

Quantum Mechanics Formulas: by R.L. Griffith@ UCB

Physical Constants

Name	Symbol	Value	Unit
Number π	π	3.14159265358979323846	
Number e	e	2.71828182845904523536	
Euler's constant	$\gamma = \lim_{n \rightarrow \infty} \left(\sum_{k=1}^n 1/k - \ln(n) \right)$	$= 0.5772156649$	
Elementary charge	e	$1.60217733 \cdot 10^{-19}$	C
Gravitational constant	G, κ	$6.67259 \cdot 10^{-11}$	$\text{m}^3\text{kg}^{-1}\text{s}^{-2}$
Fine-structure constant	$\alpha = e^2/2hc\varepsilon_0$	$\approx 1/137$	
Speed of light in vacuum	c	$2.99792458 \cdot 10^8$	m/s (def)
Permittivity of the vacuum	ε_0	$8.854187 \cdot 10^{-12}$	F/m
Permeability of the vacuum	μ_0	$4\pi \cdot 10^{-7}$	H/m
$(4\pi\varepsilon_0)^{-1}$		$8.9876 \cdot 10^9$	Nm^2C^{-2}
Planck's constant	h	$6.6260755 \cdot 10^{-34}$	Js
Dirac's constant	$\hbar = h/2\pi$	$1.0545727 \cdot 10^{-34}$	Js
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.2741 \cdot 10^{-24}$	Am^2
Bohr radius	a_0	0.52918	Å
Rydberg's constant	Ry	13.595	eV
Electron Compton wavelength	$\lambda_{Ce} = h/c$	$2.2463 \cdot 10^{-12}$	m
Proton Compton wavelength	$\lambda_{Cp} = h/m_p c$	$1.3214 \cdot 10^{-15}$	m
Reduced mass of the H-atom	μ_H	$9.1045755 \cdot 10^{-31}$	kg
Stefan-Boltzmann's constant	σ	$5.67032 \cdot 10^{-8}$	$\text{Wm}^{-2}\text{K}^{-4}$
Wien's constant	k_W	$2.8978 \cdot 10^{-3}$	mK
Molar gas constant	R	8.31441	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
Avogadro's constant	N_A	$6.0221367 \cdot 10^{23}$	mol^{-1}
Boltzmann's constant	$k = R/N_A$	$1.380658 \cdot 10^{-23}$	J/K
Electron mass	m_e	$9.1093897 \cdot 10^{-31}$	kg
Proton mass	m_p	$1.6726231 \cdot 10^{-27}$	kg
Neutron mass	m_n	$1.674954 \cdot 10^{-27}$	kg
Elementary mass unit	$m_u = \frac{1}{12}m(^{12}_6\text{C})$	$1.6605656 \cdot 10^{-27}$	kg
Nuclear magneton	μ_N	$5.0508 \cdot 10^{-27}$	J/T
Diameter of the Sun	D_\odot	$1392 \cdot 10^6$	m
Mass of the Sun	M_\odot	$1.989 \cdot 10^{30}$	kg
Rotational period of the Sun	T_\odot	25.38	days
Radius of Earth	R_A	$6.378 \cdot 10^6$	m
Mass of Earth	M_A	$5.976 \cdot 10^{24}$	kg
Rotational period of Earth	T_A	23.96	hours
Earth orbital period	Tropical year	365.24219879	days
Astronomical unit	AU	$1.4959787066 \cdot 10^{11}$	m
Light year	lj	$9.4605 \cdot 10^{15}$	m
Parsec	pc	$3.0857 \cdot 10^{16}$	m
Hubble constant	H	$\approx (75 \pm 25)$	$\text{km}\cdot\text{s}^{-1}\cdot\text{Mpc}^{-1}$

Chapter 1: The wave Function

Schrodinger Equation

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi \quad (1)$$

Probability

$$P_{ab} = \int_a^b |\psi(x, t)|^2 dx \quad (2)$$

For Normalization

$$1 = \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx, \text{ where } |\Psi(x, t)|^2 = \Psi^* \Psi \quad (3)$$

once Ψ is normalized it stays normalized for all time

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 0 \quad (4)$$

Operators for momentum and position in general form

$$\langle x \rangle = \int \Psi^* x \Psi dx \quad (5)$$

$$\langle p \rangle = \int \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx \quad (6)$$

$$\langle Q(x, p) \rangle = \int \Psi^* Q \left(x, \frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx \quad (7)$$

Expectation value of kinetic energy

$$\langle T \rangle = -\frac{\hbar^2}{2m} \int \Psi^* \frac{\partial^2 \Psi}{\partial x^2} dx \quad (8)$$

de Broglie formula

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda} \quad (9)$$

uncertainty principle

$$\sigma_x \sigma_p \geq \frac{\hbar}{2} \quad (10)$$

probability current

$$J(x, t) \equiv \frac{i\hbar}{2m} \left(\Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x} \right) \quad (11)$$

Chapter 2: Stationary States

separation of variables

$$\Psi(x, t) = \psi(x)\varphi(t) = \psi(x)e^{-iEt/\hbar} \quad (12)$$

$$\frac{d\varphi}{dt} = -\frac{iE}{\hbar}\varphi \quad (13)$$

$$\varphi(t) = e^{-iEt/\hbar} \quad (14)$$

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar} \quad (15)$$

Time Independent Schrodinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V\psi = E\psi \quad (16)$$

Hamiltonian

$$H(x, p) = \frac{p^2}{2m} + V(x) \quad (17)$$

substitute $p = (\hbar/i)(\partial/\partial x)$ and the corresponding Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x) = E\psi \quad (18)$$

$$\langle H \rangle = \int \psi^* \hat{H} \psi dx = E \quad (19)$$

You can always write the general solution of the Schrodinger equation as a linear combination of separable solutions

$$\Psi(x, 0) = \sum_{n=1}^{\infty} c_n \psi_n(x) \quad (20)$$

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar} = \sum_{n=1}^{\infty} c_n \Psi_n(x, t) \quad (21)$$

