7 The 3D Schrödinger equation

7.1 Quantum mechanics in three dimensions

We can develop quantum mechanics in three dimensions following the analogy with classical mechanics that we used to obtain the 1D Schrödinger equation. The classical state of a single particle is described by six dynamical variables: its position $\underline{x} = (x_1, x_2, x_3) = \sum_{i=1}^{3} x_i \underline{e_i}$ and momentum $\underline{p} = (p_1, p_2, p_3) = \sum_{i=1}^{3} p_i \underline{e_i}$, where $\underline{e_i}$ are the standard orthonormal basis vectors. The particle's energy is

(7.1)

(Throughout this section, we use M to denote mass, to avoid confusion with the L_3 angular momentum eigenvalue denoted by m which we introduce below.)

Proceeding by analogy with the 1D case, we can introduce operators

$$\begin{aligned} \hat{x_i} &= x_i \qquad (\text{ i.e. multiplication by } x_i)\,, \\ \hat{p_i} &= -i\hbar \frac{\partial}{\partial x_i}\,, \\ \text{or in vector form } \ \hat{\underline{x}} &= \underline{x} && (7.2) \\ \hat{\underline{p}} &= -i\hbar \underline{\nabla} && (7.3) \\ \text{and } \hat{H} &= \frac{\hat{\underline{p}}.\hat{\underline{p}}}{2M} + V(\underline{x}) \\ &= -\frac{\hbar^2}{2M}\nabla^2 + V(\underline{x})\,. && (7.4) \end{aligned}$$

Here we define a *vector operator* $\underline{A}$ to be a triple of operators (A_1, A_2, A_3) such that $\underline{A}\psi(\underline{x}) = (A_1\psi(\underline{x}), A_2\psi(\underline{x}), A_3\psi(\underline{x}))$ is a vector for all wavefunctions $\psi(\underline{x})$ and all $\underline{x}$.

We also take the wavefunction ψ to depend on 3 space and 1 time coordinates: $\psi \equiv \psi(\underline{x}, t)$. The 3D normalisation condition is

(7.5)

Following the 1D analogy gives us the *3D time-dependent Schrödinger equation*

$$\hat{H}\psi(\underline{x}, t) = i\hbar \frac{\partial}{\partial t}\psi(\underline{x}, t)\,, \tag{7.6}$$

or more explicitly, for a time-independent potential V,

(7.7)

Using the method of separation of variables, as before, we can derive the 3D time-independent Schrödinger equation

$$-\frac{\hbar^2}{2M}\nabla^2\psi(\underline{x}) + V(\underline{x})\psi(\underline{x}) = E\psi(\underline{x})\,. \tag{7.8}$$

We can define the probability density and current

(7.9)

(7.10)

and as in the 1D case (cf (3.17)) we can show that they obey a conservation equation

(7.11)

Notice that the 3D Schrödinger equation, like the 1D SE, is linear and the superposition principle thus applies to its solutions: there is a physical solution corresponding to any linear combination of two (or more) physical solutions.

The Born rule naturally extends to the 3D case: the probability of finding a particle in a small 3D volume V which contains a point $\underline{x_0}$ is

(7.12)

We define the inner product of 3D wavefunctions by

The definition of the expectation value of an observable $\hat{A}$ in terms of the corresponding hermitian operator A also naturally extends to 3D wavefunctions:

$$\langle \hat{A} \rangle_\psi = \int \psi^*(\underline{x}, t) A \psi(\underline{x}, t) d^3x = (\psi, A\psi) \,. \tag{7.13}$$

We can thus define the uncertainty $\Delta_\psi A$ as in (6.21), using the definition (7.13) for expectation values.

The proofs of theorems 6.1 and 6.2 apply to hermitian operators on 3D wavefunctions just as to hermitian operators on 1D wavefunctions.

Theorem 6.3 also extends to hermitian operators on 3D wavefunctions: the discrete and continuous sets of eigenfunctions of a hermitian operator form a complete orthogonal basis of th normalisable complex-valued functions $\psi(\underline{x})$ of 3D vectors $\underline{x}$.

7.2 Spherically symmetric potentials

The 3D time-independent Schrödinger equation simplifies considerably when the potential $V(\underline{x})$ is spherically symmetric about the origin.[20] We call this a *central* potential.

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[20] Of course, if V is spherically symmetric about any given point, we can redefine our coordinates by translation to make that point the origin.

It is convenient to use spherical polar coordinates

$$x_1 = r\sin\theta\cos\phi\,, \qquad x_2 = r\sin\theta\sin\phi\,, \qquad x_3 = r\cos\theta\,, \tag{7.14}$$

which have ranges $0 \le r < \infty$, $0 \le \phi < 2\pi$, $0 \le \theta \le \pi$.

