangle \langle\phi|\phi\rangle}, \quad (3.3)$$

a relation known as the **Schwarz inequality**.

3.1 Operators

An operator \hat{A} is a mathematical object that maps one state vector, $|\psi\rangle$, into another, $|\phi\rangle$, i.e. $\hat{A}|\psi\rangle = |\phi\rangle$. If

$$\hat{A}|\psi\rangle = a|\psi\rangle, \quad (3.4)$$

then $|\psi\rangle$ is said to be an **eigenstate** (or **eigenfunction**) of \hat{A} with eigenvalue a . For example, the plane wave state $\psi_x(x) = \langle x|\psi_p\rangle = Ae^{ipx/\hbar}$ is an eigenstate of the **momentum operator**, $\hat{p} = -i\hbar\partial_x$, with eigenvalue p . For a free particle, the plane wave is also an eigenstate of the Hamiltonian, $\hat{H} = \frac{\hat{p}^2}{2m}$ with eigenvalue $\frac{p^2}{2m}$.

In quantum mechanics, for any observable A , there is an operator \hat{A} which acts on the wavefunction so that, if a system is in a state described by $|\psi\rangle$, the expectation value of A is

$$\langle A \rangle = \langle \psi|\hat{A}|\psi \rangle = \int_{-\infty}^{\infty} dx \phi^*(x) \hat{A}\psi(x). \quad (3.5)$$

Every operator corresponding to an observable is both linear and Hermitian: That is, for any two wavefunctions $|\phi\rangle$ and $|\psi\rangle$, and any two complex numbers α and β , **linearity** implies that

$$\hat{A}(\alpha|\psi\rangle + \beta|\phi\rangle) = \alpha(\hat{A}|\psi\rangle) + \beta(\hat{A}|\phi\rangle). \quad (3.6)$$

Moreover, for any linear operator \hat{A} , the **Hermitian conjugate** operator (also known as the adjoint) is defined by the relation

$$\langle \phi|\hat{A}\psi \rangle = \int dx \phi^*(\hat{A}\psi) = \int dx \psi(\hat{A}^\dagger\phi)^* = \langle \hat{A}^\dagger\phi|\psi \rangle. \quad (3.7)$$

From the definition, $\langle \hat{A}^\dagger\phi|\psi \rangle = \langle \phi|\hat{A}\psi \rangle$, we can prove some useful relations: Taking the complex conjugate, $\langle \hat{A}^\dagger\phi|\psi \rangle^* = \langle \psi|\hat{A}^\dagger\phi \rangle = \langle \hat{A}\psi|\phi \rangle$, and then finding the Hermitian conjugate of \hat{A}^\dagger , we have

$$\langle \psi|\hat{A}^\dagger\phi \rangle = \langle (\hat{A}^\dagger)^\dagger\psi|\phi \rangle = \langle \hat{A}\psi|\phi \rangle, \quad \text{i.e. } (\hat{A}^\dagger)^\dagger = \hat{A}. \quad (3.8)$$

Therefore, if we take the Hermitian conjugate twice, we get back to the same operator. It's easy to show that $(\lambda\hat{A})^\dagger = \lambda^*\hat{A}^\dagger$ and $(\hat{A} + \hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$ just from the properties of the dot product. We can also show that $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$ from the identity, $\langle \phi|\hat{A}\hat{B}\psi \rangle = \langle \hat{A}^\dagger\phi|\hat{B}\psi \rangle = \langle \hat{B}^\dagger\hat{A}^\dagger\phi|\psi \rangle$. Note that operators are **associative** but not (in general) **commutative**,

$$\hat{A}\hat{B}|\psi\rangle = \hat{A}(\hat{B}|\psi\rangle) = (\hat{A}\hat{B})|\psi\rangle \neq \hat{B}\hat{A}|\psi\rangle. \quad (3.9)$$

It is helpful to define the **commutator** of two operators by

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}. \quad (3.10)$$

A physical variable must have real expectation values (and eigenvalues). This implies that the operators representing physical variables have some special properties. By computing the complex conjugate of the expectation value of a physical variable, we can easily show that physical operators are their own Hermitian conjugate,

$$\langle \psi | \hat{H} | \psi \rangle^* = \left[\int_{-\infty}^{\infty} \psi^*(x) \hat{H} \psi(x) dx \right]^* = \int_{-\infty}^{\infty} \psi(x) (\hat{H} \psi(x))^* dx = \langle \hat{H} \psi | \psi \rangle. \quad (3.11)$$

i.e. $\langle \hat{H} \psi | \psi \rangle = \langle \psi | \hat{H} \psi \rangle = \langle \hat{H}^\dagger \psi | \psi \rangle$, and $\hat{H}^\dagger = \hat{H}$. Operators that are their own Hermitian conjugate are called **Hermitian** (or self-adjoint).

3.1.1 Matrix Representations of Operators

Eigenfunctions of Hermitian operators $\hat{H} |i\rangle = E_i |i\rangle$ form an orthonormal (i.e. $\langle i | j \rangle = \delta_{ij}$) complete basis. For any complete basis $\{|i\rangle\}$, we can expand a state $|\psi\rangle$ as

$$|\psi\rangle = \sum_i \psi_i |i\rangle \quad (3.12)$$

This is a “representation” of $|\psi\rangle$ in this particular basis: e.g. if $\{|i\rangle\}$ are energy eigenstates, then we say that ψ_i is the “energy-representation” of $|\psi\rangle$.

To obtain an explicit form for ψ_i , we note that we can for any orthonormal complete set of states $\{|i\rangle\}$, we can always write

$$|\psi\rangle = \sum_i |i\rangle \langle i | \psi \rangle. \quad (3.13)$$

Thus, we see that the complex numbers $\langle i | \psi \rangle$ are the components of the state vector in the basis states $\{|i\rangle\}$, that is $\psi_i \equiv \langle i | \psi \rangle$.

A ‘ket’ state vector followed by a ‘bra’ state vector is an example of an operator. The **projection operator** onto a state $|j\rangle$ is given by $|j\rangle\langle j|$. First the bra vector dots into the state, giving the coefficient of $|j\rangle$ in the state, then it is multiplied by the unit vector $|j\rangle$, turning it back into a vector, with the right length to be a projection. An operator maps one vector into another vector, so this is an operator. If we sum over a complete orthonormal set of states, like the eigenstates of a Hermitian operator, we obtain the (useful) **resolution of the identity**

$$\hat{\mathbb{I}} = \sum_i |i\rangle\langle i|. \quad (3.14)$$

Using the resolution of the identity, it is possible to express any operator as

$$\hat{A} = \hat{\mathbb{I}} \hat{A} \hat{\mathbb{I}} = \sum_i \sum_j |j\rangle \langle j | \hat{A} | i \rangle \langle i|. \quad (3.15)$$

The complex numbers $A_{ji} = \langle j | \hat{A} | i \rangle$ are the “matrix representation” of \hat{A} in this basis,

$$\hat{A} = \sum_{ij} A_{ji} |j\rangle\langle i|. \quad (3.16)$$

Consider the action of \hat{A} on a state $|\psi\rangle$

$$|\phi\rangle \equiv \hat{A}|\psi\rangle \quad (3.17)$$

$$= \sum_i \sum_j |j\rangle \langle j|\hat{A}|i\rangle \langle i|\psi\rangle = \sum_{i,j} |j\rangle A_{ji} \psi_i \quad (3.18)$$

The representation of $|\psi\rangle$ in this basis is

$$\phi_i \equiv \langle i|\phi\rangle = \langle i| \left(\sum_{k,j} |j\rangle A_{jk} \psi_k \right) = \sum_{k,j} \delta_{ij} A_{jk} \psi_k \quad (3.19)$$

$$= \sum_k A_{ik} \phi_k \quad (3.20)$$

Thus the action of the operator \hat{A} is via matrix multiplication of A_{ik} on the components of the vector ψ_k . Any complete orthonormal set of vectors can be used as the basis. Each gives rise to a different (vector) representation of the states and (matrix) representation of the operators.

In the above discussion, we have assumed that the basis $\{|i\rangle\}$ is discrete (i.e. we can sum over the projectors $|i\rangle\langle i|$). How do we interpret these sums when the basis is described by a continuous variable? For example, we could consider the eigenstates $|x\rangle$ of the position operator \hat{x} , or the eigenstates $|p\rangle$ of the momentum operator \hat{p} .

For a continuous set of states, the resolution of the identity becomes

$$\hat{\mathbb{I}} = \int dx |x\rangle\langle x|. \quad (3.21)$$

and the orthonormality condition becomes

$$\langle x'|x\rangle = \delta(x - x'), \quad (3.22)$$

where $\delta(x)$ is the **Dirac delta function**. Thus, for a state $|\psi\rangle$ we can write

$$|\psi\rangle = \int dx |x\rangle \langle x|\psi\rangle = \int dx \psi(x) |x\rangle \quad (3.23)$$

If $\{|x\rangle\}$ are the position eigenstates, then the complex function $\psi(x)$ the position representation of $|\psi\rangle$. This function $\psi(x)$ is nothing but the wavefunction of the Schrödinger equation. Eq. (3.23) shows how the Schrödinger wavefunction should be interpreted within the more abstract Dirac notation.

The basis states can be formed from any complete set of orthogonal states. In particular, they can be formed from the basis states of the position or the momentum operator, i.e. $\int_{-\infty}^{\infty} dx |x\rangle\langle x| = \int_{-\infty}^{\infty} dp |p\rangle\langle p| = \hat{\mathbb{I}}$. If we apply these definitions, we can then recover the familiar Fourier representation,

$$\psi(x) = \langle x|\psi\rangle = \int_{-\infty}^{\infty} dp \underbrace{\langle x|p\rangle}_{e^{ipx/\hbar}/\sqrt{2\pi\hbar}} \langle p|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp e^{ipx/\hbar} \psi(p), \quad (3.24)$$

where $\langle x|p\rangle$ is the position representation of the momentum eigenstate $|p\rangle$.

3.1.2 Time-Evolution Operator

The ability to develop an eigenfunction expansion provides the means to explore the time evolution of a general wave packet, $|\psi\rangle$ under the action of a Hamiltonian. Formally, we can evolve a wavefunction forward in time by applying the time-evolution operator. For a Hamiltonian which is time independent, we have $|\psi(t)\rangle = \hat{U} |\psi(0)\rangle$, where

$$\boxed{\hat{U} = e^{-i\hat{H}t/\hbar},} \quad (3.25)$$

denotes the time-evolution operator.¹ By inserting the resolution of identity, $\mathbb{I} = \sum_i |i\rangle\langle i|$, where the states $|i\rangle$ are eigenstates of the Hamiltonian with eigenvalue E_i , we find that

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar} \sum_i \langle i | \langle i | \psi(0) \rangle = \sum_i \langle i | \langle i | \psi(0) \rangle e^{-iE_i t/\hbar}. \quad (3.26)$$

The time-evolution operator is an example of a **unitary operator**. The latter are defined as transformations which preserve the scalar product, $\langle \phi | \psi \rangle = \langle \hat{U} \phi | \hat{U} \psi \rangle = \langle \phi | \hat{U}^\dagger \hat{U} \psi \rangle \stackrel{!}{=} \langle \psi | \phi \rangle$, i.e.

$$\boxed{\hat{U}^\dagger \hat{U} = \hat{\mathbb{I}}} \quad (3.27)$$

3.1.2.1 Example: Evolution of Harmonic Oscillator

Consider the harmonic oscillator Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2$. Later in this chapter, we will see that the eigenstates, $|n\rangle$, have equally-spaced eigenvalues, $E_n = \hbar\omega(n + 1/2)$, for $n = 0, 1, 2, \dots$. Let us then consider the time-evolution of a general wavepacket, $|\psi(0)\rangle$, under the action of the Hamiltonian. From the equation above, we find that $|\psi(t)\rangle = \sum_n |n\rangle \langle n | \psi(0) \rangle e^{-iE_n t/\hbar}$. Since the eigenvalues are equally spaced, let us consider what happens when $t = t_r \equiv 2\pi r/\omega$, with r integer. In this case, since $e^{2\pi i n r} = 1$, we have

$$|\psi(t_r)\rangle = \sum_n |n\rangle \langle n | \psi(0) \rangle e^{-i\omega t_r/2} = (-1)^r |\psi(0)\rangle \quad (3.28)$$

From this result, we can see that, up to an overall phase, the wave packet is perfectly reconstructed at these times. This recurrence or “echo” is not generic, but is a manifestation of the equal separation of eigenvalues in the harmonic oscillator.

3.1.3 Uncertainty Principle for Non-Commuting Operators

For non-commuting Hermitian operators, $[\hat{A}, \hat{B}] \neq 0$, it is straightforward to establish a bound on the uncertainty in their expectation values. Given a state $|\psi\rangle$, the mean square uncertainty is defined as

$$(\Delta A)^2 = \langle \psi | (\hat{A} - \langle \hat{A} \rangle)^2 | \psi \rangle = \langle \psi | \hat{U}^2 | \psi \rangle, \quad (3.29)$$

$$(\Delta B)^2 = \langle \psi | (\hat{B} - \langle \hat{B} \rangle)^2 | \psi \rangle = \langle \psi | \hat{V}^2 | \psi \rangle, \quad (3.30)$$

¹This equation follows from integrating the time-dependent Schrödinger equation, $\hat{H} |\psi\rangle = i\hbar \partial_t |\psi\rangle$.

where we have defined the operators $\hat{U} = \hat{A} - \langle \hat{A} \rangle$ and $\hat{V} = \hat{B} - \langle \hat{B} \rangle$. Since $\langle \hat{A} \rangle$ and $\langle \hat{B} \rangle$ are just constants, $[\hat{U}, \hat{V}] = [\hat{A}, \hat{B}]$. Now let us take the scalar product of $\hat{U}|\psi\rangle + i\lambda\hat{V}|\psi\rangle$ with itself to develop some information about the uncertainties. As a modulus, the scalar product must be greater than or equal to zero, i.e. expanding, we have $\langle\psi|\hat{U}^2|\psi\rangle + \lambda^2\langle\psi|\hat{V}^2|\psi\rangle + i\lambda\langle\psi|\hat{U}\hat{V}|\psi\rangle - i\lambda\langle\psi|\hat{V}\hat{U}|\psi\rangle \geq 0$. Reorganising this equation in terms of the uncertainties, we thus find

$$(\Delta A)^2 + \lambda^2(\Delta B)^2 + i\lambda\langle[\hat{U}, \hat{V}]\rangle \geq 0. \quad (3.31)$$

If we minimise this expression with respect to λ , we can determine when the inequality becomes strongest. In doing so, we find

$$2\lambda(\Delta B)^2 + i\langle[\hat{U}, \hat{V}]\rangle = 0, \quad \lambda = -\frac{i}{2} \frac{\langle[\hat{U}, \hat{V}]\rangle}{(\Delta B)^2}. \quad (3.32)$$

Substituting this value of λ back into the inequality, we then find,

$$(\Delta A)^2(\Delta B)^2 \geq -\frac{1}{4}\langle[\hat{U}, \hat{V}]\rangle^2. \quad (3.33)$$

We therefore find that, for non-commuting operators, the uncertainties obey the following inequality,

$$\boxed{\Delta A \Delta B \geq \left| \frac{1}{2} \langle[\hat{A}, \hat{B}]\rangle \right|}. \quad (3.34)$$

If the commutator is a constant, as in the case of the conjugate operators $[\hat{p}, \hat{x}] = -i\hbar$, the expectation values can be dropped, and we obtain the relation, $(\Delta A)(\Delta B) \geq \frac{i}{2}[\hat{A}, \hat{B}]$. For momentum and position, this result recovers **Heisenberg's uncertainty principle**,

$$\boxed{\Delta p \Delta x \geq \left| \frac{1}{2} \langle[\hat{p}, \hat{x}]\rangle \right| = \frac{\hbar}{2}}. \quad (3.35)$$

3.1.4 Time-Evolution of Expectation Values

Finally, to close this section on operators, let us consider how their expectation values evolve. To do so, let us consider a general operator \hat{A} which may itself involve time. The time derivative of a general expectation value has three terms.

$$\frac{d}{dt} \langle\psi|\hat{A}|\psi\rangle = \partial_t(\langle\psi|\hat{A}|\psi\rangle) + \langle\psi|\partial_t\hat{A}|\psi\rangle + \langle\psi|\hat{A}(\partial_t|\psi\rangle). \quad (3.36)$$

If we then make use of the time-dependent Schrödinger equation, $i\hbar\partial_t|\psi\rangle = \hat{H}|\psi\rangle$, and the Hermiticity of the Hamiltonian, we obtain

$$\frac{d}{dt} \langle\psi|\hat{A}|\psi\rangle = \underbrace{\frac{i}{\hbar} \left(\langle\psi|\hat{H}\hat{A}|\psi\rangle - \langle\psi|\hat{A}\hat{H}|\psi\rangle \right)}_{\frac{i}{\hbar} \langle[\hat{H}, \hat{A}]\rangle} + \langle\psi|\partial_t\hat{A}|\psi\rangle. \quad (3.37)$$

$$\frac{i}{\hbar} \langle[\hat{H}, \hat{A}]\rangle \quad (3.38)$$

This is an important and general result for the time derivative of expectation values which becomes simple if the operator itself does not explicitly depend on time,

$$\boxed{\frac{d}{dt} \langle \hat{A} \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{A}] \rangle.} \quad (3.39)$$

From this result, which is known as **Ehrenfest's theorem**, we see that expectation values of operators that commute with the Hamiltonian are constants of the motion

3.1.4.1 Example: Evolution of \hat{x} and \hat{p} Operators

From the non-relativistic Schrödinger operator for a single particle moving in a potential, $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$, we can derive the quantum mechanical counterparts of Hamilton's classical equations of motion.

Suppose we wanted to know the instantaneous change in the expectation of the momentum operator \hat{p} . Using Ehrenfest's theorem, we have

$$\frac{d}{dt} \langle \hat{p} \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{p}] \rangle + \left\langle \frac{\partial}{\partial t} \hat{p} \right\rangle = \frac{i}{\hbar} \langle [V(\hat{x}), \hat{p}] \rangle, \quad (3.40)$$

since the operator \hat{p} commutes with itself and has no time dependence. By expanding the right hand side, using the identity $[F(\hat{x}), \hat{p}] = i\hbar \partial_{\hat{x}} F(\hat{x})$, we obtain

$$\frac{d}{dt} \langle \hat{p} \rangle = - \langle \partial_{\hat{x}} V(\hat{x}) \rangle = - \langle \partial_{\hat{x}} \hat{H} \rangle. \quad (3.41)$$

Similarly, we can obtain the instantaneous change in the position expectation value,

$$\frac{d}{dt} \langle \hat{x} \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{x}] \rangle + \left\langle \frac{\partial}{\partial t} \hat{x} \right\rangle = \frac{i}{2m\hbar} \langle [\hat{p}^2, \hat{x}] \rangle, \quad (3.42)$$

and thus from this we can evaluate the appropriate commutator, noting that $[\hat{p}, \hat{x}] = -i\hbar$, to give

$$\frac{d}{dt} \langle \hat{x} \rangle = \frac{1}{m} \langle \hat{p} \rangle = \langle \partial_{\hat{p}} \hat{H} \rangle. \quad (3.43)$$

Although, at first glance, it might appear that the Ehrenfest theorem is saying that the quantum mechanical expectation values obey Newton's classical equations of motion, this is not actually the case. This result does not say that the pair $\{\langle \hat{x} \rangle, \langle \hat{p} \rangle\}$ satisfies Newton's second law, because the right-hand side of the formulae (3.41) and (3.43) are of the form $\langle F(\hat{x}, t) \rangle$ rather than $F(\langle \hat{x} \rangle, t)$. Nevertheless, for states that are highly localised in space, the expected position and momentum will approximately follow classical trajectories, which may be understood as an instance of the correspondence principle.

3.2 The Heisenberg Picture

Until now, the time dependence of an evolving quantum system has been placed within the wavefunction while the operators have remained constant - this is the **Schrödinger picture** or **representation**. However, it is sometimes useful to transfer the time-dependence

to the operators. To see how, let us consider the expectation value of some operator \hat{B} ,

$$\langle \psi(t) | \hat{B} | \psi(t) \rangle = \langle e^{-i\hat{H}t/\hbar} \psi(0) | \hat{B} | e^{-i\hat{H}t/\hbar} \psi(0) \rangle = \langle \psi(0) | e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} | \psi(0) \rangle. \quad (3.44)$$

According to rules of associativity, we can multiply operators together before using them. If we define the operator $\hat{B}(t) = e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}$, the time dependence of the expectation values has been transferred from the wavefunction. This is called the **Heisenberg picture** or **representation** and in it, the operators evolve with time (even if, as in this case, they have no explicit time dependence) while the wavefunctions remain constant. In this representation, the time derivative of the operator is given by

$$\frac{d}{dt} \langle \hat{B} \rangle = \frac{i\hat{H}}{\hbar} e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} - e^{i\hat{H}t/\hbar} \hat{B} \frac{i\hat{H}}{\hbar} e^{-i\hat{H}t/\hbar} \quad (3.45)$$

$$= \frac{i}{\hbar} e^{i\hat{H}t/\hbar} [\hat{H}, \hat{B}] e^{-i\hat{H}t/\hbar} \quad (3.46)$$

$$= \frac{i}{\hbar} [\hat{H}, \hat{B}(t)]. \quad (3.47)$$

3.3 Quantum Harmonic Oscillator

As we will see time and again in this course, the harmonic oscillator assumes a privileged position in quantum mechanics and quantum field theory finding numerous and sometimes unexpected applications. It is useful to us now in that it provides a platform for us to implement some of the technology that has been developed in this chapter. In the one-dimensional case, the quantum harmonic oscillator Hamiltonian takes the form,

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2, \quad (3.48)$$

where $\hat{p} = -i\hbar\partial_x$. To find the eigenstates of the Hamiltonian, we could look for solutions of the linear second order differential equation corresponding to the time-independent Schrödinger equation, $\hat{H}\psi = E\psi$, where $\hat{H} = -\frac{\hbar^2}{2m}\partial_x^2 + \frac{1}{2}m\omega^2\hat{x}^2$. The integrability of the Schrödinger operator in this case allows the stationary states to be expressed in terms of a set of orthogonal functions known as Hermite polynomials. However, the complexity of the exact eigenstates obscure a number of special and useful features of the harmonic oscillator system. To identify these features, we will instead follow a method based on an operator formalism.

The form of the Hamiltonian as the sum of the squares of momenta and position suggests that it can be recast as the “square of an operator”. To this end, let us introduce the operator

$$a = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + i \frac{\hat{p}}{m\omega} \right), \quad a^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - i \frac{\hat{p}}{m\omega} \right), \quad (3.49)$$

where, for notational convenience, we have not drawn hats on the operators a and its Hermitian conjugate a^\dagger . Making use of the identity,

$$a^\dagger a = \frac{m\omega}{2\hbar} \hat{x}^2 + \frac{\hat{p}^2}{2\hbar m\omega} + \frac{i}{2\hbar} [\hat{x}, \hat{p}] = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2} \quad (3.50)$$

and the parallel relation, $aa^\dagger = \frac{\hat{H}}{\hbar\omega} + \frac{1}{2}$, we see that the operators fulfil the commutation relations

$$\boxed{[a, a^\dagger] \equiv aa^\dagger - a^\dagger a = 1.} \quad (3.51)$$

Then, setting $\hat{n} = a^\dagger a$, the Hamiltonian can be cast in the form

$$\boxed{\hat{H} = \hbar\omega(n + 1/2).} \quad (3.52)$$

Since the operator $\hat{n} = a^\dagger a$ must lead to a positive definite result, we see that the eigenstates of the harmonic oscillator must have energies of $\hbar\omega/2$ or higher. Moreover, the ground state $|0\rangle$ can be identified by finding the state for which $a|0\rangle = 0$. Expressed in the coordinate basis, this translates to the equation,²

$$\left(x + \frac{\hbar}{m\omega} \partial_x\right) \psi_0(x) = 0, \quad \psi_0(x) = \langle x|0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}. \quad (3.54)$$

Since $\hat{n}|0\rangle = a^\dagger a|0\rangle = 0$, this state is an eigenstate with energy $\hbar\omega/2$. The higher lying states can be found by acting upon this state with the operator a^\dagger . The proof runs as follows: If $\hat{n}|n\rangle = n|n\rangle$, we have

$$\hat{n}(a^\dagger|n\rangle) = a^\dagger \underbrace{aa^\dagger}_{a^\dagger a + 1} |n\rangle = (a^\dagger \underbrace{a^\dagger a}_{\hat{n}} + a^\dagger) |n\rangle = (n+1)a^\dagger |n\rangle \quad (3.55)$$

or, equivalently, $[\hat{n}, a^\dagger] = a^\dagger$. In other words, if $|n\rangle$ is an eigenstate of \hat{n} with eigenvalue n , then $a^\dagger|n\rangle$ is an eigenstate with eigenvalue $n+1$.

From this result, we can deduce that the eigenstates for a “tower” $|0\rangle, |1\rangle = C_1 a^\dagger|0\rangle, |2\rangle = C_2 (a^\dagger)^2|0\rangle$, etc., where C_n denotes the normalisation. If $\langle n|n\rangle = 1$ we have

$$\langle n|aa^\dagger|n\rangle = \langle n|(\hat{n} + 1)|n\rangle = (n+1). \quad (3.56)$$

Therefore, with $|n+1\rangle = \frac{1}{\sqrt{n+1}}a^\dagger|n\rangle$ the state $|n+1\rangle$ is also normalised, $\langle n+1|n+1\rangle = 1$. By induction, we can deduce the general normalisation,

$$\boxed{|n\rangle = \frac{1}{\sqrt{n!}}(a^\dagger)^n|0\rangle,} \quad (3.57)$$

with $\langle n|n'\rangle = \delta_{nn'}$, $\hat{H}|n\rangle = \hbar\omega(n + 1/2)|n\rangle$ and

$$\boxed{a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, \quad a|n\rangle = \sqrt{n}|n-1\rangle.} \quad (3.58)$$

The operators a and a^\dagger represent **ladder operators** and have the effect of lowering or raising the energy of the state.

²Formally, in coordinate basis, we have $\langle x'|a|x\rangle = \delta(x' - x)(a + \frac{\hbar}{m\omega}\partial_x)$ and $\langle x|0\rangle = \psi_0(x)$. Then making use of the resolution of identity $\int dx |x\rangle\langle x| = \mathbb{I}$, we have

$$\langle x|a|0\rangle = 0 = \int dx \langle x|a|x'\rangle \langle x'|0\rangle = \left(x + \frac{\hbar}{m\omega}\partial_x\right) \psi_0(x). \quad (3.53)$$

In fact, the operator representation achieves something quite remarkable and, as we will see, unexpectedly profound. The quantum harmonic oscillator describes the motion of a single particle in a one-dimensional potential well. Its eigenvalues turn out to be equally spaced - a ladder of eigenvalues, separated by a constant energy $\hbar\omega$. If we are energetic, we can of course translate our results into a coordinate representation $\psi_n(x) = \langle x|n\rangle$.³ However, the operator representation affords a second interpretation, one that lends itself to further generalisation in quantum field theory. We can instead interpret the quantum harmonic oscillator as a simple system involving many fictitious particles, each of energy $\hbar\omega$. In this representation, known as the **Fock space**, the vacuum state $|0\rangle$ is one involving no particles, $|1\rangle$ involves a single particle, $|2\rangle$ has two and so on. These fictitious particles are created and annihilated by the action of the raising and lowering operators, a^\dagger and a with canonical commutation relations, $[a, a^\dagger] = 1$. Later in the course, we will find that these commutation relations are the hallmark of **bosonic** quantum particles and this representation, known as the **second quantisation** underpins the quantum field theory of the electromagnetic field.

This completes our abridged survey of operator methods in quantum mechanics.

³Expressed in real space, the harmonic oscillator wavefunctions are in fact described by the Hermite polynomials,

$$\psi_n(x) = \langle x|n\rangle = \sqrt{\frac{1}{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}} x\right) \exp\left[-\frac{m\omega x^2}{2\hbar}\right], \quad (3.59)$$

where $H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}$.

Quantum Mechanics in More Than One Dimension

Previously, we have explored the manifestations of quantum mechanics in one spatial dimension and discussed the properties of bound and unbound states. The concepts developed there apply equally to higher dimension. However, for a general two or three-dimensional potential, without any symmetry, the solutions of the Schrödinger equation are often inaccessible. In such situations, we may develop approximation methods to address the properties of the states (e.g. WKB method, and see chapter 7). However, in systems where there is a high degree of symmetry, the quantum mechanics of the system can often be reduced to a tractable low-dimensional theory.

4.1 Rigid Diatomic Molecule

As a pilot example let us consider the quantum mechanics of a rigid diatomic molecule with nuclear masses m_1 and m_2 , and (equilibrium) bond length, R_e . Since the molecule is rigid, its coordinates can be specified by its centre of mass, $\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}$, and internal orientation, $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ (with $|\mathbf{r}| = R_e$). Defining the total mass $M = m_1 + m_2$, and moment of inertia, $I = \mu R_e^2$, where $\mu = m_1 m_2 / (m_1 + m_2)$ denotes the reduced mass, the corresponding Hamiltonian can be then separated into the kinetic energy associated with the centre of mass motion and the rotational kinetic energy,

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{L}}^2}{2I}, \quad (4.1)$$

where $\hat{\mathbf{P}} = -i\hbar\nabla_{\mathbf{R}}$ and $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ denotes the angular momentum associated with the internal degrees of freedom. Since the internal and centre of mass degrees of freedom separate, the wavefunction can be factorized as $\psi(\mathbf{r}, \mathbf{R}) = e^{i\mathbf{K}\cdot\mathbf{R}}Y(\mathbf{r})$, where the first factor accounts for the free particle motion of the body, and the second factor relates to the internal angular degrees of freedom.

As a result of the coordinate separation, we have reduced the problem of the rigid diatomic molecule to the study of the quantum mechanics of a particle moving on a sphere – the **rigid rotor**,

$$\hat{H}_{\text{rot}} = \frac{\hat{\mathbf{L}}^2}{2I}. \quad (4.2)$$

The eigenstates of this component of the Hamiltonian are simply the states of the angular momentum operator. Indeed, in *any* quantum mechanical system involving a radial potential, the angular momentum will be conserved, i.e. $[\hat{H}, \hat{\mathbf{L}}] = 0$ meaning that the angular component of the wavefunction can be indexed by the states of the angular momentum operator. We therefore now digress to discuss the quantum mechanics of angular momentum

4.2 Angular momentum

4.2.1 Commutation Relations

Following the usual canonical quantization procedure, the angular momentum operator is defined by $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ where, as usual $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ obey the commutation relations, $[\hat{p}_i, \hat{r}_j] = -i\hbar\delta_{ij}$. Using this relation, one may then show that the angular momentum operators obey the **spin commutation relations**,

$$[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k. \quad (4.3)$$

where, as usual, ϵ_{ijk} denotes the totally antisymmetric tensor - the Levi Civita symbol.¹

4.2.2 Eigenvalues of Angular Momentum

In the following, we will construct a basis set of angular momentum states. Since the angular momentum is a *vector* quantity, it may be characterised by its magnitude and direction. For the former, let us define the operator $\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$. With the latter, since the separate components of the angular momentum are all mutually non-commuting, we cannot construct a common set of eigenstates for any two of them. They do, however, commute with $\hat{\mathbf{L}}^2$. Therefore, in the following, we will look for an eigenbasis of $\hat{\mathbf{L}}^2$ and *one* direction, say \hat{L}_z ,

$$\hat{\mathbf{L}}^2 |a, b\rangle = a |a, b\rangle, \quad \hat{L}_z |a, b\rangle = b |a, b\rangle. \quad (4.4)$$

To find $|a, b\rangle$, we could simply proceed by looking for a suitable coordinate basis to represent $\hat{\mathbf{L}}^2$ and \hat{L}_z in terms of differential operators. However, although we will undertake such a programme in due course, before getting to this formalism, we can make substantial progress without resorting to an explicit coordinate representation.

4.2.2.1 Raising and Lowering Operators for Angular Momentum

The set of eigenvalues a and b can be obtained by making use of a trick based on a “ladder operator” formalism which parallels that used in the study of the quantum harmonic oscillator in section 3.3. Specifically, let us define the raising and lowering operators,

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y. \quad (4.5)$$

With this definition, one may then show that

$$[\hat{L}_z, \hat{L}_{\pm}] = \pm\hbar\hat{L}_{\pm}. \quad (4.6)$$

¹Recall that $\epsilon_{ijk} = 1$ if $\{i, j, k\}$ is an even permutation of $\{1, 2, 3\}$, -1 if it is an odd permutation, and 0 if any index is repeated.

Since each component of the angular momentum commutes with $\hat{\mathbf{L}}^2$, we can deduce that the action of \hat{L}_\pm on $|a, b\rangle$ cannot affect the value of a relating to the magnitude of the angular momentum. However, they do affect the projection:

$$\hat{L}_z \hat{L}_\pm |a, b\rangle = \hat{L}_\pm \hat{L}_z |a, b\rangle + [\hat{L}_z, \hat{L}_\pm] |a, b\rangle = (b \pm \hbar) |a, b\rangle. \quad (4.7)$$

Therefore, if $|a, b\rangle$ is an eigenstate of \hat{L}_z with eigenvalue b , $\hat{L}_\pm |a, b\rangle$ is either zero, or an eigenstate of \hat{L}_z with eigenvalue $b \pm \hbar$, i.e. $\hat{L}_\pm |a, b\rangle = C_\pm(a, b) |a, b \pm \hbar\rangle$ where $C_\pm(a, b)$ is a normalisation constant.

To fix the normalisation, we may note that the norm,

$$\|\hat{L}_\pm |a, b\rangle\|^2 = \langle a, b | \hat{L}_\pm^\dagger \hat{L}_\pm |a, b\rangle = \langle a, b | \hat{L}_\mp \hat{L}_\pm |a, b\rangle, \quad (4.8)$$

where we have used the identity $\hat{L}_\pm^\dagger = \hat{L}_\mp$. Then, making use of the relation $\hat{L}_\mp \hat{L}_\pm = \hat{L}_x^2 + \hat{L}_y^2 \pm i[\hat{L}_x, \hat{L}_y] = \hat{\mathbf{L}}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z$, and the presumed normalisation, $\langle a, b | a, b\rangle = 1$, one finds

$$\|\hat{L}_\pm |a, b\rangle\|^2 = \langle a, b | (\hat{\mathbf{L}}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z) |a, b\rangle = a - b^2 \mp \hbar b. \quad (4.9)$$

As a represents the eigenvalue of a sum of squares of Hermitian operators, it is necessarily non-negative. Moreover, b is real. Therefore, for a given a , b must be bounded: there must be a b_{max} and a (negative or zero) b_{min} . In particular,

$$\|\hat{L}_+ |a, b_{max}\rangle\|^2 = a - b_{max}^2 \mp \hbar b_{max} \quad (4.10)$$

$$\|\hat{L}_- |a, b_{min}\rangle\|^2 = a - b_{min}^2 \mp \hbar b_{min} \quad (4.11)$$

For a given a , b_{max} and b_{min} are determined uniquely – there cannot be two states with the same a but different b annihilated by \hat{L}_+ . It also follows immediately that $a = b_{max}(b_{max} + \hbar)$ and $b_{min} = -b_{max}$. Furthermore, we know that if we keep operating on $|a, b_{min}\rangle$ with \hat{L}_+ , we generate a sequence of states with \hat{L}_z eigenvalues $b_{min} + \hbar, b_{min} + 2\hbar, b_{min} + 3\hbar, \dots$. This series must terminate, and the only possible way for that to happen is for b_{max} to be equal to $b_{min} + n\hbar$ with n integer, from which it follows that b_{max} is either an integer or half an odd integer times \hbar .

At this point, we switch to the standard notation. We have established that the eigenvalues of \hat{L}_z form a finite ladder, with spacing \hbar . We write them as $m\hbar$, and ℓ is used to denote the maximum value of m , so the eigenvalue of $\hat{\mathbf{L}}^2$, $a = \ell(\ell + 1)\hbar^2$. Both ℓ and m will be integers or half odd integers, but the spacing of the ladder of m values is always unity. Although we have been writing $|a, b\rangle$ with $a = \ell(\ell + 1)\hbar^2$, $b = m\hbar$ we shall henceforth follow convention and write $|\ell, m\rangle$.

In summary, the operators $\hat{\mathbf{L}}^2$ and \hat{L}_z have a common set of orthonormal eigenstates $|\ell, m\rangle$ with

$$\boxed{\hat{\mathbf{L}}^2 |\ell, m\rangle = \ell(\ell + 1)\hbar^2 |\ell, m\rangle, \quad \hat{L}_z |\ell, m\rangle = m\hbar |\ell, m\rangle,} \quad (4.12)$$

where ℓ, m are integers or half-integers. The allowed quantum numbers m form a ladder with step spacing unity, the maximum value of m is ℓ , and the minimum value is $-\ell$.

With these results, we may then return to the normalisation of the raising and lowering operators. In particular, making use of Eq. (4.9), we have

$$\begin{aligned}\hat{L}_+ |\ell, m\rangle &= \hbar\sqrt{\ell(\ell+1) - m(m+1)} |\ell, m+1\rangle \\ \hat{L}_- |\ell, m\rangle &= \hbar\sqrt{\ell(\ell+1) - m(m-1)} |\ell, m-1\rangle\end{aligned}\quad (4.13)$$

The use of m to denote the component of angular momentum in one direction came about because a Bohr-type electron in orbit is a current loop, with a magnetic moment parallel to its angular momentum. So the m measured the component of magnetic moment in a chosen direction, usually along an external magnetic field. For this reason, m is often termed the **magnetic quantum number**.

4.2.3 Representation of the Angular Momentum States

Having established expressions for the eigenvalues of the angular momentum operators, it is now necessary to establish (angular) coordinate representations for the corresponding eigenstates, $Y_{\ell m}(\theta, \phi) = \langle \theta, \phi | \ell, m \rangle$. Here the angles θ and ϕ denote the spherical coordinates parameterising the unit sphere. Previously, we obtained the eigenvalues of the angular momentum operator by making use of the raising and lowering operators in a manner that paralleled the study of the quantum harmonic oscillator. Similarly, to obtain explicit expressions for the eigenstates, we must make use of the coordinate representation of these operators. With $\mathbf{r} = r\hat{\mathbf{e}}_r$, the gradient operator can be written in spherical polar coordinates as

$$\nabla = \hat{\mathbf{e}}_r \partial_r + \hat{\mathbf{e}}_\theta \frac{1}{r} \partial_\theta + \hat{\mathbf{e}}_\phi \frac{1}{r \sin \theta} \partial_\phi. \quad (4.14)$$

From this result, we thus obtain

$$\hat{L}_z = -i\partial_\phi, \quad \hat{L}_\pm \hbar e^{\pm i\phi} (\pm \partial_\theta + i \cot \theta \partial_\phi), \quad (4.15)$$

and, at least formally,

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \partial_\theta (\sin \theta \partial_\theta) + \frac{1}{\sin^2 \theta} \partial_\phi^2 \right]. \quad (4.16)$$

Beginning with the eigenstates of \hat{L}_z , the eigenvalue equation (4.12), and making use of the expression above, we have

$$-i\hbar \partial_\phi Y_{\ell m}(\theta, \phi) = m\hbar Y_{\ell m}(\theta, \phi). \quad (4.17)$$

Since the left hand side depends only on ϕ , the solution is separable and takes the form $Y_{\ell m}(\theta, \phi) = F(\theta)e^{im\phi}$. Note that, provided m is integer, the continuity of the wavefunction, $Y_{\ell m}(\theta, \phi + 2\pi) = Y_{\ell m}(\theta, \phi)$, is ensured. Thus, the condition that the co-ordinate representation of the wavefunction be singlevalued requires m to be integer, and hence ℓ to be integer. (As discussed in Chapter 5, for “spin” angular momentum half-integer ℓ is possible.)

To determine the second component of the eigenstates, $F(\theta)$, we could immediately turn to the eigenvalue equation involving the differential operator for $\hat{\mathbf{L}}^2$,

$$\left[\frac{1}{\sin \theta} \partial_\theta (\sin \theta \partial_\theta) - \frac{m^2}{\sin^2 \theta} \right] F(\theta) = \ell(\ell+1)F(\theta) \quad (4.18)$$

However, to construct the states, it is easier to draw upon the properties of the angular momentum raising and lowering operators (much in the same way that the Hermite polynomials are generated by the action of ladder operators in the harmonic oscillator problem).

Consider then the state of maximal m , $|\ell, \ell\rangle$, for which $\hat{L}_+ |\ell, \ell\rangle = 0$. Making use of the coordinate representation of the raising operator above together with the separability of the wavefunction, this relation implies that

$$0 = \langle \theta, \phi | \hat{L}_+ | \ell, \ell \rangle = \hbar e^{i\phi} (\partial_\theta + i \cot \theta \partial_\phi) Y_{\ell\ell}(\theta, \phi) = \hbar e^{i(\ell+1)\phi} (\partial_\theta - \ell \cot \theta) F(\theta). \quad (4.19)$$

From this result it follows that $\partial_\theta F(\theta) = \ell \cot \theta F(\theta)$ with the solution $F(\theta) = C \sin^\ell \theta$, and C a constant of normalization. States with values of m lower than ℓ can then be obtained simply by repeated application of the angular momentum lowering operator \hat{L}_- to the state $|\ell, \ell\rangle$. This amounts to the relation

$$Y_{\ell m}(\theta, \phi) = C(\hat{L}_-)^{\ell-m} [\sin^\ell \theta e^{i\ell\phi}] \quad (4.20)$$

$$= C(-\partial_\theta + \ell \cot \theta)^{\ell-m} [\sin^\ell \theta e^{i\ell\phi}]. \quad (4.21)$$

The eigenfunctions produced by this procedure are well known and referred to as the **spherical harmonics**. In particular, one finds that the normalised eigenstates take the form,

$$Y_{\ell m}(\theta, \phi) = (-1)^{m+|m|} \left[\frac{2\ell+1}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!} \right]^{1/2} P_\ell^{|m|}(\cos \theta) e^{im\phi} \quad (4.22)$$

where

$$P_\ell^m(\xi) = \frac{(1-\xi^2)^{m/2}}{2^\ell \ell!} \frac{d^{m+\ell}}{d\xi^{m+\ell}} (\xi^2 - 1)^\ell, \quad (4.23)$$

represent the **associated Legendre polynomials**. In particular, for the first few angular momentum states, we have

$$\begin{aligned} Y_{00} &= \frac{1}{\sqrt{4\pi}}, \\ Y_{10} &= \sqrt{\frac{3}{4\pi}} \cos \theta, & Y_{11} &= -\sqrt{\frac{3}{8\pi}} e^{i\phi} \sin \theta, \\ Y_{20} &= \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1), & Y_{21} &= -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta, & Y_{22} &= \sqrt{\frac{15}{32\pi}} e^{2i\phi} \sin^2 \theta. \end{aligned} \quad (4.24)$$

As a complete basis set, the spherical harmonics can be used as a resolution of the identity

$$\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} |\ell, m\rangle \langle \ell, m| = \hat{\mathbb{I}}. \quad (4.25)$$

In terms of the angular position eigenstates $|\theta, \phi\rangle$, we have

$$\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi |\theta, \phi\rangle \langle \theta, \phi| = \hat{\mathbb{I}}, \quad (4.26)$$

where the integration measure $\sin \theta \, d\theta \, d\phi$ weights all directions equally. The normalisation condition is

$$\langle \theta', \phi' | \theta, \phi \rangle = \frac{1}{\sin \theta} \delta(\theta - \theta') \delta(\phi - \phi'), \quad (4.27)$$

as may be readily verified by requiring $\hat{\mathbb{I}}^2 = \hat{\mathbb{I}}$ from (4.26).

Thus, expressing the angular momentum eigenstates in the coordinate basis, we have

$$\sum_{\ell=0}^{\infty} Y_{\ell,m}^*(\theta', \phi') Y_{\ell,m}(\theta, \phi) = \frac{1}{\sin \theta} \delta(\theta - \theta') \delta(\phi - \phi'), \quad (4.28)$$

Similarly, we have the orthogonality condition,

$$\int_0^{\pi} \sin \theta \, d\theta \int_0^{2\pi} d\phi Y_{\ell,m}^*(\theta', \phi') Y_{\ell,m}(\theta, \phi) = \delta_{\ell\ell'} \delta_{mm'}. \quad (4.29)$$

After this lengthy digression, we may now return to the problem of the quantum mechanical rotor Hamiltonian and the rigid diatomic molecule. From the analysis above, we have found that the eigenstates of the Hamiltonian (4.1) are given by $\psi(\mathbf{R}, \mathbf{r}) = \frac{1}{\sqrt{2\pi}} e^{i\mathbf{K} \cdot \mathbf{R}} Y_{\ell,m}(\theta, \phi)$ with eigenvalues

$$E_{\mathbf{K},\ell} = \frac{\hbar^2 \mathbf{K}^2}{2m} + \frac{\hbar^2}{2I} \ell(\ell+1), \quad (4.30)$$

where each \mathbf{K}, ℓ value has a $2\ell + 1$ -fold degeneracy.

CHAPTER 5

Spin

Until we have focussed on the quantum mechanics of particles which are “featureless”, carrying no internal degrees of freedom. However, a relativistic formulation of quantum mechanics shows that particles can exhibit an intrinsic angular momentum component known as spin. However, the discovery of the spin degree of freedom marginally predates the development of relativistic quantum mechanics by Dirac and was achieved in a ground-breaking experiment by Stern and Gerlach (1922). In their experiment, they passed a well-collimated beam of silver atoms through a region of inhomogeneous field before allowing the particles to impact on a photographic plate. The magnetic field was directed perpendicular to the beam, and has a strong gradient, $\partial_z B_z \neq 0$ so that a beam comprised of atoms with a magnetic moment would be bent towards the z or $-z$ axis. As the magnetic moment will be proportional to the total angular momentum, such an experiment can be thought of as a measurement of its projection along z .

At the time of the experiment, there was an expectation that the magnetic moment of the atom was generated in its entirety by the orbital angular momentum. Within that expectation, the result was qualitatively consistent with the model of Bohr – that orbits of the electron are quantised. Hence the congratulations on the postcard. However, as we have seen, the full quantum theory (of Schrödinger, developed after 1922) leads one to expect that the angular momentum is $\ell = 0, 1, 2, \dots$ so there should be a minimum of 3 possible values of l_z . As such, one would expect that there would be an odd number of possible z -components of angular momentum: $2\ell + 1$ with ℓ integer. Curiously, Stern and Gerlach’s experiment showed that the beam of silver atoms split into two! This discovery, which caused great discussion and surprise in subsequent years, presented a puzzle.

However, in our derivation of allowed angular momentum eigenvalues we found that, although for any system the allowed values of m form a ladder with spacing \hbar , we could not rule out half-integral values of m . The lowest such case, $\ell = 1/2$, would in fact have just two allowed m values: $m = \pm 1/2$. However, such an ℓ value could not translate to an orbital angular momentum because the z -component of the orbital wavefunction, ψ has a factor $e^{im\phi} = e^{\pm i\phi/2}$, and therefore acquires a factor -1 on rotating through 2π ! This would imply that ϕ is not single-valued, which doesn’t make sense for a Schrödinger-type wavefunction.