The Infinite Square Well

$$V(x) = \begin{cases} 0, & \text{if } 0 \leq x \leq a \\ \infty, & \text{otherwise} \end{cases} \quad (22)$$

plugging this into the TISE and we get

$$\frac{d^2 \psi}{dx^2} = -k^2 \psi \quad (23)$$

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \quad (24)$$

$$\psi(x) = A \sin kx \quad (25)$$

$$k_n = \frac{n\pi}{a} \quad (26)$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad (27)$$

after normalization, the general TISE solutions for the infinite square well is

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \quad (28)$$

as a collection, the functions $\psi_n(x)$ have some interesting properties

1. They are alternately **even** and **odd**, with respect to the center of the well.

2. As you go up in energy, each successive state has one more node (zero crossing)

3. They are mutually **orthogonal**, in the sense that

$$\int \psi_m(x)^* \psi_n(x) dx = 0 \quad (29)$$

Kronecker delta

$$\int \psi_m(x)^* \psi_n(x) dx = \delta_{mn} \quad (30)$$

$$\delta_{mn} = \begin{cases} 0, & \text{if } m \neq n \\ 1, & \text{if } m = n \end{cases} \quad (31)$$

we say that ψ 's are orthonormal

4. They are complete, in the sense that any other function, $f(x)$, can be expressed as a linear combination of them:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right) \quad (32)$$

the c_n 's can be found using Fourier's trick

$$c_n = \int \psi_n(x)^* f(x) dx \quad (33)$$

$$= \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x, 0) dx \quad (34)$$

$$P_{\psi_n} = |c_n|^2 \quad (35)$$

$$\sum_{n=1}^{\infty} |c_n|^2 = 1 \quad (36)$$

$$\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n \quad (37)$$

The harmonic Oscillator

$$V(x) = \frac{1}{2} kx^2 \quad (38)$$

$$\omega \equiv \sqrt{\frac{k}{m}} \quad (39)$$

$$V(x) = \frac{1}{2} m\omega^2 x^2 \quad (40)$$

rewriting equation 18 in a more suggestive form

$$\frac{1}{2m} [p^2 + (m\omega x)^2] \psi = E\psi \quad (41)$$

we can use raising and lowering operators to solve this problem

$$a_+ \equiv \frac{1}{\sqrt{2\hbar m\omega}} (-ip + m\omega x) \quad (42)$$

$$a_- \equiv \frac{1}{\sqrt{2\hbar m\omega}} (ip + m\omega x) \quad (43)$$

$$a_- a_+ = \frac{1}{2m\hbar\omega} [p^2 + (m\omega x)^2 - im\omega(xp - px)] \quad (44)$$

commutator

$$[A, B] \equiv AB - BA \quad (45)$$

$$[x, p]f(x) = i\hbar f(x) \quad (46)$$

$$[x, p] = i\hbar \quad (47)$$

$$a_- a_+ = \frac{1}{\hbar\omega} H + \frac{1}{2} \quad (48)$$

$$H = \hbar\omega \left(a_- a_+ - \frac{1}{2} \right) \quad (49)$$

$$a_+ a_- = \frac{1}{\hbar\omega} H - \frac{1}{2} \quad (50)$$

$$[a_-, a_+] = 1 \quad (51)$$

$$H = \hbar\omega \left(a_+ a_- + \frac{1}{2} \right) \quad (52)$$

In terms of a_{\pm} , then the Schrodinger equation of the harmonic oscillator takes the form

$$\hbar\omega \left(a_{\pm} a_{\mp} \pm \frac{1}{2} \right) \psi = E\psi \quad (53)$$

$$H(a_+ \psi) = (E + \hbar\omega)(a_+ \psi) \quad (54)$$

$$H(a_- \psi) = (E - \hbar\omega)(a_- \psi) \quad (55)$$

there must be a lowest state and this occurs when

$$a_-\psi_0 = 0 \quad (56)$$

this means

$$\frac{1}{\sqrt{2\hbar m\omega}} \left(\hbar \frac{d}{dx} + m\omega x \right) \psi_0 = 0 \quad (57)$$

the genral solution for the ground state of the harmonic oscillator is

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2} \quad (58)$$

$$E_0 = \frac{1}{2}\hbar\omega \quad (59)$$

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega \quad (60)$$

$$\psi_n = A_n(a_+)^n \psi_0(x) \quad (61)$$

$$a_+a_-\psi_n = n\psi_n, \quad a_-a_+\psi_n = (n+1)\psi_n \quad (62)$$

$$a_+\psi_n = \sqrt{n+1}\psi_{n+1}, \quad a_-\psi_n = \sqrt{n}\psi_{n-1} \quad (63)$$

$$\psi_n = \frac{1}{\sqrt{n!}}(a_+)^n \psi_0 \quad (64)$$

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a_+ + a_-) \quad (65)$$

$$p = i\sqrt{\frac{\hbar m\omega}{2}}(a_+ - a_-) \quad (66)$$

The Free particle

$V(x) = 0$ everywhere

$$\Psi(x, t) = Ae^{ik(x - \frac{\hbar k}{2m}t)} + Be^{-ik(x + \frac{\hbar k}{2m}t)} \quad (67)$$

$$\Psi_k(x, t) = Ae^{i(kx - \frac{\hbar k^2}{2m}t)} \quad (68)$$

$$k \equiv \pm \frac{\sqrt{2mE}}{\hbar}, \quad \text{with } \begin{cases} k > 0 \Rightarrow \text{traveling to the right} \\ k < 0 \Rightarrow \text{traveling to the left} \end{cases} \quad (69)$$

$$p = \hbar k \quad (70)$$

$$v_{\text{quantum}} = \sqrt{\frac{E}{2m}} \quad (71)$$

$$v_{\text{classical}} = 2v_{\text{quantum}} \quad (72)$$

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)} dk \quad (73)$$

to determine $\phi(k)$ we can use the TISE which is

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx} dk \quad (74)$$

this is a classic problem in Fourier analysis; the answer is provided by **Plancherel's theorem**