In spherical polars, a central potential $V(\underline{x}) \equiv V(r,\theta,\phi)$ depends only on $r = |\underline{x}|$. Recall that in Cartesian coordinates we have $\nabla^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2}$. In spherical polars this becomes[21]

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{7.15}$$

For spherically symmetric stationary states $\psi(r)$, the time-independent SE simplifies. We have $\frac{\partial\psi}{\partial\theta} = \frac{\partial\psi}{\partial\phi} = 0$ and so

(7.16)

so we have

$$-\frac{\hbar^2}{2M}\frac{1}{r}\frac{d^2}{dr^2}(r\psi(r)) + V(r)\psi(r) = E\psi(r)\,, \tag{7.17}$$

which we can rewrite as

$$-\frac{\hbar^2}{2M}\frac{d^2}{dr^2}(r\psi(r)) + V(r)(r\psi(r)) = E(r\psi(r))\,. \tag{7.18}$$

Notice that (7.18) is the 1D time-independent SE for $\phi(r) = r\psi(r)$, on the interval $0 \le r < \infty$.

We require $\phi(r) \to 0$ as $r \to 0$, otherwise $\psi(r) \approx O(1/r)$ as $r \to 0$ and so is singular at $r = 0$. It can be shown that this means that the 3D Schrödinger equation (7.7) fails to hold there.[22]

Any solution to (7.18) with $\phi(r) \to 0$ as $r \to 0$ can be extended to an odd parity solution $\tilde{\phi}(r)$ of the 1D SE in $-\infty < r < \infty$ of the same energy, with $\tilde{\phi}(r)$ and $\frac{d\tilde{\phi}}{dr}$ continuously defined at $r = 0$, by defining

(7.19)

Conversely, any odd parity solution of the 1D SE for $-\infty < r < \infty$ defines a solution to (7.18) with $\phi(r) \to 0$ as $r \to 0$ and $\frac{d\phi}{dr}$ finite at $r = 0$. Provided that

---

[21] See IA Vector Calculus, or e.g. Collinson "Introductory Vector Analysis", Chap. 12.

[22] * See Dirac, "The Principles of Quantum Mechanics" (4th edition), Chap. VI for a full discussion. *

$V(r)$ is finite and continuous at $r = 0$, these are the correct continuity conditions for solutions of the 3D SE: they imply that ψ and ψ' are continuous at the origin.

Solving (7.18) thus becomes equivalent to finding *odd parity solutions* to the 1D SE for $-\infty < r < \infty$.

Comments We will show later (see Thm. 7.2) that the ground state (the lowest energy bound state, if there is one) of a 3D quantum system with spherically symmetric potential is itself spherically symmetric. (Cf. the 1D result that the ground state of a symmetric potential always has even parity.) Hence we can always use the method above to obtain the ground state.

One might wonder whether there might not exist even parity solutions $\phi_+(r)$ of the 1D SE with the property that $\phi_+(0) = \frac{d\phi_+}{dr}(0) = 0$, which would also define solutions to (7.18) for $0 \leq r < \infty$ with the appropriate properties. The following lemma rules this out.

Lemma 7.1. *There are no even parity solutions $\phi_+(r)$ of the 1D SE with the property that $\phi_+(0) = \frac{d\phi_+}{dr}(0) = 0$.*

Proof. If such a solution ϕ_+ were to exist, we could define a continuous odd parity solution $\phi_-(r)$ by

$$\phi_-(r) = \begin{cases} \phi_+(r) & r \geq 0\,, \\ -\phi_+(-r) & r < 0\,. \end{cases} \tag{7.20}$$

Then, by the superposition principle, $\phi(r) = \phi_+(r) - \phi_-(r)$ would also be a solution. But we have $\phi(r) = 0$ for $r > 0$, so that all derivatives of ϕ vanish for $r \geq 0$. The Schrödinger equation has no non-trivial solutions with this property: hence $\phi(r) = 0$ for all r. Hence $\phi_+(r) = \phi_-(r) = 0$ for all r, so in particular the hypothesised even parity solution ϕ_+ is not a physical solution, as it vanishes everywhere. ■

7.3 Examples of spherically symmetric potentials

7.3.1 The spherical harmonic oscillator

has potential

The general method we have just given for constructing spherically symmetric stationary states shows that its spherically symmetric stationary states are related by (7.19) to the odd parity bound states of the 1D harmonic oscillator, and have the same energies. Thus the lowest energy spherically symmetric stationary state – i.e. the ground state – has energy $\frac{3}{2}\hbar\omega$, and the higher energy (excited) spherically symmetric states have energies $(2n + \frac{3}{2})\hbar\omega$ for positive integer n.