Yet the experimental result was irrefutable. Therefore, this must be a new kind of non-orbital angular momentum - spin. Conceptually, just as the Earth has orbital angular momentum in its yearly circle around the sun, and also spin angular momentum from its daily turning, the electron has an analogous spin. But this analogy has obvious limitations: the Earth’s spin is, after all, made up of material orbiting around the axis through the poles. The electron spin cannot be imagined as arising from a rotating body, since orbital angular momenta always come in integral multiples of \hbar . Fortunately, this lack of a simple quasi-mechanical picture underlying electron spin doesn’t prevent us from using the general angular momentum machinery developed earlier, which followed just from analyzing the effect of spatial rotation on a quantum mechanical system.

5.1 Spinors, Spin Operators, Pauli Matrices

The Hilbert space of angular momentum states for spin $1/2$ is two-dimensional. Various notations are used: $|\ell, m\rangle$ becomes $|s, m\rangle$ or, more graphically,

$$\boxed{|1/2, 1/2\rangle = |\uparrow\rangle, \quad |1/2, -1/2\rangle = |\downarrow\rangle.} \quad (5.1)$$

A general state of spin can be written as the linear combination,

$$\alpha |\uparrow\rangle + \beta |\downarrow\rangle = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \quad (5.2)$$

with the normalisation condition, $|\alpha|^2 + |\beta|^2 = 1$, and this two-dimensional ket is called a spinor. Operators acting on spinors are necessarily of the form of 2×2 matrices. We shall adopt the usual practice of denoting the angular momentum components L_i by S_i for spins. (Once again, for clarity, we also drop the hats on the angular momentum operators!)

From our definition of the spinor, it is evident that the z -component of the spin can be represented as the matrix,

$$S_z = \frac{\hbar}{2}\sigma_z, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (5.3)$$

From the general formulae (4.13) for raising and lowering operators $S_{\pm} = S_x + iS_y$, with $s = 1/2$, we have $S_+ |1/2, -1/2\rangle = \hbar |1/2, 1/2\rangle$, $S_- |1/2, 1/2\rangle = \hbar |1/2, -1/2\rangle$, or, in matrix form,

$$S_x + iS_y = S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad S_x - iS_y = S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \quad (5.4)$$

It therefore follows that an appropriate matrix representation for spin $1/2$ is given by the **Pauli spin matrices**, $\mathbf{S} = \frac{\hbar}{2}\boldsymbol{\sigma}$ where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (5.5)$$

The total spin $\mathbf{S}^2 = \frac{\hbar^2}{4}\boldsymbol{\sigma}^2 = \frac{3}{4}\hbar^2$, i.e. $s(s+1)\hbar^2$ for $s = 1/2$.

5.2 Relating the Spinor to the Spin Direction

For a general state $\alpha |\uparrow\rangle + \beta |\downarrow\rangle$, how do α , β relate to which way the spin is pointing? To find out, let us assume that it is pointing up along the unit vector $\hat{\mathbf{n}} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$, i.e. in the direction (θ, ϕ) . In other words, the spin is an eigenstate of the operator $\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}$ having eigenvalue unity:

$$\begin{pmatrix} n_z & n_x - in_y \\ n_x + in_y & -n_z \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}. \quad (5.6)$$

From this expression, we find that $\alpha/\beta = (n_x - in_y)/(1 - n_z) = e^{-i\phi} \cot \theta/2$. Then, making use of the normalisation, $|\alpha|^2 + |\beta|^2 = 1$, we obtain (up to an arbitrary phase)

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} e^{-i\phi/2} \cos \theta/2 \\ e^{i\phi/2} \sin \theta/2 \end{pmatrix}. \quad (5.7)$$

Since $e^{-i\phi} \cot \theta/2$ can be used to specify any complex number with $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$, so for any possible spinor, there is an associated direction along which the spin points up.

5.2.0.1 The Spin Rotation Operator

In general, the rotation operator for rotation through an angle θ about an axis in the direction of the unit vector $\hat{\mathbf{n}}$ is given by $e^{-i\theta \hat{\mathbf{n}} \cdot \hat{\mathbf{J}}/\hbar}$ where $\hat{\mathbf{J}}$ denotes the angular momentum operator. For spin, $\hat{\mathbf{J}} = \mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\sigma}$, and the rotation operator takes the form¹ $e^{-i\theta \hat{\mathbf{n}} \cdot \hat{\mathbf{J}}/\hbar} = e^{-i(\theta/2)(\hat{\mathbf{n}} \cdot \boldsymbol{\sigma})}$. Expanding the exponential, and making use of the Pauli matrix identities, $(\hat{\mathbf{n}} \cdot \boldsymbol{\sigma})^2 = \hat{\mathbb{I}}$, one can show that

$$e^{-i(\theta/2)(\hat{\mathbf{n}} \cdot \boldsymbol{\sigma})} = \hat{\mathbb{I}} \cos \theta/2 - i\hat{\mathbf{n}} \cdot \boldsymbol{\sigma} \sin \theta/2. \quad (5.8)$$

The rotation operator is a 2×2 matrix operating on the ket space. The 2×2 rotation matrices are unitary and form a group known as $SU(2)$; the 2 refers to the dimensionality, the U to their being unitary, and the S signifying determinant +1. Note that for rotation about the z -axis, $\hat{\mathbf{n}} = (0, 0, 1)$, it is more natural to replace θ with ϕ , and the rotation operator takes the form,

$$e^{-i(\theta/2)(\hat{\mathbf{n}} \cdot \boldsymbol{\sigma})} = \begin{pmatrix} e^{-i\phi/2} & 0 \\ 0 & e^{i\phi/2} \end{pmatrix}. \quad (5.9)$$

In particular, the wavefunction is multiplied by -1 for a rotation of 2π . Since this is true for any initial wave function, it is clearly also true for rotation through 2π about any axis.

5.3 Spin Precession in a Magnetic Field

Consider a magnetized classical object spinning about its centre of mass, with angular momentum \mathbf{L} and parallel magnetic moment $\boldsymbol{\mu}$, $\boldsymbol{\mu} = \gamma\mathbf{L}$. The constant γ is called the gyromagnetic ratio. Now suppose that we impose a magnetic field \mathbf{B} along, say, the z -direction. This will exert a torque $\mathbf{T} = \boldsymbol{\mu} \times \mathbf{B} = \gamma\mathbf{L} \times \mathbf{B} = \frac{d\mathbf{L}}{dt}$. This equation is easily solved and shows that the angular momentum vector \mathbf{L} precesses about the magnetic field direction with angular velocity of precession $\boldsymbol{\omega}_0 = -\gamma\mathbf{B}$.²

In the following, we will show that precisely the same result appears in the study of the quantum mechanics of an electron spin in a magnetic field. The electron has magnetic

¹Warning: do not confuse θ - the rotation angle - with the spherical polar angle used to parameterise $\hat{\mathbf{n}}$.

²Proof: From the equation of motion, with $L_+ = L_x + iL_y$, $\frac{dL_+}{dt} = -i\gamma BL_+$, $L_+ = L_+^0 e^{-i\gamma Bt}$. Of course, $\frac{dL_z}{dt} = 0$, since $\frac{d\mathbf{L}}{dt} = \gamma\mathbf{L} \times \mathbf{B}$ is perpendicular to \mathbf{B} , which is in the z -direction.

dipole moment $\boldsymbol{\mu} = \gamma \mathbf{S}$, where $\gamma = g \frac{-e}{2m_e}$ and the gyromagnetic ratio, g , is very close to 2.³ The Hamiltonian for the interaction of the electron's dipole moment with the magnetic field is given by $\hat{H} = -\boldsymbol{\mu} \cdot \mathbf{B} = -\gamma \mathbf{S} \cdot \mathbf{B}$. Hence the time development is specified by the equation $|\psi(t)\rangle = \hat{U} |\psi(0)\rangle$, with the time-evolution operator (or propagator), $\hat{U} = e^{-i\hat{H}t/\hbar} = e^{i\gamma \mathbf{S} \cdot \mathbf{B}t/2}$. However, this is nothing but the rotation operator (as shown earlier) through an angle $-\gamma Bt$ about the direction of \mathbf{B} !

For an arbitrary initial spin orientation

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} e^{-i\phi/2} \cos \theta/2 \\ e^{i\phi/2} \sin \theta/2 \end{pmatrix}, \quad (5.10)$$

the propagator for a magnetic field in the z -direction is given by

$$\hat{U}(t) = e^{i\gamma \mathbf{S} \cdot \mathbf{B}t/2} = \begin{pmatrix} e^{-i\omega_0 t/2} & 0 \\ 0 & e^{i\omega_0 t/2} \end{pmatrix}, \quad (5.11)$$

so the time-dependent spinor is set by

$$\begin{pmatrix} \alpha(t) \\ \beta(t) \end{pmatrix} = \begin{pmatrix} e^{-i(\phi+\omega_0 t)/2} \cos \theta/2 \\ e^{i(\phi+\omega_0 t)/2} \sin \theta/2 \end{pmatrix}. \quad (5.12)$$

The angle θ between the spin and the field stays constant while the azimuthal angle around the field increases as $\phi = \phi_0 + \omega_0 t$, exactly as in the classical case. The frequency $\omega_0 = g \frac{|e|\hbar}{2m_e}$ is the Larmor frequency for spin precession. For a magnetic field of 1T, $\omega_0 \simeq 10^{11} \text{ rad s}^{-1}$.

5.4 Addition of Angular Momenta

In subsequent chapters, it will be necessary to add angular momentum, be it the addition of orbital and spin angular momenta, $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, as with the study of spin-orbit coupling in atoms, or the addition of general angular momenta, $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$ as occurs in the consideration of multi-electron atoms. In the following section, we will explore three problems: The addition of two spin 1/2 degrees of freedom; the addition of a general orbital angular momentum and spin; and the addition of spin $J = 1$ angular momenta. However, before addressing these examples in turn, let us first make some general remarks.

Without specifying any particular application, let us consider the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$ where $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ correspond to distinct degrees of freedom, $[\hat{\mathbf{J}}_1, \hat{\mathbf{J}}_2] = 0$, and the individual operators obey angular momentum commutation relations. As a result, the total angular momentum also obeys angular momentum commutation relations,

$$[\hat{J}_i, \hat{J}_j] = i\hbar \epsilon_{ijk} \hat{J}_k. \quad (5.13)$$

For each angular momentum component, the states $|j_1, m_1\rangle$ and $|j_2, m_2\rangle$ where $m_i = -j_i, \dots, j_i$, provide a basis of states of the total angular momentum operator, $\hat{\mathbf{J}}^2$ and the

³This g -factor terminology is used more widely. In general, the magnetic moment of an atom is written $\boldsymbol{\mu} = -g\mu_B(\hat{\mathbf{J}}/\hbar)$, where $\mu_B = \frac{e\hbar}{2m_e}$ is known as the **Bohr magneton**, $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ is the total (orbital and spin) angular momentum and g depends on the internal structure of the particular atom.

projection \hat{J}_{iz} . Together, they form a complete basis which can be used to span the states of the coupled spins,⁴

$$|j_1, m_1, j_2, m_2\rangle \equiv |j_1, m_1\rangle \otimes |j_2, m_2\rangle. \quad (5.14)$$

These product states are also eigenstates of \hat{J}_z with eigenvalue $\hbar(m_1 + m_2)$, but not of $\hat{\mathbf{J}}^2$. However, for practical application, we require a basis in which the total angular momentum operator $\hat{\mathbf{J}}^2$ is also diagonal. That is, we must find eigenstates $|j, m_j, j_1, j_2\rangle$ of the four mutually commuting operators $\hat{\mathbf{J}}^2$, \hat{J}_z , $\hat{\mathbf{J}}_1^2$, and $\hat{\mathbf{J}}_2^2$.

In general, the relation between the two basis can be expressed as

$$|j, m_j, j_1, j_2\rangle = \sum_{m_1, m_2} |j_1, m_1, j_2, m_2\rangle \langle j_1, m_1, j_2, m_2 | j, m_j, j_1, j_2\rangle, \quad (5.15)$$

where the matrix elements are known as **Clebsch-Gordan coefficients**. In general, the determination of these coefficients from first principles is a somewhat soul destroying exercise and one that we do not intend to pursue in great detail.⁵ In any case, for practical purposes, such coefficients have been tabulated in the literature and can be readily obtained. However, in some simple cases, these matrix elements can be determined straightforwardly. Moreover, the algorithmic programme by which they are deduced offer some new conceptual insights.

Operationally, the mechanism for finding the basis states of the total angular momentum operator follow the strategy:

1. As a unique entry, the basis state with maximal J_{\max} and $m_j = J_{\max}$ is easy to deduce from the original basis states since it involves the product of states of **highest weight**,

$$|J_{\max}, m_j = J_{\max}, j_1, j_2\rangle = |j_1, m_1 = j_1\rangle \otimes |j_2, m_2 = j_2\rangle, \quad (5.17)$$

where $J_{\max} = j_1 + j_2$.

2. From this state, we can use of the total spin lowering operator \hat{J}_- to find all states with $J = J_{\max}$ and $m_j = -J_{\max}, \dots, J_{\max}$.
3. From the state with $J = J_{\max}$ and $m_j = J_{\max} - 1$, one can then obtain the state with $J = J_{\max} - 1$ and $m_j = J_{\max} - 1$ by orthogonality. Now one can return to the second step of the programme and repeat until $J = |j_1 - j_2|$ when all $(2j_1 + 1)(2j_2 + 1)$ basis states have been obtained.

⁴Here \otimes denotes the “direct product” and shows that the two constituent spin states access their own independent Hilbert space.

⁵In fact, one may show that the general matrix element is given by

$$\begin{aligned} \langle j_1, m_1, j_2, m_2 | j, m_j, j_1, j_2 \rangle &= \delta_{m_j, m_1 + m_2} \sqrt{\frac{(j_1 + j_2 - j)!(j + j_1 - j_2)!(j + j_2 - j_1)!(2j + 1)}{(j + j_1 + j_2 + 1)!}} \\ &\times \sum_k \frac{(-1)^k \sqrt{(j_1 + m_1)!(j_1 - m_1)!(j_2 + m_2)!(j_2 - m_2)!(j + m)!(j - m)!}}{k!(j_1 + j_2 - j - k)!(j_1 - m_1 - k)!(j_2 + m_2 - k)!(j - j_2 + m_1 + k)!(j - j_1 - m_2 + k)!}. \end{aligned} \quad (5.16)$$

5.4.1 Addition of Two Spin 1/2 Degrees of Freedom

For two spin 1/2 degrees of freedom, we could simply construct and diagonalise the complete 4×4 matrix elements of the total spin. However, to gain some intuition for the general case, let us consider the programme above. Firstly, the maximal total spin state is given by

$$|S = 1, m_S = 1, s_1 = 1/2, s_2 = 1/2\rangle = |s_1 = 1/2, m_{s_1} = 1/2\rangle \otimes |s_2 = 1/2, m_{s_2} = 1/2\rangle. \quad (5.18)$$

Now, since $s_1 = 1/2$ and $s = 1/2$ is implicit, we can rewrite this equation in a more colloquial form as

$$|S = 1, m_S = 1\rangle = |\uparrow_1\rangle \otimes |\uparrow_2\rangle. \quad (5.19)$$

We now follow step 2 of the programme and subject the maximal spin state to the total spin lowering operator, $\hat{S}_- = \hat{S}_1^- + \hat{S}_2^-$. In doing so, making use of Eq. (4.13), we find

$$\hat{S}_- |S = 1, m_S = 1\rangle = \sqrt{2}\hbar |S = 1, m_S = 0\rangle = \hbar(|\downarrow_1\rangle \otimes |\uparrow_2\rangle + |\uparrow_1\rangle \otimes |\downarrow_2\rangle), \quad (5.20)$$

i.e. $|S = 1, m_S = 0\rangle = \frac{1}{\sqrt{2}}(|\downarrow_1\rangle \otimes |\uparrow_2\rangle + |\uparrow_1\rangle \otimes |\downarrow_2\rangle)$. Similarly,

$$\hat{S}_- |S = 1, m_S = 0\rangle = \sqrt{2}\hbar |S = 1, m_S = -1\rangle = \sqrt{2}\hbar |\uparrow_1\rangle \otimes |\downarrow_2\rangle, \quad (5.21)$$

i.e. $|S = 1, m_S = -1\rangle = |\uparrow_1\rangle \otimes |\downarrow_2\rangle$. This completes the construction of the manifold of spin $S = 1$ states - the **spin triplet** states. Following the programme, we must now consider the lower spin state.

In this case, the next multiplet is the unique total spin singlet state $|S = 0, m_S = 0\rangle$. The latter must be orthogonal to the spin triplet state $|S = 1, m_S = 0\rangle$. As a result, we can deduce that

$$|S = 0, m_S = 0\rangle = \frac{1}{\sqrt{2}}(|\downarrow_1\rangle \otimes |\uparrow_2\rangle - |\uparrow_1\rangle \otimes |\downarrow_2\rangle). \quad (5.22)$$

5.4.2 Addition of Angular Momentum and Spin

We now turn to the problem of the addition of angular momentum and spin, $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$. In the original basis, for a given angular momentum ℓ , one can identify $2 \times (2\ell + 1)$ product states $|\ell, m_\ell\rangle \otimes |\uparrow\rangle$ and $|\ell, m_\ell\rangle \otimes |\downarrow\rangle$, with $m_\ell = -\ell, \dots, \ell$, involving eigenstates of $\hat{\mathbf{L}}^2$, \hat{L}_z , $\hat{\mathbf{S}}^2$ and \hat{S}_z , but not $\hat{\mathbf{J}}^2$. From these basis states, we are looking for eigenstates of $\hat{\mathbf{J}}^2$, \hat{J}_z , $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$. To undertake this programme, it is helpful to recall the action of the angular momentum raising and lower operators,

$$\hat{L}_\pm |\ell, m_\ell\rangle = ((\ell \pm m_\ell + 1)(\ell \mp m_\ell))^{1/2} \hbar |\ell, m_\ell \pm 1\rangle \quad (5.23)$$

as well as the identity

$$\hat{\mathbf{J}}^2 = \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + \overbrace{2\hat{L}_z\hat{S}_z + \hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+}^{2\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}}. \quad (5.24)$$

For the eigenstates of $\hat{\mathbf{J}}^2$, \hat{J}_z , $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$ we will adopt the notation $|j, m_j, \ell\rangle$ leaving the spin $S = 1/2$ implicit. The maximal spin state is given by⁶

⁶The proof runs as follows:

$$\hat{J}_z |\ell, \ell\rangle \otimes |\uparrow\rangle = (\hat{L}_z + \hat{S}_z) |\ell, \ell\rangle \otimes |\uparrow\rangle = (\ell + 1/2)\hbar |\ell, \ell\rangle \otimes |\uparrow\rangle, \quad (5.25)$$

5.4.3 Addition of two angular momenta $J = 1$

As mentioned above, for the general case the programme is algebraically technical and unrewarding. However, for completeness, we consider here the explicit example of the addition of two spin 1 degrees of freedom. Once again, the maximal spin state is given by

$$|J = 2, m_J = 2, j_1 = 1, j_2 = 1\rangle = |j_1 = 1, m_1 = 1\rangle \otimes |j_2 = 1, m_2 = 1\rangle, \quad (5.28)$$

or, more concisely, $|2, 2\rangle = |1\rangle \otimes |1\rangle$, where we leave j_1 and j_2 implicit. Once again, making use of Eq. (4.13) and an economy of notation, we find

$$\begin{cases} |2, 2\rangle = |1\rangle \otimes |1\rangle \\ |2, 1\rangle = \frac{1}{\sqrt{2}}(|0\rangle \otimes |1\rangle + |1\rangle \otimes |0\rangle) \\ |2, 0\rangle = \frac{1}{\sqrt{6}}(|-1\rangle \otimes |1\rangle + 2|0\rangle \otimes |0\rangle + |1\rangle \otimes |-1\rangle) \\ |2, -1\rangle = \frac{1}{\sqrt{2}}(|0\rangle \otimes |-1\rangle + |-1\rangle \otimes |0\rangle) \\ |2, -2\rangle = |-1\rangle \otimes |-1\rangle \end{cases} \quad (5.29)$$

Then, from the expression for $|2, 1\rangle$, we can construct the next maximal spin state $|1, 1\rangle = \frac{1}{\sqrt{2}}(|0\rangle \otimes |1\rangle - |1\rangle \otimes |0\rangle)$, from the orthogonality condition. Once again, acting on this state with the total spin lowering operator, we obtain the remaining members of the multiplet,

$$\begin{cases} |1, 1\rangle = \frac{1}{\sqrt{2}}(|0\rangle \otimes |1\rangle - |1\rangle \otimes |0\rangle) \\ |1, 0\rangle = \frac{1}{\sqrt{2}}(|-1\rangle \otimes |1\rangle - |1\rangle \otimes |-1\rangle) \\ |1, -1\rangle = \frac{1}{\sqrt{2}}(|-1\rangle \otimes |0\rangle - |0\rangle \otimes |-1\rangle) \end{cases} \quad (5.30)$$

Finally, finding the state orthogonal to $|1, 0\rangle$ and $|1, 0\rangle$, we obtain the final state,

$$|0, 0\rangle = \frac{1}{\sqrt{3}}(|-1\rangle \otimes |1\rangle - |0\rangle \otimes |0\rangle + |1\rangle \otimes |-1\rangle). \quad (5.31)$$

and

$$\hat{\mathbf{J}}^2 |\ell, \ell\rangle \otimes |\uparrow\rangle = \hbar^2(\ell(\ell+1) + \frac{1}{2}(\frac{1}{2}+1) + 1 + 2\ell\frac{1}{2}) |\ell, \ell\rangle \otimes |\uparrow\rangle \quad (5.26)$$

$$= \hbar^2(\ell + \frac{1}{2})(\ell + \frac{3}{2}) |\ell, \ell\rangle \otimes |\uparrow\rangle. \quad (5.27)$$

CHAPTER 6

Motion in a Magnetic Field

Hitherto, we have focussed on applications of quantum mechanics to free particles or particles confined by scalar potentials. In the following, we will address the influence of a magnetic field on a charged particle. Classically, the force on a charged particle in an electric and magnetic field is specified by the **Lorentz force law**:

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}), \quad (6.1)$$

where q denotes the charge and \mathbf{v} the velocity. (Here we will adopt a convention in which q denotes the charge (which may be positive or negative) and $e \equiv |e|$ denotes the modulus of the electron charge, i.e. for an electron, the charge $q_e = -e = -1.602176487 \times 10^{-19} \text{C}$.) The velocity-dependent force associated with the magnetic field is quite different from the conservative forces associated with scalar potentials, and the programme for transferring from classical to quantum mechanics – replacing momenta with the appropriate operators – has to be carried out with more care. As preparation, it is helpful to revise how the Lorentz force arises in the Lagrangian formulation of classical mechanics.

6.1 Classical Mechanics of a Particle in a Field

For a system with m degrees of freedom specified by coordinates q_1, \dots, q_m , the classical action is determined from the Lagrangian $L(q_i, \dot{q}_i)$ by

$$S[q_i] = \int dt L(q_i, \dot{q}_i) \quad (6.2)$$

The action is said to be a **functional** of the coordinates $q_i(t)$. According to **Hamilton's extremal principle** (also known as the **principle of least action**), the dynamics of a classical system is described by the equations that minimise the action. These equations of motion can be expressed through the classical Lagrangian in the form of the Euler-Lagrange equations,

$$\frac{d}{dt}(\partial_{\dot{q}_i} L(q_i, \dot{q}_i)) - \partial_{q_i} L(q_i, \dot{q}_i) = 0. \quad (6.3)$$

According to Hamilton's extremal principle, for any smooth set of curves $w_i(t)$, the variation of the action around the classical solution $q_i(t)$ is zero, i.e. $\lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} (S[q_i + \epsilon w_i] - S[q_i]) = 0$. Applied to the action, the variation implies that, for any i , $\int dt (w_i \partial_{q_i} L(q_i, \dot{q}_i) + \dot{w}_i \partial_{\dot{q}_i} L(q_i, \dot{q}_i)) = 0$. Then, integrating the second term by parts, and dropping the boundary term, one obtains

$$\int dt \left(\partial_{q_i} L(q_i, \dot{q}_i) + \frac{d}{dt} \partial_{\dot{q}_i} L(q_i, \dot{q}_i) \right) = 0. \quad (6.4)$$

Since this equality must follow for any function $w_i(t)$, the term in parentheses in the integrand must vanish leading to the Euler-Lagrange equation (6.3).

The **canonical momentum** is specified by the equation $p_i = \partial_{\dot{q}_i} L$, and the classical Hamiltonian is defined by the Legendre transform,

$$H(q_i, p_i) = \sum_i p_i \dot{q}_i - L(q_i, \dot{q}_i). \quad (6.5)$$

It is straightforward to check that the equations of motion can be written in the form of Hamilton's equations of motion,

$$\dot{q}_i = \partial_{p_i} H, \quad \dot{p}_i = -\partial_{q_i} H. \quad (6.6)$$

From these equations it follows that, if the Hamiltonian is independent of a particular coordinate q_i , the corresponding momentum p_i remains constant. For **conservative forces**,¹ the classical Lagrangian and Hamiltonian can be written as $L = T - V$, $H = T + V$, with T the kinetic energy and V the potential energy.

Any dynamical variable f in the system is some function of the phase space coordinates, the q_i s and p_i s, and (assuming it does not depend explicitly on time) its time-development is given by:

$$\frac{d}{dt} f(q_i, p_i) = \partial_{q_i} f \dot{q}_i + \partial_{p_i} f \dot{p}_i = \partial_{q_i} f \partial_{p_i} H - \partial_{p_i} f \partial_{q_i} H \equiv \{f, H\}. \quad (6.7)$$

The curly brackets are known as Poisson brackets, and are defined for any dynamical variables as $\{A, B\} = \partial_{q_i} A \partial_{p_i} B - \partial_{p_i} A \partial_{q_i} B$. From Hamilton's equations, we have shown that for any variable, $\dot{f} = \{f, H\}$. It is easy to check that, for the coordinates and canonical momenta, $\{q_i, q_j\} = 0 = \{p_i, p_j\}$, $\{q_i, p_j\} = \delta_{ij}$. This was the classical mathematical structure that led Dirac to link up classical and quantum mechanics: He realised that the Poisson brackets were the classical version of the commutators, so a classical canonical momentum must correspond to the quantum differential operator in the corresponding coordinate.

With these foundations revised, we now return to the problem at hand; the influence of an electromagnetic field on the dynamics of the charged particle.

As the Lorentz force is velocity dependent, it can not be expressed simply as the gradient of some potential. Nevertheless, the classical path traversed by a charged particle is still specified by the principle of least action. The electric and magnetic fields can be written in terms of a scalar and a vector potential as $\mathbf{B} = \nabla \times \mathbf{A}$, $\mathbf{E} = -\nabla \phi - \dot{\mathbf{A}}$. The corresponding Lagrangian takes the form:²

$$L = \frac{1}{2} m \mathbf{v}^2 - q\phi + q\mathbf{v} \cdot \mathbf{A}. \quad (6.8)$$

In this case, the general coordinates $q_i \equiv x_i = (x_1, x_2, x_3)$ are just the Cartesian coordinates specifying the position of the particle, and the \dot{q}_i are the three components

¹i.e. forces that conserve mechanical energy

²In a relativistic formulation, the interaction term here looks less arbitrary: the relativistic version would have the relativistically invariant $q \int A^\mu dx_\mu$ added to the action integral, where the four-potential $A_\mu = (\phi, \mathbf{A})$ and $dx_\mu = (ct, dx_1, dx_2, dx_3)$. This is the simplest possible invariant interaction between the electromagnetic field and the particle's four-velocity. Then, in the non-relativistic limit, $q \int A^\mu dx_\mu$ just becomes $q \int \mathbf{v} \cdot \mathbf{A} - \phi dt$.

$\dot{x}_i = (\dot{x}_1, \dot{x}_2, \dot{x}_3)$ of the particle velocities. The important point is that the *canonical* momentum

$$p_i = \partial_{\dot{x}_i} L = m\dot{x}_i + qA_i, \quad (6.9)$$

is no longer simply given by the mass \times velocity – there is an extra term!

Making use of the definition (6.5), the corresponding Hamiltonian is given by

$$H(q_i, p_i) = \sum_i (m\dot{x}_i + qA_i)\dot{x}_i - \frac{1}{2}m\mathbf{v}^2 + q\phi - q\mathbf{v} \cdot \mathbf{A} = \frac{1}{2}m\mathbf{v}^2 + q\phi. \quad (6.10)$$

Reassuringly, the Hamiltonian just has the familiar form of the sum of the kinetic and potential energy. However, to get Hamilton's equations of motion, the Hamiltonian has to be expressed solely in terms of the coordinates and canonical momenta, i.e.

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A}(\mathbf{r}, t))^2 + q\phi(\mathbf{r}, t). \quad (6.11)$$

Let us now consider Hamilton's equations of motion, $\dot{x}_i = \partial_{p_i} H$ and $\dot{p}_i = -\partial_{x_i} H$. The first equation recovers the expression for the canonical momentum while second equation yields the Lorentz force law. To understand how, we must first keep in mind that dp/dt is not the acceleration: The A -dependent term also varies in time, and in a quite complicated way, since it is the field at a point moving with the particle. More precisely,

$$\dot{p}_i = m\ddot{x}_i + q\dot{A}_i = m\ddot{x}_i + q(\partial_t A_i + v_j \partial_{x_j} A_i), \quad (6.12)$$

where we have assumed a summation over repeated indices. The right-hand side of the second of Hamilton's equation, $\dot{p}_i = -\frac{\partial H}{\partial x_i}$, is given by

$$-\partial_{x_i} H = \frac{1}{m}(\mathbf{p} - q\mathbf{A}(\mathbf{r}, t))q\partial_{x_i} \mathbf{A} - q\partial_{x_i} \phi(\mathbf{r}, t) = qv_j \partial_{x_i} A_j - q\partial_{x_i} \phi. \quad (6.13)$$

Together, we obtain the equation of motion, $m\ddot{x}_i = -q(\partial_t A_i + v_j \partial_{x_j} A_i) + qv_j \partial_{x_i} A_j - q\partial_{x_i} \phi$. Using the identity $\mathbf{v} \times (\nabla \times \mathbf{A}) = \nabla(\mathbf{v} \cdot \mathbf{A}) - (\mathbf{v} \cdot \nabla)\mathbf{A}$, and the expressions for the electric and magnetic fields in terms of the potentials, one recovers the Lorentz equation

$$m\ddot{x}_i = \mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad (6.14)$$

With these preliminary discussions of the classical system in place, we are now in a position to turn to the quantum mechanic.

6.2 Quantum Mechanics of a Particle in a Field

To transfer to the quantum mechanical regime, we must implement the canonical quantization procedure setting $\hat{\mathbf{p}} = -i\hbar\nabla$, so that $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$. However, in this case, $\hat{p}_i \neq m\hat{v}_i$ \wedge $\hat{p}_i \neq m\hat{v}_i$. This leads to the novel situation that the velocities in different directions do not commute.³ To explore influence of the magnetic field on the particle dynamics, it is helpful to assess the relative weight of the A -dependent contributions to the quantum Hamiltonian,

$$\hat{H} = \frac{1}{2m}(\mathbf{p} - q\mathbf{A}(\mathbf{r}, t))^2 + q\phi(\mathbf{r}, t). \quad (6.15)$$

³With $m\hat{v}_i = -i\hbar\partial_{x_i} - qA_i$, it is easy to verify that $[\hat{v}_x, \hat{v}_y] = \frac{i\hbar q}{m^2}B$.

6.3 Gauge Invariance and the Aharonov-Bohm Effect

Our derivation above shows that the quantum mechanical Hamiltonian of a charged particle is defined in terms of the vector potential, \mathbf{A} . Since the latter is defined only up to some gauge choice, this suggests that the wavefunction is not a gauge invariant object. Indeed, it is only the observables associated with the wavefunction which must be gauge invariant. To explore this gauge freedom, let us consider the influence of the **gauge transformation**,

$$\mathbf{A} \mapsto \mathbf{A}' = \mathbf{A} + \nabla\Lambda, \quad \phi \mapsto \phi' = \phi - \partial_t\Lambda, \quad (6.16)$$

where $\Lambda(\mathbf{r}, t)$ denotes a scalar function. Under the gauge transformation, one may show that the corresponding wavefunction gets transformed as

$$\psi'(\mathbf{r}, t) = \exp \left[i \frac{q}{\hbar} \Lambda(\mathbf{r}, t) \right] \psi(\mathbf{r}, t). \quad (6.17)$$

The gauge transformation introduces an additional space and time-dependent phase factor into the wavefunction. However, since the observable translates to the probability density, $|\phi|^2$, this phase dependence seems invisible.

One physical manifestation of the gauge invariance of the wavefunction is found in the **Aharonov-Bohm effect**. Consider a particle with charge q travelling along a path, P , in which the magnetic field, $\mathbf{B} = 0$ is identically zero. However, a vanishing of the magnetic field does not imply that the vector potential, \mathbf{A} is zero. Indeed, as we have seen, any $\Lambda(\mathbf{r})$ such that $\mathbf{A} = \nabla\Lambda$ will translate to this condition. In traversing the path, the wavefunction of the particle will acquire the phase factor $\varphi = \frac{q}{\hbar} \int_P \mathbf{A} \cdot d\mathbf{r}$, where the line integral runs along the path.

If we consider now two separate paths P and P' which share the same initial and final points, the relative phase of the wavefunction will be set by

$$\Delta\varphi = \frac{q}{\hbar} \int_P \mathbf{A} \cdot d\mathbf{r} - \frac{q}{\hbar} \int_{P'} \mathbf{A} \cdot d\mathbf{r} = \frac{q}{\hbar} \oint \mathbf{A} \cdot d\mathbf{r} = \frac{q}{\hbar} \int_A \mathbf{B} \cdot d^2\mathbf{r}, \quad (6.18)$$

where the line integral \oint runs over the loop involving paths P and P' , and \int_A runs over the area enclosed by the loop. The last relation follows from the application of Stokes' theorem. This result shows that the relative phase $\Delta\varphi$ is fixed by the factor q/\hbar multiplied by the magnetic flux $\Phi = \int_A \mathbf{B} \cdot d^2\mathbf{r}$ enclosed by the loop.⁴ In the absence of a magnetic field, the flux vanishes, and there is no additional phase.

However, if we allow the paths to enclose a region of non-vanishing magnetic field, *even if the field is identically zero on the paths P and P'* , the wavefunction will acquire a non-vanishing relative phase. This flux-dependent phase difference translates to an observable shift of interference fringes when on an observation plane. Since the original proposal, the Aharonov-Bohm effect has been studied in several experimental contexts. Of these, the most rigorous study was undertaken by Tonomura in 1986. Tonomura fabricated a doughnut-shaped (toroidal) ferromagnet six micrometers in diameter, and covered it with a niobium superconductor to completely confine the magnetic field within

⁴Note that the phase difference depends on the magnetic flux, a function of the magnetic field, and is therefore a gauge invariant quantity.

the doughnut, in accordance with the Meissner effect.⁵ With the magnet maintained at 5K, they measured the phase difference from the interference fringes between one electron beam passing through the hole in the doughnut and the other passing on the outside of the doughnut. Interference fringes are displaced with just half a fringe of spacing inside and outside of the doughnut, indicating the existence of the Aharonov-Bohm effect. Although electrons pass through regions free of any electromagnetic field, an observable effect was produced due to the existence of vector potentials.

The observation of the half-fringe spacing reflects the constraints imposed by the superconducting toroidal shield. When a superconductor completely surrounds a magnetic flux, the flux is quantised to an integral multiple of quantised flux $\hbar/2e$, the factor of two reflecting that fact that the superconductor involves a condensate of electron pairs. When an odd number of vortices are enclosed inside the superconductor, the relative phase shift becomes $\pi \pmod{2\pi}$ – half-spacing! For an even number of vortices, the phase shift is zero.⁶

6.4 Free Electron in a Magnetic Field

Finally, to complete our survey of the influence of a uniform magnetic field on the dynamics of charged particles, let us consider the problem of a free quantum particle. In this case, the classical electron orbits can be macroscopic and there is no reason to neglect the diamagnetic contribution to the Hamiltonian. Previously, we have worked with a gauge in which $\mathbf{A} = (-y, x, 0)B/2$, giving a constant field B in the z -direction. However, to address the Schrödinger equation for a particle in a uniform perpendicular magnetic field, it is convenient to adopt the **Landau gauge**, $\mathbf{A}(\mathbf{r}) = (-By, 0, 0)$.

In this case, the stationary form of the Schrödinger equation is given by

$$\hat{H}\psi(\mathbf{r}) = \frac{1}{2m}[(\hat{p}_x^2 + qBy)^2 + \hat{p}_y^2 + \hat{p}_z^2]\psi(\mathbf{r}) = E\psi(\mathbf{r}). \quad (6.19)$$

Since \hat{H} commutes with both \hat{p}_x and \hat{p}_z , both operators have a common set of eigenstates reflecting the fact that p_x and p_z are conserved by the dynamics. The wavefunction must therefore take the form, $\psi(\mathbf{r}) = e^{i(p_x x + p_z z)/\hbar}\chi(y)$, with $\chi(y)$ defined by the equation,

$$\left[\frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega_c^2(y - y_0)^2 \right] \chi(y) = \left(E - \frac{p_z^2}{2m} \right) \chi(y). \quad (6.20)$$

Here $y_0 = -p_x/qB$ and $\omega_c = |q|B/m$ coincides with the **cyclotron frequency** of the classical charged particle. We now see that the conserved canonical momentum p_x in the x -direction is in fact the coordinate of the centre of a simple harmonic oscillator potential in the y -direction with frequency ω_c . As a result, we can immediately infer that the eigenvalues of the Hamiltonian are comprised of a free particle component associated with motion parallel to the field, and a set of harmonic oscillator states,

$$E_{n,p_z} = (n + 1/2)\hbar\omega_c + \frac{p_z^2}{2m}. \quad (6.21)$$

⁵Perfect diamagnetism, a hallmark of superconductivity, leads to the complete expulsion of magnetic fields – a phenomenon known as the Meissner effect.

⁶The superconducting flux quantum was actually predicted prior to Aharonov and Bohm, by Fritz London in 1948 using a phenomenological theory.

The quantum numbers, n , specify states known as **Landau levels**.

Let us confine our attention to states corresponding to the lowest oscillator (Landau level) state, (and, for simplicity, $p_z = 0$), $E_0 = \hbar\omega_c/2$. What is the degeneracy of this Landau level? Consider a rectangular geometry of area $A = L_x \times L_y$ and, for simplicity, take the boundary conditions to be periodic. The centre of the oscillator wavefunction, $y_0 = -p_x/qB$, must lie between 0 and L_y . With periodic boundary conditions $e^{ip_x L_x/\hbar} = 1$, so that $p_x = n2\pi\hbar/L_x$. This means that y_0 takes a series of evenly-spaced discrete values, separated by $\Delta y_0 = \hbar/qBL_x$. So, for electron degrees of freedom, $q = -e$, the total number of states $N_{\text{states}} = L_y/|\Delta y_0|$, i.e.

$$N_{\text{states}} = \frac{L_x L_y}{\hbar/eB} = A \frac{B}{\Phi_0}, \quad (6.22)$$

where $\Phi_0 = \hbar/e$ denotes the “flux quantum”. So the total number of states in the lowest energy level coincides with the total number of flux quanta making up the field B penetrating the area A .

The Landau level degeneracy, N_{states} , depends on field; the larger the field, the more electrons can be fit into each Landau level. In the physical system, each Landau level is spin split by the Zeeman coupling, with (6.22) applying to one spin only. Finally, although we treated x and y in an asymmetric manner, this was merely for convenience of calculation; no physical quantity should differentiate between the two due to the symmetry of the original problem.

6.4.0.1 Integer Quantum Hall Effect

Until now, we have considered the impact of just a magnetic field. Consider now the Hall effect geometry in which we apply a crossed electric, \mathbf{E} and magnetic field, \mathbf{B} . Taking into account both contributions, the total current flow is given by

$$\mathbf{j} = \sigma_0 \left(\mathbf{E} - \frac{\mathbf{j} \times \mathbf{B}}{ne} \right), \quad (6.23)$$

where σ_0 denotes the conductivity, and n is the electron density. With the electric field oriented along y , and the magnetic field along z , the latter equation may be rewritten as

$$\begin{pmatrix} 1 & \frac{\sigma_0 B}{ne} \\ -\frac{\sigma_0 B}{ne} & 1 \end{pmatrix} \begin{pmatrix} j_x \\ j_y \end{pmatrix} = \sigma_0 \begin{pmatrix} 0 \\ E_y \end{pmatrix}. \quad (6.24)$$

Inverting these equations, one finds that

$$j_x = \underbrace{\frac{-\sigma_0^2 B/ne}{1 + (\sigma_0 B/ne)^2}}_{\sigma_{xy}} E_y, \quad j_y = \underbrace{\frac{\sigma_0}{1 + (\sigma_0 B/ne)^2}}_{\sigma_{xy}} E_x. \quad (6.25)$$

These provide the classical expressions for the longitudinal and Hall conductivities, σ_{yy} and σ_{xy} in the crossed field. Note that, for these classical expressions, σ_{xy} is proportional to B .

How does quantum mechanics revise this picture? For the classical model – **Drude theory**, the random elastic scattering of electrons impurities leads to a constant drift velocity in the presence of a constant electric field, $\sigma_0 = \frac{ne^2\tau}{m_e}$, where τ denotes the mean time between collisions. Now let us suppose the magnetic field is chosen so that the electrons exactly fill all of the states in the first ν Landau levels, i.e. the total number of electrons nL_xL_y is

$$nL_xL_y = \nu N_{\text{states}} \implies n = \nu \frac{eB}{h}. \quad (6.26)$$

The scattering of electrons must lead to a transfer between quantum states. However, if all states of the same energy are filled,⁷ elastic (energy conserving) scattering becomes impossible. Moreover, since the next accessible Landau level energy is a distance $\hbar\omega_c$ away, at low enough temperatures, inelastic scattering becomes frozen out. As a result, the scattering rate $1/\tau$ vanishes at special values of the field, i.e. $\sigma_{yy} \rightarrow 0$ and

$$\sigma_{xy} \rightarrow \frac{ne}{B} = \nu \frac{e^2}{h}. \quad (6.27)$$

At critical values of the field, the Hall conductivity is quantised in units of e^2/h . Inverting the conductivity tensor, one obtains the resistivity tensor,

$$\begin{pmatrix} \rho_{xx} & \rho_{xy} \\ -\rho_{xy} & \rho_{yy} \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ -\sigma_{xy} & \sigma_{yy} \end{pmatrix}^{-1}, \quad (6.28)$$

where

$$\rho_{xx} = \frac{\sigma_{xx}}{\sigma_{xx}^2 + \sigma_{xy}^2}, \quad \rho_{xy} = \frac{\sigma_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2}, \quad (6.29)$$

So, when $\sigma_{xx} = 0$ and $\sigma_{xy} = \nu e^2/h$, $\rho_{xx} = 0$ and $\rho_{xy} = h/\nu e^2$. The quantum Hall state describes dissipationless current flow in which the Hall conductance σ_{xy} is quantised in units of e^2/h . Experimental measurements of these values provides the best determination of fundamental ratio e^2/h , better than 1 part in 10^7 .

⁷Note that electrons are subject to Pauli's exclusion principle restricting the occupancy of each state to unity

Approximation Methods for Stationary States

7.1 Time-independent Perturbation Theory

While we have succeeded in deriving formal analytical solutions for stationary states of the Schrödinger operator in a variety of settings, in the majority of practical applications, *exact* solutions are inaccessible.¹ For example, if an atom is placed in an external electric field, the energy levels shift, and the wavefunctions become distorted — the Stark effect. The new energy levels and wavefunctions could in principle be obtained by writing down a complete Hamiltonian, including the external field. Indeed, such a programme may be achieved for the hydrogen atom. But even there, if the external field is small compared with the electric field inside the atom (which is billions of volts per metre) it is easier to compute the changes in the energy levels and wavefunctions within a scheme of successive corrections to the zero-field values. This method, termed perturbation theory, is the single most important method for solving problems in quantum mechanics, and is widely used in atomic physics, condensed matter and particle physics.

It should be acknowledged that there are – typically very interesting – problems which cannot be solved using perturbation theory, even when the perturbation is very weak; although such problems are the exception rather than the rule. One such case is the one-dimensional problem of free particles perturbed by a localised potential of strength λ . As we found earlier in chapter (2), switching on an arbitrarily weak attractive potential causes the $k = 0$ free particle wavefunction to drop below the continuum of plane wave energies and become a localised bound state with binding energy of order λ^2 . However, on changing the sign of λ to give a repulsive potential, there is no bound state; the lowest energy plane wave state stays at energy zero. Therefore the energy shift on switching on the perturbation cannot be represented as a power series in λ , the strength of the perturbation. This particular difficulty does not typically occur in three dimensions, where arbitrarily weak potentials do not in general lead to bound states.

7.1.1 The Perturbation Series

Let us then consider an unperturbed Hamiltonian, $\hat{H}^{(0)}$, having known (orthonormal) eigenstates $|n^{(0)}\rangle$ and eigenvalues $E_n^{(0)}$,

$$\hat{H}^{(0)} |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle. \quad (7.1)$$

In the following we will address the question of how the eigenstates and eigenenergies are modified by the imposition of a small perturbation, $\hat{H}^{(1)}$ (such as that imposed by an

¹Indeed, even if such a solution is formally accessible, its complexity may render it of no practical benefit.

external electric or magnetic field on a charged particle, or the deformation of some other external potential). In short, we are interested in the solution of the Schrödinger equation,

$$\left(\hat{H}^{(0)} + \hat{H}^{(1)}\right) |n\rangle = E_n |n\rangle \quad (7.2)$$

If the perturbation is small, $\langle n^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle \ll E_n^{(0)}$, it seems natural to suppose that, on turning on $\hat{H}^{(1)}$, the eigenfunctions and eigenvalues will change adiabatically from their unperturbed to their perturbed values, a situation described formally as “adiabatic continuity”,

$$|n^{(0)}\rangle \mapsto |n\rangle, \quad E_n^{(0)} \mapsto E_n. \quad (7.3)$$

However, note that this is not always the case. For example, as mentioned above, an infinitesimal perturbation has the capacity to develop a bound state not present in the unperturbed system. For now, let us proceed with the perturbative expansion and return later to discuss its potential range of validity.

The basic assumption that underpins the perturbation theory is that, for $\hat{H}^{(1)}$ small, the leading corrections are of the same order of magnitude as $\hat{H}^{(1)}$ itself. The perturbed eigenenergies and eigenvectors can then be obtained to a greater accuracy by a successive series of corrections, each of order $\langle \hat{H}^{(1)} \rangle / \langle \hat{H}^{(0)} \rangle$ compared with the previous. To identify terms of the same order in $\langle \hat{H}^{(1)} \rangle / \langle \hat{H}^{(0)} \rangle$, it is convenient to extract from $\hat{H}^{(1)}$ a dimensionless parameter λ , characterising the relative magnitude of the perturbation against $\hat{H}^{(0)}$, and then expand $|n\rangle$ and E_n as a power series in λ , i.e.

$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots = \sum_{m=0}^{\infty} \lambda^m |n^{(m)}\rangle, \quad (7.4)$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots = \sum_{m=0}^{\infty} \lambda^m E_n^{(m)}. \quad (7.5)$$

One may think of the parameter λ as an artificial book-keeping device to organize the perturbative expansion, and which is eventually set to unity at the end of the calculation.