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) e^{ikx} dk \quad (75)$$

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx \quad (76)$$

so the solution to the generic quantum problem, for the free particle is equation 74, with

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, 0) e^{-ikx} dx \quad (77)$$

The Delta-Function Potential

$$\begin{cases} E < 0 & \Rightarrow \text{bound state} \\ E > 0 & \Rightarrow \text{scattering state} \end{cases} \quad (78)$$

$$\delta(x) \equiv \begin{cases} 0, & \text{if } x \neq 0 \\ \infty, & \text{if } x = 0 \end{cases}, \quad \text{with } \int_{-\infty}^{\infty} \delta(x) dx = 1 \quad (79)$$

$$\int_{-\infty}^{\infty} f(x) \delta(x-a) dx = f(a) \int_{-\infty}^{\infty} \delta(x-a) dx = f(a) \quad (80)$$

thats the most important property of the delta function: Under the integral sign it serves to “pick out” the value of $f(x)$ at the point a .

Let's consider a potential of the form

$$V(x) = -\alpha \delta(x) \quad (81)$$

plugging this into equation 18 in the region $x < 0$, $V(x) = 0$ so

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = k^2\psi \quad (82)$$

where

$$k \equiv \frac{\sqrt{-2mE}}{\hbar} \quad (83)$$

for bound states $E < 0$ the general solution is when $x < 0$

$$\psi(x) = Ae^{-kx} + Be^{kx} \quad (84)$$

the first term blows up as $x \rightarrow -\infty$ so we must choose $A=0$

$$\psi(x) = Be^{kx} \quad (85)$$

for bound states $E < 0$ the general solution is when $x > 0$

$$\psi(x) = Fe^{-kx} + Ge^{kx} \quad (86)$$

the second term blows up as $x \rightarrow \infty$ so we must choose $G=0$

$$\psi(x) = Fe^{-kx} \quad (87)$$

It remains only to stitch these two functions together, using the appropriate boundary conditions at $x = 0$, the standard boundary conditions for ψ

1. ψ is always continuous 2. $d\psi/dx$ is continuous except at points where the potential is infinite

in this case the first boundary condition tells us that $F = B$, so

$$\psi(x) = \begin{cases} Be^{kx}, & (x \leq 0) \\ Be^{-kx}, & (x \geq 0) \end{cases} \quad (88)$$

the second boundary condition gives

$$\Delta \left(\frac{d\psi}{dx} \right) = -\frac{2m\alpha}{\hbar^2}\psi(0) \quad (89)$$

Evidently the delta-function well, regardless of its “strength” α , has exactly one bound state

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x|/\hbar^2}; \quad E = -\frac{m\alpha^2}{2\hbar^2} \quad (90)$$

What about scattering states, with $E > 0$? For $x < 0$ the Schrodinger equation read

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi \quad (91)$$

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \quad (92)$$

is real and positive. The general solution is for $x < 0$

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad (93)$$

and this time we cannot rule out either term, since neither blows up. and similarly for $x > 0$

$$\psi(x) = Fe^{ikx} + Ge^{-ikx} \quad (94)$$

for boundary condition number 1 this implies

$$F + G = A + B \quad (95)$$

the derivatives are

$$\begin{cases} d\psi/dx = ik(Fe^{ikx} + Ge^{-ikx}), & \text{for } (x > 0), \text{ so } d\psi/dx|_+ = ik(F - G) \\ d\psi/dx = ik(Ae^{ikx} + Be^{-ikx}), & \text{for } (x < 0), \text{ so } d\psi/dx|_- = ik(A - B) \end{cases} \quad (96)$$

and hence $\Delta(d\psi/dx) = ik(F - G - A + B)$, meanwhile $\psi(0) = (A + B)$, so the second boundary condition says

$$ik(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}(A + B) \quad (97)$$

or more compactly

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta), \quad \text{where } \beta \equiv \frac{m\alpha}{\hbar^2 k} \quad (98)$$

having imposed both boundary condition we are left with two equations and four unknowns. it follows A is the amplitude of a wave coming from the right, B is the amplitude of the wave returning to the left, F is the amplitude of the wave traveling of to the right, and G is the amplitude of the wave coming in from the right.

$$G = 0, \quad \text{for scattering from the left} \quad (99)$$

$$A = 0, \quad \text{for scattering from the right} \quad (100)$$

for scattering from the left, A is the amplitude of the **incident wave**, B is the amplitude of the **reflected wave**, and F is the amplitude of the **transmitted wave** solving equations 95 and 98 for B and F , we find

$$B = \frac{i\beta}{1 - i\beta}A, \quad F = \frac{1}{1 - i\beta}A \quad (101)$$

The reflection coefficient is

$$R \equiv \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2} \quad (102)$$

and the transmission coefficient is

$$T \equiv \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2} \quad (103)$$

and the sum should be one

$$R + T = 1 \quad (104)$$

R and T are functions of β and hence functions of E

$$R = \frac{1}{1 + (2\hbar^2 E / m\alpha^2)} \quad (105)$$

$$T = \frac{1}{1 + (m\alpha^2 / 2\hbar^2 E)} \quad (106)$$

The Finite Square Well

$$V(x) = \begin{cases} -V_0, & \text{for } -a \leq x \leq a \\ 0, & \text{for } |x| > a \end{cases} \quad (107)$$

This potential admits both bound states and scattering states. we will look at the bound states first. in the region $x < -a$ the potential is zero, so the Schrodinger equation reads