7.3.2 The spherical square well

has potential

(7.21)

By the above argument, spherically symmetric stationary states correspond to odd parity bound states of the 1D square well potential

$$V(x) = \begin{cases} -U & |x| < a\,, \\ 0 & |x| > a\,. \end{cases} \tag{7.22}$$

These, if they exist, can be obtained by the graphical method used earlier to obtain 1D square well potential bound states. In particular, one can show (cf. section 4 above and example sheet I, question 10) that there exists an odd parity bound state if and only if

$$\sqrt{\frac{2MU}{\hbar^2}} \geq \frac{\pi}{2a} \,. \qquad (7.23)$$

So, if this condition is not satisfied, the 3D spherical square well does not have a spherically symmetric stationary state: i.e. it does not have a ground state, and thus does not have any bound states.

As this illustrates, 3D potential wells (continuous potentials with $V(x) \leq 0$ for all x, $V(x) < 0$ for some x, and $V(x) = 0$ for $|x| > a$, for some finite a) do **not** necessarily have bound states. This is in contrast to the 1D case:

Exercise (important!): Show that all 1D potential wells have at least one bound state.

7.4 Spherically symmetric bound states of the hydrogen atom

We model the hydrogen atom by treating the proton as infinitely massive and at rest.[23]

We seek spherically symmetric bound state wavefunctions $\psi(r)$ for the electron orbiting in a Coulomb potential $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$:

$$-\frac{\hbar^2}{2M}\left(\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr}\right) - \frac{e^2}{4\pi\epsilon_0 r}\psi(r) = E\psi(r) \,, \qquad (7.24)$$

for some $E < 0$. Writing $a = \frac{e^2 M}{2\pi\epsilon_0\hbar^2}$, $b = \frac{\sqrt{-2ME}}{\hbar}$, we have

$$\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr} + \frac{a}{r}\psi - b^2\psi = 0 \,. \qquad (7.25)$$

If we try the ansatz

(7.26)

we see the first and fourth terms dominate the other two for large r, and cancel one another precisely. This suggests trying an ansatz of the form $\psi(r) = f(r)\exp(-br)$, with $f(r) = \sum_{n=0}^{\infty} a_n r^n$, in the hope of finding values of the coefficients a_n such that the four terms cancel precisely to all orders. (Cf. our first solution to the harmonic oscillator.)

Our previous discussion assumed that $V(r)$ is nonsingular as $r \to 0$. Since here $V(r)$ diverges as $r \to 0$, we cannot use the same justification as previously to argue that that $\phi(r) = r\psi(r) \to 0$ as $r \to 0$. However, we still require $\psi(r)$ to define a normalisable 3D wavefunction, so that

$$0 < \int_{r=0}^{\infty} r^2 |\psi(r)|^2 dr < \infty \,.$$

This implies that $\psi(r) = O(r^{-1})$ as $r \to 0$, i.e. that ψ can at worst have a singularity of order r^{-1} at zero. We also require that ψ should correspond to a continuous wavefunction. This excludes a singularity of order r^{-1}, so we require that ψ is regular — i.e. has a finite limit — as $r \to 0$.

---

[23] *This can be shown to be an excellent approximation (see Part II Principles of Quantum Mechanics): it gives the correct energy levels up to an overall constant factor (the same for each energy level) of order $1 + (m_e/m_p) \approx 1.0005$.*

We have

$$\frac{d^2f}{dr^2}+(\frac{2}{r}-2b)\frac{df}{dr}+\frac{1}{r}(a-2b)f(r)=0\,. \tag{7.27}$$

Hence

$$\sum_{n=0}^{\infty}(a_n n(n-1)r^{n-2}+2a_n n r^{n-2}-2ba_n n r^{n-1}+(a-2b)a_n r^{n-1})=0 \tag{7.28}$$

and taking the coefficient of r^{n-2} we have

$$a_n n(n-1)+2a_n n-2ba_{n-1}(n-1)+(a-2b)a_{n-1}=0 \text{ for } n\geq 1\,. \tag{7.29}$$

This gives

(7.30)

We thus have that $a_n \to \frac{2b}{n}a_{n-1}$ for large n. If the coefficients do not vanish for large n, this means they have the asymptotic behaviour of the coefficients of $\exp(2br)$, i.e. $f(r)\approx C\exp(2br)$. This would give $\psi(r)\approx C\exp(2br)\exp(-br)=\exp(br)$, leading to an unnormalisable and thus unphysical wavefunction. So there must be some integer $N\geq 1$ for which $a_N=0$, and we can take N to be the smallest such integer.

Then $a_{N-1}\neq 0$, so that $a_N=0$ implies $2bN=a$ or $b=a/2N$, and so

(7.31)

which is precisely the energy spectrum of the Bohr orbits, but now derived from quantum mechanics (though still with an assumption of spherical symmetry, which we will need to relax to obtain the general orbital wavefunction).