Applied to the stationary form of the Schrödinger equation (7.2), an expansion of this sort leads to the relation

$$\begin{aligned} & \left(\hat{H}^{(0)} + \hat{H}^{(1)}\right) \left(|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots\right) \\ &= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots\right) \left(|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots\right) \end{aligned} \quad (7.6)$$

From this equation, we must relate terms of equal order in λ . At the lowest order, $\mathcal{O}(\lambda^0)$, we simply recover the unperturbed equation (7.1). In practical applications, one is usually interested in determining the first non-zero perturbative correction. In the following, we will explore the form of the first and second order perturbative corrections.

7.1.2 First Order Perturbation Theory

Isolating terms from (7.6) which are first order in λ ,

$$\hat{H}^{(0)} |n^{(1)}\rangle + \hat{H}^{(1)} |n^{(0)}\rangle = E_n^{(0)} |n^{(1)}\rangle + E_n^{(1)} |n^{(0)}\rangle. \quad (7.7)$$

and taking the inner product with the unperturbed states $\langle n^{(0)} |$, one obtains

$$\langle n^{(0)} | \hat{H}^{(0)} | n^{(1)} \rangle + \langle n^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle = \langle n^{(0)} | E_n^{(0)} | n^{(1)} \rangle + \langle n^{(0)} | E_n^{(1)} | n^{(0)} \rangle. \quad (7.8)$$

Noting that $\langle n^{(0)} | \hat{H}^{(0)} = \langle n^{(0)} | E_n^{(0)}$, and exploiting the normalisation $\langle n^{(0)} | n^{(0)} \rangle = 1$, one finds that the first order shift in energy is given simply by the expectation value of the perturbation taken with respect to the unperturbed eigenfunctions,

$$\boxed{E_n^{(1)} = \langle n^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle.} \quad (7.9)$$

Turning to the wavefunction, if we instead take the inner product of (7.7) with $\langle m^{(0)} |$ (with $m \neq n$), we obtain

$$\langle m^{(0)} | \hat{H}^{(0)} | n^{(1)} \rangle + \langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle = \langle m^{(0)} | E_n^{(0)} | n^{(1)} \rangle + \langle m^{(0)} | E_n^{(1)} | n^{(0)} \rangle. \quad (7.10)$$

Once again, with $\langle m^{(0)} | \hat{H}^{(0)} = \langle m^{(0)} | E_m^{(0)}$ and the orthogonality condition on the wavefunctions, $\langle m^{(0)} | n^{(0)} \rangle = 0$, one obtains an expression for the first order shift of the wavefunction expressed in the unperturbed basis,

$$\boxed{\langle m^{(0)} | n^{(1)} \rangle = \frac{\langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}.} \quad (7.11)$$

In summary, setting $\lambda = 1$, to first order in perturbation theory, we have the eigenvalues and eigenfunctions,

$$E_n \simeq E_n^{(0)} + \langle n^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle, \quad (7.12)$$

$$|n\rangle \simeq |n^{(0)}\rangle + \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}. \quad (7.13)$$

Before turning to the second order of perturbation theory, let us first consider a simple application of the method.

7.1.2.1 Ground State Energy of the Helium Atom

For the Helium atom, two electrons are bound to a nucleus of two protons and two neutrons. If one neglects altogether the Coulomb interaction between the electrons, in the ground state, both electrons would occupy the ground state hydrogenic wavefunction (scaled appropriately to accommodate the doubling of the nuclear charge) and have opposite spin. Treating the Coulomb interaction between electrons as a perturbation, one may then use the basis above to estimate the shift in the ground state energy with

$$\hat{H}^{(1)} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (7.14)$$

The hydrogenic wave functions are specified by three quantum numbers, n , ℓ , and m . In the ground state, the corresponding wavefunction takes the spatially isotropic form,

$$\langle \mathbf{r} | n = 1, \ell = 0, m = 0 \rangle = \psi_{100}(\mathbf{r}) = \left(\frac{1}{\pi a^3} \right)^{1/2} e^{-r/a}, \quad (7.15)$$

where $a = \frac{4\pi\epsilon_0 \hbar^2}{Ze^2 m_e} = \frac{a_0}{Z}$ denotes the atomic Bohr radius for a nuclear charge Z . For the Helium atom ($Z = 2$), the symmetrised ground state of the unperturbed Hamiltonian is given by the spin singlet ($S = 0$) electron wavefunction,

$$| \text{g.s.}^{(0)} \rangle = \frac{1}{\sqrt{2}} (|100, \uparrow\rangle \otimes |100, \downarrow\rangle - |100, \downarrow\rangle \otimes |100, \uparrow\rangle). \quad (7.16)$$

Here we have used the **direct product** \otimes to discriminate between the two electrons. Then, applying the perturbation theory formula above (7.9), to first order in the Coulomb interaction, the energy shift is given by

$$E_n^{(1)} = \langle \text{g.s.}^{(0)} | \hat{H}^{(1)} | \text{g.s.}^{(0)} \rangle = \frac{e^2}{4\pi\epsilon_0} \frac{1}{(\pi a^3)^2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{e^{-2(r_1+r_2)/a}}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{e^2}{4\pi\epsilon_0} \frac{C_0}{2a}, \quad (7.17)$$

where we have defined the dimensionless constant $C_0 = \frac{1}{(4\pi)^2} \int d\mathbf{z}_1 d\mathbf{z}_2 \frac{e^{-(z_1+z_2)}}{|\mathbf{z}_1 - \mathbf{z}_2|}$. Then, making use of the identity,

$$\frac{1}{(4\pi)^2} \int d\Omega_1 d\Omega_2 \frac{1}{|\mathbf{z}_1 - \mathbf{z}_2|} = \frac{1}{\max(z_1, z_2)}, \quad (7.18)$$

where the integrations run over the angular coordinates of the vectors \mathbf{z}_1 and \mathbf{z}_2 , and $z_{1,2} = |\mathbf{z}_{1,2}|$, one finds that $C_0 = 2 \int_0^\infty dz_1 z_1^2 e^{-z_1} \int_{z_1}^\infty dz_2 z_2 e^{-z_2} = 5/4$. As a result, noting that the Rydberg energy, $\text{Ry} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{2a_0}$, we obtain the first order energy shift $\Delta E = \frac{5}{4} Z \text{Ry} \simeq 34 \text{eV}$ for $Z = 2$. This leads to a total ground state energy of $(2Z^2 - \frac{5}{4}Z) \text{Ry} = -5.5 \text{Ry} \simeq -74.8 \text{eV}$ compared to the experimental value of -5.807Ry .

7.1.3 Second Order Perturbation Theory

With the first order of perturbation theory in place, we now turn to consider the influence of the second order terms in the perturbative expansion (7.6). Isolating terms of order λ^2 , we have

$$\hat{H}^{(0)} |n^{(2)}\rangle + \hat{H}^{(1)} |n^{(1)}\rangle = E_n^{(0)} |n^{(2)}\rangle + E_n^{(1)} |n^{(1)}\rangle + E_n^{(2)} |n^{(0)}\rangle. \quad (7.19)$$

As before, taking the inner product with $\langle n^{(0)} |$, one obtains

$$\begin{aligned} \langle n^{(0)} | \hat{H}^{(0)} | n^{(2)} \rangle + \langle n^{(0)} | \hat{H}^{(1)} | n^{(1)} \rangle \\ = \langle n^{(0)} | E_n^{(0)} | n^{(2)} \rangle + \langle n^{(0)} | E_n^{(1)} | n^{(1)} \rangle + \langle n^{(0)} | E_n^{(2)} | n^{(0)} \rangle. \end{aligned} \quad (7.20)$$

Noting that the first two terms on the left and right hand sides cancel, we are left with the result

$$E_n^{(2)} = \langle n^{(0)} | \hat{H}^{(1)} | n^{(1)} \rangle - E_n^{(1)} \langle n^{(0)} | n^{(1)} \rangle. \quad (7.21)$$

Previously, we have made use of the normalisation of the basis states, $|n^{(0)}\rangle$. We have said nothing so far about the normalisation of the exact eigenstates, $|n\rangle$. Of course, eventually, we would like to ensure normalisation of these states too. However, to facilitate the perturbative expansion, it is operationally more convenient to impose a normalisation on $|n\rangle$ through the condition $\langle n^{(0)}|n\rangle = 1$. Substituting the λ expansion for $|n\rangle$, we thus have

$$\langle n^{(0)}|n\rangle = 1 = \langle n^{(0)}|n^{(0)}\rangle + \lambda \langle n^{(0)}|n^{(1)}\rangle + \lambda^2 \langle n^{(0)}|n^{(2)}\rangle + \dots \quad (7.22)$$

From this relation, it follows that $\langle n^{(0)}|n^{(1)}\rangle = \langle n^{(0)}|n^{(2)}\rangle = \dots = 0$. We can therefore drop the term $E_n^{(1)} \langle n^{(0)}|n^{(1)}\rangle$ from consideration. As a result, we obtain

$$E_n^{(2)} = \langle n^{(0)}|\hat{H}^{(1)}|n^{(1)}\rangle = \langle n^{(0)}|\hat{H}^{(1)} \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} \quad (7.23)$$

i.e.

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}}. \quad (7.24)$$

From this result, we can conclude that,

- for the ground state, the second order shift in energy is always negative;
- if the matrix elements of $\hat{H}^{(1)}$ are of comparable magnitude, neighbouring levels make a larger contribution than distant levels;
- Levels that lie in close proximity tend to be **repelled**;
- If a fraction of the states belong to a continuum, the sum in Eq. (7.24) should be replaced by an integral.

Once again, to illustrate the utility of the perturbative expansion, let us consider a concrete physical example.

7.1.3.1 The Quadratic Stark Effect

Consider the influence of an external electric field on the ground state of the hydrogen atom. As the composite electron and proton are drawn in different directions by the field, the relative displacement of the electron cloud and nucleus results in the formation of a dipole which serves to lower the overall energy. In this case, the perturbation due to the external field takes the form

$$\hat{H}^{(1)} = -q\mathcal{E}z = e\mathcal{E}r \cos \theta, \quad (7.25)$$

where $q = -e$ denotes the electron charge, and the electric field, $\mathcal{E} = \mathcal{E}\hat{e}_z$ is oriented along the z -axis. With the non-perturbed energy spectrum given by $E_{n\ell m}^{(0)} \equiv E_n^{(0)} = -\text{Ry}/n^2$, the ground state energy is given by $E^{(0)} \equiv E_{100}^{(0)} = -\text{Ry}$. At first order in the electric field

strength, \mathcal{E} , the shift in the ground state energy is given by $E^{(1)} = \langle 100 | e\mathcal{E}z | 100 \rangle$ where the ground state wavefunction was defined above (7.15). Since the potential perturbation is antisymmetric in z , it is easy to see that the energy shift vanishes at this order.

We are therefore led to consider the contribution second order in the field strength. Making use of Eq. (7.24), and neglecting the contribution to the energy shift from the continuum of unbound positive energy states, we have

$$E^{(2)} = \sum_{n \neq 1, \ell, m} \frac{|\langle n\ell m | e\mathcal{E}z | 100 \rangle|^2}{E_1^{(0)} - E_n^{(0)}}, \quad (7.26)$$

where $|n\ell m\rangle$ denote the set of bound state hydrogenic wavefunctions. Although the expression for $E^{(2)}$ can be computed exactly, the programme is somewhat tedious. However, we can place a strong bound on the energy shift through the following argument: Since, for $n > 2$, $|E_1^{(0)} - E_n^{(0)}| > |E_1^{(0)} - E_2^{(0)}|$, we have

$$|E^{(2)}| < \frac{1}{E_2^{(0)} - E_1^{(0)}} \sum_{n \neq 1, \ell, m} \langle 100 | e\mathcal{E}z | n\ell m \rangle \langle n\ell m | e\mathcal{E}z | 100 \rangle. \quad (7.27)$$

Since $\sum_{n, \ell, m} |n\ell m\rangle\langle n\ell m| = \hat{\mathbb{I}}$, we have $\sum_{n \neq 1, \ell, m} |n\ell m\rangle\langle n\ell m| = \hat{\mathbb{I}} - |100\rangle\langle 100|$. Finally, since $\langle 100 | z | 100 \rangle = 0$, we can conclude that $|E^{(2)}| < \frac{1}{E_2^{(0)} - E_1^{(0)}} \langle 100 | (e\mathcal{E}z)^2 | 100 \rangle$. With $\langle 100 | z^2 | 100 \rangle = a_0^2$, $E_1^{(0)} = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2a_0} = -Ry$, and $E_2^{(0)} = E_1^{(0)}/4$, we have

$$|E^{(2)}| < \frac{1}{\frac{3}{4}e^2/8\pi\epsilon_0 a_0} (e\mathcal{E})^2 a_0^2 = \frac{8}{3} 4\pi\epsilon_0 \mathcal{E}^2 a_0^3. \quad (7.28)$$

Furthermore, since all terms in the perturbation series for $E^{(2)}$ are negative, the first term in the series sets a lower bound, $|E^{(2)}| > \frac{|\langle 210 | e\mathcal{E}z | 100 \rangle|^2}{E_2^{(0)} - E_1^{(0)}}$. From this result, one can show that $0.55 \times \frac{8}{3} 4\pi\epsilon_0 \mathcal{E}^2 a_0^3 < |E^{(2)}| < \frac{8}{3} 4\pi\epsilon_0 \mathcal{E}^2 a_0^3$.

7.2 Degenerate Perturbation Theory

The perturbative analysis above is reliable providing that the successive terms in the expansion form a convergent series. A necessary condition is that the matrix elements of the perturbing Hamiltonian must be smaller than the corresponding energy level differences of the original Hamiltonian. If it has different states with the same energy (i.e. degeneracies), and the perturbation has nonzero matrix elements between these degenerate levels, then clearly the theory breaks down. However, the problem is easily fixed. To understand how, let us consider a particular example.

Recall that, for the simple harmonic oscillator, $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2$, the ground state wavefunction is given by $\langle x | 0 \rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\xi^2/2}$, where $\xi = x\sqrt{m\omega/\hbar}$ and the first excited state by $\langle x | 1 \rangle = \left(\frac{4m\omega}{\pi\hbar}\right)^{1/4} \xi e^{-\xi^2/2}$. The wavefunctions for the two-dimensional harmonic oscillator,

$$\hat{H}^{(0)} \equiv \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2) + \frac{1}{2}m\omega^2(x^2 + y^2), \quad (7.29)$$

are given simply by the product of two one-dimensional oscillators. So, setting $\eta = y\sqrt{m\omega/\hbar}$, the ground state is given by $\langle x, y|0, 0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-(\xi+\eta)^2/2}$, and the two *degenerate* first excited states, an energy $\hbar\omega$ above the ground state, are given by

$$\begin{cases} \langle x, y|1, 0\rangle \\ \langle x, y|0, 1\rangle \end{cases} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-(\xi+\eta)^2/2} \begin{cases} \xi \\ \eta \end{cases}. \quad (7.30)$$

Suppose now we add to the Hamiltonian a perturbation

$$\hat{H}^{(1)} = \alpha m\omega^2 xy = \alpha \hbar\omega \xi \eta, \quad (7.31)$$

controlled by a small parameter α . Notice that, by symmetry, the following matrix elements all vanish, $\langle \hat{H}^{(1)}|0, 0\rangle = \langle \hat{H}^{(1)}|1, 0\rangle = \langle \hat{H}^{(1)}|0, 1\rangle = 0$. Therefore, according to a naïve perturbation theory, there is no first-order correction to the energies of these states. However, on proceeding to consider the second-order correction to the energy, the theory breaks down. The off-diagonal matrix element $\langle 1, 0|\hat{H}^{(1)}|0, 1\rangle$ is non-zero, but the two states $|0, 1\rangle$ and $|1, 0\rangle$ have the same energy! This gives an infinite term in the series for $E_{n=1}^{(2)}$.

Yet we know that a small perturbation of this type will not wreck a two-dimensional simple harmonic oscillator – so what is wrong with our approach? To understand the origin of the problem and its fix, it is helpful to plot the original harmonic oscillator potential $\frac{1}{2}m\omega^2(x^2 + y^2)$ together with the perturbing potential $\alpha m\omega^2 xy$. The first of course has circular symmetry, the second has two symmetry axes oriented in the directions $x = \pm y$, climbing most steeply from the origin along $x = y$, falling most rapidly in the directions $x = -y$. If we combine the two potentials into a single quadratic form,

$$\frac{1}{2}m\omega^2(x^2 + y^2) + \alpha m\omega^2 xy = \frac{1}{2}m\omega^2 \left[(1 + \alpha) \left(\frac{x+y}{2} \right)^2 + (1 - \alpha) \left(\frac{x-y}{2} \right)^2 \right]. \quad (7.32)$$

the original circles of constant potential become ellipses, with their axes aligned along $x = \pm y$.

As soon as the perturbation is introduced, the eigenstates lie in the direction of the new elliptic axes. This is a large change from the original x and y bases, which is not proportional to the small parameter α . But the original unperturbed problem had circular symmetry, and there was no particular reason to choose the x and y axes as we did. If we had instead chosen as our original axes the lines $x = \pm y$, the basis states would not have undergone large changes on switching on the perturbation. The resolution of the problem is now clear: *Before switching on the perturbation, one must choose a set of basis states in a degenerate subspace in which the perturbation is diagonal.*

In fact, for the simple harmonic oscillator example above, the problem can of course be solved exactly by rearranging the coordinates to lie along the symmetry axes, $(x \pm y)/\sqrt{2}$. It is then clear that, despite the results of naïve first order perturbation theory, there is indeed a *first order shift* in the energy levels, $\hbar\omega \rightarrow \hbar\omega\sqrt{1 \pm \alpha} \approx \hbar\omega(1 \pm \alpha/2)$.

7.2.0.1 Example: Linear Stark Effect

As with the two-dimensional harmonic oscillator discussed above, the hydrogen atom has a non-degenerate ground state, but degeneracy in its lowest excited states. Specifically, there are four $n = 2$ states, all having energy $-\frac{1}{4}\text{Ry}$. In spherical coordinates, these wavefunctions are given by

$$\begin{cases} \psi_{200}(\mathbf{r}) \\ \psi_{210}(\mathbf{r}) \\ \psi_{21,\pm 1}(\mathbf{r}) \end{cases} = \left(\frac{1}{32\pi a_0^3}\right)^{1/2} e^{-r/2a_0} \begin{cases} \left(2 - \frac{r}{a_0}\right) \\ \frac{r}{a_0} \cos \theta \\ \frac{r}{a_0} e^{\pm i\phi} \sin \theta \end{cases}. \quad (7.33)$$

When perturbing this system with an electric field oriented in the z -direction, $\hat{H}^{(1)} = e\mathcal{E}r \cos \theta$, a naïve application of perturbation theory predicts no first-order shift in any of these energy levels. However, to first order in E there is a non-zero matrix element between two degenerate levels $\Delta = \langle 200 | \hat{H}^{(1)} | 210 \rangle$. All the other matrix elements between these basis states in the four-dimensional degenerate subspace are zero. So the only diagonalisation necessary is within the two-dimensional degenerate subspace spanned by $|200\rangle$ and $|210\rangle$, i.e.

$$\hat{H}^{(1)} = \begin{pmatrix} 0 & \Delta \\ \Delta & 0 \end{pmatrix}, \quad (7.34)$$

with $\Delta = e\mathcal{E} \left(\frac{1}{32\pi a_0^3}\right) \int \left(2 - \frac{r}{a_0}\right) \frac{(r \cos \theta)^2}{a_0} e^{-r/a_0} r^2 dr \sin \theta d\theta d\phi = -3e\mathcal{E}a_0$.

Diagonalising $\hat{H}^{(1)}$ within this sub-space, the new basis states are given by the symmetric and antisymmetric combinations, $(|200\rangle + |210\rangle)/\sqrt{2}$ with energy shifts $\pm\Delta$, *linear* in the perturbing electric field. The states $|2\ell, \pm 1\rangle$ are not changed by the presence of the field to this level of approximation, so the complete energy map of the $n = 2$ states in the electric field has two states at the original energy of $-\text{Ry}/4$, one state moved up from that energy by Δ , and one down by Δ . Notice that the new eigenstates $(|200\rangle \pm |210\rangle)/\sqrt{2}$ are *not* eigenstates of the parity operator - a sketch of their wavefunctions reveals that, in fact, they have non-vanishing electric dipole moment \mathbf{p} . Indeed this is the reason for the energy shift, $\pm\Delta = \mp 2e\mathcal{E}a_0 = \mp \mathbf{p} \cdot \mathcal{E}$.

7.2.0.2 Nearly Free Electron Model

As a second and important example of the degenerate perturbation theory, let us consider the problem of a particle moving in one dimension and subject to a weak periodic potential, $V(x) = 2V \cos(2\pi x/a)$ - the **nearly free electron model**. This problem provides a caricature of a simple crystalline solid in which (free) conduction electrons propagate in the presence of a periodic background lattice potential. Here we suppose that the strength of the potential V is small as compared to the typical energy scale of the particle so that it may be treated as a small perturbation. In the following, we will suppose that the total one-dimensional system is of length $L = Na$, with periodic boundary conditions.

For the unperturbed free particle system, the eigenstates are simply plane waves $\psi_k(x) = \langle x | k \rangle = \frac{1}{\sqrt{L}} e^{ikx}$ indexed by the wavenumber $k = 2\pi n/L$, n integer, and the

unperturbed spectrum is given by $E_k^{(0)} = \hbar^2 k^2 / 2m$. The matrix elements of the perturbation between states of different wavevector are given by

$$\begin{aligned} \langle k | V | k' \rangle &= \frac{1}{L} \int_0^L dx e^{i(k-k')x} 2V \cos(2\pi x/a) \\ &= \frac{V}{L} \int_0^L \left(e^{i(k-k'+2\pi x/a)x} + e^{i(k-k'-2\pi x/a)x} \right) dx = V \delta_{k'-k, 2\pi/a}. \end{aligned} \quad (7.35)$$

Note that all diagonal matrix elements of the perturbation are identically zero. In general, for wavevectors k and k' separated by $G = 2\pi/a$, the unperturbed states are non-degenerate. For these states one can compute the relative energy shift within the framework of second order perturbation theory. However, for states $k = -k' = G/2 \equiv \pi/2$, the unperturbed free particle spectrum is degenerate. Here, and in the neighbourhood of these k values, we must implement a degenerate perturbation theory.

For the sinusoidal potential considered here, only states separated by $G = 2\pi/a$ are coupled by the perturbation. We may therefore consider matrix elements of the full Hamiltonian between pairs of coupled states, $|k = G/2 + q\rangle$ and $|k = -G/2 + q\rangle$

$$H = \begin{pmatrix} E_{G/2+q}^{(0)} & V \\ V & E_{-G/2+q}^{(0)} \end{pmatrix}. \quad (7.36)$$

As a result, to leading order in V , we obtain the eigenvalues,

$$E_q = \frac{\hbar^2}{2m} (q^2 + (\pi/a)^2) \pm \left(V^2 + \frac{\pi^2 \hbar^4 q^2}{4m^2 a^2} \right)^{1/2}. \quad (7.37)$$

In particular, this result shows that, for $k = \pm G/2$, the degeneracy of the free particle system is lifted by the potential. In the vicinity, $|q| \ll G$, the spectrum of eigenvalues is separated by a gap of size $2V$. The appearance of the gap mirrors the behaviour found in our study of the Kronig-Penney model of a crystal studied in section 2.2.3.

The appearance of the gap has important consequences in theory of solids. Electrons are fermions and have to obey Pauli's exclusion principle. In a metal, at low temperatures, electrons occupy the free particle-like states up to some (Fermi) energy which lies away from gap. Here, the accessibility of very low-energy excitations due to the continuum of nearby states allows current to flow when a small electric field is applied. However, when the Fermi energy lies in the gap created by the lattice potential, an electric field is unable to create excitations and induce current flow. Such systems are described as **(band) insulators**.

7.3 Variational Method

So far, in devising approximation methods for quantum mechanics, we have focused on the development of a perturbative expansion scheme in which the states of the non-perturbed system provided a suitable platform. Here, by "suitable" we refer to situations in which the states of the unperturbed system mirror those of the full system – adiabatic continuity. For example, the states of the harmonic oscillator potential with a small perturbation will

mirror those of the unperturbed Hamiltonian: The ground state will be nodeless, the first excited state will be antisymmetric having one node, and so on. However, often we working with systems where the true eigenstates of the problem may not be adiabatically connected to some simple unperturbed reference state. This situation is particularly significant in strongly interacting quantum systems where many-particle correlations can effect phase transitions to new states of matter – e.g. the development of superfluid condensates, or the fractional quantum Hall fluid. To address such systems it is often extremely effective to “guess” and then optimize a trial wavefunction. The method of optimisation relies upon a simple theoretical framework known as the variational approach. For reasons that will become clear, the variational method is particularly wellsuited to addressing the ground state.

The variational method involves the optimisation of some trial wavefunction on the basis of one or more adjustable parameters. The optimisation is achieved by minimising the expectation value of the energy on the trial function, and thereby finding the best approximation to the true ground state wave function. This seemingly crude approach can, in fact, give a surprisingly good approximation to the ground state energy but, it is usually not so good for the wavefunction, as will become clear. However, as mentioned above, the real strength of the variational method arises in the study of many-body quantum systems, where states are more strongly constrained by fundamental symmetries such as “exclusion statistics”.

To develop the method, we’ll begin with the problem of a single quantum particle confined to a potential, $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{r})$. If the particle is restricted to one dimension, and we’re looking for the ground state in any fairly localised potential well, it makes sense to start with a trial wavefunction which belongs to the family of normalised Gaussians, $\langle x|\psi(\alpha)\rangle = (\alpha/\pi)^{1/4}e^{-\alpha x^2/2}$. Such a trial state fulfils the criterion of being nodeless, and is exponentially localised to the region of the binding potential. It also has the feature that it includes the exact ground states of the harmonic binding potential.

The variation approach involves simply minimising the expectation value of the energy, $E = \langle\psi(\alpha)|\hat{H}|\psi(\alpha)\rangle$, with respect to variations of the **variational parameter**, α . (Of course, as with any minimisation, one must check that the variation does not lead to a maximum of the energy!) Not surprisingly, this programme leads to the exact ground state for the simple harmonic oscillator potential, while it serves only as an approximation for other potentials. What is perhaps surprising is that the result is only off by only ca. 30% or so for the attractive δ -function potential, even though the wavefunction looks substantially different. The Gaussian family cannot be used if there is an infinite wall anywhere: since the wavefunction must vanish where the potential is infinite, one must find a family of wavefunctions that vanishes at such a boundary.

To gain some further insight into the approach, suppose the Hamiltonian \hat{H} has a set of eigenstates, $\hat{H}|n\rangle = E_n|n\rangle$. Since the Hamiltonian is Hermitian, these states span the space of possible wave functions, including our variational family of Gaussians, so we can write, $|\psi(\alpha)\rangle = \sum_n a_n(\alpha)|n\rangle$. From this expansion, we have

$$\boxed{\frac{\langle\psi(\alpha)|\hat{H}|\psi(\alpha)\rangle}{\langle\psi(\alpha)|\psi(\alpha)\rangle} = \sum_n |a_n|^2 E_n \geq E_0.} \quad (7.38)$$

for *any* $|\psi(\alpha)\rangle$. (We don’t need the denominator if we’ve chosen a family of normalised

wavefunctions, as we did with the Gaussians above.) Evidently, minimising the left hand side of this equation as function of α provides an **upper bound** on the ground state energy.

We can see immediately that this will probably be better for finding the ground state energy than for the wavefunction: Suppose the optimum state in our family is given by, say, $|\alpha_{\min}\rangle = N(|0\rangle + 0.2|1\rangle)$ with the normalisation $N \simeq 0.98$, i.e. a 20% admixture of the first excited state. Then the wavefunction is off by ca. 20%, but the energy estimate will be too high by only $0.04(E_1 - E_0)$, usually a much smaller error.

7.3.0.1 Example: Ground State of Hydrogen Atom

To get some idea of how well the variational approach works, consider its application to the ground state of the hydrogen atom. Taking into account the spherical symmetry of the ground state, we may focus on the one-dimensional radial component of the wavefunction. Defining the trial radial wavefunction $u(\rho)$ (presumed real), where $\rho = r/a_0$, the variational energy is given by

$$E(u) = -Ry \frac{\int_0^\infty d\rho u(\rho) \left(\frac{d^2}{d\rho^2} + \frac{2}{\rho} \right) u(\rho)}{\int_0^\infty d\rho u^2(\rho)}. \quad (7.39)$$

For the three families of trial functions,

$$u_1(\rho) = \rho e^{-\alpha\rho}, \quad u_2(\rho) = \frac{\rho}{\alpha^2 + \rho^2}, \quad u_3(\rho) = \rho^2 e^{-\alpha\rho}, \quad (7.40)$$

and finds $\alpha_{\min} = 1, \pi/4$, and $3/2$ respectively. The first family, u_1 , includes the exact result, and the minimisation procedure correctly finds it. For the three families, the predicted energy of the optimal state is off by 0, 25%, and 21% respectively.

The corresponding error in the wavefunction is defined by how far the square of the overlap with the true ground state wavefunction falls short of unity. For the three families, $\varepsilon = 1 - |\langle\psi_0|\psi_{\text{var}}\rangle|^2 = 0, 0.21$, and 0.05 . Notice here that our handwaving argument that the energies would be found much more accurately than the wavefunctions seems to come unstuck. The third family has far better wavefunction overlap than the second, but only a slightly better energy estimate. Why? A key point is that the potential is singular at the origin; there is a big contribution to the potential energy from a rather small region, and the third family of trial states is the least accurate of the three there. The second family of functions are very inaccurate at large distances: the expectation value $\langle r \rangle = 1.5a_0, \infty, 1.66a_0$ for the three families. But at large distances, both kinetic and potential energies are small, so the result can still look reasonable. These examples reinforce the point that the variational method should be implemented with some caution.

In some cases, one can exploit symmetry to address the properties of higher-lying states. For example, if the one-dimensional attractive potential is symmetric about the origin, and has more than one bound state, the ground state will be even, the first excited state odd. Therefore, we can estimate the energy of the first excited state by minimizing a family of odd functions, such as $\psi(x, \alpha) = \left(\frac{\sqrt{\pi}}{2a^{3/2}} \right)^{1/2} x e^{-\alpha x^2/2}$.

7.3.0.2 Helium Atom Addressed by the Variational Approach

For the hydrogen atom, we know that the ground state energy is -1Ry , or -13.6eV . The He^+ ion (with just a single electron) has a nuclear charge of $Z = 2$, so the ground state energy of the electron, being proportional to Z^2 , will now be equal to -4Ry . Therefore, for the He atom, if we neglect their mutual interaction, the electrons will occupy the ground state wavefunction having opposite spin, leading to a total ground state energy of -8Ry or -109eV . In practice, as we have seen earlier, the repulsion between the electrons raises the ground state energy to -79eV (see Section 7.1.2.1).

To get a better estimate for the ground state energy, one can retain the form of the ionic wavefunction, $\left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/\pi a_0}$, but now with Z a variational parameter, rather than setting it equal to the nuclear charge $Z = 2$. In other words, let us accommodate the effects of electron-electron repulsion, which must “push” the wavefunctions to larger radii, by keeping exactly the same wavefunction profile but lessening the effective nuclear charge as reflected in the spread of the wavefunction from $Z = 2$ to $Z < 2$. The precise value will be set by varying it to find the minimum total energy, including the term from electron-electron repulsion.

To find the potential energy from the nuclear-electron interactions, we of course must use the actual nuclear charge $Z = 2$, but impose a variable Z for the wavefunction, so the nuclear potential energy for the two electrons is given by,

$$\text{p.e.} = -2 \times \frac{2e^2}{4\pi\epsilon_0} \int_0^\infty 4\pi r^2 dr \frac{Z^3}{\pi a_0^3} \frac{e^{-2Zr/a_0}}{r} = -Z \frac{e^2}{\pi\epsilon_0 a_0} = -8Z\text{Ry}. \quad (7.41)$$

This could have been inferred from the formula for the one electron ion of charge Z , where the potential energy for the one electron is $-2Z^2\text{Ry}$, one factor of Z being from the nuclear charge, the other from the consequent shrinking of the orbit. The kinetic energy is even easier to determine: it depends entirely on the form of the wavefunction, and not on the actual nuclear charge. So for our trial wavefunction it has to be $Z^2\text{Ry}$ per electron. Finally, making use of our calculation in Section 7.1.2.1, we can immediately write down the positive contribution to the energy expectation value from the electron-electron interaction,

$$\frac{e^2}{4\pi\epsilon_0} \frac{Z^2}{(\pi a_0^3)^2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{e^{-2Z(r_1+r_2)/a_0}}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{5}{4} \frac{e^2}{4\pi\epsilon_0} \frac{Z}{2a_0} = \frac{5}{4} Z\text{Ry}. \quad (7.42)$$

Collecting all of the terms, the total variational state energy is given by:

$$E = -2 \left(4Z - Z^2 - \frac{5}{8}Z \right) \text{Ry}. \quad (7.43)$$

Minimisation of this energy with respect to Z obtains the minimum at $Z = 2 - \frac{5}{16}$, leading to an energy of -77.5eV . This result departs from the true value by about 1eV . So, indeed, the presence of the other electron leads effectively to a shielding of the nuclear charge by an amount of ca. $(5/16)e$.

This completes our discussion of the principles of the variational approach. However, later in the course, we will find the variational methods appearing in several important applications.

Symmetry in Quantum Mechanics

Symmetry considerations are very important in quantum theory. The structure of eigenstates and the spectrum of energy levels of a quantum system reflect the symmetry of its Hamiltonian. As we will see later, the transition probabilities between different states under a perturbation, such as that imposed by an external electromagnetic field, depend in a crucial way on the transformation properties of the perturbation and lead to “selection rules”. Symmetries can be classified into two types, discrete and continuous, according to the transformations that generate them. For example, a mirror symmetry is an example of a discrete symmetry while a rotation in three-dimensional space is continuous.

Formally, the symmetries of a quantum system can be represented by a group of unitary transformations (or operators), \hat{U} , that act in the Hilbert space.¹ Under the action of such a unitary transformation, operators corresponding to observables \hat{A} of the quantum model will then transform as,

$$\hat{A} \rightarrow \hat{U}^\dagger \hat{A} \hat{U}. \quad (8.1)$$

For unitary transformations, we have seen that $\hat{U}^\dagger \hat{U} = \hat{\mathbb{I}}$, i.e. $\hat{U}^\dagger = \hat{U}^{-1}$. Under what circumstances does such a group of transformations represent a **symmetry group**? Consider a Schrödinger particle in three dimensions.² The basic observables are the position and momentum vectors, $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$. We can always define a transformation of the coordinate system, or the observables, such that a vector $\hat{\mathbf{A}} = \hat{\mathbf{r}}$ or $\hat{\mathbf{p}}$ is mapped to $\mathbf{R}[\hat{\mathbf{A}}]$.³ If \mathbf{R} is an element of the group of transformations, then this transformation will be represented by a unitary operator $\hat{U}(\mathbf{R})$, such that

$$\hat{U}^\dagger \hat{\mathbf{A}} \hat{U} = \mathbf{R}[\hat{\mathbf{A}}]. \quad (8.3)$$

Such unitary transformations are said to be **symmetries of a general operator** $\hat{O}(\hat{\mathbf{p}}, \hat{\mathbf{r}})$ if

$$\hat{U}^\dagger \hat{O} \hat{U} = \hat{O}, \quad \text{i.e. } [\hat{O}, \hat{U}] = 0. \quad (8.4)$$

If $\hat{O}(\hat{\mathbf{p}}, \hat{\mathbf{r}}) \equiv \hat{H}$, the quantum Hamiltonian, such unitary transformations are said to be symmetries of the quantum system.

¹In quantum mechanics, the possible states of a system can be represented by unit vectors (called “state vectors”) residing in “state space” known as the Hilbert space. The precise nature of the Hilbert space is dependent on the system; for example, the state space for position and momentum states is the space of square-integrable functions.

²In the following, we will focus our considerations on the realm of “low-energy” physics where the relevant space-time transformations belong to the Galilei group.

³e.g., for a clockwise spatial rotation by an angle θ around \hat{e}_z , we have,

$$\mathbf{R}[\mathbf{r}] = R_{ij} \hat{x}_j, \quad \begin{pmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (8.2)$$

Similarly, for a spatial translation by a vector \mathbf{a} , $\mathbf{R}[\mathbf{r}] = \mathbf{r} + \mathbf{a}$.

8.1 Observables as Generators of Transformations

The vector operators $\hat{\mathbf{p}}$ and $\hat{\mathbf{r}}$ for a Schrödinger particle are themselves generators of space-time transformations. From the standard commutation relations one can show that, for a constant vector \mathbf{a} , the unitary operator

$$\hat{U}(\mathbf{a}) = \exp \left[-\frac{i}{\hbar} \mathbf{a} \cdot \hat{\mathbf{p}} \right], \quad (8.5)$$

acting in the Hilbert space of a Schrödinger particle performs a spatial translation, $\hat{U}^\dagger(\mathbf{a})f(\mathbf{r})\hat{U}(\mathbf{a}) = f(\mathbf{r} + \mathbf{a})$, where $f(\mathbf{r})$ denotes a general algebraic function of \mathbf{r} .

The proof runs as follows: With $\hat{\mathbf{p}} = -i\hbar\nabla$,

$$\hat{U}^\dagger(\mathbf{a}) = e^{\mathbf{a} \cdot \nabla} = \sum_{n=0}^{\infty} \frac{1}{n!} a_{i_1} \cdots a_{i_n} \nabla_{i_1} \cdots \nabla_{i_n}, \quad (8.6)$$

where summation on the repeated indices, i_n is assumed. Then, making use of the **Baker-Hausdorff identity**

$$e^{\hat{A}} \hat{B} e^{-\hat{A}} = \hat{B} + [\hat{A}, \hat{B}] + \frac{1}{2!} [\hat{A}, [\hat{A}, \hat{B}]] + \cdots, \quad (8.7)$$

it follows that

$$\hat{U}^\dagger(\mathbf{a})f(\mathbf{r})\hat{U}(\mathbf{a}) = f(\mathbf{a}) + a_{i_1}(\nabla_{i_1} f(\mathbf{r})) + \frac{1}{2!} a_{i_1} a_{i_2} (\nabla_{i_1} \nabla_{i_2} f(\mathbf{r})) + \cdots = f(\mathbf{r} + \mathbf{a}), \quad (8.8)$$

where the last identity follows from the Taylor expansion.

Therefore, a quantum system has spatial translation as an invariance group if and only if the following condition holds,

$$\hat{U}(\mathbf{a})\hat{H} = \hat{H}\hat{U}(\mathbf{a}), \quad \text{i.e. } \hat{\mathbf{p}}\hat{H} = \hat{H}\hat{\mathbf{p}} \quad (8.9)$$

This demands that the Hamiltonian is independent of position, $\hat{H} = \hat{H}(\hat{\mathbf{p}})$, as one might have expected! Similarly, the group of unitary transformations, $\hat{U}(\mathbf{B}) = \exp \left[-\frac{i}{\hbar} \mathbf{B} \cdot \hat{\mathbf{r}} \right]$, performs translations in momentum space. Moreover, spatial rotations are generated by the transformation $\hat{U} = \exp \left[-\frac{i}{\hbar} \theta \mathbf{e}_n \cdot \hat{\mathbf{L}} \right]$, where $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ denotes the angular momentum operator. For more details see Appendix A.2.

As we have seen, **time translations** are generated by the time evolution operator, $\hat{U}(t) = \exp \left[-\frac{i}{\hbar} \hat{H}t \right]$. Therefore, every observable which commutes with the Hamiltonian is a constant of the motion (invariant under time translations),

$$\hat{H}\hat{A} = \hat{A}\hat{H} \implies e^{i\hat{H}t/\hbar} \hat{A} e^{-i\hat{H}t/\hbar} = \hat{A}, \quad \forall t. \quad (8.10)$$

We now turn to consider some examples of discrete symmetries. Amongst these, perhaps the most important in low-energy physics are parity and time-reversal. The **parity** operation, denoted \hat{P} , involves a reversal of sign on all coordinates.

$$\hat{P}\psi(\mathbf{r}) = \psi(-\mathbf{r}). \quad (8.11)$$

This is clearly a discrete transformation. Application of parity twice returns the initial state implying that $\hat{P}^2 = 1$. Therefore, the eigenvalues of the parity operation (if such exist) are ± 1 . A wavefunction will have a defined parity if and only if it is an even or odd function. For example, for $\psi(x) = \cos(x)$, $\hat{P}\psi = \cos(-x) = \cos(x) = \psi$; thus ψ is even and $P = 1$. Similarly $\psi = \sin(x)$ is odd with $P = -1$. Later, in the next chapter, we will encounter the spherical harmonic functions which have the following important symmetry under parity, $\hat{P}Y_{\ell m} = (-1)^\ell Y_{\ell m}$. Parity will be conserved if the Hamiltonian is invariant under the parity operation, i.e. if the Hamiltonian is invariant under a reversal of sign of all the coordinates.⁴

In classical mechanics, the time-reversal operation involves simply “running the movie backwards”. The time-reversed state of the phase space coordinates $(x(t), p(t))$ is defined by $(x_T(t), p_T(t))$ where $x_T(t) = x(t)$ and $p_T(t) = -p(t)$. Hence, if the system evolved from $(x(0), p(0))$ to $(x(t), p(t))$ in time t and at t we reverse the velocity, $p(t) \rightarrow -p(t)$ with $x(t) \rightarrow x(t)$, at time $2t$ the system would have returned to $x(2t) = x(0)$ while $p(2t) = -p(0)$. If this happens, we say that the system is time-reversal invariant. Of course, this is just the statement that Newton’s laws are the same if $t \rightarrow -t$. A notable case where this is not true is that of a charged particle in a magnetic field.

As with classical mechanics, time-reversal in quantum mechanics involves the operation $t \rightarrow -t$. However, referring to the time-dependent Schrödinger equation, $i\hbar\partial_t\psi(x, t) = \hat{H}\psi(x, t)$, we can see that the operation $t \rightarrow -t$ is equivalent to complex conjugation of the wavefunction, $\psi \rightarrow \psi^*$ if $\hat{H}^* = \hat{H}$. Let us then consider the time-evolution of $\psi(x, t)$,

$$\psi(x, 0) \rightarrow e^{-\frac{i}{\hbar}\hat{H}t}\psi(x, 0) \xrightarrow{\text{c.c.}} e^{+\frac{i}{\hbar}\hat{H}^*t}\psi^*(x, 0) \xrightarrow{\text{evolve}} e^{-\frac{i}{\hbar}\hat{H}t}e^{+\frac{i}{\hbar}\hat{H}^*t}\psi^*(x, 0). \quad (8.12)$$

If we require that $\psi(x, 2t) = \psi^*(x, 0)$, we must have $\hat{H}^* = \hat{H}(x)$. Therefore, \hat{H} is invariant under time-reversal if and only if \hat{H} is real.

Although the group of space-transformations covers the symmetries that pertain to “low-energy” quantum physics, such as atomic physics, quantum optics, and quantum chemistry, in nuclear physics and elementary particle physics new observables come into play (e.g. the isospin quantum numbers and the other quark charges in the standard model). They generate symmetry groups which lack a classical counterpart, and they do not have any obvious relation with space-time transformations. These symmetries are often called **internal symmetries** in order to underline this fact.

8.2 Consequences of Symmetries: Multiplets

Having established how to identify whether an operator belongs to a group of symmetry transformations, we now consider the consequences. Consider a single unitary transformation \hat{U} in the Hilbert space, and an observable \hat{A} which commutes with \hat{U} , $[\hat{U}, \hat{A}] = 0$. If \hat{A} has an eigenvector $|a\rangle$, it follows that $\hat{U}|a\rangle$ will be an eigenvector with the same eigenvalue, i.e.

$$\hat{U}\hat{A}|a\rangle = \hat{A}\hat{U}|a\rangle = a\hat{U}|a\rangle. \quad (8.13)$$

⁴In high energy physics, parity is a symmetry of the strong and electromagnetic forces, but does not hold for the weak force. Therefore, parity is conserved in strong and electromagnetic interactions, but is violated in weak interactions.

This means that either:

1. $|a\rangle$ is an eigenvector of both \hat{A} and \hat{U} , or
2. the eigenvalue a is degenerate: the linear space spanned by the vectors $\hat{U}^n |a\rangle$ (n integer) are eigenvectors with the same eigenvalue.

This mathematical argument leads to the conclusion that, given a group G of unitary operators $\hat{U}(x)$, $x \in G$, for any observable which is invariant under these transformations, i.e.

$$[\hat{U}(x), \hat{A}] = 0, \quad \forall x \in G, \quad (8.14)$$

its discrete eigenvalues and eigenvectors will show a characteristic multiplet structure: there will be a degeneracy due to the symmetry such that the eigenvectors belonging to each eigenvalue form an invariant subspace under the group of transformations.

For example, if the Hamiltonian commutes with the angular momentum operators, \hat{L}_i , $i = x, y, z$, i.e. it is invariant under three-dimensional rotations, an energy level with a given orbital quantum number ℓ is at least $(2\ell + 1)$ -fold degenerate. Such a degeneracy can be seen as the result of non-trivial actions of the operator \hat{L}_x and \hat{L}_y on an energy (and \hat{L}_z) eigenstate $|E, \ell, m\rangle$ (where m is the magnetic quantum number associated with \hat{L}_z).

8.3 Rotational Symmetry in Quantum Mechanics

Under a rotation R , the states of a quantum system transform as

$$|\psi\rangle \rightarrow |\psi'\rangle = \hat{U}(R) |\psi\rangle. \quad (8.15)$$

If all measurement outcomes remain invariant under spatial rotations, then the operator $\hat{U}(R)$ is a unitary operator:

$$\hat{U}(R)^\dagger \hat{U}(R) = \hat{\mathbb{I}}. \quad (8.16)$$

For an infinitesimal rotation described by a vector ω , it must be possible to write the unitary operator $\hat{U}(R)$ in the form

$$\hat{U}(\omega) = \hat{\mathbb{I}} + \frac{i}{\hbar} (\omega \cdot \hat{\mathbf{J}}) + \mathcal{O}(\omega^2), \quad (8.17)$$

where the generators $\hat{\mathbf{J}} = (\hat{J}_1, \hat{J}_2, \hat{J}_3)$ are a vector of Hermitian operators. The factor of $\frac{1}{\hbar}$ is introduced in order that the generators have dimension of angular momentum. Since rotations do not in general commute with each other, the generator components \hat{J}_i will not be mutually commuting (unlike the generators \hat{P}_i of spatial translations).