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = k^2\psi \quad (108)$$

where

$$k \equiv \frac{\sqrt{-2mE}}{\hbar} \quad (109)$$

the general solution as before is

$$\psi(x) = Ae^{-kx} + Be^{kx} \quad (110)$$

the first term blows up as $x \rightarrow -\infty$ so we must choose A=0

$$\psi(x) = Be^{kx}, \quad \text{for } x < -a \quad (111)$$

in the region $-a < x < a$, $V(x) = -V_0$, and the Schrodinger equation reads

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - V_0\psi = E\psi, \quad \text{or} \quad \frac{d^2\psi}{dx^2} = -l^2\psi \quad (112)$$

where

$$l \equiv \frac{\sqrt{2m(E + V_0)}}{\hbar} \quad (113)$$

and the general solution is

$$\psi(x) = C \sin(lx) + D \cos(lx), \quad \text{for } -a < x < a \quad (114)$$

when $x > a$ the genral solution is

$$\psi(x) = Fe^{-kx} + Ge^{kx} \quad (115)$$

the first term blows up as $x \rightarrow -\infty$ so we must choose G=0

$$\psi(x) = Fe^{-kx}, \quad \text{for } x > a \quad (116)$$

The next step is to impose boundary conditions: ψ and $d\psi/dx$ continuous at $-a$ and a . but we can save a little time by noting that this potential is an even function, so we can assume with no loss of generality that the solutions are either even or odd. since $\psi(-x) = \pm\psi(x)$.

for even solutions use $D \cos(lx)$ and for odd solutions use $C \sin(lx)$. I will show the even solutions

The continuity of $\psi(x)$, at $x = a$, says

$$Fe^{-ka} = D \cos(la) \quad (117)$$

and the continuity of $d\psi/dx$, says

$$-kFe^{-ka} = -lD \sin(la) \quad (118)$$

deviding equation 118 by 117, we find that

$$k = l \tan(la) \quad (119)$$

This is a formula for the allowed energies, since k and l are both functions of E . To solve for E , we first adopt a nicer notation: Let

$$z \equiv la, \quad \text{and} \quad z_0 \equiv \frac{a}{\hbar} \sqrt{2mV_0} \quad (120)$$

$$(k^2 + l^2) = \frac{2mV_0}{\hbar^2}, \quad \text{so} \quad ka = \sqrt{z_0^2 - z^2} \quad (121)$$

and now equation 119 read

$$\tan(z) = \sqrt{(z_0/z)^2 - 1} \quad (122)$$

This is a trancendental equation and can onlly be solved numerically or graphically. Two limiting cases are of special interest.

1. Wide, deep well. if z_0 is very large, the intersections occur just slightly below $z_n = n\pi/2$, with n odd it follows that

$$E_n + V_0 \cong \frac{n^2 \pi^2 \hbar^2}{2m(2a)^2} \quad (123)$$

2. Shallow, narrow well. As z_0 decreases, there are fewer and fewer bound states, until finally (for $z_0 < \pi/2$, where the lowest odd state disappears) only one remains. It is interesting to note that there is always one bound state, no matter how weak the well becomes.

Now moving on to **scattering states** where $E > 0$

the general solution as before is

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad \text{for } (x < -a) \quad (124)$$

where(as usual)

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \quad (125)$$

inside the well, where $V(x) = -V_0$ and the general solution is

$$\psi(x) = C \sin(lx) + D \cos(lx), \quad \text{for } -a < x < a \quad (126)$$

where as before

$$l \equiv \frac{\sqrt{2m(E + V_0)}}{\hbar} \quad (127)$$

To the right, assuming there is no incoming wave in this region, we have

$$\psi(x) = Fe^{ikx} \quad (128)$$

Here A is the incident amplitude, B is the reflected amplitude, and F is the transmitted amplitude.

There are four boundary conditions: Continuity of $\psi(x)$ at $-a$ says

$$Ae^{-ika} + Be^{ika} = -C \sin(la) + D \cos(la) \quad (129)$$

continuity of $d\psi/dx$ at $-a$ gives

$$ik[Ae^{-ika} - Be^{ika}] = l[C \cos(la) + D \sin(la)] \quad (130)$$

continuity of $\psi(x)$ at $+a$ yields

$$C \sin(la) + D \cos(la) = Fe^{ika} \quad (131)$$

continuity of $d\psi/dx$ at $+a$ gives

$$l[C \cos(la) - D \sin(la)] = iFe^{ika} \quad (132)$$

We can use two of these to eliminate C and D , and solve the remaining two for B and F :

$$B = i \frac{\sin(2la)}{2kl} (l^2 - k^2) F \quad (133)$$

$$F = \frac{e^{-2ika} A}{\cos(2la) - i \frac{(k^2 + l^2)}{2kl} \sin(2la)} \quad (134)$$

The transmission coefficient ($T = |F|^2/|A|^2$) expressed in terms of the original variables, is given by

$$T^{-1} = 1 + \frac{V_0^2}{4E(E + V_0)} \sin^2 \left(\frac{2a}{\hbar} \sqrt{2m(E + V_0)} \right) \quad (135)$$

Notice that $T = 1$ (the well becomes “transparent”) whenever the sine is zero, which is to say, when

$$\frac{2a}{\hbar} \sqrt{2m(E_n + V_0)} = n\pi \quad (136)$$

where n is an integer. The energies for perfect transmission, then are given by

$$E_n + V_0 = \frac{n^2 \pi^2 \hbar^2}{2m(2a)^2} \quad (137)$$

which happens to be the allowed energies for the infinite square well

Chapter 3: Formalism

The collection of all functions of x constitutes a vector space. To represent a possible physical state, the wave function Ψ must be *normalized*:

$$\int |\Psi|^2 dx = 1 \quad (138)$$

The set of all **square-integrable functions**, on a specified interval

$$f(x) \quad \text{such that} \quad \int_a^b |f(x)|^2 dx < \infty \quad (139)$$

this constitutes a (much smaller) vector space. mathematicians call it $L_2(a, b)$; physicist call it **Hilbert Space**. In quantum mechanics, then