From

$$a=2bN \qquad \text{and } a_n=a_{n-1}\frac{2bn-a}{n(n+1)} \tag{7.32}$$

we obtain

(7.33)

This gives solutions of the form

$$f(r)=\begin{cases} 1 & N=1\,,\\ (1-br) & N=2\,,\\ (1-2br+\frac{2}{3}(br)^2) & N=3\,, \end{cases} \tag{7.34}$$

and generally $f(r) = L^1_{N-1}(2br)$ where L^1_{N-1} is one of the *associated Laguerre polynomials.*[24]

The corresponding wavefunctions are $\psi(r) = CL^1_{N-1}(2br)\exp(-br)$, where the constant C is determined by normalisation.

7.5 Canonical Commutation Relations in 3D

From (7.2) we have

$$\hat{x_i} = x_i \qquad \text{(multiplication by } x_i) \,, \tag{7.35}$$

$$\hat{p_i} = -i\hbar\frac{\partial}{\partial x_i} \,, \tag{7.36}$$

and so, by calculating the action on a general wavefunction as before, we obtain

(7.37)

(7.38)

(The prefactors i on the right hand sides are $\sqrt{-1}$.)

7.6 Orbital Angular Momentum

Recall that in classical mechanics we define the angular momentum vector

$$\underline{L} = \underline{x} \wedge \underline{p} \,, \qquad L_i = \epsilon_{ijk}x_j p_k \,, \tag{7.39}$$

and that $\underline{L}$ is conserved in a spherically symmetric potential $V(r)$.

We define the quantum mechanical operators

(7.40)

and the total angular momentum

(7.41)

---

[24] *There is a simple expression for the associated Laguerre polynomials:

$$L^k_N(x) = \frac{1}{N!}e^x x^{-k}\frac{d^N}{dx^N}(x^{N+k}e^{-x}) \,.$$

Some plots of L^0_N for small N and some other information about the Laguerre polynomials (L^k_N for $k = 0$) and the associated Laguerre polynomials can be found at mathworld.wolfram.com/LaguerrePolynomial.html and at mathworld.wolfram.com/AssociatedLaguerrePolynomial.html .*

7.6.1 Angular momentum commutation relations

$$
\begin{aligned}
[\hat{L}_i, \hat{L}_j] &= -\hbar^2 \epsilon_{ilm}\epsilon_{jnp}[\hat{x}_l \frac{\partial}{\partial x_m}, \hat{x_n}\frac{\partial}{\partial x_p}] \\
&= -\hbar^2 \epsilon_{ilm}\epsilon_{jnp}([\hat{x}_l \frac{\partial}{\partial x_m}, \hat{x_n}]\frac{\partial}{\partial x_p} + \hat{x_n}[\hat{x}_l \frac{\partial}{\partial x_m}, \frac{\partial}{\partial x_p}]) \\
&= \\
&= -\hbar^2 \epsilon_{ilm}\epsilon_{jnp}(\hat{x}_l \delta_{mn}\frac{\partial}{\partial x_p} - \hat{x_n}\delta_{lp}\frac{\partial}{\partial x_m}) \\
&= -\hbar^2 \epsilon_{mil}\epsilon_{mpj}\hat{x}_l \frac{\partial}{\partial x_p} - \hbar^2 \epsilon_{pjn}\epsilon_{pmi}\hat{x_n}\frac{\partial}{\partial x_m}) \\
&= -\hbar^2(\delta_{ip}\delta_{lj} - \delta_{ij}\delta_{lp})\hat{x}_l \frac{\partial}{\partial x_p} - \hbar^2(\delta_{jm}\delta_{ni} - \delta_{ji}\delta_{nm})(\hat{x_n}\frac{\partial}{\partial x_m}) \\
&= \\
&= i\hbar\epsilon_{ijk}\hat{L}_k \,. \\
&=
\end{aligned}
$$

$$
\begin{aligned}
[\hat{L}^2, \hat{L}_i] &= [\hat{L}_j\hat{L}_j, \hat{L}_i] \\
&= \\
&= i\hbar(\epsilon_{jik}(\hat{L}_k\hat{L}_j + \hat{L}_j\hat{L}_k)) \\
&= 0 \,.
\end{aligned}
\tag{7.42}
$$

Since the $\hat{L}_i$ do not commute, they are not simultaneously diagonalisable. However, $\hat{L}^2$ and any one of the $\hat{L}_i$ can be simultaneously diagonalised, since $[\hat{L}^2, \hat{L}_i] = 0$.