Since two successive rotations, R_1 followed by R_2 , are equivalent to a single rotation described by the matrix product $R_2 R_1$, we must have

$$\hat{U}(R_2) \hat{U}(R_1) = \hat{U}(R_2 R_1). \quad (8.18)$$

To obtain the commutation relations satisfied by the components \hat{J}_i , we consider a sequence of three infinitesimal rotations:

$$R_1 = \mathbb{I} + \omega' + \cdots; \quad R_2 = \mathbb{I} + \omega + \cdots; \quad R_3 = (R_1)^{-1} = \mathbb{I} - \omega' + \cdots. \quad (8.19)$$

where we have used $(R_1)^{-1} = (R_1)^T$ and $(\omega')^T = -\omega'$. This corresponds to an overall rotation given by

$$R_3 R_2 R_1 = (\mathbb{I} - \omega' + \cdots)(\mathbb{I} + \omega + \cdots)(\mathbb{I} + \omega' + \cdots) = \mathbb{I} + \omega + \omega\omega' - \omega'\omega + \cdots, \quad (8.20)$$

where we have kept the quadratic terms of order $\omega\omega'$ and $\omega'\omega$ as these will be needed in what follows. We thus have

$$R_3 R_2 R_1 = \mathbb{I} + \omega + \Omega + \cdots, \quad (8.21)$$

where

$$\Omega \equiv \omega\omega' - \omega'\omega. \quad (8.22)$$

Explicit multiplication gives the matrix product $\omega\omega'$ as

$$\omega\omega' = \begin{pmatrix} 0 & \omega_3 & -\omega_2 \\ -\omega_3 & 0 & \omega_1 \\ \omega_2 & -\omega_1 & 0 \end{pmatrix} \begin{pmatrix} 0 & \omega'_3 & -\omega'_2 \\ -\omega'_3 & 0 & \omega'_1 \\ \omega'_2 & -\omega'_1 & 0 \end{pmatrix} \quad (8.23)$$

$$= \begin{pmatrix} 0 & \omega_2\omega'_1 - \omega_1\omega'_2 & \omega_3\omega'_1 - \omega_1\omega'_3 \\ \omega_1\omega'_2 - \omega_2\omega'_1 & 0 & \omega_3\omega'_2 - \omega_2\omega'_3 \\ \omega_1\omega'_3 - \omega_3\omega'_1 & \omega_2\omega'_3 - \omega_3\omega'_2 & 0 \end{pmatrix} \quad (8.24)$$

Thus the matrix Ω corresponds to an infinitesimal rotation,

$$\Omega = \begin{pmatrix} 0 & \Omega_3 & -\Omega_2 \\ -\Omega_3 & 0 & \Omega_1 \\ \Omega_2 & -\Omega_1 & 0 \end{pmatrix}, \quad (8.25)$$

with components

$$\Omega_1 = \omega_3\omega'_2 - \omega_2\omega'_3, \quad \Omega_2 = \omega_1\omega'_3 - \omega_3\omega'_1, \quad \Omega_3 = \omega_2\omega'_1 - \omega_1\omega'_2. \quad (8.26)$$

The equation $\hat{U}(R_3)\hat{U}(R_2)\hat{U}(R_1) = \hat{U}(R_3 R_2 R_1)$ then gives

$$\left(\hat{\mathbb{I}} - \frac{i}{\hbar}(\omega' \cdot \hat{\mathbf{J}})\right) \left(\hat{\mathbb{I}} + \frac{i}{\hbar}(\omega \cdot \hat{\mathbf{J}})\right) \left(\hat{\mathbb{I}} + \frac{i}{\hbar}(\omega' \cdot \hat{\mathbf{J}})\right) = \hat{\mathbb{I}} + \frac{i}{\hbar}(\omega \cdot \hat{\mathbf{J}}) + \frac{i}{\hbar}(\Omega \cdot \hat{\mathbf{J}}) + \cdots, \quad (8.27)$$

where $\Omega = (\Omega_1, \Omega_2, \Omega_3)$. Multiplying out the left-hand side above then gives

$$(\omega' \cdot \hat{\mathbf{J}})(\omega \cdot \hat{\mathbf{J}}) - (\omega \cdot \hat{\mathbf{J}})(\omega' \cdot \hat{\mathbf{J}}) = i\hbar(\Omega \cdot \hat{\mathbf{J}}). \quad (8.28)$$

Writing the scalar products in Eq. (8.28) explicitly in terms of the vector components, and equating the coefficients of $\omega_1\omega'_2$ on both sides, gives

$$\hat{J}_1\hat{J}_2 - \hat{J}_2\hat{J}_1 = i\hbar\hat{J}_3. \quad (8.29)$$

Similarly, equating the coefficients of $\omega_2\omega'_3$ gives

$$\hat{J}_2\hat{J}_3 - \hat{J}_3\hat{J}_2 = i\hbar\hat{J}_1, \quad (8.30)$$

and equating the coefficients of $\omega_3\omega'_1$ gives

$$\hat{J}_3\hat{J}_1 - \hat{J}_1\hat{J}_3 = i\hbar\hat{J}_2. \quad (8.31)$$

Overall, we obtain the commutation relations

$$\boxed{[\hat{J}_i, \hat{J}_j] = i\hbar\epsilon_{ijk}\hat{J}_k.} \quad (8.32)$$

The vector operator $\hat{\mathbf{J}}$ therefore satisfies the standard commutation relations for angular momentum. Since $\hat{\mathbf{J}}$ is a property of the system as a whole, rather than of a particular particle, we identify $\hat{\mathbf{J}}$ as the *total* angular momentum operator for the system.

8.3.1 Scalar Operators

A *scalar operator* is an operator whose matrix elements are invariant under rotations,

$$\langle\psi'|\hat{K}|\phi'\rangle = \langle\psi|\hat{K}|\phi\rangle, \quad (8.33)$$

for all possible states of the system, $|\psi\rangle$ and $|\phi\rangle$. Since $|\psi'\rangle = \hat{U}(R)|\psi\rangle$ and $|\phi'\rangle = \hat{U}(R)|\phi\rangle$, the left-hand side is

$$\langle\psi'|\hat{K}|\phi'\rangle = \langle\psi|\hat{U}(R)^\dagger\hat{K}\hat{U}(R)|\phi\rangle. \quad (8.34)$$

For Eq. (8.33) to hold for all possible states $|\psi\rangle$ and $|\phi\rangle$ then requires that \hat{K} satisfy the relation

$$\hat{U}(R)^\dagger\hat{K}\hat{U}(R) = \hat{K} \quad (8.35)$$

for all rotations R . Since $\hat{U}(R)$ is unitary, this is equivalent to the condition that \hat{K} commutes with $\hat{U}(R)$ for all rotations R :

$$[\hat{U}(R), \hat{K}] = 0. \quad (8.36)$$

Applying this result to the case of infinitesimal rotations, with $\hat{U}(R)$ of the form given in Eq. (8.17), then shows that \hat{K} must commute with all components of the total angular momentum operator, $\hat{\mathbf{J}}$:

$$[\hat{J}_i, \hat{K}] = 0; \quad [\hat{\mathbf{J}}, \hat{K}] = 0. \quad (8.37)$$

From this, it follows immediately that \hat{K} also commutes with $\hat{\mathbf{J}}^2$ and with the ladder operators $\hat{J}_\pm = \hat{J}_1 \pm i\hat{J}_2$:

$$[\hat{\mathbf{J}}^2, \hat{K}] = 0, \quad [\hat{J}_\pm, \hat{K}] = 0. \quad (8.38)$$

Eq. (8.37) can also serve as the *definition* of a scalar operator \hat{K} with respect to an angular momentum operator $\hat{\mathbf{J}}$.

8.3.2 Vector Operators

An operator

$$\hat{\mathbf{V}} = (\hat{V}_x, \hat{V}_y, \hat{V}_z) = (\hat{V}_1, \hat{V}_2, \hat{V}_3) \quad (8.39)$$

whose expectation values transform under rotations like an ordinary vector,

$$\langle \psi | \hat{V}_i | \psi \rangle \rightarrow \langle \psi' | \hat{V}_i | \psi' \rangle = \sum_j R_{ij} \langle \psi | \hat{V}_j | \psi \rangle, \quad (8.40)$$

is said to be a *vector operator*. The left-hand side of Eq. (8.40) is

$$\langle \psi' | \hat{V}_i | \psi' \rangle = \langle \psi | \hat{U}(R)^\dagger \hat{V}_i \hat{U}(R) | \psi \rangle \quad (8.41)$$

For Eq. (8.40) to hold for all possible states $|\psi\rangle_i$, the operator $\hat{\mathbf{V}}$ must satisfy the relation

$$\hat{U}(R)^\dagger \hat{V}_i \hat{U}(R) = \sum_j R_{ij} \hat{V}_j \quad (8.42)$$

for all possible rotations R .

For the case that R is an infinitesimal rotation, $R = \mathbb{I} + \omega$, Eq. (8.42) gives

$$\left(\mathbb{I} - \frac{i}{\hbar} (\omega \cdot \hat{\mathbf{J}}) + \dots \right) \hat{V}_i \left(\mathbb{I} + \frac{i}{\hbar} (\omega \cdot \hat{\mathbf{J}}) + \dots \right) = \hat{V}_i + \sum_j \omega_{ij} \hat{V}_j + \dots \quad (8.43)$$

Expanding the left-hand side up to first-order in ω then gives

$$\frac{i}{\hbar} \hat{V}_i (\omega \cdot \hat{\mathbf{J}}) - \frac{i}{\hbar} (\omega \cdot \hat{\mathbf{J}}) \hat{V}_i = \sum_j \omega_{ij} \hat{V}_j \quad (i = 1, 2, 3). \quad (8.44)$$

Written out explicitly, the right-hand side of the above equation is

$$\sum_j \omega_{ij} \hat{V}_j = \begin{pmatrix} 0 & \omega_3 & -\omega_2 \\ -\omega_3 & 0 & \omega_1 \\ \omega_2 & -\omega_1 & 0 \end{pmatrix} \begin{pmatrix} \hat{V}_1 \\ \hat{V}_2 \\ \hat{V}_3 \end{pmatrix} = \begin{pmatrix} \omega_3 \hat{V}_2 - \omega_2 \hat{V}_3 \\ -\omega_3 \hat{V}_1 + \omega_1 \hat{V}_3 \\ \omega_2 \hat{V}_1 - \omega_1 \hat{V}_2 \end{pmatrix}. \quad (8.45)$$

Hence, for $i = 1$, Eq. (8.44) gives

$$\hat{V}_1 (\omega \cdot \hat{\mathbf{J}}) - (\omega \cdot \hat{\mathbf{J}}) \hat{V}_1 = -i\hbar (\omega_3 \hat{V}_2 - \omega_2 \hat{V}_3). \quad (8.46)$$

Expanding $\omega \cdot \hat{\mathbf{J}} = \omega_1 \hat{J}_1 + \omega_2 \hat{J}_2 + \omega_3 \hat{J}_3$ on the left-hand side, and rearranging, we obtain

$$\omega_1 (\hat{V}_1 \hat{J}_1 - \hat{J}_1 \hat{V}_1) + \omega_2 (\hat{V}_1 \hat{J}_2 - \hat{J}_2 \hat{V}_1) + \omega_3 (\hat{V}_1 \hat{J}_3 - \hat{J}_3 \hat{V}_1) = -i\hbar (\omega_3 \hat{V}_2 - \omega_2 \hat{V}_3). \quad (8.47)$$

This relation must hold for all possible choices of ω . Equating the coefficients of ω_1 , ω_2 and ω_3 on both sides gives

$$\hat{V}_1 \hat{J}_1 - \hat{J}_1 \hat{V}_1 = 0, \quad \hat{V}_1 \hat{J}_2 - \hat{J}_2 \hat{V}_1 = i\hbar \hat{V}_3, \quad \hat{V}_1 \hat{J}_3 - \hat{J}_3 \hat{V}_1 = -i\hbar \hat{V}_2. \quad (8.48)$$

Repeating this process for $i = 2$ and $i = 3$ gives, similarly,

$$\hat{V}_2 \hat{J}_2 - \hat{J}_2 \hat{V}_2 = 0, \quad \hat{V}_2 \hat{J}_3 - \hat{J}_3 \hat{V}_2 = i\hbar \hat{V}_1, \quad \hat{V}_2 \hat{J}_1 - \hat{J}_1 \hat{V}_2 = -i\hbar \hat{V}_3, \quad (8.49)$$

$$\hat{V}_3 \hat{J}_3 - \hat{J}_3 \hat{V}_3 = 0, \quad \hat{V}_3 \hat{J}_1 - \hat{J}_1 \hat{V}_3 = i\hbar \hat{V}_2, \quad \hat{V}_3 \hat{J}_2 - \hat{J}_2 \hat{V}_3 = -i\hbar \hat{V}_1. \quad (8.50)$$

Altogether, for *any* vector operator $\hat{\mathbf{V}}$, the equations above can be written compactly as

$$[\hat{J}_i, \hat{V}_j] = i\hbar \epsilon_{ijk} \hat{V}_k \quad (8.51)$$

Equivalently, using the antisymmetry properties of ϵ_{ijk} , this is

$$[\hat{V}_i, \hat{J}_j] = i\hbar\epsilon_{ijk}\hat{V}_k \quad (8.52)$$

Explicitly, the non-zero commutation relations between the components of the operators $\hat{\mathbf{J}}$ and $\hat{\mathbf{V}}$ can be summarised as

$$\begin{aligned} [\hat{J}_1, \hat{V}_2] &= i\hbar\hat{V}_3, & [\hat{J}_2, \hat{V}_3] &= i\hbar\hat{V}_1, & [\hat{J}_3, \hat{V}_1] &= i\hbar\hat{V}_2, \\ [\hat{J}_1, \hat{V}_3] &= -i\hbar\hat{V}_2, & [\hat{J}_2, \hat{V}_1] &= -i\hbar\hat{V}_3, & [\hat{J}_3, \hat{V}_2] &= -i\hbar\hat{V}_1. \end{aligned} \quad (8.53)$$

Eq. (8.51) can also serve as the *definition* of a vector operator $\hat{\mathbf{V}}$ with respect to an angular momentum operator $\hat{\mathbf{J}}$.

8.3.2.1 Spherical Components of a Vector Operator

The *spherical components* \hat{V}_{+1} , \hat{V}_{-1} , and \hat{V}_0 of a vector operator are defined as

$$\hat{V}_{+1} \equiv -\frac{1}{\sqrt{2}}(\hat{V}_1 + i\hat{V}_2), \quad \hat{V}_{-1} \equiv \frac{1}{\sqrt{2}}(\hat{V}_1 - i\hat{V}_2), \quad \hat{V}_0 \equiv \hat{V}_3. \quad (8.54)$$

Note that the spherical component \hat{V}_{+1} is distinct from the Cartesian component $\hat{V}_1 = \hat{V}_x$ and from the ladder operator $\hat{V}_+ = \hat{V}_1 + i\hat{V}_2$.

The commutator of the spherical component \hat{V}_{+1} of $\hat{\mathbf{V}}$ with the component $\hat{J}_3 = \hat{J}_z$ of $\hat{\mathbf{J}}$ can be evaluated as

$$[\hat{J}_3, \hat{V}_{+1}] = -\frac{1}{\sqrt{2}}[\hat{J}_3, \hat{V}_1] - \frac{1}{\sqrt{2}}[\hat{J}_3, \hat{V}_2] = -\frac{1}{\sqrt{2}}(i\hbar\hat{V}_2) - \frac{i}{\sqrt{2}}(-i\hbar\hat{V}_1) = \hbar\hat{V}_{+1}. \quad (8.55)$$

For \hat{V}_{-1} we similarly obtain

$$[\hat{J}_3, \hat{V}_{-1}] = -\hbar\hat{V}_{-1}, \quad (8.56)$$

while for \hat{V}_0 we have simply

$$[\hat{J}_3, \hat{V}_0] = [\hat{J}_3, \hat{V}_3] = 0. \quad (8.57)$$

The above relations can be summarised as

$$[\hat{J}_3, \hat{V}_m] = \hbar m \hat{V}_m, \quad m = \{0, \pm 1\}. \quad (8.58)$$

The spherical component \hat{V}_{+1} commutes with the ladder operator $\hat{J}_+ = \hat{J}_1 + i\hat{J}_2$,

$$[\hat{J}_+, \hat{V}_{+1}] = -\frac{1}{\sqrt{2}}[\hat{J}_1 + i\hat{J}_2, \hat{V}_1 + i\hat{V}_2] = -\frac{1}{\sqrt{2}}(i(i\hbar\hat{V}_3) + i(-i\hbar\hat{V}_3)) = 0, \quad (8.59)$$

while for \hat{V}_{-1} and \hat{V}_0 , the commutators with \hat{J}_+ are

$$[\hat{J}_+, \hat{V}_{-1}] = \frac{1}{\sqrt{2}}[\hat{J}_1 + i\hat{J}_2, \hat{V}_1 - i\hat{V}_2] = \frac{1}{\sqrt{2}}(-i(i\hbar\hat{V}_3) + i(-i\hbar\hat{V}_3)) = \sqrt{2}\hbar\hat{V}_3 = \sqrt{2}\hbar\hat{V}_0, \quad (8.60)$$

and

$$[\hat{J}_+, \hat{V}_0] = [\hat{J}_1 + i\hat{J}_2, \hat{V}_3] = -i\hbar\hat{V}_2 + i(i\hbar\hat{V}_1) = \sqrt{2}\hbar\hat{V}_{+1}. \quad (8.61)$$

For the ladder operator $\hat{J}_- = \hat{J}_1 - i\hat{J}_2$, the equivalent expressions are

$$[\hat{J}_-, \hat{V}_{+1}] = \sqrt{2}\hbar\hat{V}_0, \quad [\hat{J}_-, \hat{V}_{-1}] = 0, \quad [\hat{J}_-, \hat{V}_0] = \sqrt{2}\hbar\hat{V}_{-1}. \quad (8.62)$$

All the above commutation relations involving the ladder operators \hat{J}_\pm can be summarised as

$$[\hat{J}_\pm, \hat{V}_m] = \hbar\sqrt{2 - m(m \pm 1)}\hat{V}_{m \pm 1}, \quad m = \{0, \pm 1\}, \quad (8.63)$$

or, equivalently, as

$$[\hat{J}_\pm, \hat{V}_m] = \hbar\sqrt{j(j+1) - m(m \pm 1)}\hat{V}_{m \pm 1}, \quad j \equiv 1, m = \{0, \pm 1\}. \quad (8.64)$$

8.3.2.2 Properties of Vector Operators

If the vector operator $\hat{\mathbf{V}}$ corresponds to an observable quantity, then its Cartesian components \hat{V}_i must all be Hermitian. It then follows directly from Eq. (8.54) that the spherical components \hat{V}_m of $\hat{\mathbf{V}}$ have Hermitian conjugates given by

$$\hat{V}_m^\dagger = (-1)^m \hat{V}_{-m}. \quad (8.65)$$

Inverting Eq. (8.54), the Cartesian components \hat{V}_i are given in terms of the spherical components \hat{V}_m as

$$\hat{V}_1 = \frac{1}{\sqrt{2}}(\hat{V}_{-1} - \hat{V}_{+1}), \quad \hat{V}_2 = \frac{i}{\sqrt{2}}(\hat{V}_{-1} + \hat{V}_{+1}), \quad \hat{V}_3 = \hat{V}_0. \quad (8.66)$$

The commutation relations between the scalar product $\hat{\mathbf{V}} \cdot \hat{\mathbf{W}} = \hat{V}_1\hat{W}_1 + \hat{V}_2\hat{W}_2 + \hat{V}_3\hat{W}_3$ of two vector operators $\hat{\mathbf{V}}$ and $\hat{\mathbf{W}}$ and the component \hat{J}_1 of $\hat{\mathbf{J}}$ can then be evaluated as

$$[\hat{J}_1, \hat{V}_1\hat{W}_1] = [\hat{J}_1, \hat{V}_1]\hat{W}_1 + \hat{V}_1[\hat{J}_1, \hat{W}_1] = 0, \quad (8.67)$$

$$[\hat{J}_1, \hat{V}_2\hat{W}_2] = [\hat{J}_1, \hat{V}_2]\hat{W}_2 + \hat{V}_2[\hat{J}_1, \hat{W}_2] = i\hbar(\hat{V}_3\hat{W}_2 + \hat{V}_2\hat{W}_3), \quad (8.68)$$

$$[\hat{J}_1, \hat{V}_3\hat{W}_3] = [\hat{J}_1, \hat{V}_3]\hat{W}_3 + \hat{V}_3[\hat{J}_1, \hat{W}_3] = -i\hbar(\hat{V}_2\hat{W}_3 + \hat{V}_3\hat{W}_2). \quad (8.69)$$

Summing the above equations shows that \hat{J}_1 commutes with the scalar product $\hat{\mathbf{V}} \cdot \hat{\mathbf{W}}$:

$$[\hat{J}_1, \hat{\mathbf{V}} \cdot \hat{\mathbf{W}}] = 0. \quad (8.70)$$

Since the choice of the component \hat{J}_1 was arbitrary, this relation must be true for all components of $\hat{\mathbf{J}}$, not just \hat{J}_1 :

$$[\hat{\mathbf{J}}, \hat{\mathbf{V}} \cdot \hat{\mathbf{W}}] = 0. \quad (8.71)$$

Hence the scalar product $\hat{\mathbf{V}} \cdot \hat{\mathbf{W}}$ of two vector operators (for example, the spin-orbit coupling product $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$) is a scalar operator. In particular, taking $\hat{\mathbf{W}} = \hat{\mathbf{V}}$, we also obtain

$$[\hat{\mathbf{J}}, \hat{\mathbf{V}}^2] = 0. \quad (8.72)$$

The scalar product $\hat{\mathbf{V}} \cdot \hat{\mathbf{W}}$ can be expressed in terms of spherical components as

$$\hat{\mathbf{V}} \cdot \hat{\mathbf{W}} = \hat{V}_1\hat{W}_1 + \hat{V}_2\hat{W}_2 + \hat{V}_3\hat{W}_3 \quad (8.73)$$

$$= \frac{1}{2}(\hat{V}_{-1} - \hat{V}_{+1})(\hat{W}_{-1} - \hat{W}_{+1}) - \frac{1}{2}(\hat{V}_{-1} + \hat{V}_{+1})(\hat{W}_{-1} + \hat{W}_{+1}) + \hat{V}_0\hat{W}_0 \quad (8.74)$$

$$= -\hat{V}_{+1}\hat{W}_{-1} - \hat{V}_{-1}\hat{W}_{+1} + \hat{V}_0\hat{W}_0. \quad (8.75)$$

Similar arguments show that the vector product $\hat{\mathbf{V}} \times \hat{\mathbf{W}}$ of two vector operators $\hat{\mathbf{V}}$ and $\hat{\mathbf{W}}$ is also a vector operator.

8.4 The Wigner-Eckart Theorem for Scalar Operators

Let \hat{K} be a scalar operator with respect to an angular momentum operator $\hat{\mathbf{J}}$:

$$[\hat{\mathbf{J}}, \hat{K}] = 0. \quad (8.76)$$

Then the Wigner-Eckart theorem states that matrix elements of \hat{K} taken between total angular momentum eigenstates $|\alpha'' j'' m''\rangle$ and $|\alpha' j' m'\rangle$ must be of the form

$$\langle \alpha'' j'' m'' | \hat{K} | \alpha' j' m' \rangle = C(\alpha'' \alpha'; j') \delta_{j'' j'} \delta_{m'' m'}, \quad (8.77)$$

where $C(\alpha'' \alpha'; j')$ is a complex constant known as the reduced matrix element which is independent of the quantum numbers m'' and m' . The quantities α'' and α' collectively label all other quantum numbers needed to uniquely identify the angular momentum eigenstates involved.

For completeness, the proof of Eq. (8.77) is provided in the Appendix A.3.

The Wigner-Eckart theorem shows that matrix elements between total angular momentum eigenstates for rotationally invariant (scalar) operators do not depend on the quantum number m . This is intuitively reasonable; the angular momentum eigenstates $|jm\rangle$ are defined with respect to a particular choice of quantisation axis, conventionally taken to be the z -axis. A different choice of axis, the x -axis for example, would result in a different set of eigenstates, $|jm_x\rangle$, which are linear combinations of the conventional z -axis states $|jm\rangle$. For a rotationally invariant operator, all spatial directions are equivalent. Hence the matrix elements of \hat{K} cannot depend on a particular choice of quantisation axis; hence they cannot depend on the quantum number m (or m_x or \dots) whose definition depends on the choice of axis.

The reduced matrix element $C(\alpha'' \alpha'; j')$ is usually written in Dirac-style notation as

$$C(\alpha'' \alpha'; j') \equiv \langle \alpha'' j'' || \hat{K} || \alpha' j' \rangle. \quad (8.78)$$

Despite its name, the reduced matrix element, $\langle \alpha'' j'' || \hat{K} || \alpha' j' \rangle$, is *not* a matrix element; it is a common, constant component of a family of $(2j+1)(2j'+1)$ matrix elements.

The product of Kronecker- δ factors in Eq. (8.77) can be expressed as a single Clebsch-Gordan coefficient. To see this, consider the (trivial) angular momentum combination $0 \otimes j'' = j''$. The connection between the total (coupled) and uncoupled eigenstates is simply

$$|j'' m''\rangle = |00\rangle \otimes |j'' m''\rangle \equiv |00\rangle |j'' m''\rangle. \quad (8.79)$$

Comparing with the expansion

$$|j'' m''\rangle = \sum_{j' m'} |00\rangle |j' m'\rangle \langle 00; j' m' | j'' m'' \rangle \quad (8.80)$$

then shows that the relevant Clebsch-Gordan coefficients are either zero or unity:

$$\langle 00; j' m' | j'' m'' \rangle = \delta_{j'' j'} \delta_{m'' m'}. \quad (8.81)$$

Eq. (8.78) and (8.81) allow the Wigner-Eckart theorem for scalar operators, Eq. (8.77), to be written in the form

$$\langle \alpha'' j'' m'' | \hat{K} | \alpha' j' m' \rangle = \langle \alpha'' j'' | \hat{K} | \alpha' j' \rangle \langle 00; j' m' | j'' m'' \rangle. \quad (8.82)$$

The reason for writing the Wigner-Eckart theorem in this way will become clear once we have also considered the equivalent result for *vector* operators.

8.4.1 Consequences of the Wigner-Eckart Theorem (for Scalars)

Consider the Hamiltonian operator \hat{H} for an isolated system. Since there can be no preferred spatial direction for an isolated system, the expectation values of \hat{H} (the energy eigenvalues) cannot depend on the spatial orientation of the system. Hence \hat{H} must be a scalar operator, commuting with (all components of) the total angular momentum operator $\hat{\mathbf{J}}$:

$$[\hat{J}_i, \hat{H}] = 0, \quad [\hat{\mathbf{J}}, \hat{H}] = 0, \quad [\hat{\mathbf{J}}^2, \hat{H}] = 0. \quad (8.83)$$

Since \hat{H} and $\hat{\mathbf{J}}$ commute, it follows from Ehrenfest's theorem that the expectation values $\langle \hat{J}_i \rangle$ of each component of $\hat{\mathbf{J}}$ are constant:

$$\frac{d}{dt} \langle \psi(t) | \hat{\mathbf{J}} | \psi(t) \rangle = 0. \quad (8.84)$$

Thus, for an isolated system, total angular momentum is conserved; this is a direct consequence of rotational symmetry.

Since \hat{H} and $\hat{\mathbf{J}}$ commute, they possess a simultaneous set of eigenstates $|\alpha j m\rangle$, where “ α ” represents all other quantum numbers needed to uniquely identify a particular energy eigenstate of \hat{H} . From the Wigner-Eckart theorem, the matrix elements of \hat{H} between these eigenstates must be of the form

$$\langle \alpha'' j'' m'' | \hat{H} | \alpha' j' m' \rangle = \langle \alpha'' j'' | \hat{H} | \alpha' j' \rangle \delta_{j'' j'} \delta_{m'' m'}, \quad (8.85)$$

where the reduced matrix element $\langle \alpha'' j'' | \hat{H} | \alpha' j' \rangle$ is a constant, independent of the quantum number m . In particular, the expectation values of \hat{H} are

$$\langle \alpha j m | \hat{H} | \alpha j m \rangle = \langle \alpha j | \hat{H} | \alpha j \rangle. \quad (8.86)$$

Hence the energy eigenvalues for an isolated system can depend only on α and j , and must be independent of m . The energy levels therefore have a degeneracy $2j + 1$ with respect to angular momentum. Further degeneracy is possible if the Hamiltonian \hat{H} possesses additional symmetry properties involving the quantum numbers α .

This illustrates a general principle, that degeneracies in quantum mechanics are hardly ever accidental, but indicate the existence of an underlying symmetry (in this case, rotational invariance).

8.5 The Wigner-Eckart Theorem for Vector Operators

Consider an operator $\hat{\mathbf{V}}$ which is a vector operator with respect to an angular momentum operator $\hat{\mathbf{J}}$, and thus satisfies Eq. (8.51):

$$[\hat{J}_i, \hat{V}_j] = i\hbar\epsilon_{ijk}\hat{V}_k. \quad (8.87)$$

Then the Wigner-Eckart theorem states that the matrix elements of $\hat{\mathbf{V}}$ between eigenstates $|\alpha'j'm'\rangle$ and $|\alpha''j''m''\rangle$ of $\hat{\mathbf{J}}$ must be of the form

$$\langle\alpha''j''m''|\hat{V}_m|\alpha'j'm'\rangle = \langle\alpha''j''||\hat{\mathbf{V}}||\alpha'j'\rangle \langle 1m; j'm'|j''m''\rangle. \quad (8.88)$$

where the quantum number m takes the values $m = \pm 1, 0$, and \hat{V}_m is a spherical component of the operator $\hat{\mathbf{V}}$. The reduced matrix element $\langle\alpha''j''||\hat{\mathbf{V}}||\alpha'j'\rangle$ is a complex constant which is independent of the quantum numbers m, m' and m'' . The final factor, $\langle 1m; j'm'|j''m''\rangle$, is a Clebsch-Gordan coefficient which can be obtained by considering the angular momentum combination $j'' = 1 \otimes j' = j', j' = \pm 1$.

For completeness, the proof of Eq. (8.88) is provided in the Appendix A.3.

The definition of the quantum numbers m, m' and m'' depends on the arbitrary choice of quantisation axis. The Wigner-Eckart theorem shows that the dependence of vector operator matrix elements on this arbitrary choice of axis is carried entirely by Clebsch-Gordan coefficients; these are independent of the particular vector operator, $\hat{\mathbf{V}}$, being considered.

The reduced matrix element $\langle\alpha''j''||\hat{\mathbf{V}}||\alpha'j'\rangle$ is a common, constant component of a set of $3(2j' + 1)(2j'' + 1)$ matrix elements, $\langle\alpha''j''m''|\hat{V}_m|\alpha'j'm'\rangle$. To determine the reduced matrix element, only *one* of the matrix elements belonging to this set needs to be evaluated explicitly. Once this has been done, all other matrix elements of $\hat{\mathbf{V}}$ are determined straightforwardly by looking up the appropriate Clebsch-Gordan coefficients.

The Wigner-Eckart theorem allows various general properties of the matrix elements of vector operators (positions, linear momenta, angular momenta, ...) to be obtained. For example, it leads directly to selection rules in atomic transitions, to general expressions for atomic energy level shifts in electric and magnetic fields (the Stark and Zeeman effects), as well as to many applications involving the scattering or decay of nuclei and elementary particles.

8.5.1 Selection Rules for Vector Operator Matrix Elements

For the case $j' = j'' = 0$, and hence also $m' = m'' = 0$, the Clebsch-Gordan coefficient $\langle 1m; j'm'|j''m''\rangle$ vanishes for all m :

$$\langle 1m; 00|00\rangle = 0, \quad m = 0, \pm 1. \quad (8.89)$$

The Wigner-Eckart theorem, Eq. (8.88), then shows that the matrix elements of any vector operator $\hat{\mathbf{V}}$ taken between eigenstates of zero angular momentum must vanish:

$$\langle \alpha'' 00 | \hat{V}_m | \alpha' 00 \rangle = 0. \quad (8.90)$$

Equivalently, this can be written as

$$\boxed{\langle \alpha'' 00 | \hat{\mathbf{V}} | \alpha' 00 \rangle = 0.} \quad (8.91)$$

For all other cases, with $j' > 0$ or $j'' > 0$, the Clebsch-Gordan coefficient $\langle 1m; j'm' | j''m'' \rangle$ vanishes unless

$$j'' = \{j', j' \pm 1\}, \quad m'' = m + m', \quad m = \{0, \pm 1\} \quad (8.92)$$

The conditions in Eq. (8.89) and (8.92) for a non-zero Clebsch-Gordan coefficient can be summarised as the *selection rules*

$$\boxed{|\Delta j| = \{0, 1\}; \quad j' + j'' \geq 1; \quad |\Delta m| = \{0, 1\}.} \quad (8.93)$$

The Wigner-Eckart theorem shows that the matrix element $\langle 1m; j'm' | j''m'' \rangle$ will vanish if these selection rules are not satisfied.

Satisfying the above selection rules does not, on its own, guarantee that the matrix element will be non-zero. The Clebsch-Gordan coefficient may anyway still vanish, for example $\langle 10; 10 | 10 \rangle = 0$, or the operator $\hat{\mathbf{V}}$ may possess additional symmetry properties which lead to additional selection rules.

8.5.2 The Landé Projection Formula

The angular momentum operator $\hat{\mathbf{J}}$ is itself a vector operator, and so must satisfy the Wigner-Eckart theorem. Therefore, matrix elements of the spherical components \hat{J}_{+1} , \hat{J}_{-1} , \hat{J}_0 of $\hat{\mathbf{J}}$ taken between angular momentum eigenstates must be of the form

$$\langle \alpha'' j'' m'' | \hat{J}_m | \alpha' j' m' \rangle = \langle \alpha'' j'' || \hat{\mathbf{J}} || \alpha' j' \rangle \langle 1m; j'm' | j''m'' \rangle, \quad (8.94)$$

where the reduced matrix element $\langle \alpha'' j'' || \hat{\mathbf{J}} || \alpha' j' \rangle$ is an overall constant which is independent of m , m' and m'' . In particular, taking $\alpha'' = \alpha'$ and $j'' = j'$, we have

$$\langle \alpha' j' m'' | \hat{J}_m | \alpha' j' m' \rangle = \langle \alpha' j' || \hat{\mathbf{J}} || \alpha' j' \rangle \langle 1m; j'm' | j'm'' \rangle. \quad (8.95)$$

Similarly, for any vector operator $\hat{\mathbf{V}}$, the Wigner-Eckart theorem gives

$$\langle \alpha' j' m'' | \hat{V}_m | \alpha' j' m' \rangle = \langle \alpha' j' || \hat{\mathbf{V}} || \alpha' j' \rangle \langle 1m; j'm' | j'm'' \rangle. \quad (8.96)$$

Eliminating the Clebsch-Gordan coefficient between Eq. (8.95) and (8.96), we obtain

$$\langle \alpha' j' m'' | \hat{V}_m | \alpha' j' m' \rangle = \frac{\langle \alpha' j' || \hat{\mathbf{V}} || \alpha' j' \rangle}{\langle \alpha' j' || \hat{\mathbf{J}} || \alpha' j' \rangle} \langle \alpha' j' m'' | \hat{J}_m | \alpha' j' m' \rangle. \quad (8.97)$$

This can equivalently be written as

$$\langle \alpha' j' m'' | \hat{\mathbf{V}} | \alpha' j' m' \rangle = \frac{\langle \alpha' j' | \hat{\mathbf{V}} | \alpha' j' \rangle}{\langle \alpha' j' | \hat{\mathbf{J}} | \alpha' j' \rangle} \langle \alpha' j' m'' | \hat{\mathbf{J}} | \alpha' j' m' \rangle. \quad (8.98)$$

This expression no longer explicitly involves the quantum number $m = \pm 1, 0$. Thus we can simplify the notation by dropping one prime throughout, and write

$$\boxed{\langle \alpha j m' | \hat{\mathbf{V}} | \alpha j m \rangle = g_{\alpha j} \langle \alpha j m' | \hat{\mathbf{J}} | \alpha j m \rangle}, \quad (8.99)$$

where $g_{\alpha j}$, the ratio of reduced matrix elements, is defined as

$$g_{\alpha j} \equiv \frac{\langle \alpha j | \hat{\mathbf{V}} | \alpha j \rangle}{\langle \alpha j | \hat{\mathbf{J}} | \alpha j \rangle}, \quad (8.100)$$

and is a constant which is independent of m and m' . Eq. (8.99) can be considered as holding for each of the *spherical* components of $\hat{\mathbf{V}}$ and $\hat{\mathbf{J}}$, or equivalently, for each of the *Cartesian* components of $\hat{\mathbf{V}}$ and $\hat{\mathbf{J}}$, with a common value of the constant $g_{\alpha j}$.

The expectation value $\langle \alpha j m | \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} | \alpha j m \rangle$ of the scalar product operator $\hat{\mathbf{V}} \cdot \hat{\mathbf{J}}$ is

$$\langle \alpha j m | \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} | \alpha j m \rangle = \sum_k \langle \alpha j m | \hat{V}_k \hat{J}_k | \alpha j m \rangle. \quad (8.101)$$

The eigenstates $|\alpha j m\rangle$ of the total angular momentum operator $\hat{\mathbf{J}}$ satisfy the completeness relation

$$\sum_{\alpha', j', m'} |\alpha' j' m'\rangle \langle \alpha' j' m'| = \hat{\mathbb{I}}. \quad (8.102)$$

Using this completeness relation to insert a factor of identity into the matrix element of Eq. (8.101) then gives

$$\langle \alpha j m | \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} | \alpha j m \rangle = \sum_{\alpha', j', m'} \langle \alpha j m | \hat{\mathbf{V}} | \alpha' j' m' \rangle \cdot \langle \alpha' j' m' | \hat{\mathbf{J}} | \alpha j m \rangle. \quad (8.103)$$

The matrix elements $\langle \alpha' j' m' | \hat{\mathbf{J}} | \alpha j m \rangle$ vanish unless $\alpha' = \alpha$ and $j' = j$:

$$\langle \alpha' j' m' | \hat{\mathbf{J}} | \alpha j m \rangle = \langle \alpha j m' | \hat{\mathbf{J}} | \alpha j m \rangle \delta_{\alpha' \alpha} \delta_{j' j}. \quad (8.104)$$

Hence the summations over α' and j' can be trivially carried out, leaving

$$\langle \alpha j m | \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} | \alpha j m \rangle = \sum_{m'} \langle \alpha j m | \hat{\mathbf{V}} | \alpha j m' \rangle \cdot \langle \alpha j m' | \hat{\mathbf{J}} | \alpha j m \rangle. \quad (8.105)$$

Substituting from Eq. (8.99) then gives

$$\langle \alpha j m | \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} | \alpha j m \rangle = g_{\alpha j} \sum_{m'} \langle \alpha j m | \hat{\mathbf{J}} | \alpha j m' \rangle \cdot \langle \alpha j m' | \hat{\mathbf{J}} | \alpha j m \rangle. \quad (8.106)$$

The sum over j' can now be reinstated, giving

$$\langle \alpha j m | \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} | \alpha j m \rangle = g_{\alpha j} \sum_{j', m'} \langle \alpha j m | \hat{\mathbf{J}} | \alpha j' m' \rangle \cdot \langle \alpha j' m' | \hat{\mathbf{J}} | \alpha j m \rangle. \quad (8.107)$$

Invoking completeness again, the summation over j' and m' just gives a factor of identity. Hence we have

$$\langle \alpha j m | \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} | \alpha j m \rangle = g_{\alpha j} \langle \alpha j m | \hat{\mathbf{J}}^2 | \alpha j m \rangle \quad (8.108)$$

$$= g_{\alpha j} j(j+1) \hbar^2. \quad (8.109)$$

Provided $j > 0$, the constant $g_{\alpha j}$ is therefore given by

$$g_{\alpha j} = \frac{\langle \alpha j m | \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} | \alpha j m \rangle}{j(j+1) \hbar^2}. \quad (8.110)$$

Although the quantum number m appears inside the matrix element on the right-hand side of Eq. (8.110), the constant $g_{\alpha j}$ is in fact independent of m , as is evident from its original definition as a ratio of reduced matrix elements in Eq. (8.100).

Substituting for $g_{\alpha j}$ in Eq. (8.99) gives (for $j > 0$) the *Landé projection formula*

$$\boxed{\langle \alpha j m' | \hat{\mathbf{V}} | \alpha j m \rangle = \frac{\langle \alpha j m | \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} | \alpha j m \rangle}{j(j+1) \hbar^2} \langle \alpha j m' | \hat{\mathbf{J}} | \alpha j m \rangle.} \quad (8.111)$$

The z -component of the projection formula is

$$\langle \alpha j m' | \hat{V}_z | \alpha j m \rangle = g_{\alpha j} m \langle \alpha j m' | \hat{J}_z | \alpha j m \rangle = g_{\alpha j} m \hbar \delta_{m'm}. \quad (8.112)$$

Taking $m' = m$ then gives the expectation values of \hat{V}_z as

$$\boxed{\langle \alpha j m | \hat{\mathbf{V}} | \alpha j m \rangle = g_{\alpha j} m \hbar.} \quad (8.113)$$

Finally, for the case $j = 0$, Eq. (8.91) gives simply

$$\langle \alpha 0 0 | \hat{\mathbf{V}} | \alpha 0 0 \rangle = 0. \quad (8.114)$$

Thus in Eq. (8.99), for $j = 0$, the Landé g -factor vanishes:

$$\boxed{g_{\alpha 0} = 0.} \quad (8.115)$$

8.6 Magnetic Dipole Moments

The Hamiltonian operator describing the motion of a particle of charge q and mass m in a magnetic field \mathbf{B} includes an interaction which can be described in terms of an orbital magnetic dipole moment operator $\hat{\boldsymbol{\mu}}_L$ as

$$\hat{H}_B = -\hat{\boldsymbol{\mu}}_L \cdot \mathbf{B}; \quad \hat{\boldsymbol{\mu}}_L = \frac{q}{2m} \hat{\mathbf{L}}, \quad (8.116)$$

where $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = -i\hbar \hat{\mathbf{r}} \times \nabla$ is the orbital angular momentum operator for the particle. Similarly, a spin-half particle is predicted by the Dirac equation to possess an intrinsic magnetic dipole moment $\hat{\boldsymbol{\mu}}_S$ which interacts with a magnetic field as

$$\hat{H}_B = -\hat{\boldsymbol{\mu}}_S \cdot \mathbf{B}; \quad \hat{\boldsymbol{\mu}}_S = \frac{q}{m} \hat{\mathbf{S}}, \quad (8.117)$$

where $\hat{\mathbf{S}}$ is the spin operator for the particle. Thus, both orbital and spin magnetic moments have interactions with a magnetic field which are generically of the form

$$\hat{H} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B}; \quad \hat{\boldsymbol{\mu}} = \gamma \hat{\mathbf{J}}, \quad (8.118)$$

where $\hat{\mathbf{J}}$ is an angular momentum operator, and γ is a constant known as the *gyromagnetic ratio*.

The (scalar) magnetic dipole moment associated with a (vector) magnetic dipole operator $\hat{\boldsymbol{\mu}}$ is defined as

$$\mu = \langle jj | \hat{\mu}_z | jj \rangle. \quad (8.119)$$

This is the expectation value of the operator $\hat{\mu}_z$ when the particle is in its “most spin-up” state, $|jj\rangle \equiv |j, m_j = j\rangle$, for which the angular momentum quantum number m_j (defined with respect to the z -axis) takes its maximum possible value.

The state $|jj\rangle$ is an eigenstate of \hat{J}_z with eigenvalue $m_j \hbar = j \hbar$:

$$\hat{J}_z |jj\rangle = j \hbar |jj\rangle. \quad (8.120)$$

The magnetic moment μ is therefore related to the gyromagnetic ratio γ as

$$\mu = \gamma \langle jj | \hat{J}_z | jj \rangle = \gamma j \hbar \quad (8.121)$$

8.6.1 g -Factors

It is often convenient to express magnetic moments in terms of a common overall scale, typically either the Bohr magneton $\mu_B \equiv e \hbar / 2 m_e$ or the nuclear magneton $\mu_N \equiv e \hbar / 2 m_p$. In atomic physics, for example, since the magnetic moment of the electron is $\mu_e \approx -\mu_B$, the Bohr magneton μ_B is a convenient scale and it is common to set

$$\mu = -g j \mu_B, \quad (8.122)$$

where the constant g is referred to simply as the *g-factor*. In nuclear physics, the nuclear magneton μ_N is a more convenient scale, and the *g-factor* is defined using

$$\mu = g j \mu_N. \quad (8.123)$$

The signs in the expressions above reflect the most common sign conventions used in each area. Using Eq. (8.121), the connections between the gyromagnetic ratio and the *g-factor* for each choice of scale are seen to be

$$\gamma = -g \frac{\mu_B}{\hbar}; \quad \gamma = g \frac{\mu_N}{\hbar}. \quad (8.124)$$

The magnetic moment of the electron, for example, with spin $j = 1/2$, can be expressed in units of the Bohr magneton as

$$\mu_e = -\frac{1}{2} g_e \mu_B, \quad (8.125)$$

where the *g-factor* for the electron is predicted by the Dirac equation to be $g_e = 2$, while the measured value is $g_e \approx 2.0023$. The equivalent expression for the magnetic moment of the proton is

$$\mu_p = -\frac{1}{2} g_p \mu_B, \quad (8.126)$$

where the measured g -factor is $g_p \approx -0.0031$. In nuclear and particle physics applications, the proton magnetic moment is more conveniently expressed in terms of μ_N rather than μ_B , as

$$\mu_p = \frac{1}{2} g_p \mu_N, \quad (8.127)$$

In this case, the measured g -factor becomes $g_p \approx 5.586$. Similarly, the magnetic moment of the neutron is expressed as

$$\mu_n = \frac{1}{2} g_n \mu_N, \quad (8.128)$$

with $g_n \approx -3.826$.

	spin J, I	"nuclear"		"atomic"	
		μ/μ_N	g_J	μ/μ_N	g_I
e^-	1/2			-1.0011	-2.0023
e^+	1/2			+1.0011	-2.0023
p	1/2	+2.793	+5.586	+0.00152	-0.00304
n	1/2	-1.913	-3.826	-0.00104	+0.00208
^4He	0	0	0	0	0
^6Li	1	+0.822	+0.822	+0.00045	-0.00045
^7Li	3/2	+3.256	+2.171	+0.00177	-0.00118
^{12}C	0	0	0	0	0
^{85}Rb	5/2	+1.353	+0.541	+0.00074	-0.00029
^{87}Rb	3/2	+2.750	+1.833	+0.00150	-0.00100
^{107}Ag	1/2	-0.114	-0.228	-0.00006	+0.00012
^{109}Ag	1/2	-0.131	-0.262	-0.00007	+0.00014

Table 8.1: Examples of the magnetic moments and g -factors of various particles and nuclei, expressed in terms of both μ_B and μ_N .

8.6.2 Combining magnetic moments

It is often the case that we need to determine the combined effects of two or more magnetic dipole moment interactions, for example the combined effect of the orbital and spin magnetic dipole moments of a particle, or the combined effect of the spin magnetic dipole moments of two spin-half particles.