Wave functions live in Hilbert Space

We define the **inner product of two functions**, $f(x)$ and $g(x)$, as follows

$$\langle f|g \rangle \equiv \int_a^b f(x)^* g(x) dx \quad (140)$$

If f and g are both square-integrable (that is, if they are both in Hilbert space), their inner product is guaranteed to exist (the integral in equation 140 converges to a finite number). This follows from the integral **Schwarz inequality**

$$\left| \int_a^b f(x)^* g(x) dx \right| \leq \sqrt{\int_a^b |f(x)|^2 dx \int_a^b |g(x)|^2 dx} \quad (141)$$

Notice in particular that

$$\langle g|f \rangle = \langle f|g \rangle^* \quad (142)$$

Moreover, the inner product of $f(x)$ with *itself*,

$$\langle f|f \rangle = \int_a^b |f(x)|^2 dx \geq 0 \quad (143)$$

is *real* and non-negative; it's *zero* only if $f(x) = 0$

A function is said to be **normalized** if its inner product with itself is 1; two functions are **orthogonal** if their inner product is 0; and a *set* of functions, $\{f_n\}$, is **orthonormal** if they are normalized and mutually orthogonal;

$$\langle f_m|f_n \rangle = \delta_{mn} \quad (144)$$

Finally, a set of functions is **complete** if any *other* function (in Hilbert space) can be expressed as a linear combination of them

$$f(x) = \sum_{n=1}^{\infty} c_n f_n(x) \quad (145)$$

if the functions $\{f_n(x)\}$ are orthonormal, the coefficients are given by Fourier's trick

$$c_n = \langle f_n|f \rangle \quad (146)$$

Observables

The expectation value of an observable $Q(x, p)$ can be expressed very neatly in inner-product notation:

$$\langle Q \rangle = \int \Psi^* \hat{Q} \Psi dx = \langle \Psi|\hat{Q} \Psi \rangle \quad (147)$$

now the outcome of a measurement has got to be *real*, and so, *a fortiori*, is the average of many measurements:

$$\langle Q \rangle = \langle Q \rangle^* \quad (148)$$

But the complex conjugate of an inner product reverses the order

$$\langle \Psi|\hat{Q} \Psi \rangle = \langle \hat{Q} \Psi|\Psi \rangle \quad (149)$$

and this must hold true for any wave function Ψ . Thus operators representing *observables* have the very special property that

$$\langle f|\hat{Q} f \rangle = \langle \hat{Q} f|f \rangle \quad \text{for all } f(x) \quad (150)$$

we call such operator **hermitian**

Observables are represented by hermitian operators

Determinate States

$$\hat{Q} \Psi = q \Psi \quad (151)$$

This is the **eigenvalue equation** for the operator \hat{Q} ; Ψ is an **eigenfunction** of \hat{Q} , and q is the corresponding **eigenvalue**; thus

Determinate states are eigenfunctions of \hat{Q}

Measurement of q on such a state is certain to yield the eigenvalue q . The collection of all eigenvalues of an operator is called its **spectrum**. *Sometimes two (or more) linearly independent eigenfunctions share the same eigenvalue*; in that case the spectrum is said to be **degenerate**.

Eigenfunctions of Hermitian Operators Discrete Spectra

Mathematically, the normalized eigenfunctions of a hermitian operator have two important properties.

Theorem 1: Their eigenvalues are real.

$$\hat{Q} f = q f \quad (152)$$

(i.e., $f(x)$ is an eigenfunction of \hat{Q} , with eigenvalue q), and

$$\langle f|\hat{Q} f \rangle = \langle \hat{Q} f|f \rangle \quad (153)$$

then

$$q \langle f|f \rangle = q^* \langle f|f \rangle \quad (154)$$

and q must be real

Theorem 2: Eigenfunctions belonging to distinct eigenvalues are *orthogonal*.

$$\hat{Q}f = qf, \quad \text{and} \quad \hat{Q}g = q'g \quad (155)$$

and \hat{Q} is hermitian. Then $\langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle$ so

$$q'\langle f|g\rangle = q\langle f|g\rangle \quad (156)$$

again the inner product exist because the eigenfunctions are in Hilbert space by assumption. but q is real so if $q' \neq q$ it must be that $\langle f|g\rangle = 0$.

Continuous Spectrum

If the spectrum of a hermitian operator is *continuous*, the eigenfunctions are not normalizable, and the proofs of Theorems 1 and 2 fail, because the inner products may not exist.

Generalized Statistical Interpretation

If you measure an observable $Q(x, p)$ on a particle in the state $\Psi(x, t)$, you are certain to get *one of the eigenvalues* of the hermitian operator. If the spectrum is discrete, the probability of getting the particular eigenvalue q_n associated with the orthonormalized eigenfunction $f_n(x)$ is

$$|c_n|^2, \quad \text{where} \quad c_n = \langle f_n|\Psi\rangle \quad (157)$$

If the spectrum is continuous, with real eigenvalues $q(z)$ and associated Dirac orthonormalized eigenfunctions $f_z(x)$, the probability of getting result in the range dz is

$$|c(z)|^2 dz, \quad \text{where} \quad c(z) = \langle f_z|\Psi\rangle \quad (158)$$

The eigenfunctions of a hermitian operator are *complete*, so that the wave function can be written as a linear combination of them

$$\Psi(x, t) = \sum_n c_n f_n(x) \quad (159)$$

Because the eigenfunctions are *orthonormal*, the coefficients are given by Fourier's trick

$$c_n = \langle f_n|\Psi\rangle = \int f_n(x)^* \Psi(x, t) dx \quad (160)$$

Of course, the *total* probability (summed over all possible outcomes) has got to equal *one*

$$\sum_n |c_n|^2 = 1 \quad (161)$$

Similarly, the expectation value Q should be the sum over all possible outcomes of the eigenvalue times the probability of getting that eigenvalue

$$\langle Q\rangle = \sum_n q_n |c_n|^2 \quad (162)$$

The **momentum space wave function**, $\Phi(p, t)$ is essentially the *Fourier transform* of the **position space** wave function $\Psi(x, t)$, which by Plancherel's theorem is its *inverse* Fourier transform.

$$\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar} \Psi(x, t) dx \quad (163)$$