We also have

$$[\hat{L}_i, \hat{x}_j] = i\hbar\epsilon_{ijk}\hat{x}_k \,, \tag{7.43}$$

$$[\hat{L}_i, \hat{p}_j] = i\hbar\epsilon_{ijk}\hat{p}_k \,, \tag{7.44}$$

$$[\hat{L}_i, \sum_j \hat{x}_j^2] = \qquad\qquad , \tag{7.45}$$

$$[\hat{L}_i, \sum_j \hat{p}_j^2] = \tag{7.46}$$

Now we have that $\hat{r} = \sqrt{\sum_j \hat{x_j}^2}$. We also have that $[\hat{L}_i, \sum_j \hat{x_j}^2] = 0$. One can show directly from this (see part II Principles of Quantum Mechanics), or check by calculation (Exercise), that $[\hat{L}_i, \hat{r}] = 0$. More generally, one can show that $[\hat{L}_i, V(r)] = 0$ for any spherically symmetric potential $V(r)$. We also have that

$$[\hat{L}_i, \frac{\hat{p}.\hat{p}}{2m}] = [\hat{L}_i, \frac{1}{2m}\sum_j p_j^2] = 0 \,. \tag{7.47}$$

So, for any spherically symmetric potential $V(r)$, we have that

(7.48)

(7.49)

In other words, $\hat{H}, \hat{L}_i$ and $\hat{L}^2$ all commute with one another.

Comment This is an important and powerful result. Given any 3D quantum system, we can find a basis of simultaneous eigenfunctions of $\hat{H}$, $\hat{L}^2$ and $\hat{L}_3$. (The standard convention is to use $\hat{L}_3$. Of course, as the operators are related by rotational symmetry, $\hat{L}_1$ or $\hat{L}_2$ would work equally well.) As we will see, working in such a basis greatly simplifies the solution of the time-independent SE.

7.6.2 Angular momentum operators in spherical polar coordinates

We can translate the definitions of $\hat{L}_i$ to spherical polars. We have

$$x_1 = r\sin\theta\cos\phi\,, \qquad x_2 = r\sin\theta\sin\phi\,, \qquad x_3 = r\cos\theta\,. \tag{7.50}$$

Thus

$$\begin{aligned}\frac{\partial}{\partial\theta} &= \sum_i \frac{\partial x_i}{\partial\theta}\frac{\partial}{\partial x_i}\\ &= r\cos\theta\cos\phi\frac{\partial}{\partial x_1} + r\cos\theta\sin\phi\frac{\partial}{\partial x_2} - r\sin\theta\frac{\partial}{\partial x_3}\,, &(7.51)\\ \frac{\partial}{\partial\phi} &= \sum_i \frac{\partial x_i}{\partial\phi}\frac{\partial}{\partial x_i}\\ &= -r\sin\theta\sin\phi\frac{\partial}{\partial x_1} + r\sin\theta\cos\phi\frac{\partial}{\partial x_2}\,. &(7.52)\end{aligned}$$

We thus obtain

$$\begin{aligned}i\hbar(\cos\phi\cot\theta\frac{\partial}{\partial\phi} + \sin\phi\frac{\partial}{\partial\theta}) &= -i\hbar(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2})\\ &= \hat{L}_1\,, &(7.53)\\ i\hbar(\sin\phi\cot\theta\frac{\partial}{\partial\phi} + \cos\phi\frac{\partial}{\partial\theta}) &= -i\hbar(x_3\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_3})\\ &= \hat{L}_2\,, &(7.54)\\ -i\hbar\frac{\partial}{\partial\phi} &= -i\hbar(x_1\frac{\partial}{\partial x_2} - x_2\frac{\partial}{\partial x_1})\\ &= \hat{L}_3\,. &(7.55)\end{aligned}$$

Notes 1. We could obtain these identities more straightforwardly but long-windedly by first expressing $\frac{\partial}{\partial x_i}$ in terms of r, θ, ϕ, $\frac{\partial}{\partial r}$, $\frac{\partial}{\partial\theta}$, $\frac{\partial}{\partial\phi}$ and thus converting the definitions of the $\hat{L}_i$ into spherical polars.

2. Observe in particular that the $\hat{L}_i$ are all independent of $\frac{\partial}{\partial r}$, as we expect from the commutation relation $[\hat{L}_i, r] = 0$.