Thus, in general, we are led to consider the combined effect of two magnetic dipole moment operators, $\hat{\boldsymbol{\mu}}_1 = \gamma_1 \hat{\mathbf{J}}_1$ and $\hat{\boldsymbol{\mu}}_2 = \gamma_2 \hat{\mathbf{J}}_2$. In a magnetic field \mathbf{B} , the Hamiltonian contains the sum of the two interaction terms

$$\hat{H}_B = -\hat{\boldsymbol{\mu}}_1 \cdot \mathbf{B} - \hat{\boldsymbol{\mu}}_2 \cdot \mathbf{B}. \quad (8.129)$$

The overall interaction with the magnetic field is therefore

$$\hat{H}_B = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B}, \quad (8.130)$$

where $\hat{\boldsymbol{\mu}}$ is the total magnetic moment operator:

$$\hat{\boldsymbol{\mu}} = \hat{\boldsymbol{\mu}}_1 + \hat{\boldsymbol{\mu}}_2 = \gamma_1 \hat{\mathbf{J}}_1 + \gamma_2 \hat{\mathbf{J}}_2 \quad (8.131)$$

If we choose to orient the z -axis along the magnetic field direction,

$$\mathbf{B} = (0, 0, B_z), \quad (8.132)$$

then the overall interaction becomes

$$\hat{H}_B = -\hat{\mu}_z B_z, \quad \hat{\mu}_z = \gamma_1 \hat{J}_{1z} + \gamma_2 \hat{J}_{2z}. \quad (8.133)$$

In the uncoupled basis of states,

$$|\alpha j_1 m_1 j_2 m_2\rangle = |\alpha j_1 m_1\rangle \otimes |\alpha j_2 m_2\rangle, \quad (8.134)$$

finding the matrix elements of $\hat{\mu}_z$ is straightforward. We have

$$\hat{J}_{1z} |\alpha j_1 m_1 j_2 m_2\rangle = m_1 \hbar |\alpha j_1 m_1 j_2 m_2\rangle, \quad (8.135)$$

$$\hat{J}_{2z} |\alpha j_1 m_1 j_2 m_2\rangle = m_2 \hbar |\alpha j_1 m_1 j_2 m_2\rangle, \quad (8.136)$$

and hence

$$\langle \alpha j_1 m'_1 j_2 m'_2 | \hat{\mu}_z | \alpha j_1 m_1 j_2 m_2 \rangle = (\gamma_1 m_1 + \gamma_2 m_2) \hbar \delta_{m'_1 m_1} \delta_{m'_2 m_2}. \quad (8.137)$$

Thus, in the uncoupled basis, for given j_1 and j_2 , the matrix representation of $\hat{\mu}_z$ is diagonal with respect to the quantum numbers m_1 and m_2 .

This is the case that applies, for example, to the Zeeman effect at high magnetic field.

However, in other cases, for example the Zeeman effect at low magnetic field, or the determination of the magnetic moment of the proton in terms of its constituent quark magnetic moments, the matrix elements of $\hat{\mu}_z$ must be determined in the *coupled* basis $|\alpha j m\rangle$ of total angular momentum eigenstates, rather than in the uncoupled basis $|\alpha j_1 m_1 j_2 m_2\rangle$.

In the coupled basis, if the two gyromagnetic ratios involved are the same, $\gamma_1 = \gamma_2$, finding the matrix elements is trivial. We have

$$\hat{\mu} = \gamma \hat{\mathbf{J}}, \quad (8.138)$$

where $\hat{\mathbf{J}}$ is the total angular momentum of the combined system,

$$\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2, \quad (8.139)$$

and where

$$\gamma = \gamma_1 + \gamma_2. \quad (8.140)$$

The matrix elements of $\hat{\mu}_z$ in the coupled basis are then given simply by

$$\langle \alpha j m' | \hat{\mu}_z | \alpha j m \rangle = \gamma m \hbar \delta_{m' m}. \quad (8.141)$$

However, in the more general case that the gyromagnetic ratios are different, $\gamma_1 \neq \gamma_2$, the operator $\hat{\mu}$ is *not* directly proportional to the total angular momentum $\hat{\mathbf{J}}$:

$$\hat{\mu} \neq \gamma \hat{\mathbf{J}}. \quad (8.142)$$

In this case, finding the matrix elements of $\hat{\mu}_z$ between total angular momentum eigenstates is no longer straightforward. However, as we now show, the Landé projection formula allows proportionality between the operators $\hat{\mu}$ and $\hat{\mathbf{J}}$ to be *effectively* restored for states of given total angular momentum j , with a constant of proportionality γ_j which depends on j (and j_1 and j_2).

8.6.2.1 The Landé g-Factor

Since $\hat{\boldsymbol{\mu}}$ is a vector operator, the projection formula of Eq. (8.111) (obtained from the Wigner-Eckart theorem) is applicable. This gives the matrix elements of the operator $\hat{\boldsymbol{\mu}}$ between eigenstates of total angular momentum $\hat{\mathbf{J}}$ as

$$\langle \alpha j m' | \hat{\boldsymbol{\mu}} | \alpha j m \rangle = \gamma_{\alpha j} \langle \alpha j m' | \hat{\mathbf{J}} | \alpha j m \rangle, \quad (8.143)$$

where the constant $\gamma_{\alpha j}$ is independent of m and m' . The z component of this equation gives

$$\langle \alpha j m' | \hat{\mu}_z | \alpha j m \rangle = \gamma_{\alpha j} \langle \alpha j m' | \hat{J}_z | \alpha j m \rangle = \gamma_{\alpha j} m \hbar \delta_{m'm}. \quad (8.144)$$

Thus, for a given total angular momentum j , the matrix representation is diagonal with respect to m . However, we still need to find $\gamma_{\alpha j}$ in terms of γ_1 and γ_2 .

For $j > 0$, the effective gyromagnetic ratio $\gamma_{\alpha j}$ is given by Eq. (8.110) as

$$\gamma_{\alpha j} = \frac{\langle \alpha j m | \hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{J}} | \alpha j m \rangle}{j(j+1)\hbar^2}. \quad (8.145)$$

The numerator in the above expression is

$$\langle \alpha j m | \hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{J}} | \alpha j m \rangle = \gamma_1 \langle \alpha j m | \hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}} | \alpha j m \rangle + \gamma_2 \langle \alpha j m | \hat{\mathbf{J}}_2 \cdot \hat{\mathbf{J}} | \alpha j m \rangle. \quad (8.146)$$

Squaring the relation $\hat{\mathbf{J}}_2 = \hat{\mathbf{J}} - \hat{\mathbf{J}}_1$ gives the scalar product $\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}$ as

$$\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}} = \frac{1}{2} (\hat{\mathbf{J}}^2 - \hat{\mathbf{J}}_1^2 - \hat{\mathbf{J}}_2^2). \quad (8.147)$$

For given j_1 and j_2 , the state $|\alpha j m\rangle$ is an eigenstate of $\hat{\mathbf{J}}_1^2$ and $\hat{\mathbf{J}}_2^2$ (as well as of $\hat{\mathbf{J}}^2$) with

$$\hat{\mathbf{J}}_1^2 |\alpha j m\rangle = j_1(j_1+1)\hbar^2 |\alpha j m\rangle, \quad \hat{\mathbf{J}}_2^2 |\alpha j m\rangle = j_2(j_2+1)\hbar^2 |\alpha j m\rangle. \quad (8.148)$$

Hence the expectation value of $\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}$ is

$$\langle \alpha j m | \hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}} | \alpha j m \rangle = \frac{\hbar^2}{2} [j(j+1) + j_1(j_1+1) - j_2(j_2+1)]. \quad (8.149)$$

The equivalent result for $\hat{\mathbf{J}}_2 \cdot \hat{\mathbf{J}}$ is obtained by interchanging j_1 and j_2 :

$$\langle \alpha j m | \hat{\mathbf{J}}_2 \cdot \hat{\mathbf{J}} | \alpha j m \rangle = \frac{\hbar^2}{2} [j(j+1) + j_2(j_2+1) - j_1(j_1+1)]. \quad (8.150)$$

Combining the various equations above, we obtain $\gamma_{\alpha j}$ as

$$\boxed{\gamma_j = \gamma_1 \frac{j(j+1) + j_1(j_1+1) - j_2(j_2+1)}{2j(j+1)} + \gamma_2 \frac{j(j+1) + j_2(j_2+1) - j_1(j_1+1)}{2j(j+1)}}. \quad (8.151)$$

As anticipated, the constant $\gamma_{\alpha j}$ is independent of the quantum number m . Eq. (8.151) shows that it is also independent of the quantum numbers α , so we can rename $\gamma_{\alpha j} \rightarrow \gamma_j$.

Eq. (8.143) can now be written as

$$\langle \alpha j m' | \hat{\boldsymbol{\mu}} | \alpha j m \rangle = \gamma_j \langle \alpha j m' | \hat{\mathbf{J}} | \alpha j m \rangle. \quad (8.152)$$

From Eq. (8.131), we have therefore shown that, for given values of j , j_1 and j_2 , matrix elements of magnetic dipole moment operators combine as

$$\langle \alpha j m' | \gamma_1 \hat{\mathbf{J}}_1 + \gamma_2 \hat{\mathbf{J}}_2 | \alpha j m \rangle = \gamma_j \langle \alpha j m' | \hat{\mathbf{J}} | \alpha j m \rangle. \quad (8.153)$$

Thus, when a composite particle or system built from j_1 and j_2 is known to be in an eigenstate with total angular momentum quantum number j , the interaction of the composite system with a magnetic field \mathbf{B} , Eq. (8.129), is *effectively* described by the Hamiltonian

$$\hat{H}_B = -\gamma_j \hat{\mathbf{J}} \cdot \mathbf{B}. \quad (8.154)$$

Equivalently, in an angular momentum state j , the total magnetic moment operator of Eq. (8.131) is effectively given by

$$\hat{\boldsymbol{\mu}}_j = \gamma_j \hat{\mathbf{J}}. \quad (8.155)$$

The magnetic moments can be expressed in terms of g -factors rather than gyromagnetic ratios. For example, using the Bohr magneton as a common overall scale, Eq. (8.124), we can introduce g -factors for each magnetic dipole as

$$\gamma_j = -g_j \frac{\mu_B}{\hbar}, \quad \gamma_1 = -g_1 \frac{\mu_B}{\hbar}, \quad \gamma_2 = -g_2 \frac{\mu_B}{\hbar}. \quad (8.156)$$

Eq. (8.151) retains the same form; we obtain

$$g_j = g_1 \frac{j(j+1) + j_1(j_1+1) - j_2(j_2+1)}{2j(j+1)} + g_2 \frac{j(j+1) + j_2(j_2+1) - j_1(j_1+1)}{2j(j+1)}. \quad (8.157)$$

Eq. (8.151) and (8.157) apply to the case $j > 0$. For the case $j = 0$, Eq. (8.91) gives the matrix elements of $\hat{\boldsymbol{\mu}}$ as simply

$$\langle \alpha 0 0 | \hat{\boldsymbol{\mu}} | \alpha 0 0 \rangle = 0. \quad (8.158)$$

Thus a composite system in a state with zero total angular momentum has no net dipole interaction with a magnetic field \mathbf{B} ; we effectively have $\gamma = 0$.

8.6.2.2 Particular Cases

For the case that the two g -factors are equal, $g_1 = g_2$, Eq. (8.157) reduces simply to

$$g_j = g_1 = g_2, \quad (8.159)$$

as expected.

For the case $g_1 = 1$ and $g_2 = 2$, Eq. (8.157) simplifies as

$$g_j = \frac{3}{2} - \frac{1}{2} \frac{j_1(j_1+1) - j_2(j_2+1)}{j(j+1)}. \quad (8.160)$$

This case is relevant to combining the orbital ($g_\ell = 1$) and spin ($g_e = 2$) magnetic dipole moments of atomic electrons, for example. In this context, the equation above would typically be written as

$$g_J = \frac{3}{2} - \frac{1}{2} \frac{L(L+1) - S(S+1)}{J(J+1)}. \quad (8.161)$$

This applies both to a single electron, in which case $S = 1/2$, or to an N -electron system, in which case S could take any integer or half-integer value up to a maximum of $S = N/2$.

For the case $j_2 = 1/2$, and hence $j = j_1 \pm (1/2)$, Eq. (8.157) simplifies as

$$g_j = g_1 \pm \frac{g_2 - g_1}{2j_1 + 1}, \quad (j = j_1 \pm 1/2). \quad (8.162)$$

This case is relevant to combining the orbital and spin magnetic moments of a single spin-half particle. For an electron, with $j = \ell \otimes s = \ell \pm (1/2)$, and with $g_1 = g_\ell = 1$, $g_2 = g_e \approx 2$, Eq. (8.162) further simplifies as

$$g_j = 1 \pm \frac{1}{2\ell + 1}, \quad (j = \ell \pm 1/2). \quad (8.163)$$

Similarly, for a proton, we have $g_\ell = 1$ and $g_2 = g_p = 5.586$, and hence

$$g_j = 1 \pm \frac{4.586}{2\ell + 1}, \quad (j = \ell \pm 1/2). \quad (8.164)$$

For a neutron, we have $g_\ell = 0$ and $g_2 = g_n = -3.826$, and hence

$$g_j = \mp \frac{3.826}{2\ell + 1}, \quad (j = \ell \pm 1/2). \quad (8.165)$$

Eq. (8.164) and (8.165) have application in the shell model of nuclear structure.

Identical Particles

Until now, most of our focus has been on the quantum mechanical behaviour of *individual* particles, or problems which can be “factorised” into independent single-particle systems.¹ However, most physical systems of interest involve the interaction of large numbers of particles; electrons in a solid, atoms in a gas, etc. In classical mechanics, particles are always distinguishable in the sense that, at least formally, their “trajectories” through phase space can be traced and their identity disclosed. However, in quantum mechanics, the intrinsic uncertainty in position, embodied in Heisenberg’s principle, demands a careful and separate consideration of distinguishable and indistinguishable particles. In the present section, we will consider how to formulate the wavefunction of many-particle systems, and address some of the (sometimes striking and often counter-intuitive) implications of particle indistinguishability.

9.1 Quantum Statistics

Consider then two indistinguishable particles confined to a box in one-dimension. Here, by indistinguishable, we mean that the particles can not be discriminated by some internal quantum number. For example, we might have two electrons of the same spin. The normalised two-particle wavefunction $\psi(x_1, x_2)$, which gives the probability $|\psi(x_1, x_2)|^2 dx_1 dx_2$ of finding simultaneously one particle in the interval x_1 to $x_1 + dx_1$ and another between x_2 to $x_2 + dx_2$, only makes sense if $|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2$, since we can’t know which of the two indistinguishable particles we are finding where. It follows from this that the wavefunction can exhibit two (and, generically, only two) possible symmetries under exchange: $\psi(x_1, x_2) = \psi(x_2, x_1)$ or $\psi(x_1, x_2) = -\psi(x_2, x_1)$.² If two identical particles have a symmetric wavefunction in some state, particles of that type always have symmetric wavefunctions, and are called **bosons**. (If in some other state they had an antisymmetric wavefunction, then a linear superposition of those states would be neither symmetric nor antisymmetric, and so could not satisfy the relation $|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2$.) Similarly, particles having antisymmetric wavefunctions are called **fermions**.

To construct wavefunctions for three or more fermions, let first suppose that the particles do not interact with each other, and are confined by a spin independent potential, such as the Coulomb field of a nucleus. In this case, the Hamiltonian will be symmetric

¹For example, the treatment of the hydrogen atom involves the separation of the system into centre of mass and relative motion. Each could be referred to an effective single-particle dynamics.

²We could in principle have $\psi(x_1, x_2) = e^{i\alpha} \psi(x_2, x_1)$, with α a constant phase. However, in this case we would not recover the original wavefunction on exchanging the particles twice. Curiously, in some two-dimensional theories used to describe the fractional quantum Hall effect, there exist collective excitations of the electron system – called **anyons** – that do have this kind of property. Such anyonic systems have been proposed as a strong candidate for the realisation of quantum computation. However, all ordinary “fundamental” particles are either bosons or fermions.

in the fermion degrees of freedom,

$$\hat{H} = \frac{\hat{\mathbf{p}}_1^2}{2m} + \frac{\hat{\mathbf{p}}_2^2}{2m} + \frac{\hat{\mathbf{p}}_3^2}{2m} + \cdots V(\mathbf{r}_1) + V(\mathbf{r}_2) + V(\mathbf{r}_3) + \cdots, \quad (9.1)$$

and the solutions of the Schrödinger equation will be products of eigenfunctions of the single-particle Hamiltonian $\hat{H}_s = \hat{\mathbf{p}}^2/2m + V(\mathbf{r})$. However, single products such as $\psi_a(1)\psi_b(2)\psi_c(3)$ do not have the required antisymmetry property under the exchange of any two particles. (Here a, b, c, \dots label the single-particle eigenstates of \hat{H}_s , and $1, 2, 3, \dots$ denote *both* space and spin coordinates of single particles, i.e. 1 stands for (\mathbf{r}_1, s_1) , etc.)

We could achieve the necessary antisymmetrisation for particles 1 and 2 by subtracting the same product wavefunction with the particles 1 and 2 interchanged, i.e. $\psi_a(1)\psi_b(2)\psi_c(3) \mapsto (\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1))\psi_c(3)$, ignoring the overall normalisation for now. However, the wavefunction needs to be antisymmetrised with respect to *all* possible particle exchanges. So, for 3 particles, we must add together all $3!$ permutations of 1, 2, 3 in the state a, b, c , with a factor -1 for each particle exchange necessary to get to a particular ordering from the original ordering of 1 in a , 2 in b , and 3 in c . In fact, such a sum over permutations is precisely the *definition* of the determinant. So, with the appropriate normalisation factor:

$$\psi_{abc}(1, 2, 3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_a(1) & \psi_b(1) & \psi_c(1) \\ \psi_a(2) & \psi_b(2) & \psi_c(2) \\ \psi_a(3) & \psi_b(3) & \psi_c(3) \end{vmatrix} \quad (9.2)$$

The determinantal form makes clear the antisymmetry of the wavefunction with respect to exchanging any two of the particles, since exchanging two rows of a determinant multiplies it by -1 . We also see from the determinantal form that the three states a, b, c *must* all be different, for otherwise two columns would be identical, and the determinant would be zero. This is just the manifestation of Pauli's exclusion principle: no two fermions can be in the same state.

Although these determinantal wavefunctions (known as **Slater determinants**), involving superpositions of single-particle states, are only strictly correct for non-interacting fermions, they provide a useful platform to describe electrons in atoms (or in a metal), with the electron-electron repulsion approximated by a single-particle potential. For example, the Coulomb field in an atom, as seen by the outer electrons, is partially shielded by the inner electrons, and a suitable $V(\mathbf{r})$ can be constructed self-consistently, by computing the single-particle eigenstates and finding their associated charge densities. (We shall discuss this ‘‘Hartree’’ approximation later in the course, when we study multielectron atoms.)

In the bosonic system, the corresponding many-particle wavefunction must be symmetric under particle exchange. We can obtain such a state by expanding all of the contributing terms from the Slater determinant and setting all of the signs to be positive. In other words, the bosonic wave function describes the uniform (equal phase) superposition of all possible permutations of product states. In this case, there is no requirement that the orbitals be different. (There is no exclusion principle for bosons.) One important example is the groundstate wavefunction of a collection of non-interacting gas of bosons, in which all bosons occupy the lowest energy single particle wavefunction, $\psi_0(\mathbf{r})$. The many-particle state (for N indistinguishable bosons) is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \prod_{i=1}^N \psi_0(\mathbf{r}_i) \quad (9.3)$$

This is the wavefunction for a **Bose-Einstein condensate**, with all particles condensed in the state $\psi_0(\mathbf{r})$. It describes a non-interacting gas of (spinless) bosons at zero temperature: i.e. the many-particle groundstate.

9.2 Space and spin wavefunctions

Although the methodology for constructing a basis of many-particle states outlined above is generic, it is not particularly convenient when the Hamiltonian is spin-independent. In this case we can simplify the structure of the wavefunction by factorizing the spin and spatial components. Suppose we have two electrons (i.e. fermions) in some spin-independent potential $V(\mathbf{r})$. We know that the two-electron wavefunction must be antisymmetric under particle exchange. Since the Hamiltonian has no spin-dependence, we must be able to construct a set of common eigenstates of the Hamiltonian, the total spin, and the z -component of the total spin. For two electrons, there are four basis states in the spin space, the $S = 0$ spin singlet state, $|\chi_{S=0, S_z=0}\rangle = \frac{1}{\sqrt{2}}(|\uparrow_1\downarrow_2\rangle - |\downarrow_1\uparrow_2\rangle)$, and the three $S = 1$ spin triplet states,

$$|\chi_{11}\rangle = |\uparrow_1\uparrow_2\rangle, \quad |\chi_{10}\rangle = \frac{1}{\sqrt{2}}(|\uparrow_1\downarrow_2\rangle + |\downarrow_1\uparrow_2\rangle), \quad |\chi_{1,-1}\rangle = |\downarrow_1\downarrow_2\rangle. \quad (9.4)$$

Here the first arrow in the ket refers to the spin of particle 1, the second to particle 2.

It is evident that the spin singlet wavefunction is antisymmetric under the exchange of two particles, while the spin triplet wavefunction is symmetric. For a general state, the total wavefunction for the two electrons in a common eigenstate of $\hat{\mathbf{S}}^2$, \hat{S}_z and the Hamiltonian \hat{H} then has the form:

$$\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) = \psi(\mathbf{r}_1, \mathbf{r}_2)\chi(s_1, s_2), \quad (9.5)$$

where $\chi(s_1, s_2) = \langle s_1, s_2 | \chi \rangle$. For two electron degrees of freedom, the total wavefunction, ψ , must be antisymmetric under exchange. It follows that a pair of electrons in the spin *singlet* state must have a *symmetric* spatial wavefunction, $\psi(\mathbf{r}_1, \mathbf{r}_2)$, whereas electrons in the spin *triplet* states must have an *antisymmetric* spatial wavefunction. Before discussing the physical consequences of this symmetry, let us mention how this scheme generalises to more particles.

Unfortunately, in seeking a factorisation of the Slater determinant into a product of spin and spatial components for three electrons, things become more challenging. There are now $2^3 = 8$ basis states in the spin space. Four of these are accounted for by the spin $3/2$ state with $S_z = 3/2, 1/2, -1/2, -3/2$. Since all spins are aligned, this is evidently a symmetric state, so must be multiplied by an antisymmetric spatial wavefunction, itself a determinant. So far so good. But the other four states involve two pairs of total spin $1/2$ states built up of a singlet and an unpaired spin. They are orthogonal to the symmetric spin $3/2$ state, so they can't be symmetric. But they can't be antisymmetric either, since in each such state, two of the spins must be pointing in the same direction! An example of such a state is presented by $|\chi\rangle = |\uparrow\rangle \otimes \frac{1}{\sqrt{2}}(|\uparrow_2\downarrow_3\rangle - |\downarrow_2\uparrow_3\rangle)$. Evidently, this must be multiplied by a spatial wavefunction symmetric in 2 and 3. But to recover a total wave

function with *overall* antisymmetry it is necessary to add more terms:

$$\Psi(1, 2, 3) = \chi(s_1, s_2, s_3)\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \chi(s_2, s_3, s_1)\psi(\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_1) + \chi(s_3, s_1, s_2)\psi(\mathbf{r}_3, \mathbf{r}_1, \mathbf{r}_2). \quad (9.6)$$

Requiring the spatial wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ to be symmetric in 2, 3 is sufficient to guarantee the overall antisymmetry of the total wavefunction Ψ . For more than three electrons, similar considerations hold. The mixed symmetries of the spatial wavefunctions and the spin wavefunctions which together make a totally antisymmetric wavefunction are quite complex, and are described by **Young diagrams** (or **tableaux**).

9.3 Physical Consequences of Particle Statistics

The overall antisymmetry demanded by the many-fermion wavefunction has important physical implications. In particular, it determines the magnetic properties of atoms. The magnetic moment of the electron is aligned with its spin, and even though the spin variables do not appear in the Hamiltonian, the energy of the eigenstates depends on the relative spin orientation. This arises from the electrostatic repulsion between electrons. In the spatially antisymmetric state, the probability of electrons coinciding at the same position necessarily vanishes. Moreover, the nodal structure demanded by the antisymmetry places the electrons further apart on average than in the spatially symmetric state. Therefore, the electrostatic repulsion raises the energy of the spatially symmetric state above that of the spatially antisymmetric state. It therefore follows that the lower energy state has the electron spins pointing in the same direction. This argument is still valid for more than two electrons, and leads to **Hund's rule** for the magnetisation of incompletely filled inner shells of electrons in transition metal and rare earths atoms. This is the first step in understanding ferromagnetism (see 9.4.3).

A gas of hydrogen molecules provides another manifestation of wavefunction antisymmetry. In particular, the specific heat depends sensitively on whether the two protons (spin 1/2) in H_2 have their spins parallel or antiparallel, even though that alignment involves only a very tiny interaction energy. If the proton spins occupy a spin singlet configuration, the molecule is called **parahydrogen** while the triplet states are called **orthohydrogen**. These two distinct gases are remarkably stable – in the absence of magnetic impurities, para-ortho transitions take weeks.

The actual energy of interaction of the proton spins is of course completely negligible in the specific heat. The important contributions to the specific heat are the usual kinetic energy term, and the rotational energy of the molecule. This is where the overall (space \times spin) antisymmetric wavefunction for the protons plays a role. Recall that the parity of a state with rotational angular momentum ℓ is $(-1)^\ell$. Therefore, parahydrogen, with an antisymmetric proton spin wavefunction, must have a symmetric proton *spatial* wavefunction, and so can only have even values of the rotational angular momentum. Orthohydrogen can only have odd values. The energy of the rotational level with angular momentum ℓ is $E_{\text{tot}}^\ell = 2\hbar\ell(\ell + 1)/I$, where I denotes the moment of inertia of the molecule. So the two kinds of hydrogen gas have different sets of rotational energy levels, and consequently different specific heats.

9.3.0.1 Example: Excited State Spectrum of Helium

As a final example, and one that will feed into our discussion of multielectron atoms in the next chapter, let us consider the implications of particle statistics for the excited state spectrum of Helium. After Hydrogen, Helium is the simplest atom having two protons and two neutrons in the nucleus ($Z = 2$), and two bound electrons. As a complex many-body system, we have seen already that the Schrödinger equation is analytically intractable and must be treated perturbatively. Previously, in Chapter 7, we have used the ground state properties of Helium as a vehicle to practice perturbation theory. In the absence of direct electron-electron interaction, the Hamiltonian

$$\hat{H}_0 = \sum_{n=1}^2 \left[\frac{\hat{\mathbf{p}}_n^2}{2m} + V(\mathbf{r}_n) \right], \quad V(\mathbf{r}_n) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}, \quad (9.7)$$

is separable and the wavefunction can be expressed through the states of the hydrogen atom, ψ_{nlm} . In this approximation, the ground state wavefunction involves both electrons occupying the 1s state leading to an antisymmetric spin singlet wavefunction for the spin degrees of freedom, $|\Psi_{\text{g.s.}}\rangle = (|100\rangle \otimes |100\rangle) \otimes |\chi_{00}\rangle$. In Chapter 7, we made use of both the perturbative series expansion and the variational method to determine how the ground state energy is perturbed by the repulsive electron-electron interaction,

$$\hat{H}_1 = \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (9.8)$$

Now let us consider the implications of particle statistics on the spectrum of the lowest excited states.

From the symmetry perspective, the ground state wavefunction belongs to the class of states with symmetric spatial wavefunctions, and antisymmetric spin (singlet) wavefunctions. These states are known as **parahelium**. In the absence of electron-electron interaction, the first excited states are degenerate and have the form,

$$|\psi_p\rangle = \frac{1}{\sqrt{2}}(|100\rangle \otimes |2\ell m\rangle + |2\ell m\rangle \otimes |100\rangle) \otimes |\chi_{100}\rangle. \quad (9.9)$$

The second class of states involve an antisymmetric spatial wavefunction, and symmetric (triplet) spin wavefunction. These states are known as **orthohelium**. Once again, in the absence of electron-electron interaction, the first excited states are degenerate and have the form,

$$|\psi_o\rangle = \frac{1}{\sqrt{2}}(|100\rangle \otimes |2\ell m\rangle - |2\ell m\rangle \otimes |100\rangle) \otimes |\chi_{1S_z}\rangle. \quad (9.10)$$

The perturbative shift in the ground state energy has already been calculated within the framework of first order perturbation theory. Let us now consider the shift in the excited states. Despite the degeneracy, since the off-diagonal matrix elements vanish, we can make use of the first order of perturbation theory to compute the shift. In doing so, we obtain

$$\Delta E_{n\ell}^{\text{p.o.}} = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 |\psi_{100}(\mathbf{r}_1)\psi_{n\ell 0}(\mathbf{r}_2) \pm \psi_{n\ell 0}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (9.11)$$

with the plus sign refers to parahelium and the minus to orthohelium. Since the matrix element is independent of m , the $m = 0$ value considered here applies to all values of m . Rearranging this equation, we thus obtain $\Delta E_{n\ell}^{\text{p.o.}} = J_{n\ell} \pm K_{n\ell}$ where

$$J_{n\ell} = \frac{e^2}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 \frac{|\psi_{100}(\mathbf{r}_1)|^2 |\psi_{n\ell 0}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (9.12)$$

$$K_{n\ell} = \frac{e^2}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 \frac{\psi_{100}^*(\mathbf{r}_1) \psi_{n\ell 0}^*(\mathbf{r}_2) \psi_{100}(\mathbf{r}_2) \psi_{n\ell 0}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (9.13)$$

Physically, the term $J_{n\ell}$ represents the electrostatic interaction energy associated with the two charge distributions $|\psi_{100}(\mathbf{r}_1)|^2$ and $|\psi_{n\ell 0}(\mathbf{r}_2)|^2$, and it is clearly positive. By contrast, the **exchange term**, which derives from the antisymmetry of the wavefunction, leads to a shift with opposite signs for ortho and para states. In fact, one may show that, in the present case, $K_{n\ell}$ is positive leading to a positive energy shift for parahelium and a negative shift for orthohelium. Moreover, noting that

$$2\mathbf{S}_1 \cdot \mathbf{S}_2 = (\mathbf{S}_1 + \mathbf{S}_2)^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2 = \hbar^2 \left(S(S+1) - 2 \times \frac{3}{4} \right) = \hbar^2 \begin{cases} 1/2 & \text{triplet} \\ 3/2 & \text{singlet} \end{cases} \quad (9.14)$$

the energy shift can be written as

$$\Delta E_{n\ell}^{\text{p.o.}} = J_{n\ell} - \frac{1}{2} \left(1 + \frac{4}{\hbar^2} \mathbf{S}_1 \cdot \mathbf{S}_2 \right) K_{n\ell}. \quad (9.15)$$

This result shows that the electron-electron interaction leads to an effective **ferromagnetic** interaction between spins – i.e. the spins want to be aligned.

In addition to the large energy shift between the singlet and triplet states, electric dipole decay selection rules $\Delta\ell = \pm 1$, $\Delta s = 0$ cause decays from triplet to singlet states (or vice-versa) to be suppressed by a large factor (compared to decays from singlet to singlet or from triplet to triplet). This caused early researchers to think that there were two separate kinds of Helium. The diagrams ?? shows the levels for parahelium (singlet) and for orthohelium (triplet) along with the dominant decay modes.

9.4 Many-Body Systems

An important and recurring example of a many-body system is provided by the problem of free (i.e. non-interacting) non-relativistic quantum particles in a closed system – a box. The many-body Hamiltonian is then given simply by the kinetic energy

$$\hat{H}_0 = \sum_{i=1}^N \frac{\hat{\mathbf{p}}_i^2}{2m}, \quad (9.16)$$

where $\hat{\mathbf{p}}_i = -i\hbar\nabla_i$ and m denotes the particle mass. If we take the dimensions of the box to be L^d , and the boundary conditions to be periodic³ the normalised eigenstates of the

³It may seem odd to consider such an unphysical geometry – in reality, we are invariably dealing with a closed system in which the boundary conditions translate to “hard walls” – think of electrons in a metallic sample. Here, we have taken the boundary conditions to be periodic since it leads to a slightly more simple mathematical formulation. We could equally well consider closed boundary conditions, but we would have to separately discriminate between “even and odd” states and sum them accordingly. Ultimately, we would arrive to the same conclusions!

single-particle Hamiltonian are simply given by plane waves, $\psi_{\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | \mathbf{k} \rangle = \frac{1}{L^{d/2}} e^{i\mathbf{k} \cdot \mathbf{r}}$, with wavevectors taking discrete values,⁴

$$\mathbf{k} = \frac{2\pi}{L}(n_1, n_2, \dots, n_d), \quad n_i \text{ integer.} \quad (9.17)$$

To address the quantum mechanics of the system, we start with fermions.

9.4.1 Non-interacting Fermi Gas

In the (**spinless**) **Fermi system**, Pauli exclusion inhibits multiple occupancy of single-particle states. In this case, the many-body ground state wavefunction is obtained by filling states sequentially up to the **Fermi energy**, $E_F = \hbar^2 k_F^2 / 2m$, where the **Fermi wavevector**, k_F , is fixed by the number of particles. All the plane wave states $\psi_{\mathbf{k}}$ with energies lower than E_F are filled, while all states with energies larger than E_F remain empty. Since each state is associated with a k -space volume $(2\pi/L)^d$ (see Fig. ??), in the three-dimensional system, the total number of occupied states is given by $N = \left(\frac{L}{2\pi}\right)^3 \frac{4}{3}\pi k_F^3$, i.e. defining the mean particle density $\bar{n} \equiv N/L^3 = k_F^3 / 6\pi^2$,

$$E_F = \frac{\hbar^2}{2m} (6\pi^2 \bar{n})^{2/3}. \quad (9.18)$$

The **density of states** per unit volume,

$$g(E) = \frac{1}{L^3} \frac{dN}{dE} = \frac{1}{6\pi^2} \frac{d}{dE} \left(\frac{2mE}{\hbar^2} \right)^{3/2} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}. \quad (9.19)$$

We can also integrate to obtain the total energy density of all the fermions,

$$\frac{E_{\text{tot}}}{L^3} = \frac{1}{L^3} \int_0^{k_F} \frac{4\pi k^2 dk}{(2\pi/L)^3} \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{20\pi^2 m} (6\pi^2 \bar{n})^{5/3} = \frac{3}{5} \bar{n} E_F. \quad (9.20)$$

Therefore the energy per particle is

$$\frac{E_{\text{tot}}}{\bar{n}} = \frac{E_{\text{tot}}}{\bar{n} L^3} = \frac{3}{5} E_F. \quad (9.21)$$

The groundstate wavefunction is the Slater determinant

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{\mathbf{k}_1}(\mathbf{r}_1) & \phi_{\mathbf{k}_2}(\mathbf{r}_1) & \cdots & \phi_{\mathbf{k}_N}(\mathbf{r}_1) \\ \phi_{\mathbf{k}_1}(\mathbf{r}_2) & \phi_{\mathbf{k}_2}(\mathbf{r}_2) & \cdots & \phi_{\mathbf{k}_N}(\mathbf{r}_2) \\ \vdots & \vdots & & \vdots \\ \phi_{\mathbf{k}_1}(\mathbf{r}_N) & \phi_{\mathbf{k}_2}(\mathbf{r}_N) & \cdots & \phi_{\mathbf{k}_N}(\mathbf{r}_N) \end{vmatrix} \quad (9.22)$$

formed using the plane wave states with wavevectors $|\mathbf{k}_i| \leq k_F$ (i.e. those of the filled Fermi sea).

⁴The quantisation condition follows from the periodic boundary condition, $\phi[\mathbf{r} + L(m_x \hat{\mathbf{x}} + m_y \hat{\mathbf{y}} + m_z \hat{\mathbf{z}})] = \phi(\mathbf{r})$, where $m = (m_x, m_y, m_z)$ denotes an arbitrary vector of integers.

9.4.2 Interacting Fermi Gas

For realistic metals or (doped) semiconductors, it is unreasonable to treat the electrons as non-interacting fermions. After all, they have electric charge e , so interact via the Coulomb interactions. As a result, in addition to the kinetic energy (9.16) in the Hamiltonian one should add an interaction⁵

$$\hat{V}_1 = \frac{1}{2} \sum_{i \neq j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V_{\text{bg}}(\mathbf{r}_i), \quad (9.23)$$

The first term describes the electron-electron repulsion. In the second term, $V_{\text{bg}}(\mathbf{r})$ is the average (attractive) background potential due to the charged ions; this is required in order to make the system overall charge neutral.

Let us estimate how large this interaction energy is. For a gas with density \bar{n} , the typical interparticle spacing is $\bar{a} \equiv \bar{n}^{-1/3}$. Therefore, by dimensional analysis, the mean interaction energy per particle must be of order

$$\frac{\langle \hat{V}_1 \rangle}{N} \sim \frac{e^2}{4\pi\epsilon_0 \bar{a}} \quad (9.24)$$

(We shall discuss the size of the prefactor below.) On the other hand, we derived the kinetic energy per particle for the groundstate of the spinless Fermi gas,

$$\frac{\langle \hat{H}_0 \rangle}{N} = \frac{3}{5} E_F \sim \frac{\hbar^2}{m \bar{a}^2} \quad (9.25)$$

where we have used $E_F \sim \hbar^2/(m \bar{a}^2)$.

The ratio of the mean interaction energy to the mean kinetic energy is

$$\frac{\langle \hat{V}_1 \rangle}{\langle \hat{H}_0 \rangle} \sim \frac{e^2/(4\pi\epsilon_0 \bar{a})}{\hbar^2/(m \bar{a}^2)} = \frac{\bar{a}}{a_0} \quad (9.26)$$

where $a_0 = \frac{4\pi\hbar^2\epsilon_0}{me^2}$ is the Bohr radius. We can understand the properties of the interacting Fermi gas in two simple limiting cases.

1. **Weak interactions:** For $\bar{a} \ll a_0$ the typical interaction energy is small compared to the kinetic energy. In this case, one can treat the interactions as a perturbative correction to the groundstate of the kinetic energy. As discussed above, this groundstate is the filled Fermi sea. For weak interactions, the perturbative corrections are small and the interacting electron gas has the same qualitative properties as the non-interacting (ideal) Fermi gas. This case is typical for “good” metals such as copper.

⁵The electrons move in the background potential of the ionic cores of the atoms. This is a periodic potential acting on each electron, and leads to a more complicated band structure: with a new “effective mass” m^* and with band gaps at the Brillouin zone boundaries, *etc.* This can have important quantitative effects on the properties of the metal. Here we focus on the *qualitative* effects of electron-electron interactions. Therefore, for simplicity, we neglect this periodic potential.

2. **Strong interactions:** : For $\bar{a} \gg a_0$ the typical interaction energy is large compared to the kinetic energy. In this case, one should treat the kinetic energy as a perturbative correction to the groundstate of the interaction potential (9.23). The interaction potential is minimized by keeping the electrons as far apart from each other as possible. At a fixed average density \bar{n} , this is achieved by placing the electrons at points located at the sites of a regular lattice. This unperturbed wavefunction is therefore a *crystal of electrons*. Provided the kinetic energy is small ($\bar{a} \gg a_0$), the perturbation by \hat{H}_0 acts only to move the electrons a small distance from the sites of the crystalline lattice. The integrity of the lattice remains, as a so-called **Wigner crystal**. This limit of strong interactions is *not* achieved in typical metallic systems for which the density is too high. However, in two-dimensional electron gases (formed both in doped semiconductor devices and on the surface of liquid helium) there is evidence for the appearance of a 2D Wigner crystal in experiment.

The two limiting cases described above are simple to understand, since we can use perturbation theory. However, many metallic systems are in an intermediate regime, with $\bar{a} \simeq a_0$, where perturbation theory in either \hat{V}_1 or \hat{H}_0 is inappropriate. This case of intermediate coupling poses a very difficult challenge to theory, and few results are known with certainty. One technique that one can always fall back on is the **variational** approach. One can “guess” what possible phases of the electron system might appear, and construct trial wavefunctions for each of these phases. By comparing the expectation values of the total energy for these different trial wavefunctions, one obtains an indication of which of them best describes the groundstate and therefore what phase the electron system may be in. For example, this technique has been used to determine at what (numerical) value of \bar{a}/a_0 the transition between the Wigner crystal and Fermi-gas states occurs.

Another important example of the application of variational approach is in understanding **ferromagnetism** of an itinerant spin-1/2 Fermi gas. In this case, the two representative states to consider are: (1) a filled Fermi sea of spin-polarized electrons, say with all spins “up”; and (2) a filled Fermi sea of both spin components. By fixing the occupation numbers to be filled Fermi seas, these states have no remaining variational parameters. A more general class of wavefunctions is provided by “Hartree-Fock” theory, in which the orbitals in the Slater determinants are viewed as variational parameters.

1. Case (1), the spin-polarized Fermi sea, was discussed in detail above. For a density \bar{n} the states are filled out to the Fermi wavevector $k_f = (6\pi\bar{n})^{1/3}$. A direct calculation of the mean energy per particle in this spin-polarised Fermi gas gives

$$\frac{E_{\text{tot}}^{\text{pol.}}}{N} \equiv \frac{\langle \hat{H}_0 \rangle + \langle \hat{V}_1 \rangle}{N} = \frac{3}{5} \frac{\hbar^2}{2m\bar{a}^2} (6\pi^2)^{2/3} - \frac{3(6\pi^2)^{1/3}}{4\pi} \frac{e^2}{4\pi\epsilon_0\bar{a}} \quad (9.27)$$

The prefactor of the interaction term arises from a straightforward but lengthy calculation (not shown here!). The negative sign of the interaction term indicates that the energy is lowered by the electrons residing in the material, and thereby neutralising the background charge density of the ions. The overall size of the energy reduction is influenced by the extent to which the electrons repel each other.

2. Case (2), the spin-unpolarised Fermi gas, follows similar considerations. Note now that a total density \bar{n} will consist of density $\bar{n}/2$ of spin-up electrons and a density

$\bar{n}/2$ of spin-down electrons. Since there is no Pauli exclusion between these two spin states, each spin-state can fill its own Fermi sea. The resulting Fermi wavevector (for both spin-up and spin-down) is therefore $K'_F = (6\pi\bar{n}/2)^{1/3} = k_F/2^{1/3}$. A direct calculation of the mean energy per particle in this spin-unpolarised Fermi gas leads to

$$\frac{E_{\text{tot}}^{\text{unpol.}}}{N} \equiv \frac{\langle \hat{H}_0 \rangle + \langle \hat{V}_1 \rangle}{N} = \frac{3}{5} \frac{\hbar^2}{2m\bar{a}^2} (3\pi^2)^{2/3} - \frac{3(6\pi^2)^{1/3}}{4\pi 2^{1/3}} \frac{e^2}{4\pi\epsilon_0\bar{a}} \quad (9.28)$$

Compared to the polarised case, the kinetic energy is smaller. This is due to the fact that, since both spin states are occupied, the electrons are not forced up to such a high Fermi energy as in the polarized case. However, note also that the reduction in the energy due to the interactions is smaller. That is, the total interaction energy of the electrons is larger for the spin-unpolarised case than for the spin-polarised case. For the polarised Fermi gas, the wavefunction must vanish when any two electrons approach each other. This effectively keeps the electrons far apart from each other, and reduces the electron-electron repulsion. For the unpolarised Fermi gas, the wavefunction must vanish when any two particles of the same spin approach each other. However, particles of opposite spin can be located nearby in space, and can contribute a larger Coulomb energy.

For high density (small \bar{a}), the kinetic energy dominates and favours the unpolarised Fermi gas. For low density (large \bar{a}), the interaction energy dominates and favours the polarised Fermi gas. A comparison of the total energies of the two variational states shows that the transition between these is at

$$\frac{\bar{a}}{a_0} = \frac{2\pi}{5} (3\pi^2)^{1/3} (1 + 2^{1/3}) \simeq 8.8. \quad (9.29)$$

This provides a simple variational estimate for the condition **ferromagnetism** in the interacting Fermi gas. This competition is responsible for the ferromagnetism of iron and other metallic magnets. (For even larger values of \bar{a}/a_0 there should be a transition from the polarised Fermi gas into a Wigner crystal.)

9.4.3 Non-interacting Bose gas

For the case of non-interacting bosons, confined in the same box, the nature of the ground-state is even simpler. There is no exclusion principle, so the groundstate is obtained by putting all bosons in the lowest energy single particle state, $\phi_{\mathbf{k}=0}(\mathbf{r})$. This single particle state has vanishing kinetic energy. Thus, the many-particle groundstate has energy

$$E_{\text{tot}} = 0. \quad (9.30)$$

The groundstate wavefunction is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \prod_{i=1}^N \phi_{\mathbf{k}=0}(\mathbf{r}_i) \quad (9.31)$$

9.4.4 Interacting Bose Gas

For the BECs formed in cold atomic gases, there are residual interactions between the particles. To a good approximation, these can be represented by contact interactions, with

$$\hat{V}_1 = \frac{1}{2} \sum_{i \neq j} g \delta(\mathbf{r}_i - \mathbf{r}_j). \quad (9.32)$$

A simple variational approach for the interacting Bose gas is provided by the **Gross-Pitaevskii** approximation. One assumes that the groundstate is a condensate, Eq. (9.3), and treats the (normalised) condensate wavefunction $\psi(\mathbf{r})$ as the variational function. The mean energy per particle (for $N \gg 1$) is

$$\frac{\langle \hat{H}_0 + \hat{V}_1 \rangle}{N} = \int \left[\frac{\hbar^2}{2m} |\nabla \psi|^2 + V_{\text{ext}}(\mathbf{r}) |\psi|^2 \right] d^3\mathbf{r} + \frac{1}{2} g N \int |\psi|^4 d^3\mathbf{r} \quad (9.33)$$

for the BEC in an external trapping potential $V_{\text{ext}}(\mathbf{r})$. The optimal condensate wavefunction $\psi(\mathbf{r})$ is found by minimising the energy per particle, subject to the normalisation $\langle \psi | \psi \rangle = 1$. This constraint can be imposed by introducing a Lagrange multiplier, $-E \int |\psi|^2 d^3\mathbf{r}$, with minimisation over ψ then leading to

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + [V_{\text{ext}}(\mathbf{r}) + gN|\psi|^2] \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (9.34)$$

Since $\psi(\mathbf{r})$ is normalised, the mean particle density is $n(\mathbf{r}) = N|\psi|^2$. The interaction term can be viewed as contributing to an effective potential to $V_{\text{total}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + gn(\mathbf{r})$ in which $n(\mathbf{r})$ is a function of $\psi(\mathbf{r})$ and must therefore be self-consistently determined.

Atomic Structure

10.1 The Non-Relativistic Hydrogen Atom

The quantum mechanics of atomic hydrogen, and hydrogen-like atoms is characterized by a large degeneracy with eigenvalues separating into multiplets of n^2 -fold degeneracy, where n denotes the principal quantum number. However, although the idealised Schrödinger Hamiltonian,

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m} + V(r), \quad V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}, \quad (10.1)$$

provides a useful platform from which develop our intuition, there are several important effects which mean that the formulation is a little too naïve. These “corrections”, which derive from several sources, are important as they lead to physical ramifications which extend beyond the realm of atomic physics. Here we outline some of the effects which need to be taken into account even for atomic hydrogen, before moving on to discuss the quantum physics of multielectron atoms. In broad terms, the effects to be considered can be grouped into those caused by the internal properties of the nucleus, and those which derive from relativistic corrections.

To orient our discussion, it will be helpful to summarise some of key aspects of the solutions of the non-relativistic Schrödinger equation, $\hat{H}_0\psi = E\psi$ on which we will draw:

10.1.0.1 Hydrogen Atom Revisited

- As with any centrally symmetric potential, the solutions of the Schrödinger equation take the form $\psi_{\ell m_\ell}(\mathbf{r}) = R(r)Y_{\ell, m_\ell}(\theta, \phi)$, where the spherical harmonic functions $Y_{\ell, m_\ell}(\theta, \phi)$ depend only on spherical polar coordinates, and $R(r)$ represents the radial component of the wavefunction. Solving the radial wave equation introduces a radial quantum number, $n_r \geq 0$. In the case of a Coulomb potential, the energy depends on the principal quantum number $n = n_r + \ell + 1 \geq 1$, and not on n_r and ℓ separately.
- For atomic hydrogen ($Z = 1$), the energy levels of the Hamiltonian (10.1) are given by

$$E_n = -\frac{\text{Ry}}{n^2}, \quad \text{Ry} = \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m}{2\hbar} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{2a_0} = \frac{1}{2}mc^2\alpha^2, \quad (10.2)$$

where $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{e^2 m}$ is the Bohr radius, $\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c}$ denotes the **fine structure constant**, and m represents the reduced mass of the electron and proton. Applied to single electron ions with higher atomic weight, such as He^+ , Li^{2+} , etc., the Bohr radius is reduced by a factor $1/Z$, where Z denotes the nuclear charge, and the energy is given by $E_n = -\frac{Z^2}{n^2}\text{Ry} = -\frac{1}{2n^2}mc^2(Z\alpha)^2$.