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{ipx/\hbar} \Phi(p, t) dp \quad (164)$$

$$(165)$$

According to the generalized statistical interpretation, the probability that a measurement of the momentum would yield a result in the range dp is

$$|\Phi(p, t)|^2 dp \quad (166)$$

The Uncertainty Principle

The generalized uncertainty principle is

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2 \quad (167)$$

The energy-time uncertainty principle

$$\frac{d}{dt} \langle Q\rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle \quad (168)$$

Chapter 4: Quantum Mechanics in Three Dimensions

The generalization to three dimensions is straightforward. Schrodinger's equation says

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad (169)$$

the Hamiltonian operator H is obtained from the classical energy

$$\frac{1}{2}mv^2 + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V \quad (170)$$

by the standard prescription (applied now to y and z , as well as x)

$$p_x \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x}, \quad p_y \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial y}, \quad p_z \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial z} \quad (171)$$

or

$$\mathbf{p} \rightarrow \frac{\hbar}{i} \nabla \quad (172)$$

thus

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi \quad (173)$$

where

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (174)$$

is the **Laplacian**, in cartesian coordinates. The potential V and the wave function Ψ are now functions of $\mathbf{r} = (x, y, z)$ and t .

the normalization condition reads

$$\int |\Psi|^2 d^3\mathbf{r} = 1 \quad (175)$$

with the integral taken over all space. if the potential is independent of time, there will be a complete set of stationary states

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) e^{-iE_n t/\hbar} \quad (176)$$

where the spatial wave function ψ_n satisfies the time-independent Schrodinger

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = E \psi \quad (177)$$

The general solution to the time-dependent Schrodinger equation is

$$\Psi(\mathbf{r}, t) = \sum c_n \psi_n(\mathbf{r}) e^{-iE_n t/\hbar} \quad (178)$$

Seperation Of variables Typically, the potential is a function only of the distance from the origin. In that case it is natural to adopt **spherical coordinates**, (r, θ, ϕ) . In spherical coordinates the Laplacian takes the form

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \quad (179)$$

We begin by looking for solutions that are seperable by products

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi) \quad (180)$$

.. **The Angular Equation**

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -l(l+1) \sin^2 \theta Y \quad (181)$$

you might recognize this equation, it occurs in the solution to Laplace's equation in classical electrodynamics. as always, we try seperation of variables

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi) \quad (182)$$

plugging this in and deviding by $\Theta \Phi$ gives us two solutions

$$\frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1) \sin^2 \theta = m^2 \quad (183)$$

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2 \quad (184)$$

The ϕ equation is easy

$$\frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi \Rightarrow \Phi(\phi) = e^{\pm i m \phi} \quad (185)$$

Now when ϕ advances by 2π , we return to the same point in space, so it is natural to require that

$$\Phi(\phi + 2\pi) = \Phi(\phi) \quad (186)$$

from this it follows that m must be an integer

$$m = 0, \pm 1, \pm 2, \dots \quad (187)$$

The θ equation is not so simple, the solution is

$$\Theta(\theta) = A P_l^m(\cos \theta) \quad (188)$$

where P_l^m is the associated **Legendre function**, defined by

$$P_l^m(x) \equiv (1-x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x) \quad (189)$$

and $P_l(x)$ is the l th **Legendre polynomial**, defined by the **Rodrigues formula**

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2 - 1)^l \quad (190)$$

Now, the volume element in spherical coordinates is

$$d^3 \mathbf{r} = r^2 \sin \theta dr d\theta d\phi \quad (191)$$

so the normalization condition becomes

$$\int |\psi|^2 r^2 dr d\theta d\phi = \int |R|^2 r^2 dr \int |Y|^2 \sin \theta d\theta d\phi = 1 \quad (192)$$

It is convenient to normalize R and Y separately

$$\int_0^\infty |R|^2 r^2 dr = 1 \quad (193)$$

$$\int_0^{2\pi} \int_0^\pi |Y|^2 \sin \theta d\theta d\phi = 1 \quad (194)$$

The normalized angular wave functions are called **spherical harmonics**

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} e^{im\phi} P_l^m(\cos \theta) \quad (195)$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. As we shall prove later on, they are automatically orthogonal.

The Radial Equation Notice that the angular part of the wave function, $Y(\theta, \phi)$, is the same for all spherically symmetric potentials; the actual *shape* of the potential, $V(r)$, affects only the *radial* part of the wave function, $R(r)$, which is determined by

$$u(r) \equiv rR(r) \quad (196)$$

using this relationship we can now write the radial equation as

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu \quad (197)$$

the normalization condition becomes

$$\int_0^\infty |u|^2 dr = 1 \quad (198)$$

this is as far as we can go until a specific potential $V(r)$ is provided.

The infinite spherical well

$$V(r) = \begin{cases} 0, & \text{if } r \leq a \\ \infty, & \text{if } r > a \end{cases} \quad (199)$$

Outside the well, the wave function is zero; inside the well, the radial equation says

$$\frac{d^2 u}{dr^2} = \left[\frac{l(l+1)}{r^2} - k^2 \right] u \quad (200)$$

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \quad (201)$$

as usual. Our problem is to solve this equation, subject to the boundary condition $u(a) = 0$. The case $l = 0$ is easy

$$\frac{d^2 u}{dr^2} = -k^2 u \Rightarrow u(r) = A \sin(kr) + B \cos(kr) \quad (202)$$

we must choose $B = 0$ because $r \rightarrow 0$ the radial wave function blows up. The boundary condition then requires $\sin(ka) = 0$, and hence $ka = n\pi$, for some integer n . The allowed energies are evidently

$$E_{n0} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}, \quad (n = 1, 2, 3, \dots) \quad (203)$$

the same as for the one-dimensional infinite square well. The general solution to equation 200 (for an arbitrary integer l) is not as familiar

$$u(r) = A r j_l(kr) + B r n_l(kr) \quad (204)$$

where $j_l(x)$ is the **spherical Bessel function** of order l , and $n_l(x)$ is the **spherical Neumann function** of order l . They are defined as follows

$$j_l(x) \equiv (-x)^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \frac{\sin x}{x} \quad (205)$$

$$n_l(x) \equiv -(-x)^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \frac{\cos x}{x} \quad (206)$$