We can also obtain

$$
\begin{aligned}
\hat{L}^2 &= \sum_i \hat{L}_i^2 = (\hat{L}_1 + i\hat{L}_2)(\hat{L}_1 - i\hat{L}_2) + i[\hat{L}_1, \hat{L}_2] + \hat{L}_3^2 \\
&= (\hat{L}_1 + i\hat{L}_2)(\hat{L}_1 - i\hat{L}_2) - \hbar\hat{L}_3 + \hat{L}_3^2 \\
&= -\hbar^2(\cot\theta e^{i\phi}\frac{\partial}{\partial\phi} - ie^{i\phi}\frac{\partial}{\partial\theta})(\cot\theta e^{-i\phi}\frac{\partial}{\partial\phi} + ie^{-i\phi}\frac{\partial}{\partial\theta}) \\
&\quad + i\hbar^2\frac{\partial}{\partial\phi} - \hbar^2\frac{\partial^2}{\partial\phi^2} \\
&= -\hbar^2(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}) \\
&= -\hbar^2(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2})\,. \qquad (7.56)
\end{aligned}
$$

Recall that $[\hat{L}^2, \hat{L}_3] = 0$. We have

$$
\begin{aligned}
\hat{L}^2 &= -\hbar^2(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2})\,, \\
\hat{L}_3 &= -i\hbar\frac{\partial}{\partial\phi}\,. \qquad (7.57)
\end{aligned}
$$

We can thus seek simultaneous eigenfunctions of the form $Y(\theta)\exp(im\phi)$, since $\hat{L}_3\exp(im\phi) = \hbar m\exp(im\phi)$. As ϕ is defined modulo 2π, we need $e^{im(\phi+2\pi)} = e^{im\phi}$, so $e^{i2m\pi} = 1$ and m is an integer.

This leaves us with an eigenvalue equation for $\hat{L}^2$:

(7.58)

From a physics perspective, the key fact about this equation is that we can show it has non-singular solutions if and only if $\lambda = \hbar^2 l(l+1)$ for some integers $l \geq 0$ and m such that m is in the range $-l \leq m \leq l$.

Less crucial for now are the details, although it is interesting to see them. The solutions are called the *associated Legendre functions* $P_{l,m}(\theta)$. They can be obtained by reducing the equation to a standard form, using the substitution $w = \cos\theta$. Since θ is in the range $0 \leq \theta \leq \pi$, we have $-1 \leq w \leq 1$. We obtain the equation

$$
-\hbar^2\frac{d}{dw}((1-w^2)\frac{dY}{dw}) - (\lambda - \frac{m^2}{1-w^2})Y = 0\,. \qquad (7.59)
$$

For $m = 0$ and $\lambda = \hbar^2 l(l+1)$ this is Legendre's differential equation for functions of degree l, which has solution $P_l(w)$. For general m it's an associated Legendre differential equation.[25]

The associated Legendre functions can be obtained from the Legendre polynomials P_l by

$$
P_{l,m}(\theta) = (\sin\theta)^{|m|}\frac{d^{|m|}}{d(\cos\theta)^{|m|}}P_l(\cos\theta)\,. \qquad (7.60)
$$

We thus have the overall solution given by the *spherical harmonic* with *total angular momentum quantum number* l and $\hat{L}_3$ *quantum number* m:

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[25] Details can be found in Whittaker and Watson, "A course of modern analysis", 4th edition, (C.U.P., 1996).

an eigenfunction of $\hat{L}^2$ and $\hat{L}_3$ with eigenvalues $\hbar^2 l(l+1)$ and $\hbar m$ respectively.

(For plots of some spherical harmonics see e.g. mathworld.wolfram.com/SphericalHarmonic.html.)

7.7 Solving the 3D Schrödinger equation for a spherically symmetric potential

The time-independent SE is

$$-\frac{\hbar^2}{2M}\nabla^2\psi + V(r)\psi = E\psi\,. \tag{7.61}$$

Recall that in spherical polar coordinates

$$\begin{aligned}\nabla^2 &= \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\\ \hat{L}^2 &= -\hbar^2(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2})\,.\end{aligned} \tag{7.62}$$

So we have

(7.63)

We can thus rewrite the SE as

$$-\frac{\hbar^2}{2M}(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}) + \frac{1}{2Mr^2}\hat{L}^2)\psi(r,\theta,\phi) + V(r)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)\,. \tag{7.64}$$

If we separate variables, writing $\psi(r,\theta,\phi) = \psi(r)Y_{l,m}(\theta,\phi)$, this gives

(7.65)

So, we have a standard 1D radial Schrödinger equation for $\psi(r)$, with the modified potential

Comments:

- We have seen that we can find a basis of simultaneous eigenfunctions of $\hat{H}$, $\hat{L}^2$ and $\hat{L}_3$, with eigenvalues E, l and m respectively. Since the modified potential depends on l but not m, if an energy eigenspace with eigenvalue E contains any state with $\hat{L}^2$ eigenvalue l, it must contain states with *all* the associated $\hat{L}_3$ eigenvalues: $m = -l, -l+1, \ldots, l$. This greatly simplifies the analysis of orbital angular momentum eigenstates associated with a given energy level.
- If the angular momentum $l = 0$ then also $m = 0$, and the function $Y_{00}(\theta,\phi)$ is constant. Thus all zero angular momentum states are spherically symmetric. Conversely, since the Y_{lm} for $l \neq 0$ are orthogonal to Y_{00}, all spherically symmetric states have zero angular momentum. This makes sense physically, since a state ψ with $\langle \underline{L}\rangle_\psi \neq \underline{0}$ by definition has a nonzero vector associated with it, which breaks spherical symmetry.