- Since $n \geq 1$ and $n_r \geq 0$, the allowed combinations of quantum numbers are shown in table 10.1, where we have introduced the conventional notation whereby values of $\ell = 0, 1, 2, 3, 4, \dots$ are represented by letters s, p, d, f, g, \dots respectively.

n	ℓ	Subshell(s)
1	0	1s
2	0, 1	2s, 2p
3	0, 1, 2	3s, 3p, 3d
4	0, 1, 2, 3	4s, 4p, 4d, 4f
n	$0, \dots, (n-1)$	ns, \dots

Table 10.1: Hydrogen subshell designations for principal quantum numbers

- Since E_n depends only on n , this implies, for example, an exact degeneracy of the 2s and 2p, and of the 3s, 3p and 3d levels.

These results emerge from a treatment of the non-relativistic hydrogen atom which is inherently non-relativistic. In fact, the Hamiltonian (10.1) represents only the leading term in an expansion in $v^2/c^2 \simeq (Z\alpha)^2$ of the full relativistic Hamiltonian (see below). Higher order terms provide relativistic corrections, which impact significantly in atomic and condensed matter physics, and lead to a lifting of the degeneracy. In the following we will discuss and obtain the hierarchy of leading relativistic corrections.¹ This discussion will provide a platform to describe multi-electron atoms.

To see that $v^2/c^2 \simeq (Z\alpha)^2$, we may invoke the **virial theorem** (For a discussion of the form and proof of this theorem, refer to Appendix A.4.). The latter shows that the average kinetic energy is related to the potential energy as $\langle T \rangle = -\frac{1}{2} \langle V \rangle$. Therefore, the average energy is given by $\langle E \rangle = \langle T \rangle + \langle V \rangle = -\langle T \rangle \equiv -\frac{1}{2}mv^2$. We therefore have that $\frac{1}{2}mv^2 = \text{Ry} \equiv \frac{1}{2}mc^2(Z\alpha)^2$ from which follows the relation $v^2/c^2 \simeq (Z\alpha)^2$.

10.1.1 The Zeeman Effect

We start by exploring how the spectrum of the hydrogen atom is influenced by a uniform magnetic field, \mathbf{B} . There are two main effects:

1. The magnetic field couples to the magnetic moment associated with the *spin* of the electron.² This gives rise to an additional term in the Hamiltonian

$$\hat{H}_{\text{spin}} = -\boldsymbol{\mu}_e \cdot \mathbf{B} = g \frac{e}{2m} \hat{\mathbf{S}} \cdot \mathbf{B} \quad (10.3)$$

where we have used the spin magnetic dipole moment of the electron $\boldsymbol{\mu}_e = -g\mu_B(\mathbf{S}/\hbar)$ where $\mu_B \equiv e\hbar/(2m)$ is the Bohr magneton, and g the electron g -factor which is close to $g = 2$.³

¹It may seem odd to discuss relativistic corrections without introducing the Dirac equation and the relativistic formulation of quantum mechanics. However, such a discussion would present a lengthy and complex digression. We will therefore follow the normal practice of discussing relativistic corrections as perturbations to the familiar non-relativistic theory.

²There is also a coupling to the nuclear magnetic moment. Since $\mu_N/\mu_e \sim 10^{-3}$ this is a much weaker effect. However, it can be important in the hyperfine structure.

³The Dirac equation for the electron leads to the prediction that $g = 2$ exactly. Experimental measurements show $g = 2[1.0011596521884(\pm 43)]$. The small correction is known as the anomalous magnetic dipole moment of the electron. It arises from the electron's interaction with virtual photons in quantum electrodynamics, and can be accurately computed within that theory.

2. The field couples to the orbital motion of the (charged) electron. This is accounted for by replacing the kinetic energy with

$$\frac{1}{2m}\hat{\mathbf{p}}^2 \rightarrow \frac{1}{2m}(\hat{\mathbf{p}} + e\mathbf{A}(\hat{\mathbf{r}}))^2. \quad (10.4)$$

giving an additional change in the Hamiltonian

$$\hat{H}_{\text{orbital}} = \frac{1}{2m} \left[e(\hat{\mathbf{p}} \cdot \mathbf{A} + \mathbf{A} \cdot \hat{\mathbf{p}}) + e^2 |\mathbf{A}|^2 \right] \quad (10.5)$$

Let us explore further the effects of these orbital terms. The term linear in \mathbf{A} is known as the **paramagnetic term**, and the quadratic term the **diamagnetic** contribution. For a constant magnetic field, the vector potential can be as $\mathbf{A} = -\hat{\mathbf{r}} \times \mathbf{B}/2$. In this case, the paramagnetic component takes the form

$$-\frac{ie\hbar}{m}\mathbf{A} \cdot \nabla = -\frac{ie\hbar}{2m}(\hat{\mathbf{r}} \times \nabla) \cdot \mathbf{B} = \frac{e}{2m}\hat{\mathbf{L}} \cdot \mathbf{B}, \quad (10.6)$$

where $\hat{\mathbf{L}}$ denotes the angular momentum operator. Similarly, the diamagnetic term leads to

$$\frac{e^2}{2m}\mathbf{A}^2 = \frac{e^2}{8m}(\hat{\mathbf{r}}^2\mathbf{B}^2 - (\hat{\mathbf{r}} \cdot \mathbf{A})^2) = \frac{e^2 B^2}{2m}(\hat{x}^2 + \hat{y}^2), \quad (10.7)$$

where, here, we have chosen the magnetic field to lie along the z -axis.

Before addressing the role of these separate contributions in atomic hydrogen, let us first estimate their relative magnitude. With $\langle \hat{x}^2 + \hat{y}^2 \rangle \simeq a_0^2$, where a_0 denotes the Bohr radius, and $\langle \hat{L}_z \rangle \simeq \hbar$, the ratio of the diamagnetic to paramagnetic terms is

$$\frac{(e^2/8m_e) \langle \hat{x}^2 + \hat{y}^2 \rangle B^2}{(e/2m_e) \langle \hat{L}_z \rangle B} = \frac{e a_0^2 B}{4 \hbar} \simeq 10^{-6} B/\text{T}. \quad (10.8)$$

Therefore, provided the electron is bound in an orbital of size $\sim a_0$, for fields that can be achieved in the laboratory ($B \simeq 1\text{T}$) the diamagnetic term is negligible compared to the paramagnetic term.

Thus, for typical laboratory magnetic fields, the diamagnetic term can be neglected and the net change to the Hamiltonian is

$$\hat{H}_{\text{Zeeman}} \equiv \hat{H}_{\text{spin}} \hat{H}_{\text{orbital}} \simeq \frac{e}{2m} (g\hat{\mathbf{S}} + \hat{\mathbf{L}}) \cdot \mathbf{B} \quad (10.9)$$

The overall Hamiltonian for an electron moving in a Coulomb potential in the presence of a constant magnetic field $\mathbf{B} = B\hat{z}$ becomes

$$\hat{H} \simeq \hat{H}_0 + \frac{eB}{2m} (g\hat{S}_z + \hat{L}_z), \quad (10.10)$$

where $\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}$. Since $[\hat{H}_0, \hat{S}_z] = [\hat{H}_0, \hat{S}_z] = 0$, the eigenstates of the unperturbed hamiltonian, $\psi_{n\ell m_\ell m_s}$, remain eigenstates of \hat{H} and the corresponding energy levels are

$$E_{n\ell m_\ell m_s} \simeq -\frac{Ry}{n^2} + \hbar\omega_L(gm_s + m_\ell) \quad (10.11)$$

where $\omega_L = \frac{eB}{2m}$ denotes the **Larmor frequency**. From this result, we expect that a constant magnetic field will lead to a splitting of the $2 \times (2\ell + 1)$ - fold degeneracy of the energy levels. Before the knowledge of the existence of electron spin, one would have expected the level to split into $(2\ell + 1)$ levels, due to the orbital Zeeman effect. The fact that experiment showed an additional two-fold splitting, was one of the key insights that led to the identification of electron spin.

10.2 The “Real” Hydrogen Atom

The relativistic corrections (sometimes known as the **fine-structure corrections**) to the spectrum of hydrogen-like atoms derive from three different sources:

- relativistic corrections to the kinetic energy;
- coupling between spin and orbital degrees of freedom;
- a contribution known as the Darwin term.

In the following, we will discuss each of these corrections in turn.

10.2.1 Relativistic Correction to the Kinetic Energy

Previously, we have taken the kinetic energy to have the familiar non-relativistic form, $\frac{\mathbf{p}^2}{2m}$. However, from the expression for the relativistic energy-momentum invariant, $p_\mu p^\mu = (mc)^2$, we can already anticipate that the leading correction to the non-relativistic Hamiltonian appears at order \mathbf{p}^4 ,

$$E = \sqrt{\mathbf{p}^2 c^2 + m^2 c^4} = mc^2 + \frac{\mathbf{p}^2}{2m} - \frac{1}{8} \frac{(\mathbf{p}^2)^2}{m^3 c^2} + \dots \quad (10.12)$$

As a result, we can infer the following perturbation to the kinetic energy of the electron,

$$\hat{H}_1 = -\frac{1}{8} \frac{(\mathbf{p}^2)^2}{m^3 c^2}. \quad (10.13)$$

When compared with the non-relativistic kinetic energy, $\mathbf{p}^2/2m$, one can see that the perturbation is smaller by a factor of $p^2/m^2 c^2 = v^2/c^2 \simeq (Z\alpha)^2$, i.e. \hat{H}_1 is only a small perturbation for small atomic number, $Z \ll 1/\alpha \simeq 137$. We can therefore make use of a perturbative analysis to estimate the scale of the correction.

In principle, the large-scale degeneracy of the hydrogen atom would demand an analysis based on the degenerate perturbation theory. However, fortunately, since the off-diagonal matrix elements vanish,⁴

$$\langle n\ell m_\ell | \hat{H}_1 | n\ell' m'_\ell \rangle = 0, \quad \text{for } \ell \neq \ell' \quad \text{or} \quad m_\ell \neq m'_\ell, \quad (10.14)$$

⁴Proof: Since $[\hat{H}_1, \hat{\mathbf{L}}^2] = 0$, $\hbar[\ell'(\ell' + 1) + \ell(\ell + 1)] \langle n\ell m_\ell | \hat{H}_1 | n\ell' m'_\ell \rangle = 0$. Similarly, since $[\hat{H}_1, \hat{L}_z] = 0$, $\hbar(m'_\ell - m_\ell) \langle n\ell m_\ell | \hat{H}_1 | n\ell' m'_\ell \rangle = 0$.

degenerate states are uncoupled and such an approach is unnecessary. Then making use of the identity, $\hat{H}_1 = -\frac{1}{2mc^2}[\hat{H}_0 - V(r)]^2$, the scale of the resulting energy shift can be obtained from first order perturbation theory,

$$\langle \hat{H}_1 \rangle_{n\ell m_\ell} \equiv \langle n\ell m_\ell | \hat{H}_1 | n\ell m_\ell \rangle = -\frac{mc^2}{2} (E_n^2 - 2E_n \langle V(r) \rangle_{n\ell} + \langle V^2(r) \rangle_{n\ell}). \quad (10.15)$$

Since the calculation of the resulting expectation values is not particularly illuminating, we refer to the literature for a detailed exposition⁵ and present here only the required identities (right). From these considerations, we obtain the following expression for the first order energy shift

$$\langle \hat{H}_1 \rangle_{n\ell m_\ell} = -\frac{mc^2}{2} \left(\frac{Z\alpha}{n} \right)^4 \left(\frac{n}{\ell + 1/2} - \frac{3}{4} \right). \quad (10.16)$$

From this term alone, we expect the degeneracy between states with different values of total angular momentum ℓ to be lifted. However, as we will see, this conclusion is a little hasty. We need to gather all terms of the same order of perturbation theory before we can reach a definite conclusion. We can, however, confirm that (as expected) the scale of the correction is of order $\langle \hat{H}_1 \rangle_{n\ell m_\ell} / E_n \sim (Z\alpha/n)^2$. We now turn to the second important class of corrections.

10.2.2 Spin-Orbit Coupling

As well as revealing the existence of an internal spin degree of freedom, Dirac’s relativistic formulation of quantum mechanics shows that there is a further relativistic correction to the Schrödinger operator which involves a coupling between the spin and orbital degrees of freedom. For a general potential $V(r)$, this spin-orbit coupling takes the form,

$$\hat{H}_2 = \frac{1}{2m^2c^2} \frac{1}{r} (\partial_r V(r)) \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}. \quad (10.17)$$

For a hydrogen-like atom, $v(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$, and

$$\hat{H}_2 = \frac{1}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^3} \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}. \quad (10.18)$$

Physically, the origin of the spin-orbit interaction can be understood from the following considerations. As the electron is moving through the electric field of the nucleus then, in its rest frame, it will experience this as a magnetic field. There will be an additional energy term in the Hamiltonian associated with the orientation of the spin magnetic moment with respect to this field. We can make an estimate of the spin-orbit interaction energy as follows: If we have a central field determined by an electrostatic potential $\phi(r)$, the corresponding electric field is given by $\mathbf{E} = -\nabla\phi(r) = -\hat{\mathbf{e}}_r(\partial_r\phi) = +\hat{\mathbf{e}}_r(\partial_rV)/e$ where in the last step we introduce the potential energy of the electron $V = -e\phi$. For an electron moving at velocity v , this translates to an effective magnetic field $\mathbf{B} = -\frac{1}{c^2} \mathbf{v} \times \mathbf{E}$. The magnetic moment of the electron associated with its spin is equal to $\boldsymbol{\mu}_s = g_s \frac{-e}{2m} \hat{\mathbf{S}} \equiv -\frac{e}{m} \hat{\mathbf{S}}$, and thus the interaction energy is given by, and thus the interaction energy is given by

$$-\boldsymbol{\mu} \cdot \mathbf{B} = -\frac{e}{mc^2} \mathbf{S} \cdot (\mathbf{v} \times \mathbf{E}) = -\frac{1}{(mc)^2} \mathbf{S} \cdot (\mathbf{p} \times \mathbf{e}_r(\partial_rV)) = +\frac{1}{(mc)^2} \frac{1}{r} (\partial_rV) \mathbf{L} \cdot \mathbf{S}, \quad (10.19)$$

where we have used the relation $\mathbf{p} \times \mathbf{e}_r = \mathbf{p} \times \frac{\mathbf{r}}{r} = -\frac{\mathbf{L}}{r}$. In fact this isn't quite correct; there is a relativistic effect connected with the precession of axes under rotation, called **Thomas precession** which multiplies the formula by a further factor of $1/2$.

Once again, we can estimate the effect of spin-orbit coupling by treating \hat{H}_2 as a perturbation. In the absence of spin-orbit interaction, one may express the eigenstates of hydrogen-like atoms in the basis states of the mutually commuting operators, \hat{H}_0 , $\hat{\mathbf{L}}^2$, \hat{L}_z , $\hat{\mathbf{S}}^2$, and \hat{S}_z . However, in the presence of spin-orbit coupling, the total Hamiltonian no longer commutes with \hat{L}_z or \hat{S}_z . It is therefore helpful to make use of the degeneracy of the unperturbed Hamiltonian to switch to a new basis in which the angular momentum components of the perturbed system are diagonal. This can be achieved by turning to the basis of eigenstates of the operators, \hat{H}_0 , $\hat{\mathbf{J}}^2$, \hat{J}_z , $\hat{\mathbf{L}}^2$, and $\hat{\mathbf{S}}^2$, where $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ denotes the total angular momentum. (For a discussion of the form of these basis states, we refer back to Chapters 4 and 5.)

Making use of the relation, $\hat{\mathbf{J}}^2 = \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$, in this basis, it follows that,

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2). \quad (10.20)$$

Combining the spin and angular momentum, the total angular momentum takes values $j = \ell \pm 1/2$. The corresponding basis states $|j = \ell \pm 1/2, m_j, \ell\rangle$ (with $s = 1/2$ implicit) therefore diagonalise the operator,

$$\hat{\mathbf{S}} \cdot \hat{\mathbf{L}} |j = \ell \pm 1/2, m_j, \ell\rangle = \frac{\hbar^2}{2} \begin{Bmatrix} \ell \\ -1 - \ell \end{Bmatrix} |\ell \pm 1/2, m_j, \ell\rangle, \quad (10.21)$$

where the curly brackets index $j = \ell + 1/2$ (top) and $j = \ell - 1/2$ (bottom). As for the radial dependence of the perturbation, once again, the off-diagonal matrix elements vanish circumventing the need to invoke degenerate perturbation theory. As a result, at first order in perturbation theory, one obtains

$$\langle \hat{H}_2 \rangle_{n,j=\ell \pm 1/2, m_j, \ell} = \frac{1}{2m^2c^2} \frac{\hbar^2}{2} \begin{Bmatrix} \ell \\ -1 - \ell \end{Bmatrix} \frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r^3} \right\rangle_{n\ell}. \quad (10.22)$$

Then making use of the identity

$$\left\langle \frac{1}{r^3} \right\rangle_{n\ell} = \left(\frac{m\alpha Z}{\hbar n} \right)^3 \frac{1}{\ell(\ell + \frac{1}{2})(\ell + 1)}, \quad (10.23)$$

one obtains

$$\langle \hat{H}_2 \rangle_{n,j=\ell \pm 1/2, m_j, \ell} = \frac{1}{4} mc^2 \left(\frac{Z\alpha}{n} \right)^4 \frac{n}{j + 1/2} \begin{Bmatrix} \frac{1}{j} \\ -\frac{1}{j+1} \end{Bmatrix}. \quad (10.24)$$

Note that, for $\ell = 0$, there is no orbital angular momentum with which to couple! Then, if we rewrite the expression for $\langle \hat{H}_1 \rangle$ (10.16) in the new basis,

$$\langle \hat{H}_1 \rangle_{n,j=\ell \pm 1/2, m_j, \ell} = -\frac{1}{2} mc^2 \left(\frac{Z\alpha}{n} \right)^4 \begin{Bmatrix} \frac{n}{j} - \frac{3}{4} \\ -\frac{n}{j+1} - \frac{3}{4} \end{Bmatrix}, \quad (10.25)$$

and combining both of these expressions, for $\ell > 0$, we obtain

$$\langle \hat{H}_1 + \hat{H}_2 \rangle_{n,j=\ell \pm 1/2, m_j, \ell} = \frac{1}{2} mc^2 \left(\frac{Z\alpha}{n} \right)^4 \left(\frac{3}{4} - \frac{n}{j + 1/2} \right), \quad (10.26)$$

while for $\ell = 0$, we retain just the kinetic energy term (10.16).

10.2.2.1 The Zeeman Effect Revisited

Our theory of the Zeeman effect in Section 10.1.1 was based on the effect of a uniform magnetic field as a perturbation to the *non-relativistic* Hamiltonian \hat{H}_0 . How are these conclusions affected by the additional physics from spin-orbit coupling?

We showed that the effect of a magnetic field $\mathbf{B} = B\mathbf{z}$ on a one-electron atom is to produce an additional term

$$\hat{H}_{\text{Zeeman}} = \frac{eB}{2m}(\hat{L}_z + g\hat{S}_z). \quad (10.27)$$

This denotes the Zeeman energy associated with the coupling of the spin and orbital angular momentum degrees of freedom to the magnetic field. Depending on the scale of the magnetic field, the Zeeman term \hat{H}_{Zeeman} or the spin-orbit term \hat{H}_2 may dominate the spectrum of the atom.

We have just seen that, to leading order, the relativistic corrections lead to a fine-structure energy shift of

$$\Delta E_{n,j}^{\text{rel.}} = \frac{1}{2}mc^2 \left(\frac{Z\alpha}{n} \right)^4 \left(\frac{3}{4} - \frac{n}{j+1/2} \right), \quad (10.28)$$

for states $|n, j = \ell \pm 1/2, m_j, \ell\rangle$. For weak magnetic fields, we can treat the Zeeman energy as a perturbation to this spectrum. Here, although states with common j values are degenerate, the two spatial wavefunctions have different parities, since they have orbital angular momenta ($\ell = j - 1/2$ or $\ell = j + 1/2$) that differ by 1. (For example, for a given shell, with $n \geq 1$, a $j = 1/2$ state can be formed either from the $\ell = 0$ orbital or from the $\ell = 1$ orbital.) As a consequence of the differing parities of the spatial wavefunctions, the off-diagonal matrix element of \hat{H}_{Zeeman} coupling these states vanishes. We may therefore avoid using degenerate perturbation theory. Making use of the relation,

$$\langle n, j = \ell \pm 1/2, m_j, \ell | \hat{S}_z | n, j = \ell \pm 1/2, m_j, \ell \rangle = \pm \frac{\hbar m_j}{2\ell + 1}, \quad (10.29)$$

we obtain the following expression for the first order energy shift,

$$\Delta E_{j=\ell \pm 1/2, m_j, \ell}^{\text{Zeeman}} = \mu_B B m_j \left(1 \pm \frac{1}{2\ell + 1} \right), \quad (10.30)$$

where μ_B denotes the Bohr magneton. Therefore, we see that all degenerate levels are split due to the magnetic field. In contrast to the “normal” Zeeman effect, the magnitude of the splitting depends on ℓ .

If the **field is strong**, the Zeeman energy becomes large in comparison with the spin-orbit contribution. In this case, we must work with the basis states $|n, \ell, m_\ell, m_s\rangle = |n, \ell, m_\ell\rangle \otimes |m_s\rangle$ in which both \hat{H}_0 and \hat{H}_{Zeeman} are diagonal. Within first order of perturbation theory, one then finds that

$$\Delta E_{n, \ell, m_\ell, m_s} = \mu_B (m_\ell + m_s) + \frac{1}{2} \left(\frac{Z\alpha}{n} \right)^4 \left(\frac{3}{4} - \frac{n}{\ell + 1/2} - \frac{nm_\ell m_s}{\ell(\ell + 1/2)(\ell + 1)} \right), \quad (10.31)$$

the first term arising from the Zeeman energy and the remaining terms from $\hat{H}^{\text{rel.}}$. At intermediate values of the field, we have to apply degenerate perturbation theory to the states involving the linear combination of $|n, j = \ell \pm 1/2, m_j, \ell\rangle$.

10.2.3 Darwin Term

The final contribution to the Hamiltonian from relativistic effects is known as the Darwin term and arises from the “**Zitterbewegung**” of the electron – trembling motion – which smears the effective potential felt by the electron. Such effects lead to a perturbation of the form,

$$\hat{H}_3 = \frac{\hbar^2}{8m^2c^2} \nabla^2 V = \frac{\hbar^2}{8m^2c^2} \left(\frac{e}{\epsilon_0} Q_{\text{nuclear}}(\mathbf{r}) \right) = \frac{Ze^2}{4\pi\epsilon_0} \frac{\hbar^2}{8(mc)^2} 4\pi\delta^{(3)}(\mathbf{r}), \quad (10.32)$$

where $Q_{\text{nuclear}}(\mathbf{r}) = Ze\delta^{(3)}(\mathbf{r})$ denotes the nuclear charge density. Since the perturbation acts only at the origin, it affects only states with $\ell = 0$. As a result, one finds that

$$\langle \hat{H}_3 \rangle_{njm_j\ell} = \frac{Ze^2}{4\pi\epsilon_0} \frac{\hbar^2}{8(mc)^2} 4\pi |\psi_{\ell n}(0)|^2 = \frac{1}{2} mc^2 \left(\frac{Z\alpha}{n} \right)^4 n \delta_{\ell,0}. \quad (10.33)$$

Intriguingly, this term is formally identical to that which would be obtained from $\langle \hat{H}_2 \rangle$ at $\ell = 0$. As a result, combining all three contributions, the total energy shift is given simply by

$$\Delta E_{n,j=\ell\pm 1/2,m_\ell,\ell} = \frac{1}{2} mc^2 \left(\frac{Z\alpha}{n} \right)^4 \left(\frac{3}{4} - \frac{n}{j+1/2} \right), \quad (10.34)$$

a result that is independent of ℓ and m_j .

To discuss the predicted energy shifts for particular states, it is helpful to introduce some nomenclature from atomic physics. For a state with principal quantum number n , total spin s , orbital angular momentum ℓ , and total angular momentum j , one may use **spectroscopic notation** $n^{2s+1}L_j$ to define the state. For a hydrogen-like atom, with just a single electron, $2s+1=2$. In this case, the factor $2s+1$ is often just dropped for brevity.

If we apply our perturbative expression for the relativistic corrections (10.34), how do we expect the levels to shift for hydrogen-like atoms? As we have seen, for the non-relativistic Hamiltonian, each state of given n exhibits a $2n^2$ -fold degeneracy. For a given multiplet specified by n , the relativistic corrections depend only on j and n . For $n=1$, we have $\ell=0$ and $j=1/2$: Both $1S_{1/2}$ states, with $m_j=1/2$ and $-1/2$, experience a negative energy shift by an amount $\Delta E_{1,1/2,m_j,0} = -\frac{1}{4}Z^4\alpha^2\text{Ry}$. For $n=2$, ℓ can take the values of 0 or 1. With $j=1/2$, both the former $2S_{1/2}$ state, and the latter $2P_{1/2}$ states share the same negative shift in energy, $\Delta E_{2,1/2,m_j,0} = \Delta E_{2,1/2,m_j,1} = -\frac{5}{64}Z^4\alpha^2\text{Ry}$, while the $2P_{3/2}$ experiences a shift of $\Delta E_{2,3/2,m_j,1} = -\frac{1}{64}Z^4\alpha^2\text{Ry}$. Finally, for $n=3$, ℓ can take values of 0, 1 or 2. Here, the pairs of states $3S_{1/2}$ and $3P_{1/2}$, and $3P_{3/2}$ and $3D_{3/2}$ each remain degenerate while the state $3D_{5/2}$ is unique. These predicted shifts are summarized in Figure ??.

This completes our discussion of the relativistic corrections which develop from the treatment of the Dirac theory for the hydrogen atom. However, this does not complete our description of the “real” hydrogen atom. Indeed, there are further corrections which derive from quantum electrodynamics and nuclear effects which we now turn to address.

10.2.4 Lamb Shift

According to the perturbation theory above, the relativistic corrections which follow from the Dirac theory for hydrogen leave the $2S_{1/2}$ and $2P_{1/2}$ states degenerate. However, in 1947, a careful experimental study by Willis Lamb and Robert Retherford discovered that this was not in fact the case: $2P_{1/2}$ state is slightly lower in energy than the $2S_{1/2}$ state resulting in a small shift of the corresponding spectral line – the Lamb shift. It might seem that such a tiny effect would be deemed insignificant, but in this case, the observed shift (which was explained by Hans Bethe in the same year) provided considerable insight into quantum electrodynamics.

In quantum electrodynamics, a quantised radiation field has a zero-point energy equivalent to the mean-square electric field so that even in a vacuum there are fluctuations. These fluctuations cause an electron to execute an oscillatory motion and its charge is therefore smeared. If the electron is bound by a non-uniform electric field (as in hydrogen), it experiences a different potential from that appropriate to its mean position. Hence the atomic levels are shifted. In hydrogen-like atoms, the smearing occurs over a length scale,

$$\langle (\delta \mathbf{r})^2 \rangle \simeq \frac{2\alpha}{\pi} \left(\frac{\hbar}{mc} \right)^2 \ln \left(\frac{1}{\alpha Z} \right), \quad (10.35)$$

some five orders of magnitude smaller than the Bohr radius. This causes the electron spin g -factor to be slightly different from 2,

$$g_s = 2 \left(1 + \frac{\alpha}{2\pi} - 0.328 \frac{\alpha^2}{\pi^2} + \dots \right). \quad (10.36)$$

There is also a slight weakening of the force on the electron when it is very close to the nucleus, causing the $2S_{1/2}$ electron (which has penetrated all the way to the nucleus) to be slightly higher in energy than the $2P_{1/2}$ electron. Taking into account these corrections, one obtains a positive energy shift

$$\Delta E_{\text{Lamb}} \simeq \left(\frac{Z}{n} \right)^4 n \alpha^2 \text{Ry} \times \left(\frac{8}{3\pi} \alpha \ln \left(\frac{1}{\alpha Z} \right) \right) \delta_{\ell,0}, \quad (10.37)$$

for states with $\ell = 0$.

10.2.5 Hyperfine Structure

So far, we have considered the nucleus as simply a massive point charge responsible for the large electrostatic interaction with the charged electrons which surround it. However, the nucleus has a spin angular momentum which is associated with a further set of **hyperfine corrections** to the atomic spectra of atoms. As with electrons, the protons and neutrons that make up a nucleus are fermions, each with intrinsic spin $1/2$. This means that a nucleus will have some total nuclear spin which is labelled by the quantum number, I . The latter leads to a nuclear magnetic moment,

$$\boldsymbol{\mu}_N = g_N \frac{Ze}{2M_N} \mathbf{I}, \quad (10.38)$$

where M_N denotes the mass of the nucleus, and g_N denotes the nuclear g -factor. Since the nucleus has internal structure, the nuclear g -factor is not simply 2 as it (nearly) is for the electron. For the proton, the sole nuclear constituent of atomic hydrogen, $g_P \approx 5.56$. Even though the neutron is charge neutral, its g -factor is about -3.83 . (The constituent quarks have g -factors of 2 (plus corrections) like the electron but the problem is complicated by the strong interactions which make it hard to define a quark's mass.) We can compute (to some accuracy) the g -factor of nuclei from that of protons and neutrons as we can compute the proton's g -factor from its quark constituents. Since the nuclear mass is several orders of magnitude higher than that of the electron, the nuclear magnetic moment provides only a small perturbation.

According to classical electromagnetism, the magnetic moment generates a magnetic field

$$\mathbf{B} = \frac{\mu_0}{4\pi r^3} (3(\boldsymbol{\mu}_N \cdot \mathbf{e}_r)\mathbf{e}_r - \boldsymbol{\mu}_N) + \frac{2\mu_0}{3} \boldsymbol{\mu}_N \delta^{(3)}(\mathbf{r}). \quad (10.39)$$

To explore the effect of this field, let us consider just the s-electrons, i.e. $\ell = 0$, for simplicity. In this case, the interaction of the magnetic moment of the electrons with the field generated by the nucleus, gives rise to the hyperfine interaction,

$$\hat{H}_{hyp} = -\boldsymbol{\mu}_e \cdot \mathbf{B} = \frac{e}{m} \hat{\mathbf{S}} \cdot \mathbf{B}. \quad (10.40)$$

For the $\ell = 0$ state, the first contribution to \mathbf{B} vanishes while second leads to the first order correction,

$$\langle \hat{H}_{hyp} \rangle_{n,1/2,0} = \left(\frac{Z}{n} \right)^4 n \alpha^2 \text{Ry} \times \frac{8}{3} g_N \frac{m}{M_N} \frac{1}{\hbar^2} \hat{\mathbf{S}} \cdot \mathbf{I}. \quad (10.41)$$

Once again, to evaluate the expectation values on the spin degrees of freedom, it is convenient to define the total spin $\mathbf{F} = \mathbf{I} + \mathbf{S}$. We then have

$$\begin{aligned} \frac{1}{\hbar^2} \hat{\mathbf{S}} \cdot \mathbf{I} &= \frac{1}{2\hbar^2} (\mathbf{F}^2 - \mathbf{S}^2 - \mathbf{I}^2) = \frac{1}{2} (F(F+1) - 3/4 - I(I+1)) \\ &= \frac{1}{2} \begin{cases} I & F = I + 1/2 \\ -I - 1 & F = I - 1/2 \end{cases} \end{aligned} \quad (10.42)$$

Therefore, the $1s$ state of Hydrogen is split into two, corresponding to the two possible values $F = 0$ and 1 . The transition between these two levels has frequency 1420MHz , or wavelength 21cm , so lies in the radio waveband. It is an important transition for radio astronomy. A further contribution to the hyperfine structure arises if the **nuclear shape** is not spherical thus distorting the Coulomb potential; this occurs for deuterium and for many other nuclei.

Finally, before leaving this section, we should note that the nucleus is not point-like but has a small size. The effect of **finite nuclear size** can be estimated perturbatively. In doing so, one finds that the s ($\ell = 0$) levels are those most affected, because these have the largest probability of finding the electron close to the nucleus; but the effect is still very small in hydrogen. It can be significant, however, in atoms of high nuclear charge Z , or for **muonic** atoms. A muon is a particle somewhat like an electron, but about 200 times heavier. If a muon is captured by an atom, the corresponding Bohr radius is 200 times smaller, thus enhancing the nuclear size effect.

This completes our discussion of the “one-electron” theory. We now turn to consider the properties of multi-electron atoms.

10.3 Multi-Electron Atoms

To address the electronic structure of a multi-electron atom, we might begin with the hydrogenic energy levels for an atom of nuclear charge Z , and start filling the lowest levels with electrons, accounting for the exclusion principle. The degeneracy for quantum numbers (n, ℓ) is $2 \times (2\ell + 1)$, where $(2\ell + 1)$ is the number of available m_ℓ values, and the factor of 2 accounts for the spin degeneracy. Hence, the number of electrons accommodated in shell, n , would be $2 \times n^2$,

n	ℓ	Degeneracy in shell	Cumulative Total
1	0	2	2
2	0, 1	$(1 + 3) \times 2 = 8$	10
3	0, 1, 2	$(1 + 3 + 5) \times 2 = 18$	28
4	0, 1, 2, 3	$(1 + 3 + 5 + 7) \times 2 = 32$	60

Table 10.2: The number of electrons accommodated due to degeneracy in shell n .

We would therefore expect that atoms containing 2, 10, 28 or 60 electrons would be especially stable, and that in atoms containing one more electron than this, the outermost electron would be less tightly bound. In fact, if we look at data ?? recording the first ionisation energy of atoms, i.e. the minimum energy needed to remove one electron, we find that the noble gases, having $Z = 2, 10, 18, 36, \dots$ are especially tightly bound, and the elements containing one more electron, the alkali metals, are significantly less tightly bound.

The reason for the failure of this simple-minded approach is that we have neglected the repulsion between electrons. In fact, the first ionisation energies of atoms show a relatively weak dependence on Z ; this tells us that the outermost electrons are almost completely shielded from the nuclear charge.⁵ Indeed, when we treated the Helium atom as an example of the variational method in section 7.3.0.2 we found that the effect of electron-electron repulsion was sizeable, and really too large to be treated accurately by perturbation theory.

10.3.1 Central Field Approximation

Leaving aside for now the influence of spin or relativistic effects, the Hamiltonian for a multi-electron atom can be written as

$$\hat{H} = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} \right] + \sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}}, \quad (10.43)$$

⁵In fact, the shielding is not completely perfect. For a given energy shell, the effective nuclear charge varies for an atomic number Z as $Z_{\text{eff}} \sim (1 + \alpha)^Z$ where $\alpha > 0$ characterises the ineffectiveness of screening. This implies that the ionization energy $I_Z = -E_Z \sim Z_{\text{eff}}^2 \sim (1 + 2\alpha Z)$. The near-linear dependence of I_Z on Z is reflected in ??

where $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$. The first term represents the “single-particle” contribution to the Hamiltonian arising from interaction of each electron with the nucleus, while the last term represents the mutual Coulomb interaction between the constituent electrons. It is this latter term that makes the generic problem “many-body” in character and therefore very complicated. Yet, as we have already seen in the perturbative analysis of the excited states of atomic Helium, this term can have important physical consequences both on the overall energy of the problem and on the associated spin structure of the states.

The **central field approximation** is based upon the observation that the electron interaction term contains a large central (spherically symmetric) component arising from the “core electrons”. From the following relation,

$$\sum_{m_\ell=-\ell}^{\ell} |Y_{\ell m_\ell}(\theta, \phi)|^2 = \text{const.} \quad (10.44)$$

it is apparent that a closed shell has an electron density distribution which is isotropic (independent of θ and ϕ). We can therefore develop a perturbative scheme by setting $\hat{H} = \hat{H}_0 + \hat{H}_1$, where

$$\hat{H}_0 = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} + U_i(r_i) \right], \quad \hat{H}_1 = \sum_{i<j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r_i). \quad (10.45)$$

Here the one-electron potential, $U_i(r)$, which is assumed central (see below), incorporates the “average” effect of the other electrons. Before discussing how to choose the potentials $U_i(r)$, let us note that \hat{H}_0 is separable into a sum of terms for each electron, so that the total wavefunction can be factorised into components for each electron. The basic idea is first to solve the Schrödinger equation using \hat{H}_0 , and then to treat \hat{H}_1 as a small perturbation.

On general grounds, since the Hamiltonian \hat{H}_0 continues to commute with the angular momentum operator, $[\hat{H}_0, \hat{\mathbf{L}}] = 0$, we can see that the eigenfunctions of \hat{H}_0 will be characterised by quantum numbers (n, ℓ, m_ℓ, m_s) . However, since the effective potential is no longer Coulomb-like, the ℓ values for a given n need not be degenerate. Of course, the difficult part of this procedure is to estimate $U_i(r)$; the potential energy experienced by each electron depends on the wavefunction of all the other electrons, which is only known after the Schrödinger equation has been solved. This suggests that an iterative approach to solving the problem will be required.

To understand how the potentials $U_i(r)$ can be estimated – the **self-consistent field method** – it is instructive to consider a variational approach due originally to Hartree. If electrons are considered independent, the wavefunction can be factorised into the product state,

$$\Psi(\{\mathbf{r}_i\}) = \psi_{i_1}(\mathbf{r}_1) \psi_{i_2}(\mathbf{r}_2) \cdots \psi_{i_N}(\mathbf{r}_N), \quad (10.46)$$

where the quantum numbers, $i_k \equiv (n\ell m_\ell m_s)_k$, indicate the individual state occupancies. Note that this product state is not a properly antisymmetrised Slater determinant – the exclusion principle is taken into account only in so far as the energy of the ground state is taken to be the lowest that is consistent with the assignment of different quantum numbers, $n\ell m_\ell m_s$ to each electron. Nevertheless, using this wavefunction as a trial state,

the variational energy is then given by

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_i \int d^3r \psi_i^* \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right) \psi_i + \frac{1}{4\pi\epsilon_0} \sum_{i < j} \int d^3r \int d^3r' \psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_j(\mathbf{r}') \psi_i(\mathbf{r}). \quad (10.47)$$

Now, according to the variational principle, we must minimise the energy functional by varying $E[\psi_i]$ with respect to the complex wavefunction, ψ_i , subject to the normalisation condition, $\langle \psi | \psi \rangle = 1$. The latter can be imposed using a set of Lagrange multipliers, ε_i , i.e.

$$\frac{\delta}{\delta \psi_i^*} \left[E - \varepsilon_i \left(\int d^3r |\psi_i(\mathbf{r})|^2 - 1 \right) \right] = 0. \quad (10.48)$$

Following the variation,⁶ one obtains the **Hartree equations**,

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right) \psi_i + \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3r' |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (10.49)$$

Then according to the variational principle, amongst all possible trial functions ψ_i , the set that minimises the energy are determined by the effective potential,

$$U_i(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3r' |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (10.50)$$

Eq. (10.49) has a simple interpretation: The first two terms relate to the nuclear potential experienced by the individual electrons, while the third term represents the electrostatic potential due to the other electrons. However, to simplify the procedure, it is useful to engineer the radial symmetry of the potential by replacing $U_i(\mathbf{r})$ by its spherical average,

$$U_i(\mathbf{r}) \mapsto U_i(r) = \int \frac{d\Omega}{4\pi} U_i(\mathbf{r}). \quad (10.51)$$

Finally, to relate the Lagrange multipliers, ε_i (which have the appearance of one-electron energies), to the total energy, we can multiply Eq. (10.49) by $\psi_i^*(\mathbf{r})$ and integrate,

$$\varepsilon_i = \int d^3r \psi_i^* \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right) \psi_i + \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3r' \int d^3r |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\psi_i(\mathbf{r})|^2. \quad (10.52)$$

If we compare this expression with the variational state energy, we find that

$$E = \sum_i \varepsilon_i - \sum_{i < j} \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3r' \int d^3r |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\psi_i(\mathbf{r})|^2. \quad (10.53)$$

To summarise, if we wish to implement the central field approximation to determine the states of a multi-electron atom, we must follow the algorithm:

⁶Note that, in applying the variation, the wavefunction ψ_i^* can be considered independent of ψ_i

1. Firstly, one makes an initial “guess” for a (common) central potential, $U(r)$. As $r \rightarrow 0$, screening becomes increasingly ineffective and we expect $U(r) \rightarrow 0$. As $r \rightarrow \infty$, we anticipate that $U(r) \rightarrow \frac{1}{4\pi\epsilon_0} \frac{(Z-1)e^2}{r}$, corresponding to perfect screening. So, as a starting point, we make take some smooth function $U(r)$ interpolating between these limits. For this trial potential, we can solve (numerically) for the eigenstates of the single-particle Hamiltonian. We can then use these states as a platform to build the product wavefunction and in turn determine the self-consistent potentials, $U_i(r)$.
2. With these potentials, $U_i(r)$, we can determine a new set of eigenstates for the set of Schrödinger equations,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} + U_i(r) \right] \psi_i = \varepsilon_i \psi_i. \quad (10.54)$$

3. An estimate for the ground state energy of an atom can be found by filling up the energy levels, starting from the lowest, and taking account of the exclusion principle.
4. Using these wavefunctions, one can then make an improved estimate of the potentials $U_i(r_i)$ and return to step 2 iterating until convergence.

An improvement to this procedure, known the **Hartree-Fock** method, takes account of exchange interactions. In order to do this, it is necessary to ensure that the wavefunction, including spin, is antisymmetric under interchange of any pair of electrons. This is achieved by introducing the **Slater determinant**. Writing the individual electron wavefunction for the i th electron as $\psi_k(r_i)$, where $i = 1, 2, \dots, N$ and k is shorthand for the set of quantum numbers $(n\ell m_\ell m_s)$, the overall wavefunction is given by

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \psi_1(\mathbf{r}_3) & \cdots \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \psi_2(\mathbf{r}_3) & \cdots \\ \psi_3(\mathbf{r}_1) & \psi_3(\mathbf{r}_2) & \psi_3(\mathbf{r}_3) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix}. \quad (10.55)$$

Note that each of the $N!$ terms in Ψ is a product of wavefunctions for each individual electron. The $1/\sqrt{N!}$ factor ensures the wavefunction is normalised. A determinant changes sign if any two columns are exchanged, corresponding to $\mathbf{r}_i \leftrightarrow \mathbf{r}_j$ (say); this ensures that the wavefunction is antisymmetric under exchange of electrons i and j . Likewise, a determinant is zero if any two rows are identical; hence all the ψ_k s must be different and the Pauli exclusion principle is satisfied.⁷ In this approximation, a variational analysis leads to the Hartree-Fock equations,

$$\begin{aligned} \varepsilon_i \psi_i(\mathbf{r}) = & \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} \right] \\ & + \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3r_j \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_j^*(\mathbf{r}') \left[\psi_j(\mathbf{r}') \psi_i(\mathbf{r}) - \psi_j(\mathbf{r}) \psi_i(\mathbf{r}') \delta_{m_{s_i}, m_{s_j}} \right]. \end{aligned} \quad (10.56)$$

⁷Note that for $N = 2$, the determinant reduces to the familiar antisymmetric wavefunction, $1/\sqrt{2}[\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)]$.

The first term in the last set of brackets translates to the ordinary Hartree contribution above and describes the influence of the charge density of the other electrons, while the second term describes the non-local **exchange** contribution, a manifestation of particle statistics.

The outcome of such calculations is that the eigenfunctions are, as for hydrogen, characterised by quantum numbers n, ℓ, m_ℓ , with $\ell < n$, but that the states with different ℓ for a given n are not degenerate, with the lower values of ℓ lying lower. This is because, for the higher ℓ values, the electrons tend to lie further from the nucleus on average, and are therefore more effectively screened. The states corresponding to a particular value of n are generally referred to as a **shell**, and those belonging to a particular pair of values of n, ℓ are usually referred to as a **subshell**. The energy levels are ordered as in Table 10.3 below (with the lowest lying on the left):

Subshell name	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	...
$n =$	1	2	2	3	3	4	3	4	5	4	...
$\ell =$	0	0	1	0	1	0	2	1	0	2	...
Degeneracy	2	2	6	2	6	2	10	6	2	10	...
Cumulative	2	4	10	12	18	20	30	36	38	48	...

Table 10.3: Ordering of Hydrogen orbitals for each shell n , where ℓ denotes the subshell.

Note that the values of Z corresponding to the noble gases, 2, 10, 18, 36, at which the ionisation energy is unusually high, now emerge naturally from this filling order, corresponding to the numbers of electrons just before a new shell (n) is entered. There is a handy mnemonic to remember this filling order. By writing the subshells down as shown in figure ??, the order of states can be read off along diagonals from lower right to upper left, starting at the bottom.

We can use this sequence of energy levels to predict the ground state electron configuration of atoms. We simply fill up the levels starting from the lowest, accounting for the exclusion principle, until the electrons are all accommodated (the **aufbau principle**). A few examples are contained in table 10.4. Since it is generally the outermost electrons

Z	Element	Configuration	$^{2S+1}L_J$	Ionis. Pot. (eV)
1	H	(1s)	$^2S_{1/2}$	13.6
2	He	(1s) ²	1S_0	24.6
3	Li	He (2s)	$^2S_{1/2}$	5.4
4	Be	He (2s) ²	1S_0	9.3
5	B	He (2s) ² (2p)	$^2P_{1/2}$	8.3
6	C	He (2s) ² (2p) ²	3P_0	11.3
7	N	He (2s) ² (2p) ³	$^4S_{3/2}$	14.5
8	O	He (2s) ² (2p) ⁴	3P_2	13.6
9	F	He (2s) ² (2p) ⁵	$^2P_{3/2}$	17.4
10	Ne	He (2s) ² (2p) ⁶	1S_0	21.6
11	Na	Ne (3s)	$^2S_{1/2}$	5.1

Table 10.4: Electronic subshell configuration, according to the aufbau principle.

which are of most interest, contributing to chemical activity or optical spectra, one often omits the inner closed shells, and just writes O as $(2p)^4$, for example. However, the configuration is not always correctly predicted, especially in the heavier elements, where levels may be close together. It may be favourable to promote one or even two electrons one level above that expected in this simple picture, in order to achieve a filled shell. For example, Cu ($Z = 29$) would be expected to have configuration $\cdots(4s)^2(3d)^9$, and actually has configuration $\cdots(4s)^1(3d)^{10}$. There are several similar examples in the transition elements where the d subshells are being filled, and many among the lanthanides (rare earths) and actinides where f subshells are being filled.

Since the assignment of an electron configuration requires only the enumeration of the values of n and ℓ for all electrons, but not those of m_ℓ and m_s , each configuration will be accompanied by a **degeneracy** g . If $\nu_{n\ell}$ denotes the number of electrons occupying a given level $E_{n,\ell}$, and $\delta_\ell = 2 \times (2\ell + 1)$ is the degeneracy of that level, there are

$$d_{n\ell} = \frac{\delta_\ell!}{\nu_{n\ell}!(\delta_\ell - \nu_{n\ell})!} \quad (10.57)$$

ways of distributing the $\nu_{n\ell}$ electrons among the δ_ℓ individual states. The total degeneracy, g , is then obtained from the product.