Notice that the Bessel functions are finite at the origin, but *Neumann* functions blow up at the origin. Accordingly, we must have $B_l = 0$, and hence

$$R(r) = A j_l(kr) \quad (207)$$

There remains the boundary condition, $R(a) = 0$. Evidently k must be chosen such that

$$j_l(ka) = 0 \quad (208)$$

the boundary condition requires that

$$k = \frac{1}{a} \beta_{nl} \quad (209)$$

where β_{nl} is the n th zero of the l th spherical Bessel function. The allowed energies then, are given by

$$E_{nl} = \frac{\hbar^2}{2ma^2} \beta_{nl}^2 \quad (210)$$

and the wave functions are

$$\psi_{nlm}(r, \theta, \phi) = A_{nl}(\beta_{nl}r/a) Y_l^m(\theta, \phi) \quad (211)$$

with the constant A_{nl} to be determined by normalization.

The Hydrogen Atom

From Coulomb's law, the potential energy is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \quad (212)$$

and the radial equation says

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu \quad (213)$$

our problem is to solve this equation for $u(r)$, and determine the allowed energies. Our first task is to tidy up the notation. Let

$$k \equiv \frac{\sqrt{-2mE}}{\hbar} \Rightarrow E = -\frac{\hbar^2 k^2}{2m} \quad (214)$$

dividing equation 213 by E gives

$$\frac{1}{k^2} \frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0 \hbar^2 k} \frac{1}{(kr)} + \frac{l(l+1)}{(kr)^2} \right] u \quad (215)$$

This suggest that we introduce

$$\rho \equiv kr \quad \text{and} \quad \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0 \hbar^2 k} \quad (216)$$

so that

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u \quad (217)$$

Next we examine the asymptotic form of the solutions. As $\rho \rightarrow \infty$, the constant term in the brackets dominate, so approximately

$$\frac{d^2u}{d\rho^2} = u \quad (218)$$

The general solution is

$$u(\rho) = Ae^{-\rho} + Be^{\rho} \quad (219)$$

but e^{ρ} blows up (as $\rho \rightarrow \infty$), so $B = 0$, evidently

$$u(\rho) \sim Ae^{-\rho} \quad (220)$$

for large ρ . On the other hand, as $\rho \rightarrow 0$ the centrifugal term dominates, approximately then

$$\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u \quad (221)$$

the general solution is

$$u(\rho) = C\rho^{l+1} + D\rho^{-l} \quad (222)$$

let $D = 0$, because ρ^{-l} blows up as $\rho \rightarrow 0$, thus

$$u(\rho) \sim C\rho^{l+1} \quad (223)$$

The next step is to peel off the asymptotic behaviour, introducing the new function $v(\rho)$

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) \quad (224)$$

Finally, we assume the solution, $v(\rho)$, can be expressed as a power series in ρ

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \quad (225)$$

$$c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j \quad (226)$$

This recursion formula determines the coefficients, and hence the function $v(\rho)$. Now lets see what the coefficients look like for large j (this corresponds to large ρ , where the higher power dominate). In this regime the recursion formula says

$$c_{j+1} \cong \frac{2j}{j(j+1)}c_j = \frac{2}{j+1}c_j \quad (227)$$

suppose for a moment that this were *exact*. Then

$$c_j = \frac{2^j}{j!}c_0 \quad (228)$$

so

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j \quad (229)$$

and hence

$$u(\rho) = c_0 \rho^{l+1} e^{\rho} \quad (230)$$

which blows up at large ρ . The series must terminate. There must occur some maximal integer, j_{max} such that

$$c_{j_{max}+1} = 0 \quad (231)$$

(and beyond which all coefficients vanish automatically). equation 226 becomes

$$2(j_{max} + l + 1) - \rho_0 = 0 \quad (232)$$

Defining

$$n \equiv j_{max} + l + 1 \quad (233)$$

(the so-called **principal quantum number**), we have

$$\rho_0 = n \quad (234)$$

But ρ_0 determines E

$$E = -\frac{k^2 \hbar^2}{2m} = -\frac{m e^4}{8\pi^2 \epsilon^2 \hbar^2 \rho_0^2} \quad (235)$$

so the allowed energies are

$$E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2} \quad n = 1, 2, \dots \quad (236)$$

This is the famous **Bohr Formula**. combining equation 216 and 234 we get

$$k = \left(\frac{m e^2}{4\pi\epsilon_0 \hbar^2} \right) \frac{1}{n} = \frac{1}{a n} \quad (237)$$

where

$$a \equiv \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = 0.529 \times 10^{-10} m \quad (238)$$

is called the Bohr radius. it follows that

$$\rho = \frac{r}{a n} \quad (239)$$

The spatial wave functions for hydrogen are labeled by three quantum numbers (n, l , and m)

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi) \quad (240)$$

and

$$R_{nl}(r) = \frac{1}{r} \rho^{l+1} e^{-\rho} v(\rho) \quad (241)$$

and $v(\rho)$ is a polynomial of degree $j_{max} = n - l - 1$ in ρ , whose coefficients are determined by the recursion formula

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} c_j \quad (242)$$

The polynomial $v(\rho)$ is a function well known to mathematicians; apart from normalization, it can be written as

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho) \quad (243)$$

where

$$L_{q-p}^p(x) \equiv (-1)^p \left(\frac{d}{dx} \right)^p L_q(x) \quad (244)$$

is an **associated Laguerre polynomial**, and

$$L_q(x) \equiv e^x \left(\frac{d}{dx} \right)^q (e^{-x} x^q) \quad (245)$$

is the q th **Laguerre polynomial**, the normalized hydrogen wave functions are

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na} \right)^l [L_{n-l-1}^{2l+1}(2r/na)] Y_l^m(\theta, \phi) \quad (246)$$