- *The fact that, in quantum mechanics, we can express $-\hbar^2\nabla^2$ in terms of a differential operator involving only r together with a term proportional to the operator L^2 is a consequence of the fact that, in classical mechanics, kinetic energy can be expressed as a sum of terms proportional to the radial momentum squared and the angular momentum squared. However, to derive the first result from the second requires addressing one or two subtleties beyond our scope. (A discussion can be found in Dirac's book "The Principles of Quantum Mechanics", 4th edition, Section 38.)*
- *We can understand qualitatively why we should expect the radial SE to depend on the angular momentum l, by noting that the "extra potential energy" term $\frac{l(l+1)\hbar^2}{2Mr^2}$ corresponds to the potential needed to produce the centripetal force $\frac{L^2}{mr^3}$ which would keep a classical particle of angular momentum L in a circular orbit, if we set $L = \hbar\sqrt{l(l+1)}$.*

7.7.1 Degeneracies

As noted above, the values of E for which this equation is solvable clearly may depend on l but not on m. As there are $(2l+1)$ possible values of $m = -l, -l+1, \ldots, l$, each energy level would have degeneracy $(2l+1)$, assuming there are no further degeneracies.

The ground state We can now prove a result we stated earlier.

Theorem 7.2. *The ground state (i.e. lowest energy bound state) solution of the 3D Schrödinger equation for a spherically symmetric potential must have $l = m = 0$ and is thus spherically symmetric.*

Proof. The proof is by contradiction. Suppose that $\psi(r,\theta,\phi) = \psi(r)Y_{lm}(\theta,\phi)$, for some $l > 0$, is the lowest energy solution and has energy E. We have that

(7.66)

Now as $\hat{H}$, $\hat{L}^2$ and $\hat{L}_3$ are commuting hermitian operators, the space of wavefunctions is spanned by their simultaneous eigenstates. In particular, the space of zero angular momentum wavefunctions is spanned by orthonormal eigenstates $\psi_i(r,\theta,\phi)$ of $\hat{H}$ with $E = E_i$ and $l = m = 0$, which have the form

(7.67)

(In other words, the eigenstates ψ_i are all spherically symmetric solutions.) We can thus write $\psi(r) = \sum_i c_i\psi_i(r)$ for some constants c_i such that $\sum_i |c_i|^2 = 1$.

$$
\begin{aligned}
E = & \int_{r=0}^{\infty} \psi^*(r)(-\frac{\hbar^2}{2M}(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr})\psi(r) \\
& + (\frac{\hbar^2}{2Mr^2} l(l+1)) + V(r))\psi(r)) \qquad (7.68) \\
= & \int_{r=0}^{\infty} \psi^*(r)(-\frac{\hbar^2}{2M}(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + V(r)))\psi(r) \\
& + \int_{r=0}^{\infty} \psi^*(r)(\frac{\hbar^2}{2Mr^2} l(l+1))\psi(r) \qquad (7.69) \\
> & \int_{r=0}^{\infty} \psi^*(r)(-\frac{\hbar^2}{2M}(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + V(r)))\psi(r) \\
= & \int_{r=0}^{\infty} \sum_i c_i \psi_i^*(r)(-\frac{\hbar^2}{2M}(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + V(r))) \sum_j c_j \psi_j(r)\,. \qquad (7.70)
\end{aligned}
$$

Now this last term is

(7.71)

Since we have that $E > \sum_i |c_i|^2 E_i$ and that $\sum_i |c_i|^2 = 1$, we must have that $E > E_i$ for at least one value of i. Hence E is not the lowest energy eigenvalue, in contradiction to our original assumption. ■

7.8 The Hydrogen atom

We can now obtain the general bound state solution for particles in the potential $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$.

As we did in obtaining spherically symmetric solutions, we define the quantities $a = \frac{e^2 M}{2\pi\epsilon_0\hbar^2}$, $b = \frac{\sqrt{-2ME}}{\hbar}$. We obtain from Eqn. (7.65) the equation

$$
(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr})\psi(r) + (-\frac{1}{r^2} l(l+1)) + \frac{a}{r})\psi(r) = b^2\psi(r)\,. \qquad (7.72)
$$

As we saw in discussing Eqn. (7.26), we see that the ansatz $\psi(r) \approx \exp(-br)$ means that the two terms which are largest asymptotically (the first term on the LHS and the term on the RHS) cancel. This again suggests trying an ansatz of the form $\psi(r) = f(r)\exp(-br)$, for a power series $f(r)$.