This scheme provides a basis to understand the periodic table of elements. We would expect that elements which have similar electron configurations in their outermost shells (such as Li, Na, K, Rb, Cs, Fr which all have $(ns)^1$ or F, Cl, Br, I, which all have $(np)^5$) would have similar chemical properties, such as valency, since it is the unpaired outer electrons which especially participate in chemical bonding. Therefore, if one arranges the atoms in order of increasing atomic number Z (which equals the number of electrons in the atom), periodic behaviour is seen whenever a new subshell of a given ℓ is filled.

10.3.2 Spin-Orbit Coupling

The procedure outlined above allows us to predict the occupation of subshells in an atomic ground state. This is not in general sufficient to specify the ground state fully. If there are several electrons in a partially filled subshell, then their spins and orbital angular momenta can combine in several different ways, to give different values of total angular momentum, with different energies. In order to deal with this problem, it is necessary to consider the spin-orbit interaction as well as the residual Coulomb interaction between the outer electrons.

Schematically we can write the Hamiltonian for this system as follows:

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r_i)}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}, \quad (10.58)$$

where \hat{H}_0 includes the kinetic energy and central field terms, \hat{H}_1 is the residual Coulomb interaction, and (with $\xi_i(r) = \frac{1}{2m^2c^2} \frac{1}{r} (\partial_r V(r))$) \hat{H}_2 is the spin-orbit interaction. We can then consider two possible scenarios:

- $\hat{H}_2 \ll \hat{H}_1$: This tends to apply in the case of light atoms. In this situation, one considers first the eigenstates of $\hat{H}_0 + \hat{H}_1$, and then treats \hat{H}_2 as a perturbation. This leads to a scheme called **LS** (or **Russell-Saunders**) **coupling**.
- $\hat{H}_2 \gg \hat{H}_1$: This can apply in very heavy atoms, or in heavily ionised light atoms, in which the electrons are moving at higher velocities and relativistic effects such as the spin-orbit interaction are more important. In this case, a scheme called *jj* coupling applies.

It is important to emphasise that both of these scenarios represent approximations; real atoms do not always conform to the comparatively simple picture which emerges from these schemes.

10.3.2.1 LS Coupling Scheme

In this approximation, we start by considering the eigenstates of $\hat{H}_0 + \hat{H}_1$. We note that this Hamiltonian must commute with the total angular momentum $\hat{\mathbf{J}}^2$ (because of invariance under rotations in space), and also clearly commutes with the total spin $\hat{\mathbf{S}}^2$. It also commutes with the total orbital angular momentum $\hat{\mathbf{L}}^2$, since \hat{H}_1 only involves internal interactions, and must therefore be invariant under global rotation of all the electrons. Therefore the energy levels can be characterised by the corresponding total angular momentum quantum numbers L, S, J . Their ordering in energy is given by Hund's rules:

1. Combine the spins of the electrons to obtain possible values of total spin S . The largest permitted value of S lies lowest in energy.
2. For this value of S , find the possible values of total angular momentum L . The largest value of L lies lowest in energy.
3. Couple the values of L and S to obtain the values of J (hence the name of the scheme). If the subshell is less than half full, the smallest value of J lies lowest; otherwise, the largest value of J lies lowest.

In deciding on the permitted values of L and S , in addition to applying the usual rules for adding angular momenta, one also has to ensure that the exclusion principle is respected, as we will see later when considering some examples.

These rules are empirical; there are exceptions, especially to the L and J rules (2 and 3). Nevertheless, Hund's rules are a useful guide, and we should try to understand their physical origin.

1. Maximising S makes the spin wavefunction as symmetric as possible. This tends to make the spatial wavefunction antisymmetric, and hence reduces the Coulomb repulsion, as we saw when discussing the exchange interactions in Helium and the origin of itinerant ferromagnetism.

2. Maximising L also tends to keep the electrons apart. This is less obvious, though a simple classical picture of electrons rotating round the nucleus in the same or different senses makes it at least plausible.
3. The separation of energies for states of different J arises from treating the spin-orbit term \hat{H}_2 as a perturbation (fine structure). It can be shown (using the Wigner-Eckart theorem) that

$$\begin{aligned}
 \langle J, m_J, L, S | \sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}} | J, m_J, L, S \rangle \\
 = \zeta(L, S) \langle \hat{\mathbf{L}} J, m_J, L, S \cdot \hat{\mathbf{S}} \rangle \\
 = \frac{\zeta(L, S)}{2} [J(J+1) - L(L+1) - S(S+1)], \quad (10.59)
 \end{aligned}$$

where the matrix element $\zeta(L, S)$ depends on the total L and S values. Since one may show that the sign of $\zeta(L, S)$ changes according to whether the subshell is more or less than half-filled, the third Hund's rule is established.

To understand the application of LS coupling, it is best to work through some examples. Starting with the simplest multi-electron atom, helium, the ground state has an electron configuration $(1s)^2$, and must therefore have $L = S = J = 0$. In fact, for any completely filled subshell, we have $L = S = 0$ and hence $J = 0$, since the total m_L and m_S must equal zero if all substates are occupied. Consider now an excited state of helium, e.g. $(1s)^1(2p)^1$, in which one electron has been excited to the $2p$ level. We can now have $S = 1$ or $S = 0$, with the $S = 1$ state lying lower in energy according to Hund's rules. Combining the orbital angular momenta of the electrons yields $L = 1$ and thus, with $S = 0$, $J = 1$, while with $S = 1$, $J = 0, 1, 2$ with $J = 0$ lying lowest in energy.

Once again, as with the hydrogen-like states, we may index the states of multi-electron atoms by spectroscopic term notation, $^{2S+1}L_J$. The superscript $2S+1$ gives the multiplicity of J values into which the level is split by the spin-orbit interaction; the L value is represented by a capital letter, S, P, D , etc., and J is represented by its numerical value. Thus, for the $(1s)^1(2p)^1$ state of helium, there are four possible states, with terms:

$$^3P_0 \ ^3P_1 \ ^3P_2 \quad ^1P_1, \quad (10.60)$$

where the three 3P states are separated by the spin-orbit interaction, and the singlet 1P state lies much higher in energy owing to the Coulomb interaction. The separations between the 3P_2 and 3P_1 and the 3P_1 and 3P_0 should be in the ratio 2 : 1. This is an example of the **Landé interval rule**, which states that the separation between a pair of adjacent levels in a fine structure multiplet is proportional to the larger of the two J values involved. This is easily shown using Eq. (10.59) – the separation in energy between states J and $J-1$ is

$$\propto J(J+1) - (J-1)J = 2J. \quad (10.61)$$

Actually in the case of helium the situation is a bit more complicated, because it turns out that the spin-orbit interaction between *different* electrons makes a non-negligible additional contribution to the fine structure. Other excited states of helium, of the form $(1s)^1(n\ell)^1$, can be handled similarly, and again separate into singlet and triplet states.

We next consider the case of carbon, which has ground state electron configuration $(1s)^2(2s)^2(2p)^2$. This introduces a further complication; we now have two identical electrons in the same unfilled subshell, and we need to ensure that their wavefunction is antisymmetric with respect to electron exchange. The total spin can either be the singlet $S = 0$ state, which has an antisymmetric wavefunction $\frac{1}{\sqrt{2}}[|\uparrow_1\rangle \otimes |\downarrow_2\rangle - |\downarrow_1\rangle \otimes |\uparrow_2\rangle]$, or one of the triplet $S = 1$ states, which are symmetric, $\frac{1}{\sqrt{2}}[|\uparrow_1\rangle \otimes |\downarrow_2\rangle + |\downarrow_1\rangle \otimes |\uparrow_2\rangle]$, $|\uparrow_1\rangle \otimes |\uparrow_2\rangle$, or $|\downarrow_1\rangle \otimes |\downarrow_2\rangle$. We must therefore choose values of L with the appropriate symmetry to partner each value of S . To form an antisymmetric state, the two electrons must have different values of m_ℓ , so the possibilities are as shown in table 10.5. Inspecting the values of m_L we can deduce that $L = 1$.⁸ By contrast, to form a symmetric total angular momentum state, the two electrons may have any values of m_ℓ , leading to the possibilities shown in table 10.6. Inspecting the values of m_L we infer that $L = 2$ or 0 .

$m_\ell^{(1)}$	$m_\ell^{(2)}$	m_L
1	0	1
1	-1	0
0	-1	-1

Table 10.5: Possibilities of m_ℓ values for electrons to form an antisymmetric total angular momentum state.

$m_\ell^{(1)}$	$m_\ell^{(2)}$	m_L
1	1	2
1	0	1
1	-1	0
0	0	0
0	-1	-1
-1	-1	-2

Table 10.6: Possibilities of m_ℓ values for electrons to form an symmetric total angular momentum state.

We must therefore take $S = 1$ with $L = 1$ and $S = 0$ with $L = 2$ or 0 . Finally, to account for the fine structure, we note that the states with $S = 1$ and $L = 1$ can be combined into a single $J = 0$ state, three $J = 1$ states, and five $J = 2$ states leading to the terms 3P_0 , 3P_1 , and 3P_2 respectively. Similarly the $S = 0$, $L = 2$ state can be combined to give five $J = 2$ states, 1D_2 , while the $S = 0$, $L = 0$ state gives the single $J = 0$ state, 1S_0 . Altogether we recover the $1 + 3 + 5 + 5 + 1 = 15$ possible states (cf. Eq. (10.57) with the ordering in energy given by Hund's rules, shown in table 10.7. The experimental energy values are given using the conventional spectroscopic units of inverse wavelength. Note that the Landé interval rule is approximately obeyed by the fine structure triplet, and that the separation between L and S values caused by the electron-electron repulsion is *much* greater than the spin-orbit effect. In an excited state of carbon, e.g. $(2p)^1(3p)^1$, the electrons are no longer equivalent, because they have different radial wavefunctions. So now one can combine any of $S = 0, 1$ with any of $L = 0, 1, 2$, yielding the following

⁸This result would also be apparent if we recall that angular momentum states are eigenstates of the parity operator with eigenvalue $(-1)^L$. Since there are just two electrons, this result shows that both the $L = 0$ and $L = 2$ wavefunction must be symmetric under exchange.

	E/cm^{-1}
1S_0	20649
1D_2	10195
3P_2	43
3P_1	16
3P_0	0

Table 10.7: Experimental energy ordering of Carbon states using spectroscopy.

terms (in order of increasing energy, according to Hund's rules):

$$^3D_{1,2,3} \quad ^3P_{0,1,2} \quad ^3S_1 \quad ^1D_2 \quad ^1P_1 \quad ^1S_0. \quad (10.62)$$

For **nitrogen**, the electron configuration is given by $(1s)^2(2s)^2(2p)^3$. The maximal value of spin is $S = 3/2$ while L can take values 3, 2, 1 and 0. Since the spin wavefunction (being maximal) is symmetric, the spatial wavefunction must be completely antisymmetric. This demands that all three states with $m_\ell = 1, 0, -1$ must be involved. We must therefore have $L = 0$, leading to $J = 3/2$ and the term, $^4S_{3/2}$.

As a final example, let us consider the ground state of **oxygen**, which has electron configuration $(2p)^4$. Although there are four electrons in the $(2p)$ subshell, the maximum value of $S = 1$. This is because there are only three available values of $m_\ell = \pm 1, 0$, and therefore one of these must contain two electrons with opposite spins. Therefore, the maximum value of $S = 1$, achieved by having electrons with $m_s = +\frac{1}{2}$ in both the other m_ℓ states. By pursuing this argument, it is quite easy to see that the allowed values of L , S and J are the same as for carbon $(2p)^2$. This is in fact a general result – the allowed quantum numbers for a subshell with n electrons are the same as for that of a subshell with n “holes”. Therefore, the energy levels for the oxygen ground state configuration are the same as for carbon, except that the fine structure multiplet is inverted, in accordance with Hund's third rule.

10.3.3 jj Coupling Scheme

When relativistic effects take precedence over electron interaction effects, we must start by considering the eigenstates of $\hat{H}_0 + \hat{H}_2 = \hat{H}_0 + \sum_i \zeta_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i$. These must be eigenstates of $\hat{\mathbf{J}}^2$ as before, because of the overall rotational invariance, and also of $\hat{\mathbf{J}}_i^2$ for each electron. Therefore, in this case, the coupling procedure is to find the allowed j values of individual electrons, whose energies will be separated by the spin-orbit interaction. Then these individual j values are combined to find the allowed values of total J . The effect of the residual Coulomb interaction will be to split the J values for a given set of j s. Sadly, in this case, there are no simple rules to parallel those of Hund.

As an example, consider a configuration $(np)^2$ in the jj coupling scheme, to be compared with the example of carbon which we studied in the LS scheme. Combining $s = 1/2$ with $\ell = 1$, each electron can have $j = 1/2$ or $3/2$. If the electrons have the same j value, they are equivalent, so we have to take care of the symmetry of the wavefunction. We therefore have the following possibilities:

- $j_1 = j_2 = 3/2 \implies J = 3, 2, 1, 0$, of which $J = 2, 0$ are antisymmetric.
- $j_1 = j_2 = 1/2 \implies J = 1, 0$, of which $J = 0$ is antisymmetric.
- $j_1 = 1/2, j_2 = 3/2 \implies J = 2, 1$.

In jj coupling, the term is written $(j_1, j_2)_J$, so we have the following terms in our example:

$$(1/2, 1/2)_0 \quad (3/2, 1/2)_1 (3/2, 1/2)_2 \quad (3/2, 3/2)_2 (3/2, 3/2)_0 \quad (10.63)$$

in order of increasing energy. Note that both LS and jj coupling give the same values of J (in this case, two states with $J = 0$, two with $J = 2$ and one with $J = 1$) and in the same order. However, the pattern of levels is different; in LS coupling we found a triplet and two singlets, while in this ideal jj scenario, we have two doublets and a singlet. The sets of states in the two coupling schemes must be expressible as linear combinations of one another, and the physical states for a real atom are likely to differ from either approximation.

In fact, this idealized form of jj coupling is not seen in the heaviest such atom in the periodic table, lead $(6p)^2$. However, it is seen in some highly ionised states, for example in Cr^{18+} , which has the same electron configuration $(2p)^2$ as carbon, but where, because of the larger unscreened charge on the nucleus, the electrons are moving more relativistically, enhancing the spin-orbit effect. However, a classic example of the transition from LS to jj coupling is seen in the series C-Si-Ge-Sn-Pb in the excited states $(2p)(3s), (3p)(4s), \dots, (6p)(7s)$. Here, the electrons are not in the same subshell, so their wavefunctions overlap less, and the Coulomb repulsion is reduced compared to the spin-orbit interaction. Analysing this situation in the LS coupling approximation, one expects a triplet and a singlet:

$$^3P_{0,1,2} \quad ^1P_1, \quad (10.64)$$

while in the jj scheme one expects two doublets:

$$(1/2, 1/2)_{0,1} \quad (1/2, 3/2)_{2,1}. \quad (10.65)$$

Experimentally, C and Si conform to the LS expectation and Pb to the jj scheme, while Ge and Sn are intermediate.

10.3.4 Zeeman Effect

For a multi-electron atom in a weak magnetic field, the appropriate unperturbed states are given by $|J, M_J, L, S\rangle$, where J, L, S refer to the total angular momenta. To determine the Zeeman energy shift, we need to determine the matrix element of \hat{S}_z . To do so, we can make use of the following argument. Since $2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2$, this operator is diagonal in the basis of states, $|J, M_J, L, S\rangle$. Therefore, the matrix element of the operator (recall that $[\hat{S}_i, \hat{S}_j] = i\hbar\epsilon_{ijk}\hat{S}_k$ and $[\hat{L}_i, \hat{S}_k] = 0$),

$$-i\hbar\hat{\mathbf{S}} \times \hat{\mathbf{L}} \equiv \hat{\mathbf{S}}(\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}) - (\hat{\mathbf{L}} \cdot \hat{\mathbf{S}})\hat{\mathbf{S}} \quad (10.66)$$

must vanish. Moreover, from the identity $[\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{\mathbf{J}}] = 0$, it follows that the matrix element of the vector product,

$$-i\hbar(\hat{\mathbf{S}} \times \hat{\mathbf{L}}) \times \hat{\mathbf{J}} = \hat{\mathbf{S}} \times \hat{\mathbf{J}}(\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}) - (\hat{\mathbf{L}} \cdot \hat{\mathbf{S}})\hat{\mathbf{S}} \times \hat{\mathbf{J}}, \quad (10.67)$$

must also vanish. If we expand the left hand side, we thus find that the matrix element of

$$(\hat{\mathbf{S}} \times \hat{\mathbf{L}}) \times \hat{\mathbf{J}} = \hat{\mathbf{L}}(\hat{\mathbf{S}} \cdot \hat{\mathbf{J}}) - \hat{\mathbf{S}}(\hat{\mathbf{L}} \cdot \hat{\mathbf{J}}) \stackrel{\hat{\mathbf{L}}=\hat{\mathbf{J}}-\hat{\mathbf{S}}}{=} \hat{\mathbf{J}}(\hat{\mathbf{S}} \cdot \hat{\mathbf{J}}) - \hat{\mathbf{S}}\hat{\mathbf{J}}^2, \quad (10.68)$$

also vanishes. Therefore, it follows that $\langle \hat{\mathbf{S}}\hat{\mathbf{J}}^2 \rangle = \langle \hat{\mathbf{J}}(\hat{\mathbf{S}} \cdot \hat{\mathbf{J}}) \rangle$, where the expectation value is taken over the basis states. Then, with $\hat{\mathbf{S}} \cdot \hat{\mathbf{J}} = \frac{1}{2}(\hat{\mathbf{J}}^2 + \hat{\mathbf{S}}^2 - \hat{\mathbf{L}}^2)$, we have that

$$\langle \hat{S}_z \rangle = \langle \hat{J}_z \rangle \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (10.69)$$

As a result, we can deduce that, at first order in perturbation theory, the energy shift arising from the Zeeman term is given by

$$\Delta E_{J,M_J,L,S} = \mu_B g_J M_J B, \quad (10.70)$$

where

$$g_J = \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}, \quad (10.71)$$

denotes the effective **Landé g -factor**, which lies between 1 and 2. Note that, in the special case of hydrogen, where $S = 1/2$ and $J = L \pm 1/2$, we recover our previous result. The predicted Zeeman splitting for sodium is shown in figure ??.

In the **strong field limit**, where the influence of Zeeman term dominates, the appropriate basis states are set by $|L, M_L, A, M_S\rangle$, in which the operators $\hat{\mathbf{L}}^2$, \hat{L}_z , $\hat{\mathbf{S}}^2$, \hat{S}_z , and \hat{H}_{Zeeman} are diagonal. In this case, the energy splitting takes the form

$$\Delta E_{J,M_J,L,S} = \mu_B B(M_L + 2M_S) + \frac{1}{2}mc^2 \left\{ \frac{Z\alpha}{n} \right\}^4 \frac{nM_L M_S}{\ell(\ell+1/2)(\ell+1)}, \quad (10.72)$$

where the second term arises from the spin-orbit interaction.

From Molecules to Solids

In the previous section, we studied the quantum mechanics of multi-electron atoms – the subject of atomic physics. In this section, we will begin to explore how these concepts get translated into systems with many atoms, from simple molecular structures to the solid state. As with atomic physics, the subjects of molecular and solid state physics represent fields in their own right and it would fanciful to imagine that we could do more than touch on the basic principles. Nevertheless, in establishing the foundations of these subjects, we will see two things: firstly, by organising the hierarchy of approximation schemes, much can be understood about the seemingly complex quantum dynamics of many-particle systems. Secondly, we will find that constraints imposed by symmetries (such as translation) allow a simple phenomenology to emerge from complex solid state systems. We begin our discussion with the molecular system.

A molecule consists of electrons moving in the complicated potential set up by all the constituent electric charges. Even in classical mechanics, it would be extremely difficult to solve the equations of motion of the internal molecular degrees of freedom. Fortunately, for most purposes, we can treat the motion of the electrons and nuclei separately, due to their very different masses. As the forces on a nucleus are similar in magnitude to those that act on an electron, so the electrons and nuclei must have comparable momenta. Therefore the nuclei are typically moving much more slowly than the electrons. In studying the motion of the electrons, we can therefore treat the nuclei as being “nailed down” in fixed positions. Conversely, in studying the nuclear motion (vibrations and rotations of the molecule) we can assume, as a first approximation, that the electrons adjust instantly to changes in the *molecular conformation* defined by the positions of the nuclei. This picture forms the basis of the **Born-Oppenheimer approximation**.

In quantum mechanics, the wavefunction of a molecule, $\Psi(\{\mathbf{r}_n\}, \{\mathbf{R}_N\})$, is a function of the positions of all the electrons and nuclei, and the Hamiltonian has the form

$$\hat{H} = \sum_n \frac{\hat{\mathbf{p}}_n^2}{2m_e} + \sum_N \frac{\hat{\mathbf{p}}_N^2}{2m_N} + V(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}), \quad (11.1)$$

where, as usual, the momentum operators, $\hat{\mathbf{p}}_n^2$ and $\hat{\mathbf{p}}_N^2$, act only on the corresponding coordinates. Here we have labelled electrons by lower case letters $n = 1, 2, \dots$ to distinguish them from nuclei which are denoted by capitals, $N = a, b, \dots$. The statement that the electrons and nuclei have comparable momenta translates into the fact that $\nabla_n^2 \Psi$ and $\nabla_N^2 \Psi$ will be comparable. Therefore the second term in the Hamiltonian above, the sum over nuclear kinetic energies, can be neglected as a first approximation when we solve for the dependence of Ψ on the electron position vectors $\{\mathbf{r}_n\}$.

In the Born-Oppenheimer approximation, the time-independent Schrödinger equation for the electronic motion is therefore given by

$$\left[-\sum_n \frac{\hbar \nabla_n^2}{2m_e} + V(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}) \right] \psi_k(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}) = E_k(\{\mathbf{R}_N\}) \psi_k(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}), \quad (11.2)$$

where the eigenfunctions ψ_k , with $k = 0, 1, 2, \dots$, describe the electronic ground state and excited states with the nuclei nailed down at positions $\mathbf{R}_a, \mathbf{R}_b, \dots$; E_k are the corresponding energy levels. Notice that the nuclear positions appear as parameters in ψ_k and E_k . As the molecular conformation is varied by changing $\mathbf{R}_a, \mathbf{R}_b, \dots$, the ground state energy E_0 follows a curve called the molecular potential energy curve and the minimum of this curve defines the equilibrium conformation of the molecule.

11.1 The H_2^+ Ion

The simplest system that exhibits molecular properties is the hydrogen ion H_2^+ , which consists of two protons with positions $\mathbf{R}_a, \mathbf{R}_b$ and one electron at \mathbf{r} . With the potential energy

$$V(\mathbf{r}, \mathbf{R}_a, \mathbf{R}_b) = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{|\mathbf{R}_a - \mathbf{R}_b|} - \frac{1}{|\mathbf{r} - \mathbf{R}_a|} - \frac{1}{|\mathbf{r} - \mathbf{R}_b|} \right), \quad (11.3)$$

the Schrödinger equation takes the form,

$$\left[-\frac{\hbar^2 \nabla_n^2}{2m_e} + V(\mathbf{r}, \mathbf{R}_a, \mathbf{R}_b) \right] \psi(\mathbf{r}; \mathbf{R}_a, \mathbf{R}_b) = E \psi(\mathbf{r}; \mathbf{R}_a, \mathbf{R}_b). \quad (11.4)$$

Although this equation can be solved exactly using elliptical polar coordinates, it will be more instructive for our purposes to seek an approximate method of solution. Since there is no obvious parameter in which to develop a perturbative expansion, we will instead follow a variational route to explore the low energy states of system.

If the electron is close to one of the protons, one would expect the other proton to have a small influence on its dynamics, and that the wavefunction in this region would be close to that of a hydrogen atomic orbital. Therefore, in seeking the ground state of the H_2^+ ion, we may take a trial wavefunction that is a linear combination of the ground state ($1s$) wavefunctions centred on the two protons,

$$\psi(\mathbf{r}; \mathbf{R}_a, \mathbf{R}_b) = \alpha \psi_a(\mathbf{r}; \mathbf{R}_a) + \beta \psi_b(\mathbf{r}; \mathbf{R}_b), \quad (11.5)$$

where $\psi_{a,b} = (\pi a_0^3)^{-1/2} \exp[-|\mathbf{r} - \mathbf{R}_{a,b}|/a_0]$, represents the corresponding hydrogenic wavefunction with a_0 the atomic Bohr radius. In this case, the coefficients α and β can be taken as real. The variational expression to be minimised in order to estimate the ground state energy is given by

$$\langle E \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\alpha^2 H_{aa} + \beta^2 H_{bb} + 2\alpha\beta H_{ab}}{\alpha^2 + \beta^2 + 2\alpha\beta S} \quad (11.6)$$

where $H_{aa} = \langle \psi_a | \hat{H} | \psi_a \rangle = H_{bb} = \langle \psi_b | \hat{H} | \psi_b \rangle$, and $H_{ab} = \langle \psi_a | \hat{H} | \psi_b \rangle = \langle \psi_b | \hat{H} | \psi_a \rangle$. Note that the matrix elements $H_{aa} = H_{bb}$ because \hat{H} is symmetric with respect to \mathbf{R}_a and \mathbf{R}_b . Moreover, since ψ_a and ψ_b are not orthogonal we have to introduce the **overlap integral**, $S = \langle \psi_a | \psi_b \rangle$, which measures the overlap between the two atomic wavefunctions. In fact we can simplify this expression further, because the potential is symmetric about the mid-point between the two protons. The wavefunction must therefore be either symmetric or antisymmetric, $\alpha = \pm\beta$, and hence,

$$E_0 \leq \langle E \rangle = \frac{H_{aa} \pm H_{bb}}{1 \pm S}. \quad (11.7)$$

The matrix elements in this expression can be evaluated in closed form, though the calculation is rather tedious.¹

We have, therefore, found two possible wavefunctions for the H_2^+ ion,

$$\psi_g = \frac{\psi_a + \psi_b}{\sqrt{2(1+S)}}, \quad \psi_u = \frac{\psi_a - \psi_b}{\sqrt{2(1-S)}}, \quad (11.10)$$

with energies $E_g = \frac{H_{aa}+H_{bb}}{1+S}$, $E_u = \frac{H_{aa}-H_{bb}}{1-S}$. The subscript g refers to the term *gerade* (German for even) used in molecular physics to denote a state that is even under the operation of inverting the electronic wavefunction through the centre of symmetry of the molecule, without changing the positions of the nuclei. Such an inversion changes $\mathbf{r} \rightarrow \mathbf{R}_a + \mathbf{R}_b - \mathbf{r}$, which interchanges ψ_a and ψ_b . Note that this is not the same as parity inversion, which would also affect the nuclear coordinates. The *ungerade* (odd) state is denoted by subscript u . Note that ψ_g and ψ_u are orthogonal, even though ψ_a and ψ_b are not. In fact, ψ_g and ψ_u are just the orthonormal states that diagonalise the Hamiltonian, if we limit ourselves to linear combinations of ψ_a and ψ_b . In chemistry, ψ_g and ψ_u are called **molecular orbitals** and the assumption that they are linear combinations of atomic stationary states is called the **linear combination of atomic orbitals** (LCAO) approximation.

The state ψ_g has the lower energy, while ψ_u represents an excited state of the molecular ion. Physically, the reason for this is that, in the ψ_g state, the two atomic wavefunctions interfere constructively in the region between the protons, giving an enhanced electron density in the region where the electron is attracted strongly by both protons, which serves to screen the two protons from each other. Conversely, in ψ_u we have destructive interference in the region between the protons. If we plot E_g and E_u as functions of the nuclear separation $R = |\mathbf{R}_a - \mathbf{R}_b|$, the results are as shown in figure ???. For both curves, we have plotted $E + \text{Ry}$ since $-\text{Ry}$ is the ground state energy of the hydrogen *atom*. The curve of $E_g + \text{Ry}$ in the LCAO approximation has a minimum value of -1.8eV at $R = R_0 = 130\text{pm}$, which is the predicted equilibrium nuclear separation. The predicted energy required to dissociate the molecular ion into a hydrogen atom and a free proton is thus 1.8eV . The curve of $E_u + \text{Ry}$ does not have a minimum, suggesting that the odd wavefunction ψ_u does not correspond to a bound molecular state.

As the variational method provides an upper limit on the ground state energy, it is no surprise that the true molecular potential energy curve (shown dotted) lies below the LCAO one. The true values of the equilibrium separation and dissociation energy are 106pm and 2.8eV respectively. Clearly the LCAO wavefunction ψ_g is not a very accurate approximation to the true ground state. We could improve it by introducing further variational parameters or additional atomic orbitals. For example, when R becomes very small the true wavefunction should approach that of a He^+ ion; we could include such a

¹We simply quote the results here:

$$S = \left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\right)e^{-R/a_0}, \quad H_{aa} = -\text{Ry} + \frac{e^2}{4\pi\epsilon_0} \left(1 + \frac{R}{a_0}\right)e^{-2R/a_0}, \quad (11.8)$$

$$H_{ab} = \frac{e^2}{4\pi\epsilon_0 a_0} \left(1 + \frac{R}{a_0}\right)e^{-R/a_0} + S \left(-\text{Ry} + \frac{e^2}{4\pi\epsilon_0}\right), \quad (11.9)$$

where $R = |\mathbf{R}_a - \mathbf{R}_b|$ and Ry is the Rydberg constant, the binding energy of the Hydrogen atom in its ground state.

term in the trial function. We could also include an **effective charge parameter** in ψ_a and ψ_b , which is equivalent to replacing the Bohr radius a_0 by a free parameter.

Although not very reliable quantitatively, the LCAO wavefunction ψ_g does however exhibit a number of important features of the true ground state: (i) it is even (g) with respect to inversion of the electron wavefunction; (ii) there is constructive interference which leads to an enhanced probability of finding the electron in the region between the two nuclei. These features will be important when we come to discuss **bonding**. Since the odd u -states are orthogonal to the even g -states, and the true ground state is a g -state, the curve of E_u actually represents an upper limit on the energy of the lowest u -state. Thus the fact that the curve has no minimum does not really prove that there are no bound u -states; but this does turn out to be the case. The LCAO wavefunction ψ_u shows the characteristic feature of an **anti-bonding** state: there is destructive interference in the region between the two nuclei, so that the electron is actually forced out of the region of overlap of the two atomic wavefunctions.

At this stage, it is helpful to introduce some notation to **label the molecular orbitals**. Although the wavefunctions $\psi_{g,u}$ that we have been discussing are formed in the LCAO approximation from linear combinations of atomic $1s$ ($n = 1, \ell = 0$) states, with no orbital angular momentum, they do not themselves necessarily have zero orbital angular momentum. An $\ell = 0$ state must be proportional to Y_{00} , i.e., it must have no dependence on θ and ϕ , giving an isotropic probability distribution. But these states are certainly not isotropic: they have a ‘dumbbell’ shape, concentrated around the two protons. They do not have unique electronic orbital angular momentum because the operator $\hat{\mathbf{L}}^2$ for the electron does not commute with the Hamiltonian on account of the non-central terms $1/|\mathbf{r} - \mathbf{R}_a|$ and $1/|\mathbf{r} - \mathbf{R}_b|$ in the potential.

The only component of $\hat{\mathbf{L}}$ that does commute with these terms is \hat{L}_z , provided we choose the z -axis parallel to the internuclear axis $\mathbf{R}_a - \mathbf{R}_b$. Therefore instead of classifying the states as s, p, d, \dots orbitals according to whether $\ell = 0, 1, 2, \dots$, we call them $\sigma, \pi, \delta, \dots$ orbitals according to whether $\Lambda = 0, 1, 2, \dots$, where $\Lambda = |m_\ell|$. A subscript u or g denotes whether the state is even or odd under inversion; this notation can be applied to all *homonuclear* diatomic molecules, in which the potential is symmetric about the median plane of the molecule. Thus the ground state of the hydrogen molecular ion is σ_g and the corresponding odd state is σ_u^* , where the star signifies an antibonding orbital. In the LCAO approximation used above, these molecular orbitals are linear combinations of $1s$ atomic orbitals and so they can be written as $1s\sigma_g$ and $1s\sigma_u^*$. To get some insight into how this notation applies, it is helpful to refer to figure ??.

11.2 The H_2 molecule

We now turn to consider the hydrogen molecule. One might imagine that this would be a trivial extension of the H_2^+ ion, but in fact several new features arise when we consider this simple molecule. For two electrons with positions $\mathbf{r}_{1,2}$ and two protons at $\mathbf{R}_{a,b}$, in the Born-Oppenheimer approximation, the Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_{r_1}^2 + \nabla_{r_2}^2) + \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} \right], \quad (11.11)$$

Approximation	B.E./eV	R_0 /pm
Experiment	4.75	74.1
MO fixed charge	2.70	85.2
MO variable charge	3.49	73.0
VB variable charge	3.68	74.6
Variable λ and charge	4.03	75.7
13 variable parameters	4.72	74.1

Table 11.1: Binding energy and equilibrium nuclear separation of the hydrogen molecule in various approximations.

where $r_{1b} = |\mathbf{r}_1 - \mathbf{R}_b|$, etc. This is just the sum of two Hamiltonians for H_2^+ ions, plus the additional term $\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} - \frac{1}{r_{ab}} \right)$. It is plausible that the expectation values of $1/r_{12}$ and $1/r_{ab}$ will be comparable and therefore the extra term can be treated as a perturbation. Thus, as a first approximation we neglect it and assign each electron to one of the H_2^+ molecular orbitals defined above. There are four ways of filling the two orbitals σ_g and σ_u^* , which we can represent by

$$\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2), \quad \psi_g(\mathbf{r}_1)\psi_u^*(\mathbf{r}_2), \quad \psi_u^*(\mathbf{r}_1)\psi_g(\mathbf{r}_2), \quad \psi_u^*(\mathbf{r}_1)\psi_u^*(\mathbf{r}_2). \quad (11.12)$$

Of these, we would expect the first to be the ground state.

However, at this stage, we have given no consideration to the constraints imposed by particle statistics. In fact, since the electrons are identical fermions, the wavefunction must be antisymmetric with respect to their interchange. Taking into account the spin degree of freedom, for both electrons to occupy the bonding σ_g molecular orbital, they must have opposite spins and occupy the singlet spin state, $X_{0,0} = \frac{1}{\sqrt{2}}(\chi_+(1)\chi_-(2) - \chi_-(1)\chi_+(2))$.

If we calculate the energy of the state $\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2)X_{0,0}$ as a function of the nuclear separation R , the minimum ground state energy occurs at $R_0 = 85\text{pm}$ and corresponds to a binding energy of 2.7eV. The true molecule is smaller and more tightly bound. Allowing for more variation in the atomic orbitals, in the form of a variable effective charge, gives an equilibrium value of R_0 much closer to experiment, but a binding energy that is still not high enough (see Table 11.1). The reason is that the σ_g^2 configuration alone is not a very good representation of the ground state. To understand why, consider the following.

If we multiply out the spatial part of the σ_g^2 wavefunction in the LCAO approximation, we see that it has a rather strange form,

$$\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2) \propto [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] + [\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_b(\mathbf{r}_2)]. \quad (11.13)$$

The terms in the first square bracket correspond to the two electrons being shared between the two hydrogen atoms. This is the **covalent bonding** picture of the bound state. In the other square bracket, however, both electrons are assigned to the same atom, corresponding to **ionic bonding**. Since all the terms have equal coefficients, the ionic and covalent contributions are equal, which seems rather constraining, if not implausible. For example, it means that, when the two protons are pulled apart, the system is just as likely to be found to consist of an H^+ and an H^- ion as two neutral atoms.

If we go to the pure **valence bonding** (VB) approximation and drop the ionic part of the wavefunction altogether, we find that the predicted binding energy and nuclear separation are both improved (see Table 11.1). Including a small parameter λ for the amplitude of the ionic component, i.e., taking

$$\psi^{\text{VB}} \propto [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] + \lambda[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_b(\mathbf{r}_2)]. \quad (11.14)$$

we find that the variational method gives an optimal value of λ of about 1/6, meaning only about a 3% probability of finding the ionic configuration. Still, even with this refinement, the agreement with experiment is far from perfect. However, this doesn't mean quantum mechanics is failing; by taking enough free parameters in the trial function an excellent result can be obtained, as shown in the Table 11.1.

As mentioned above, there are four possible ways of putting two electrons into the $1s\sigma_g$ and $1s\sigma_u^*$ molecular orbitals. From these four two-electron states we can make three states that are symmetric under interchange of the positions of the electrons, all of which need to be combined with the antisymmetric spin state $X_{0,0}$,

$$^1\Sigma_g : \quad X_{0,0}\sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2) \quad (11.15)$$

$$^1\Sigma_u : \quad X_{0,0}[\sigma_g(\mathbf{r}_1)\sigma_u^*(\mathbf{r}_2) + \sigma_u^*(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)]/\sqrt{2} \quad (11.16)$$

$$^1\Sigma_g : \quad X_{0,0}\sigma_u^*(\mathbf{r}_1)\sigma_u^*(\mathbf{r}_2). \quad (11.17)$$

In addition we can make a triplet of states from an antisymmetric spatial wavefunction and the symmetric triplet spin states X_{1,m_S} ($m_S = 0, \pm 1$),

$$^3\Sigma_u : \quad X_{0,0}[\sigma_g(\mathbf{r}_1)\sigma_u^*(\mathbf{r}_2) - \sigma_u^*(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)]/\sqrt{2}. \quad (11.18)$$

We have introduced to the left of these equations a new notation, called the molecular term, to describe the overall quantum numbers of the molecule, all of which must be good quantum numbers because they correspond to operators which commute with the molecular Hamiltonian. It derives from a historic spectroscopic notation used in atomic physics. The term is written $^{2S+1}\Lambda_{u/g}$. The prefix $2S+1$ denotes the multiplicity of the total spin state of the electrons, hence 1 for a singlet and 3 for a triplet state. The central greek capital letter represents the magnitude of the total \hat{L}_z quantum number, $\Lambda = 0, 1, 2, \dots$, being represented by $\Sigma, \Pi, \Delta, \dots$. In the case of the molecular orbitals above based on the $1s$ atomic orbitals, all the wavefunctions clearly have zero orbital angular momentum about the internuclear axis and hence they are all Σ states. The g or u suffix means even or odd under inversion, and is only meaningful for homonuclear molecules. Notice that since $(\pm 1)^2 = +1$ we get a g -state by combining two g or two u -states, and a u -state by combining a g and a u -state.

In terms of the molecular orbital approach, the VB approximation implies that the ground state is not simply the σ_g^2 configuration but rather a mixture of the two $^1\Sigma_g$ states,

$$\psi^{\text{VB}} \propto (1 + \lambda)(1 + S)\sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2) - (1 - \lambda)(1 - S)\sigma_u^*(\mathbf{r}_1)\sigma_u^*(\mathbf{r}_2). \quad (11.19)$$

Thus there is **configuration mixing** in the hydrogen molecule. The two states can mix because they have the same overall quantum numbers. At large nuclear separations the energy eigenstates are clearly separated into those that are almost a pair of neutral atoms and those consisting of an H^+ and an H^- ion. In the case of the u -states, we can see

by expanding the spatial wave functions that $^3\Sigma_u$ is of the former type and $^1\Sigma_u$ of the latter. Since these configurations have different resultant electron spins they do not mix significantly (just like singlet and triplet states of atomic helium). Also the u - and g -states are prevented from mixing by their different inversion symmetry. However, the two $^1\Sigma_g$ configurations have the same electron spin and symmetry and can mix to give the above covalent-bonded ground state and an orthogonal excited state that is more ionic.

11.3 From molecules to solids

With these basic principles in hand, we could go on to discuss the orbital and electronic structure of more complicated molecules. In doing so, we would sink deeper into the realm of quantum chemistry. Instead, we will use these simple ideas of molecular bonding to develop a surprisingly versatile and faithful description of the ordered solid state. With *ca.* 10^{23} nuclei and electrons now involved such an enterprise seems foolhardy. However, we will see that, by exploiting symmetries, we can capture many of the basic principles of the solid state.

Let us then consider the electronic structure of an ordered crystalline array of equivalent atoms. (The consideration of more complicated periodic structures would not present conceptual challenges, but would bring unnecessary complications to the discussion.) Once again, we can draw upon the Born-Oppenheimer approximation and focus solely on the motion of electrons around an otherwise ordered array of nuclei. Even then, we are confronted with a many-particle Hamiltonian of apparently great complexity,

$$\hat{H} = -\sum_n \frac{\hbar^2 \nabla_n^2}{2m_e} - \sum_{n,N} \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_{nN}} + \sum_{m<n} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{mn}}. \quad (11.20)$$

Here the second term represents the interaction of the electrons with the constituent nuclei, and the third term involves the electron-electron interaction. In a physical system, we would have to take into account the influence of further relativistic corrections which would introduce additional spin-orbit couplings.

To address the properties of such a complex interacting system, we will have to draw upon many of the insights developed previously. To begin, it is helpful to partition the electrons into those which are bound to the core and those which are able to escape the potential of the individual atomic nuclei and propagate “freely” through the lattice. The electrons which are tightly bound to the nuclei screen the nuclear charge leading to a modified nuclear potential, $V_{\text{eff}}(r)$. Focussing on those electrons which are free, the effective Hamiltonian can be written as, $\hat{H} \simeq \sum_n \hat{H}_n + \sum_{m,n} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{mn}}$, where

$$\hat{H}_n = -\frac{\hbar^2 \nabla_n^2}{2m_e} + V_{\text{eff}}(r) \quad (11.21)$$

represents the single-particle Hamiltonian experienced by each of the electrons – i.e. \hat{H}_n describes the motion of an electron moving in a periodic lattice potential, $V_{\text{eff}}(\mathbf{r}) = V_{\text{eff}}(\mathbf{r} + \mathbf{R})$ with \mathbf{R} belonging to the set of periodic lattice vectors.

Despite engineering this approximation, we are still confronted by a challenging many-particle problem. Firstly, the problem remains coupled through the electron-electron

Coulomb interaction. Secondly, the electrons move in a periodic potential. However, if we assume that the electrons remain mobile – the jargon is **itinerant** – and free to propagate through the lattice, they screen each other and diminish the effect of the Coulomb interaction.² Therefore, in these circumstances, we can proceed by neglecting the Coulomb interaction altogether. Of course, we still have to contend with the constraints placed by Pauli exclusion and wavefunction antisymmetry. But we are now in the realm of the molecular orbital theory, and can proceed analogously using the variational LCAO approach.

In particular, we can building a trial wavefunction by combining orbital states of the single ion, $V_{\text{ion}}(r)$, where $V_{\text{eff}}(\mathbf{r}) = \sum_{\mathbf{R}} V_{\text{ion}}(\mathbf{r} - \mathbf{R})$. As with the hydrogen molecule, the Hamiltonian for the individual nuclei, $\hat{H}_0 = -\frac{\hbar^2 \nabla^2}{2m_e} + V_{\text{ion}}(\mathbf{r})$ are associated with a set of atomic orbitals, ψ_q , characterised by a set of quantum numbers, q . In the atomic limit, when the atoms are far-separated, these will mirror the simple hydrogenic states. To find the variational ground state of the system, we can then build a trial state from a linear combination of these atomic orbitals. Taking only the lowest orbital, $q = 0$, into account we have,

$$\Psi(\mathbf{r}) = \sum_{\mathbf{R}} \alpha_{\mathbf{R}} \psi(\mathbf{r} - \mathbf{R}), \quad (11.22)$$

where, as before, $\alpha_{\mathbf{R}}$ represent the set of variational coefficients, one for each site (and, in principle, each atomic orbital if we had taken more than one!).

Once again, we can construct the variational state energy,

$$\langle E \rangle = \frac{\langle \Psi | \hat{H}_{1e} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_{\mathbf{R}, \mathbf{R}'} \alpha_{\mathbf{R}}^* H_{\mathbf{R}, \mathbf{R}'} \alpha_{\mathbf{R}'}}{\sum_{\mathbf{R}, \mathbf{R}'} \alpha_{\mathbf{R}}^* S_{\mathbf{R}, \mathbf{R}'} \alpha_{\mathbf{R}'}} \quad (11.23)$$

where, as before, $H_{\mathbf{R}, \mathbf{R}'} = \int d^d r \psi^*(\mathbf{r} - \mathbf{R}) \hat{H}_{1e} \psi(\mathbf{r} - \mathbf{R}')$ denote the matrix elements of the orbital wavefunction on the Hamiltonian $\hat{H}_{1e} = -\frac{\hbar^2 \nabla^2}{2m_e} + V_{\text{eff}}(\mathbf{r})$ and $S_{\mathbf{R}, \mathbf{R}'} = \int d^d r \psi^*(\mathbf{r} - \mathbf{R}) \psi(\mathbf{r} - \mathbf{R}')$ represent the overlap integrals. Then, varying the energy with respect to $\alpha_{\mathbf{R}}^*$, we find that the coefficients obey the **secular equation**

$$\sum_{\mathbf{R}'} [H_{\mathbf{R}, \mathbf{R}'} - E S_{\mathbf{R}, \mathbf{R}'}] \alpha_{\mathbf{R}'} = 0. \quad (11.24)$$

Note that, if the basis functions were orthogonal, this would just be an eigenvalue equation.

To develop this idea, let us first see how the method relates to back to the problem of H_2^+ : In this case, the secular equation translates to the 2×2 matrix equation,

$$\begin{pmatrix} H_{aa} - E & H_{ab} - ES \\ H_{ab} - ES & H_{bb} - E \end{pmatrix} \alpha = \mathbf{0}. \quad (11.25)$$

where the notation and symmetries of matrix elements follow from section 11.1. As a result, we find that the states α divide into even and odd states as expected.

Now let us consider a one-dimensional periodic lattice system. If we assume that the atoms are well-separated, it is evident that both the overlap integrals and matrix elements will decay exponentially fast with orbital separation. The dominant contribution to the

²This screening is effective for $\bar{a} \ll a_0$, in the notation of section 9.4.3.

energy will then derive from matrix elements coupling only neighbouring states. In this case, the secular equation separates into the coupled sequence of equations,

$$(\varepsilon - E)\alpha_n - (t + ES)(\alpha_{n+1} + \alpha_{n-1}) = 0, \quad (11.26)$$

for each n , where $H_{nn} = \varepsilon$ denotes the atomic orbital energy, $H_{n,n+1} = H_{n+1,n} = -t$ is the matrix element between neighbouring states, $S_{n,n} = 1$ and $S_{n,n+1} = S_{n+1,n} = S$. All other matrix elements are exponentially small. Here we consider a system with N lattice sites and impose the periodic boundary condition, $\alpha_{n+N} = \alpha_n$. The periodicity of the secular equation suggests a solution of the form $\alpha_n = \frac{1}{\sqrt{N}} e^{ikna}$, where $k = 2\pi m/Na$ denote a discrete set of N wavevectors with m integer lying in the range $-N/2 < m \leq N/2$. (The size of this range, $k_{max} - k_{min}$, is fixed by the magnitude of the **reciprocal lattice vector** for the one-dimensional lattice, $2\pi/a$.) Substitution confirms that this is a solution with energies,

$$E_k = \frac{\varepsilon - 2t \cot ka}{1 + 2S \cot ka}. \quad (11.27)$$

The wavevector k parameterises a **band** of states.

Then, according to the LCAO approximation, for a single electron, distributed throughout the system, the lowest energy state is predicted to be the uniform state $\alpha_n = \frac{1}{\sqrt{N}}$ with the energy $E_0 = \frac{\varepsilon - 2t}{1 + 2S}$. (Here we have assumed that the matrix element, t , is positive – in the atomic limit, consider why this is a sound assumption.) However, if we suppose that each atom contributes a non-zero fraction of electrons to the system, we must consider the influence of Pauli exclusion and particle statistics.