However, the new singular term $(\frac{1}{r^2} l(l+1))$ means that the previously obtained solutions are not generally valid.

It turns out to be convenient to write the power series in the form $f(r) = \sum_{n=0}^{\infty} a_n r^{n+\sigma}$, where σ, a constant to be determined, is chosen so that $a_0 \neq 0$: i.e. the power series begins with a term proportional to r^σ.

Considering the coefficient of $r^{\sigma-2}$, we have $-(\sigma(\sigma-1) + 2\sigma) + l(l+1) = 0$ or $\sigma(\sigma+1) = l(l+1)$, a quadratic equation with roots $\sigma = l$ and $\sigma = -(l+1)$. As $l \geq 0$, we choose $\sigma = l$ to avoid a divergence at $r = 0$.

We now have

(7.73)

As before, if the power series does not terminate this reduces to $a_n \approx \frac{2b}{n} a_{n-1}$ for large n, which would give us $f(r) \approx \exp(2br)$ and

$$\psi(r) \approx \exp(2br)\exp(-br) \approx \exp(br)\,,$$

a divergent and unnormalisable wavefunction, which is physically unacceptable.

The power series must thus terminate, so we have $a = 2b(n+l)$, for some $n \geq 1$. Rewriting, we have $b = \frac{a}{2N}$ for some $N \geq l+1$, giving the same overall set of solutions for b, and thus the same energy levels (i.e. the Bohr energy levels), as the spherically symmetric case with $l = 0$ we considered earlier:

$$E = -\frac{Me^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{N^2}\,.$$

7.8.1 Energy level degeneracies

Each value of N is consistent with

$$l = 0, 1, \ldots (N-1)\,; \tag{7.74}$$

each value of l is consistent with

$$m = -l, -(l-1), \ldots, l\,. \tag{7.75}$$

(The first of these degeneracies occurs only for a Coulomb force law; the second, as we have seen, holds for any central potential.) The total number of values of (m, l) consistent with N is thus

(7.76)

In fact, the true degeneracy of the Nth energy level of the hydrogen atom in a full non-relativistic quantum mechanical treatment is $2N^2$: the extra factor of 2 arises from an intrinsically quantum mechanical degree of freedom, the electron *spin*, which has no direct classical analogue. (This is covered in the Part II Principles of Quantum Mechanics course.)

7.9 Towards the periodic table

We could try to generalize this discussion to atoms other than hydrogen. These have a nucleus with charge $+Ze$, orbited by Z independent electrons, where the *atomic number* Z is an integer greater than one.

If we take the nucleus to be fixed, as we did with hydrogen, this means we need to solve the Schrödinger equation for Z independent electrons in a central Coulomb potential. This is not so simple, since the electrons also interact with each other. If we ignore this temporarily, we can obtain solutions of the form

$$\psi(\mathbf{x_1}, \ldots, \mathbf{x_Z}) = \psi_1(\mathbf{x_1}) \ldots \psi_Z(\mathbf{x_Z})\,, \tag{7.77}$$

where the ψ_j are rescaled solutions for the hydrogen atom (the rescaling is because the nucleus has charge $+Ze$ instead of $+e$). The energy is just the sum

$$E = \sum_{i=1}^{Z} E_i\,. \tag{7.78}$$

It turns out that for relatively small atoms this gives qualitatively the right form, with corrections arising from the electron-electron interactions that can be calculated using perturbation theory.[26] However, we also need to allow for the *Pauli exclusion principle*, which implies that no two electrons in the same atom can be in the same state. So the lowest overall energy state is given by filling up the energy levels in order of increasing energy, starting with the lowest. Allowing for the twofold degeneracy arising from spin, as above, we have $2N^2$ states in the Nth energy level. This gives us an atom with a full energy level with $Z = 2, 10 = 8+2, \ldots$ for $N = 1, 2, \ldots$; these are the elements helium, neon, ... The elements with outer electrons in the 1st and 2nd energy levels fill out the corresponding first two rows of the periodic table. The analysis gets more complicated as atoms get larger, because electron-electron interactions become more important, and this qualitative picture is not adequate for the third and higher rows of the periodic table.

We can understand that helium and neon are chemically inert (unreactive) as a consequence of the fact that they have full energy levels, which turns out to be a very stable state that does not easily undergo transitions by capturing or losing electrons.

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[26] See Part II Principles of Quantum Mechanics for details.