Since the electrons are fermions, each state k can host two electrons in a total spin singlet configuration. The lowest energy state is then obtained by adding electron pairs sequentially into states of increasing k until all electrons are accounted for. If the maximum k value, known as the Fermi wavevector, k_F , lies within the band of states, elementary excitations of the electrons cost vanishingly small energy leading to **metallic** behaviour. On the other hand, if the system is stoichiometric, with each atom contributing an integer number of electrons, the Fermi wavevector may lie at a **band gap** between two different band of states. In this case, the system has a gap to excitations and the material forms a **band insulator**.

To add flesh to these ideas, let us then consider a simple, but prominent problem from the realm of quantum condensed matter physics. In recent years, there has been great interest in the properties of **graphene**, a single layer of graphite. (These developments were recognised by the award of the 2010 Nobel prize in physics to Geim and Novoselov.) Remarkably, high quality single crystals of graphene can be obtained by running graphite – a pencil! – over an adhesive layer. The resulting electron states of the single layer compound have been of enormous interest to physicists. To understand why, let us implement the LCAO technology to explore the valence electron structure of graphene.

Graphene forms a periodic two-dimensional honeycomb lattice structure with two atoms per each unit cell. With an electron configuration $1s^2 2s^2 2p^2$, the two $1s$ electrons are bound tightly to the nucleus. The remaining $2s$ electrons **hybridise** with one of the p orbitals to form three sp^2 hybridised orbitals. These three orbitals form the basis of a strong covalent bond of σ orbitals that constitute the honeycomb lattice. The remaining

electron, which occupies the out-of-plane p_z orbital, is then capable of forming an itinerant band of electron states. It is this band which we now address.

Once again, let us suppose that the wavefunction of this band involves the basis of single p_z orbital states localised to each lattice site,

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} [\alpha_{\mathbf{R}} \psi_1(\mathbf{r} - \mathbf{R}) + \beta_{\mathbf{R}} \psi_2(\mathbf{r} - \mathbf{R})]. \quad (11.28)$$

Here the p_z orbital wavefunction ψ_1 is centred on one of the atoms in the unit cell, and ψ_2 is centred on the other. Once again, taking into account matrix elements involving only nearest neighbours, the trial wavefunction translates to the secular equation,

$$(\varepsilon - E)\alpha_{\mathbf{R}} - (t + ES)(\beta_{\mathbf{R}} + \beta_{\mathbf{R}-\mathbf{a}_1} + \beta_{\mathbf{R}-\mathbf{a}_2}) = 0, \quad (11.29)$$

$$(\varepsilon - E)\beta_{\mathbf{R}} - (t + ES)(\alpha_{\mathbf{R}} + \alpha_{\mathbf{R}-\mathbf{a}_1} + \alpha_{\mathbf{R}-\mathbf{a}_2}) = 0, \quad (11.30)$$

where the lattice vectors $\mathbf{a}_1 = (\sqrt{3}/2, 1/2)a$ and $\mathbf{a}_2 = (\sqrt{3}/2, -1/2)a$, with a the lattice spacing, are shown in figure ???. Note that the off-diagonal matrix elements involve only couplings between atoms on different sublattices. Once again, we can make the ansatz that the solutions are of the form of plane waves with $\alpha_{\mathbf{R}} = \frac{\alpha_{\mathbf{k}}}{\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{R}}$ and $\beta_{\mathbf{R}} = \frac{\beta_{\mathbf{k}}}{\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{R}}$. Notice that, in this case, we must allow for different relative weights, $\alpha_{\mathbf{k}}$ and $\beta_{\mathbf{k}}$. Substituting, we find that this ansatz is consistent if

$$(\varepsilon - E)\alpha_{\mathbf{k}} - (t + ES)f_{\mathbf{k}}\beta_{\mathbf{k}} = 0 \quad (11.31)$$

$$(\varepsilon - E)\beta_{\mathbf{k}} - (t + ES)f_{\mathbf{k}}^* \alpha_{\mathbf{k}} = 0 \quad (11.32)$$

where $f_{\mathbf{k}} = 1 + 2e^{-i\sqrt{3}k_x a/2} \cos(k_y a/2)$. Although this equation can be solved straightforwardly, it takes a particularly simple form when the overlap integral between neighbouring sites, S , is neglected. In this case, one obtains,

$$E_{\mathbf{k}} = \varepsilon \pm |f_{\mathbf{k}}|t. \quad (11.33)$$

The corresponding band structure is shown right as a function of \mathbf{k} . In particular, one may note that, at the band centre, the dispersion relation for the electrons becomes point-like (see Fig. ??).

In the half-filled system, where each carbon atom contributes a single electron to the band, the Fermi level lies precisely at the centre of the band where the dispersion, $E_{\mathbf{k}}$ is point like. Doping electrons into (or removing electrons from) the system results in (two copies) of a linear dispersion, $E_{\mathbf{k}} \simeq c|\mathbf{k}|$, where c is a constant (velocity). Such a linear dispersion relation is the hallmark of a relativistic particle (cf. a photon). Of course, in this case, the electrons are not moving at relativistic velocities. But their properties will mirror the behaviour of relativistic particles. And herein lies the interest that these materials have drawn.

Finally, let us comment on the influence of the electron-electron interaction effects that were neglected in our treatment above. In principle, we could adopt a Hartree or Hartree-Fock scheme to address the effects of electron interaction in a perturbative manner. Indeed, such a programme would lead to interaction corrections which would modify the electronic band structure derived above. It is a surprising yet robust feature of Fermi systems that the properties of the non-interacting ground state wavefunction remain qualitatively

correct over an unreasonably wide range of interaction strengths.³ This rigidity can be ascribed to the constraints on the nodal structure of the wavefunction imposed by particle statistics. However, in some cases, the manifestations of electron interactions translate to striking modifications in the observable properties. We have already discussed the possibility of electron-electron interactions leading to Wigner crystallisation or to itinerant ferromagnetism; other effects include interaction-driven electron localisation (the “Mott transition”), local moment formation, quantum Hall fluids, and superconductivity. Such phases, which by their nature lie outside any perturbative scheme built around the non-interacting ground state, form the field of quantum condensed matter and solid state physics

³This feature is embodied in the theory of the electron liquid known as **Landau’s Fermi liquid theory**.

CHAPTER 12

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APPENDIX A

Appendix

A.1 Additional Proofs

A.1.1 Number of Modes

cm notes + thermo

A.1.2 Probability Current

Consider the expression

$$i\hbar \frac{\partial}{\partial t} \int_{\mathcal{V}} P(\mathbf{r}, t) dV = i\hbar \frac{\partial}{\partial t} \int_{\mathcal{V}} \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) dV; \quad (\text{A.1})$$

apart from the factor $i\hbar$, this is the rate of change of the probability of finding the particle in a closed region (V):

A.2 Symmetry Transformations

When a measurement of an observable \hat{A} is carried out on a quantum system which is initially in a state $|\psi\rangle$, the probabilities of the various possible measurement outcomes are given by

$$P(\psi \rightarrow \phi_i) = |\langle \phi_i | \psi \rangle|^2 \quad (\text{A.2})$$

where the $|\phi_i\rangle$ are the eigenstates of \hat{A} . A *symmetry transformation* can be implemented by introducing an operator \hat{U} which transforms all the states of the system such that

$$|\psi\rangle \rightarrow |\psi'\rangle = \hat{U} |\psi\rangle, \quad |\phi\rangle \rightarrow |\phi'\rangle = \hat{U} |\phi\rangle. \quad (\text{A.3})$$

The probabilities of the various possible measurement outcomes are left unchanged (invariant) under the symmetry operation if, for all states $|\phi_i\rangle$, we have

$$|\langle \phi'_i | \psi' \rangle|^2 = |\langle \phi_i | \psi \rangle|^2. \quad (\text{A.4})$$

A theorem due to Wigner states that the condition above can be satisfied in two distinct ways. The first possibility is that the overlaps themselves remain invariant,

$$\langle \phi'_i | \psi' \rangle = \langle \phi_i | \psi \rangle. \quad (\text{A.5})$$

In this case, we have

$$\langle \phi'_i | \psi' \rangle = \langle \hat{U} \phi_i | \hat{U} \psi \rangle = \langle \phi_i | \hat{U}^\dagger \hat{U} | \psi \rangle = \langle \phi_i | \psi \rangle, \quad (\text{A.6})$$

and the operator \hat{U} must be linear and unitary:

$$\hat{U} |\lambda\phi_i\rangle = \lambda |\phi'_i\rangle, \quad \hat{U}^\dagger \hat{U} = \hat{\mathbb{I}}. \quad (\text{A.7})$$

The second possibility is that the overlaps pick up a complex conjugation,

$$\langle \phi'_i | \psi' \rangle = \langle \phi_i | \psi \rangle^*. \quad (\text{A.8})$$

in which case the operator \hat{U} is antilinear and antiunitary:

$$\hat{U} |\lambda\phi_i\rangle = \lambda^* |\phi'_i\rangle, \quad \hat{U}^* \hat{U} = \hat{\mathbb{I}}. \quad (\text{A.9})$$

The symmetries we shall consider are all covered by the first possibility; they are described by linear, unitary operators \hat{U} . An important example of a symmetry requiring an antiunitary, rather than unitary, operator \hat{U} is timereversal invariance, $t \rightarrow -t$.

For continuous symmetries, such as spatial translations or rotations, the symmetry operation can be taken arbitrarily close to the identity operation (for example, a rotation through an infinitesimal angle). For such symmetries, the operator \hat{U} can be taken arbitrarily close to the identity operator $\hat{\mathbb{I}}$, in which case it must take the form

$$\hat{U}(\epsilon) = \hat{\mathbb{I}} + i\epsilon\hat{T} + \mathcal{O}(\epsilon^2), \quad (\text{A.10})$$

where ϵ is an arbitrary, real number. Since the identity operator $\hat{\mathbb{I}}$ is unitary, continuous symmetries must always be described by operators \hat{U} which are unitary, rather than antiunitary. We then have

$$\hat{U}^\dagger(\epsilon)\hat{U}(\epsilon) = \left(\hat{\mathbb{I}} - i\epsilon\hat{T}^\dagger + \mathcal{O}(\epsilon^2)\right)\left(\hat{\mathbb{I}} + i\epsilon\hat{T} + \mathcal{O}(\epsilon^2)\right) = \hat{\mathbb{I}} + i\epsilon(\hat{T} - \hat{T}^\dagger) + \mathcal{O}(\epsilon^2), \quad (\text{A.11})$$

from which it follows that the operator \hat{T} must be Hermitian:

$$\hat{T} = \hat{T}^\dagger. \quad (\text{A.12})$$

(The factor of i was introduced in Eq. (A.10) for convenience, to ensure that \hat{T} is Hermitian rather than anti-Hermitian). The operator \hat{T} is known as the *generator* of the symmetry. In general, a symmetry will be described by a set of parameters ϵ_k , and as a result, the symmetry will possess a set of generators \hat{T}_k .

Any finite transformation \hat{U} can be built up from an infinite number of infinitesimal transformations. To see this, take $\epsilon = \theta/N$, where θ is a finite, N independent parameter, and apply N successive infinitesimal transformations, ϵ . This corresponds to applying the operator

$$\left(\hat{\mathbb{I}} + \frac{i\theta\hat{T}}{N}\right)^N = \hat{\mathbb{I}} + N\left(\frac{i\theta\hat{T}}{N}\right) + \frac{1}{2!}N(N-1)\left(\frac{i\theta\hat{T}}{N}\right)^2 + \frac{1}{3!}N(N-1)(N-2)\left(\frac{i\theta\hat{T}}{N}\right)^3 + \dots \quad (\text{A.13})$$

Taking the limit $N \rightarrow \infty$ (and hence $\epsilon \rightarrow 0$) then gives

$$\left(\hat{\mathbb{I}} + \frac{i\theta\hat{T}}{N}\right)^N \rightarrow \exp(i\theta\hat{T}). \quad (\text{A.14})$$

Thus, for finite θ , the symmetry operator \hat{U} can be written as

$$\hat{U}(\theta) = \exp(i\theta\hat{T}). \quad (\text{A.15})$$

Under a symmetry transformation, a matrix element of an observable \hat{A} transforms as

$$\langle\phi|\hat{A}|\psi\rangle \rightarrow \langle\phi'|\hat{A}|\psi'\rangle = \langle\hat{A}\phi|\hat{A}|\hat{U}\psi\rangle = \langle\phi|\hat{U}^\dagger\hat{A}\hat{U}|\psi\rangle. \quad (\text{A.16})$$

Hence the transformation properties of matrix elements can be found by subjecting operators to a *similarity transform*

$$\hat{A} \rightarrow \hat{U}^\dagger\hat{A}\hat{U}, \quad (\text{A.17})$$

while leaving the states of the system unaltered.

For an infinitesimal transformation, the similarity transformation is

$$\hat{A} \rightarrow \left(\hat{\mathbb{I}} - i\epsilon\hat{T}^\dagger + \mathcal{O}(\epsilon^2)\right)\hat{A}\left(\hat{\mathbb{I}} + i\epsilon\hat{T} + \mathcal{O}(\epsilon^2)\right), \quad (\text{A.18})$$

and hence

$$\hat{A} \rightarrow \hat{A} - i\epsilon[\hat{T}, \hat{A}] + \mathcal{O}(\epsilon^2). \quad (\text{A.19})$$

In the particular case that the magnitudes of all matrix elements of an observable \hat{A} are left unaltered by the symmetry transformation, we have

$$\left|\langle\phi|\hat{A}|\psi\rangle\right|^2 = \left|\langle\phi|\hat{U}^\dagger\hat{A}\hat{U}|\psi\rangle\right|^2. \quad (\text{A.20})$$

For this to hold for all possible choices of the states $|\phi\rangle$ and $|\psi\rangle$, the operator \hat{A} must satisfy the condition

$$\hat{A} = \hat{U}^\dagger\hat{A}\hat{U}. \quad (\text{A.21})$$

Since \hat{U} is unitary, this implies that \hat{A} must commute with \hat{U} , and hence also with the generator \hat{T} :

$$[\hat{A}, \hat{U}] = 0, \quad [\hat{A}, \hat{T}] = 0. \quad (\text{A.22})$$

In particular, if all matrix elements of the Hamiltonian \hat{H} of a system are unchanged by a symmetry transformation, then we must have

$$[\hat{H}, \hat{U}] = 0, \quad [\hat{H}, \hat{T}] = 0. \quad (\text{A.23})$$

Ehrenfest's theorem then immediately implies that, for any state of the system, the expectation value of the generator \hat{T} must remain constant:

$$\frac{d}{dt} \langle\psi|\hat{T}|\psi\rangle = 0. \quad (\text{A.24})$$

Thus invariance of a system under a symmetry operation leads directly to a corresponding conservation law

A.2.1 Spatial Translations

A spatial translation of a system through a vector displacement \mathbf{a} changes the expectation value of the position \mathbf{r}_n of the n 'th particle for any state $|\psi\rangle$ of the system such that

$$\langle\psi'|\mathbf{r}_n|\psi'\rangle = \langle\psi|\mathbf{r}_n|\psi\rangle + \mathbf{a}. \quad (\text{A.25})$$

Introducing the symmetry operator $\hat{U}(\mathbf{a})$ defined such that

$$|\psi'\rangle = \hat{U}(\mathbf{a}) |\psi\rangle \quad (\text{A.26})$$

then gives

$$\langle\psi|\hat{U}^\dagger(\mathbf{a})\mathbf{r}_n\hat{U}(\mathbf{a})|\psi\rangle = \langle\psi|\mathbf{r}_n|\psi\rangle + \langle\psi|\mathbf{a}|\psi\rangle. \quad (\text{A.27})$$

For this relation to hold for all possible choices of the state $|\psi\rangle$ then requires that

$$\hat{U}^\dagger(\mathbf{a})\mathbf{r}_n\hat{U}(\mathbf{a}) = \mathbf{r}_n + \mathbf{a}. \quad (\text{A.28})$$

If the probabilities of all measurement outcomes are left unchanged by the spatial translation, then $\hat{U}(\mathbf{a})$ must be unitary:

$$\hat{U}^\dagger(\mathbf{a})\hat{U}(\mathbf{a}) = \hat{\mathbb{I}}. \quad (\text{A.29})$$

For an infinitesimal translation, the operator $\hat{U}(\mathbf{a})$ must take the form

$$\hat{U}(\mathbf{a}) = \hat{\mathbb{I}} - \frac{i}{\hbar}(\hat{\mathbf{P}} \cdot \mathbf{a}) + \mathcal{O}(a^2), \quad (\text{A.30})$$

where $\hat{\mathbf{P}} = (\hat{P}_x, \hat{P}_y, \hat{P}_z)$ is a vector containing the generators \hat{P}_k of spatial translations. The factor $1/\hbar$ has been introduced in order that the operator $\hat{\mathbf{P}}$ has dimensions of momentum. Substituting Eq. (A.30) into Eq. (A.28) gives

$$\left(\hat{\mathbb{I}} - \frac{i}{\hbar}(\hat{\mathbf{P}} \cdot \mathbf{a}) + \mathcal{O}(a^2)\right)\hat{\mathbf{r}}_n\left(\hat{\mathbb{I}} - \frac{i}{\hbar}(\hat{\mathbf{P}} \cdot \mathbf{a}) + \mathcal{O}(a^2)\right) = \hat{\mathbf{r}}_n + \mathbf{a}. \quad (\text{A.31})$$

Multiplying out, and keeping only terms up to $\mathcal{O}(a)$, we obtain the commutation relation

$$\frac{i}{\hbar}[(\hat{\mathbf{P}} \cdot \mathbf{a}), \hat{\mathbf{r}}_n] = \mathbf{a}. \quad (\text{A.32})$$

The k 'th component of the above equation is

$$\frac{i}{\hbar} \left[\sum_{j=1}^3 (\hat{P}_j a_j), \hat{r}_{nk} \right] = a_k, \quad (\text{A.33})$$

or, equivalently

$$\frac{i}{\hbar} \sum_{j=1}^3 [\hat{P}_j, \hat{r}_{nk}] a_j = \sum_{j=1}^3 \delta_{jk} a_j. \quad (\text{A.34})$$

For this relation to hold for all possible translations \mathbf{a} , the coefficients of a_j on each side of the equation must be equal:

$$[\hat{r}_{nk}, \hat{P}_j] = i\hbar\delta_{jk}. \quad (\text{A.35})$$

The commutation relation of the operator $\hat{\mathbf{P}}$ with the position operator $\hat{\mathbf{r}}_n$ is the same for all particles in the system; we therefore interpret $\hat{\mathbf{P}}$ as the *total* momentum operator for the system.

The order in which two distinct spatial translations defined by vectors \mathbf{a} and \mathbf{b} are applied to a system is immaterial. The corresponding symmetry operators $\hat{U}(\mathbf{a})$ and $\hat{U}(\mathbf{b})$ therefore commute with each other:

$$\hat{U}(\mathbf{b})\hat{U}(\mathbf{a}) = \hat{U}(\mathbf{a})\hat{U}(\mathbf{b}). \quad (\text{A.36})$$

If \mathbf{a} and \mathbf{b} are both infinitesimal translations, this becomes

$$\left(\hat{\mathbb{I}} - \frac{i}{\hbar}(\hat{\mathbf{P}} \cdot \mathbf{b}) + \dots\right) \left(\hat{\mathbb{I}} - \frac{i}{\hbar}(\hat{\mathbf{P}} \cdot \mathbf{a}) + \dots\right) = \left(\hat{\mathbb{I}} - \frac{i}{\hbar}(\hat{\mathbf{P}} \cdot \mathbf{a}) + \dots\right) \left(\hat{\mathbb{I}} - \frac{i}{\hbar}(\hat{\mathbf{P}} \cdot \mathbf{b}) + \dots\right). \quad (\text{A.37})$$

Multiplying out, we obtain

$$(\hat{\mathbf{P}} \cdot \mathbf{b})(\hat{\mathbf{P}} \cdot \mathbf{a}) = (\hat{\mathbf{P}} \cdot \mathbf{a})(\hat{\mathbf{P}} \cdot \mathbf{b}). \quad (\text{A.38})$$

Writing the above equation in component form, and equating the coefficients of $a_i b_j$ on both sides then shows that the components $\hat{P}_x, \hat{P}_y, \hat{P}_z$ of the total momentum operator $\hat{\mathbf{P}}$ are mutually commuting:

$$[\hat{P}_i, \hat{P}_j] = 0. \quad (\text{A.39})$$

If the expectation values of an operator \hat{A} are invariant under translations for all possible states of the system,

$$\langle \phi' | \hat{A} | \psi' \rangle = \langle \phi | \hat{A} | \psi \rangle, \quad (\text{A.40})$$

then we must have

$$\hat{U}^\dagger(\mathbf{a})\hat{A}\hat{U}(\mathbf{a}) = \hat{A}. \quad (\text{A.41})$$

Since $\hat{U}(\mathbf{a})$ is unitary, this implies that \hat{A} commutes with $\hat{U}(\mathbf{a})$:

$$[\hat{A}, \hat{U}(\mathbf{a})] = 0. \quad (\text{A.42})$$

Taking $\hat{U}(\mathbf{a})$ to correspond to an infinitesimal translation, as in Eq. (A.30), then gives

$$[\hat{A}, \hat{\mathbf{P}} \cdot \mathbf{a}] = 0. \quad (\text{A.43})$$

For this to hold for all possible translations \mathbf{a} , the operator \hat{A} must commute with the generators of the translation:

$$[\hat{A}, \hat{P}_i] = 0, \quad [\hat{A}, \hat{\mathbf{P}}] = 0. \quad (\text{A.44})$$

In particular, if the expectation values of the Hamiltonian \hat{H} are invariant under spatial translation for all states of the system (as they must be for an isolated system, for example), then we have

$$[\hat{H}, \hat{P}_i] = 0. \quad (\text{A.45})$$

From Ehrenfest's theorem, the expectation values, $\langle \hat{P}_x \rangle, \langle \hat{P}_y \rangle, \langle \hat{P}_z \rangle$, of each component of the total linear momentum are therefore conserved:

$$\frac{d\langle \hat{P}_i \rangle}{dt} = 0. \quad (\text{A.46})$$

We thus establish that conservation of total linear momentum for an isolated system is a consequence of invariance under spatial translations.

A.2.2 Spatial Rotations

A spatial rotation is a real, linear transformation of spatial three-vectors $\mathbf{r} = (r_x, r_y, r_z) = (r_1, r_2, r_3)$ of the form

$$r_i \rightarrow r'_i = \sum_{j=1}^3 R_{ij} r_j \quad (\text{A.47})$$

that leaves all three-vector scalar products $\mathbf{x} \cdot \mathbf{y}$ invariant:

$$\sum_i \left(\sum_j R_{ij} x_j \right) \left(\sum_k R_{ik} y_k \right) = \sum_i x_i y_i. \quad (\text{A.48})$$

Writing the right-hand side of the above equation as

$$\sum_i x_i y_i = \sum_i \left(\sum_j \delta_{ij} x_j \right) \left(\sum_k \delta_{ik} y_k \right), \quad (\text{A.49})$$

and equating the coefficients of $x_j y_k$ on both sides then gives

$$\sum_i R_{ij} R_{ik} = \delta_{jk}. \quad (\text{A.50})$$

In matrix notation, this is

$$R^T R = \mathbb{I}, \quad (\text{A.51})$$

where R and R^T are matrices which contain the elements

$$[R]_{ij} = [R^T]_{ji} = R_{ij}. \quad (\text{A.52})$$

Using the identities $\det(R^T R) = \det(R^T) \det(R)$ and $\det(R^T) = \det(R)$, Eq. (A.51) then implies that the determinant of R is

$$\det(R) = \pm 1. \quad (\text{A.53})$$

Transformations with $\det(R) = +1$ are spatial rotations; transformations with $\det(R) = -1$ are spatial inversions.

For an infinitesimal rotation, we can write the matrix R in the form

$$R = \mathbb{I} + \omega + \mathcal{O}(\omega^2); \quad R_{ij} = \delta_{ij} + \omega_{ij} + \mathcal{O}(\omega^2), \quad (\text{A.54})$$

where the ω_{ij} are infinitesimal parameters. The condition in Eq. (A.51) then gives

$$\mathbb{I} = [\mathbb{I} + \omega^T + \mathcal{O}(\omega^2)] [\mathbb{I} + \omega + \mathcal{O}(\omega^2)] = \mathbb{I} + \omega^T + \omega + \mathcal{O}(\omega^2). \quad (\text{A.55})$$

Hence the matrix ω must satisfy the constraint

$$\omega^T = -\omega, \quad \omega_{ji} = -\omega_{ij}, \quad (\text{A.56})$$

and so is of the form

$$\omega = \begin{pmatrix} 0 & \omega_{12} & \omega_{13} \\ -\omega_{12} & 0 & \omega_{23} \\ -\omega_{13} & -\omega_{23} & 0 \end{pmatrix}. \quad (\text{A.57})$$

To find the explicit form of the matrix ω for a general infinitesimal rotation, we begin by considering a rotation through a finite angle ϕ about the z -axis. The rotation matrix R_z corresponding to such a rotation is

$$R_z = \begin{pmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (\text{A.58})$$

This can be considered to be either an *active* rotation of the position vector \mathbf{r} , keeping the coordinate axes fixed, or, equivalently, a *passive* rotation of the coordinate axes, keeping all positions (the apparatus) fixed.

The sign convention in Eq. (A.58) corresponds to the left-hand rule (right-hand rule) for active (passive) rotations: when the thumb is oriented along the rotation axis (the $+z$ direction), the direction of the fingers gives the sense of the rotation for positive $\phi > 0$.

When the angle ϕ is infinitesimal, the matrix R_z becomes, to leading order,

$$R_z = \begin{pmatrix} 1 & \phi & 0 \\ -\phi & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \mathcal{O}(\phi^2), \quad \omega = \begin{pmatrix} 0 & \phi & 0 \\ -\phi & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (\text{A.59})$$

To find the corresponding matrices for rotations about the x and y axes, cycle the coordinates as $(x, y, z) \rightarrow (y, z, x) \rightarrow (z, x, y)$:

FIGURE

For example, the matrix element $[R_z]_{xy}$ (equal to $\sin \phi$) for a rotation about the z -axis becomes the matrix element $[R_y]_{zx}$ for a rotation about the y -axis. This gives

$$R_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \phi & \sin \phi \\ 0 & -\sin \phi & \cos \phi \end{pmatrix}, \quad R_y = \begin{pmatrix} \cos \phi & 0 & -\sin \phi \\ 0 & 1 & 0 \\ \sin \phi & 0 & \cos \phi \end{pmatrix}. \quad (\text{A.60})$$

For a general infinitesimal rotation, combining three matrices of the forms given in Eq. (A.59) and (A.60) then gives

$$\omega = \begin{pmatrix} 0 & \omega_3 & -\omega_2 \\ -\omega_3 & 0 & \omega_1 \\ \omega_2 & -\omega_1 & 0 \end{pmatrix} \quad (\text{A.61})$$

This corresponds to a rotation through an infinitesimal angle $|\omega|$ about an axis oriented in the direction of the vector $\omega = (\omega_1, \omega_2, \omega_3)$.

For two successive rotations R_1 and R_2 , satisfying $R_1^T R_1 = \mathbb{I}$ and $R_2^T R_2 = \mathbb{I}$, we have

$$(R_2 R_1)^T (R_2 R_1) = (R_1)^T (R_2)^T (R_2 R_1) = R_1^T R_1 = \mathbb{I}. \quad (\text{A.62})$$

Thus the matrix product $R_2 R_1$ satisfies the condition in Eq. (A.51), showing that two successive rotations correspond to a single, overall spatial rotation.

Since, in general, matrices do not commute, neither do rotations; applying R_1 followed by R_2 will in general give a different overall rotation to applying R_2 followed by R_1 .

A.3 The Wigner-Eckart Theorem

Proofs of the Wigner-Eckart theorem for the particular cases of a scalar operator, \hat{K} , and a vector operator, $\hat{\mathbf{V}}$, are presented below.

A.3.1 Scalar and Vector Operators

The Wigner-Eckart theorem dictates the form of matrix elements such as $\langle \alpha'' j'' m'' | \hat{K} | \alpha' j' m' \rangle$ and $\langle \alpha'' j'' m'' | \hat{\mathbf{V}} | \alpha' j' m' \rangle$ between eigenstates $|\alpha j m\rangle$ of an angular momentum operator $\hat{\mathbf{J}}$. In this context, the operator $\hat{\mathbf{J}}$ is any operator whose components $(\hat{J}_1, \hat{J}_2, \hat{J}_3)$ satisfy the commutation relations

$$[\hat{J}_i, \hat{J}_j] = i\hbar \epsilon_{ijk} \hat{J}_k. \quad (\text{A.63})$$

An operator \hat{K} is a scalar operator with respect to $\hat{\mathbf{J}}$ if it commutes with all components of $\hat{\mathbf{J}}$:

$$[\hat{J}_i, \hat{K}] = 0; \quad [\hat{\mathbf{J}}, \hat{K}] = 0; \quad [\hat{\mathbf{J}}^2, \hat{K}] = 0. \quad (\text{A.64})$$

An operator $\hat{\mathbf{V}} = (\hat{V}_1, \hat{V}_2, \hat{V}_3)$ is a vector operator with respect to $\hat{\mathbf{J}}$ if its components satisfy the commutation relations

$$[\hat{J}_i, \hat{V}_j] = i\hbar \sum_k \epsilon_{ijk} \hat{V}_k. \quad (\text{A.65})$$

Eq. (A.63)–(A.65) are the only requirements which the operators $\hat{\mathbf{J}}$, \hat{K} and $\hat{\mathbf{V}}$ must satisfy in order for the Wigner-Eckart theorem to be applicable.

A.3.2 Angular Momentum Relations

The operators $\hat{\mathbf{J}}^2$ and $\hat{J}_z = \hat{J}_3$ possess a set of simultaneous eigenstates, $|\alpha j m\rangle$, such that

$$\hat{\mathbf{J}}^2 |\alpha j m\rangle = j(j+1)\hbar^2 |\alpha j m\rangle, \quad \hat{J}_z |\alpha j m\rangle = m\hbar |\alpha j m\rangle, \quad (\text{A.66})$$

where j and m are the usual angular momentum quantum numbers, and α collectively labels all other quantum numbers needed to uniquely identify the states. The ladder operators $\hat{J}_{\pm} \equiv \hat{J}_1 \pm i\hat{J}_2$ acting on the state $|\alpha j m\rangle$ raise or lower the index m by ± 1 :

$$\hat{J}_{\pm} |\alpha j m\rangle = \hbar \sqrt{j(j+1) - m(m \pm 1)} |\alpha j, m \pm 1\rangle. \quad (\text{A.67})$$

Noting that $(\hat{J}_{\pm})^{\dagger} = \hat{J}_{\mp}$, the conjugate of this relation is

$$\langle \alpha j m | \hat{J}_{\mp} = \hbar \sqrt{j(j+1) - m(m \pm 1)} \langle \alpha j, m \pm 1 |. \quad (\text{A.68})$$

Writing this equation in terms of \hat{J}_{\pm} rather than \hat{J}_{\mp} (i.e. interchanging all “ \pm ” and “ \mp ” signs), we obtain

$$\langle \alpha j m | \hat{J}_{\pm} = \hbar \sqrt{j(j+1) - m(m \mp 1)} \langle \alpha j, m \mp 1 |. \quad (\text{A.69})$$

A.3.3 The Wigner-Eckart Theorem for Scalar Operators

Since the scalar operator \hat{K} commutes with \hat{J}_z , we have, for any pair of total angular momentum eigenstates $|\alpha''j''m''\rangle$ and $|\alpha'j'm'\rangle$,

$$0 = \langle \alpha''j''m'' | [\hat{J}_z, \hat{K}] | \alpha'j'm' \rangle \quad (\text{A.70})$$

$$= \hbar(m'' - m') \langle \alpha''j''m'' | \hat{K} | \alpha'j'm' \rangle. \quad (\text{A.71})$$

Therefore, if $m'' \neq m'$, the matrix element $\langle \alpha''j''m'' | \hat{K} | \alpha'j'm' \rangle$ must vanish. Similarly, since \hat{K} commutes with $\hat{\mathbf{J}}^2$, we have

$$0 = \langle \alpha''j''m'' | [\hat{\mathbf{J}}^2, \hat{K}] | \alpha'j'm' \rangle = \hbar^2[j''(j''+1) - j'(j'+1)] \langle \alpha''j''m'' | \hat{K} | \alpha'j'm' \rangle. \quad (\text{A.72})$$

Hence, if $j'' \neq j'$, the matrix element $\langle \alpha''j''m'' | \hat{K} | \alpha'j'm' \rangle$ must vanish. Overall therefore, we must have

$$\langle \alpha''j''m'' | \hat{K} | \alpha'j'm' \rangle = \delta_{j''j'} \delta_{m''m'} C(\alpha''\alpha'; j'm'), \quad (\text{A.73})$$

where $C(\alpha''\alpha'; j'm')$ is a constant. For $j'' = j'$ and $m'' = m'$, the equation above becomes

$$\langle \alpha''j'm' | \hat{K} | \alpha'j'm' \rangle = C(\alpha''\alpha'; j'm'). \quad (\text{A.74})$$

Since \hat{K} commutes with the ladder operators \hat{J}_{\pm} , we have

$$\langle \alpha''j''m'' | \hat{J}_{\pm} \hat{K} | \alpha'j'm' \rangle = \langle \alpha''j''m'' | \hat{K} \hat{J}_{\pm} | \alpha'j'm' \rangle. \quad (\text{A.75})$$

Using Eq. (A.67) and (A.69) then gives

$$\begin{aligned} & \sqrt{j''(j''+1) - m''(m'' \mp 1)} \langle \alpha''j'', m'' \mp 1 | \hat{K} | \alpha'j'm' \rangle \\ &= \sqrt{j'(j'+1) - m'(m' \pm 1)} \langle \alpha''j''m'' | \hat{K} | \alpha'j', m' \pm 1 \rangle. \end{aligned} \quad (\text{A.76})$$

For $j'' = j'$ and $m'' = m' \pm 1$, the square-root factors on either side of the equation above are equal to each other; cancelling these factors then leaves

$$\langle \alpha''j'm' | \hat{K} | \alpha'j'm' \rangle = \langle \alpha''j', m' \pm 1 | \hat{K} | \alpha'j', m' \pm 1 \rangle. \quad (\text{A.77})$$

Comparing with Eq. (A.74) then gives

$$C(\alpha''\alpha'; j'm') = C(\alpha''\alpha'; j', m' \pm 1). \quad (\text{A.78})$$

Thus the constants $C(\alpha''\alpha'; j'm')$ are, in fact, independent of the quantum number m' , and can be written as $C(\alpha''\alpha'; j')$. Eq. (A.73) then gives the *Wigner-Eckart theorem* for scalar operators,

$$\boxed{\langle \alpha''j''m'' | \hat{K} | \alpha'j'm' \rangle = C(\alpha''\alpha'; j') \delta_{j''j'} \delta_{m''m'}.} \quad (\text{A.79})$$

as in Eq. (8.77).

A.3.4 The Wigner-Eckart Theorem for Vector Operators

The commutation relations of the vector operator $\hat{\mathbf{V}}$ with the ladder operators \hat{J}_{\pm} were obtained in Eq. (8.64):

$$[\hat{J}_{\pm}, \hat{V}_m] = \hbar \sqrt{j(j+1) - m(m \pm 1)} \hat{V}_{m \pm 1}, \quad (j \equiv 1, m = 0, \pm 1). \quad (\text{A.80})$$

Taking matrix elements of Eq. (8.64) between eigenstates $|\alpha' j' m'\rangle$ and $|\alpha'' j'' m''\rangle$ of the total angular momentum operator $\hat{\mathbf{J}}$ gives

$$\langle \alpha'' j'' m'' | (\hat{J}_{\pm} \hat{K}_m - \hat{K}_m \hat{J}_{\pm}) | \alpha' j' m' \rangle = \hbar \sqrt{j(j+1) - m(m \pm 1)} \langle \alpha'' j'' m'' | \hat{K}_{m \pm 1} | \alpha' j' m' \rangle, \quad (\text{A.81})$$

where

$$j \equiv 1, \quad m = 0, \pm 1. \quad (\text{A.82})$$

From Eq. (A.67) and (A.69), the ladder operators act on the states $\langle \alpha'' j'' m'' |$ and $|\alpha' j' m'\rangle$ as

$$\langle \alpha'' j'' m'' | \hat{J}_{\pm} = \hbar \sqrt{j''(j''+1) - m''(m'' \mp 1)} \langle \alpha'' j'', m'' \mp 1 |, \quad (\text{A.83})$$

$$\hat{J}_{\pm} |\alpha' j' m'\rangle = \hbar \sqrt{j'(j'+1) - m'(m' \pm 1)} |\alpha' j', m' \pm 1\rangle. \quad (\text{A.84})$$

Substituting the above into the left-hand side of Eq. (A.81) and rearranging, we obtain the following relation between spherical component matrix elements:

$$\begin{aligned} & \sqrt{j''(j''+1) - m''(m'' \mp 1)} \langle \alpha'' j'', m'' \mp 1 | \hat{V}_m | \alpha' j' m' \rangle \\ &= \sqrt{j(j+1) - m(m \pm 1)} \langle \alpha'' j'' m'' | \hat{V}_{m \pm 1} | \alpha' j' m' \rangle \\ &+ \sqrt{j'(j'+1) - m'(m' \pm 1)} \langle \alpha'' j'' m'' | \hat{V}_m | \alpha' j', m' \pm 1 \rangle. \end{aligned} \quad (\text{A.85})$$

This relation connects matrix elements with common values of j' and j'' throughout, but with varying m , m' and m'' .

Now consider the addition of two angular momentum operators $\hat{\mathbf{J}}$ and $\hat{\mathbf{J}}'$ to form a combined angular momentum $\hat{\mathbf{J}}''$:

$$|jm; j'm'\rangle \equiv |jm\rangle \otimes |j'm'\rangle. \quad (\text{A.86})$$

The action of the ladder operator $\hat{J}_{\pm}'' = \hat{J}_{\pm} + \hat{J}'_{\pm}$ on these product states is

$$\begin{aligned} \hat{J}_{\pm}'' |jm; j'm'\rangle &= \hbar \sqrt{j(j+1) - m(m \pm 1)} |j, m \pm 1; j'm'\rangle \\ &+ \hbar \sqrt{j'(j'+1) - m'(m' \pm 1)} |jm; j', m' \pm 1\rangle. \end{aligned} \quad (\text{A.87})$$

Premultiplying by an eigenstate $\langle j'' m'' |$ of $\hat{\mathbf{J}}''$ then gives

$$\begin{aligned} \langle j'' m'' | \hat{J}_{\pm}'' |jm; j'm'\rangle &= \hbar \sqrt{j(j+1) - m(m \pm 1)} \langle j'' m'' | j, m \pm 1; j'm'\rangle \\ &+ \hbar \sqrt{j'(j'+1) - m'(m' \pm 1)} \langle j'' m'' | jm; j', m' \pm 1\rangle. \end{aligned} \quad (\text{A.88})$$

Taking the complex conjugate of the above equation, and using $(\hat{J}_\pm'')^\dagger = \hat{J}_\mp''$, we obtain

$$\begin{aligned} \langle jm; j'm' | \hat{J}_\mp'' | j''m'' \rangle &= \hbar \sqrt{j(j+1) - m(m \pm 1)} \langle j, m \pm 1; j'm' | j''m'' \rangle \\ &\quad + \hbar \sqrt{j'(j'+1) - m'(m' \pm 1)} \langle jm; j'm', \pm 1 | j''m'' \rangle. \end{aligned} \quad (\text{A.89})$$

The matrix element on the left-hand side can be evaluated using

$$\hat{J}_\mp'' | j''m'' \rangle = \hbar \sqrt{j''(j''+1) - m''(m'' \mp 1)} | j'', m'' \pm 1 \rangle. \quad (\text{A.90})$$

Hence we obtain the following relation between Clebsch-Gordan coefficients of fixed j , j' and j'' , but varying m , m' and m'' :

$$\begin{aligned} \sqrt{j''(j''+1) - m''(m'' \mp 1)} \langle jm; j'm' | j'', m'' \pm 1 \rangle \\ = \hbar \sqrt{j(j+1) - m(m \pm 1)} \langle j, m \pm 1; j'm' | j''m'' \rangle \\ + \hbar \sqrt{j'(j'+1) - m'(m' \pm 1)} \langle jm; j'm', \pm 1 | j''m'' \rangle. \end{aligned} \quad (\text{A.91})$$

This relation is *identical in form* to Eq. (A.85), under the replacements

$$\langle \alpha'' j'' m'' | \hat{V}_{m \pm 1} | \alpha' j' m' \rangle \longleftrightarrow \langle j, m \pm 1; j'm' | j''m'' \rangle. \quad (\text{A.92})$$

Thus Eq. (A.85) and (A.91) represent two identical sets of linear, homogenous equations of the form

$$\sum_j A_{ij} x_j = 0, \quad \sum_j A_{ij} y_j = 0. \quad (\text{A.93})$$

In the first set of equations, the quantities x_j are matrix elements $\langle \alpha'' j'' m'' | \hat{V}_{m \pm 1} | \alpha' j' m' \rangle$ of $\hat{\mathbf{V}}$. In the second set, the y_j are Clebsch-Gordan coefficients $\langle j, m \pm 1; j'm' | j''m'' \rangle$. The matrix A_{ij} contains all the factors of the form $\sqrt{j(j+1) - m(m \pm 1)}$, and is common to both sets of equations.

The solution to linear equations of the form given in Eq. (A.93) is unique up to an overall constant. Hence the solutions x_j and y_j must be directly proportional to each other:

$$\langle \alpha'' j'' m'' | \hat{V}_{m \pm 1} | \alpha' j' m' \rangle = C(\alpha'' \alpha'; j'' j') \langle j, m \pm 1; j'm' | j''m'' \rangle. \quad (\text{A.94})$$

The (complex) constant of proportionality, $C(\dots)$, must be independent of m , m' and m'' because these parameters vary from element to element within the matrix A_{ij} . On the other hand, the parameters α'' , α' , j'' and j' are common to all the elements A_{ij} .

Replacing $m \pm 1$ by m throughout Eq. (A.94), we obtain the Wigner-Eckart theorem for a vector operator $\hat{\mathbf{V}}$:

$$\langle \alpha'' j'' m'' | \hat{V}_m | \alpha' j' m' \rangle = C(\alpha'' \alpha'; j'' j') \langle jm; j'm' | j''m'' \rangle. \quad (\text{A.95})$$

The constant $C(\alpha'' \alpha'; j'' j')$, the reduced matrix element, is usually written in Dirac-style notation as $\langle \alpha'' j'' || \hat{\mathbf{V}} || \alpha' j' \rangle$, giving the Wigner-Eckart Theorem in standard form as

$$\boxed{\langle \alpha'' j'' m'' | \hat{V}_m | \alpha' j' m' \rangle = \langle \alpha'' j'' || \hat{\mathbf{V}} || \alpha' j' \rangle \langle jm; j'm' | j''m'' \rangle,} \quad (\text{A.96})$$

as in Eq. (8.88). In the equation above, the quantum number j is, by definition, $j \equiv 1$, and the quantum number m takes the values $m = \pm 1, 0$.

A.4 Virial Theorem

The virial theorem is an important theorem for a system of moving particles both in classical physics and quantum physics. The virial Theorem is useful when considering a collection of many particles and has a special importance to central-force motion. For a general system of mass points with position vectors \mathbf{r}_i and applied forces \mathbf{F}_i , consider the scalar product G

$$G \equiv \sum_i \mathbf{p}_i \cdot \mathbf{r}_i, \quad (\text{A.97})$$

where i sums over all particles. The time derivative of G is

$$\frac{dG}{dt} = \sum_i \mathbf{p}_i \cdot \dot{\mathbf{r}}_i + \sum_i \dot{\mathbf{p}}_i \cdot \mathbf{r}_i. \quad (\text{A.98})$$

However,

$$\sum_i \mathbf{p}_i \cdot \dot{\mathbf{r}}_i = \sum_i m \dot{\mathbf{r}}_i \cdot \dot{\mathbf{r}}_i = \sum_i m v_i^2 = 2T. \quad (\text{A.99})$$

Also, since

$$\sum_i \dot{\mathbf{p}}_i \cdot \mathbf{r}_i = \sum_i \mathbf{F}_i \cdot \mathbf{r}_i. \quad (\text{A.100})$$

Thus,

$$\frac{dG}{dt} = 2T + \sum_i \mathbf{F}_i \cdot \mathbf{r}_i. \quad (\text{A.101})$$

The time average over a period τ is

$$\frac{1}{\tau} \int_0^\tau \frac{dG}{dt} dt = \frac{G(\tau) - G(0)}{\tau} = \langle 2T \rangle + \left\langle \sum_i \mathbf{F}_i \cdot \mathbf{r}_i \right\rangle. \quad (\text{A.102})$$

where the $\langle \rangle$ brackets refer to the time average. Note that if the motion is periodic and the chosen time τ equals a multiple of the period, then $\frac{G(\tau) - G(0)}{\tau} = 0$. Even if the motion is not periodic, if the constraints and velocities of all the particles remain finite, then there is an upper bound to G . This implies that choosing $\tau \rightarrow \infty$ means that $\frac{G(\tau) - G(0)}{\tau} \rightarrow 0$. In both cases the left-hand side of the equation tends to zero giving the virial theorem:

$$\langle T \rangle = -\frac{1}{2} \left\langle \sum_i \mathbf{F}_i \cdot \mathbf{r}_i \right\rangle. \quad (\text{A.103})$$

The right-hand side of this equation is called the virial of the system. For a single particle subject to a conservative central force $\mathbf{F} = -\nabla U$ the virial theorem equals

$$\langle T \rangle = \frac{1}{2} \langle \nabla U \cdot \mathbf{r} \rangle = \frac{1}{2} \left\langle r \frac{\partial U}{\partial r} \right\rangle. \quad (\text{A.104})$$

If the potential is of the form $U = kr^{n+1}$ that is, $\mathbf{F} = -k(n+1)r^n$, then $r \frac{\partial U}{\partial r} = (n+1)U$. Thus for a single particle in a central potential $U = kr^{n+1}$ the virial theorem reduces to

$$\langle T \rangle = \frac{n+1}{2} \langle U \rangle. \quad (\text{A.105})$$

The following two special cases are of considerable importance in physics.

- **Hooke's Law:** Note that for a linear restoring force $n = 1$ then

$$\langle T \rangle = + \langle U \rangle \quad (\text{A.106})$$

Which should be familiar, for simple harmonic motion where the average kinetic and potential energies are the same and both equal half of the total energy.

- **Inverse-Square Law:** The other interesting case is for the inverse square law $n = -2$ where

$$\langle T \rangle = -\frac{1}{2} \langle U \rangle \quad (\text{A.107})$$

The virial theorem is useful for solving problems in that knowing the exponent n of the field makes it possible to write down directly the average total energy in the field. For example, for

$$\langle E \rangle = \langle T \rangle + \langle U \rangle \quad (\text{A.108})$$

$$= -\frac{1}{2} \langle U \rangle + \langle U \rangle = \frac{1}{2} \langle U \rangle \quad (\text{A.109})$$

This occurs for the Bohr model of the hydrogen atom where the kinetic energy of the bound electron is half of the potential energy. The same result occurs for planetary motion in the solar system.