The spectrum of Hydrogen

An electron may undergo a **transition** to some other energy state, either by absorbing energy or emitting energy, the difference in energy between the initial and final states are

$$Y_\gamma = E_i - E_f = 13.6\text{eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (247)$$

Now, according to the **Planck formula**, the energy of a photon is proportional to its frequency

$$E_\gamma = h\nu \quad (248)$$

Meanwhile, the *wavelength* is given by $\lambda = c/\nu$, so

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (249)$$

where

$$R \equiv \frac{m}{4\pi c \hbar^3} \left(\frac{e^2}{4\pi \epsilon_0} \right)^2 = 1.097 \times 10^7 \text{m}^{-1} \quad (250)$$

is known as the **Rydberg constant**

Angular Momentum

Classically, the angular momentum of a particle (with respect to the origin) is given by the formula

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad (251)$$

which is to say

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x \quad (252)$$

The corresponding quantum operators are obtained by the standard prescription $p_x \rightarrow -i\hbar\partial/\partial x$ etc.

Eigenvalues

The operators L_x and L_y do not commute; in fact

$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y \quad (253)$$

Notice that L_x, L_y , and L_z are *incompatible* observables and it would therefore be futile to look for states that are simultaneously eigenfunctions of L_x and L_y . On the other hand, the *square* of the *total* angular momentum

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2 \quad (254)$$

does commute with L_x

$$[L^2, L_x] = 0, \quad [L^2, L_y] = 0, \quad [L^2, L_z] = 0 \quad (255)$$

or, more compactly,

$$[L^2, \mathbf{L}] = 0 \quad (256)$$

So L^2 is compatible with each component of \mathbf{L} , and we can hope to find simultaneous eigenstates of L^2 and (say) L_z

$$L^2 f = \lambda f \quad \text{and} \quad L_z f = \mu f \quad (257)$$

We'll use a *ladder operator* technique. Let

$$L_\pm \equiv L_x \pm iL_y \quad (258)$$

The commutator with L_z is

$$[L_z, L_\pm] = \pm\hbar(L_x \pm iL_y) \quad (259)$$

so

$$[L_z, L_\pm] = \pm\hbar L_\pm \quad (260)$$

And of course,

$$[L^2, L_\pm] = 0 \quad (261)$$

I claim that if f is an eigenfunction of L^2 and L_z , so also is $L_\pm f$ equation 261 says

$$L^2(L_\pm f) = L_\pm(L^2 f) = L_\pm(\lambda f) = \lambda(L_\pm f) \quad (262)$$

so if $L_\pm f$ is an eigenfunction of L^2 , with the same eigenvalue λ , and equation 260 says

$$L_z(L_\pm f) = (L_z L_\pm - L_\pm L_z) f + L_\pm L_z f = \pm\hbar L_\pm f + L_\pm(\mu f) \quad (263)$$

$$= (\mu \pm \hbar)(L_\pm f) \quad (264)$$

so $L_\pm f$ is an eigenfunction of L_z , with the *new* eigenvalue $\mu \pm \hbar$. we call L_+ the *raising* operator, because it *increases* the eigenvalue of L_z by \hbar , and L_- the *lowering* operator, because it *lowers* the eigenvalue by \hbar . When using the raising operator we will eventually reach a state for which the *z*-component exceeds the *total*

$$L_\pm f_t = 0 \quad (265)$$

let $\hbar l$ be the eigenvalue of L_z at this top rung.

$$L_z f_t = \hbar l f_t; \quad L^2 f_t = \lambda f_t \quad (266)$$

Now,

$$L_{\pm}L_{\mp} = L^2 - L_z^2 \mp i(\hbar L_z) \quad (267)$$

or putting it the other way around

$$L^2 = L_{\pm}L_{\mp} + L_z^2 \mp \hbar L_z \quad (268)$$

it follows that

$$L^2 f_t = (L_-L_+ + L_z^2 + \hbar L_z) f_t = \hbar^2 l(l+1) f_t \quad (269)$$

and hence

$$\lambda = \hbar^2 l(l+1) \quad (270)$$

This tells us the eigenvalue of L^2 in terms of the *maximum* eigenvalue of L_z . Evidently the eigenvalues of L_z are $m\hbar$, where m goes from $-l$ to l in N integer steps. In particular, it follows that $l = -l + N$, and hence $l = N/2$, so l must be an integer or a half-integer. The eigenfunctions are characterized by the numbers l and m

$$L^2 f_l^m = \hbar^2 l(l+1) f_l^m; \quad L_z f_l^m = \hbar m f_l^m \quad (271)$$

where

$$l = 0, 1/2, 1, 3/2, \dots; \quad m = -l, -l+1, \dots, l-1, l \quad (272)$$

Eigenfunctions

First of all we need to rewrite L_x, L_y , and L_z in spherical coordinates. Now, $\mathbf{L} = (\hbar/i)(\mathbf{r} \times \nabla)$, and the gradient, in spherical coordinates, is

$$\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \quad (273)$$

meanwhile, $\mathbf{r} = r\hat{r}$, so

$$\mathbf{L} = \frac{\hbar}{i} \left[r(\hat{r} \times \hat{r}) \frac{\partial}{\partial r} + (\hat{r} \times \hat{\theta}) \frac{\partial}{\partial \theta} + (\hat{r} \times \hat{\phi}) \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right] \quad (274)$$

But $(\hat{r} \times \hat{r}) = 0$, $(\hat{r} \times \hat{\theta}) = \hat{\phi}$, and $(\hat{r} \times \hat{\phi}) = -\hat{\theta}$ and hence

$$\mathbf{L} = \frac{\hbar}{i} \left(\hat{\phi} \frac{\partial}{\partial \theta} - \hat{\theta} \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right) \quad (275)$$

The unit vectors $\hat{\theta}$ and $\hat{\phi}$ can be resolved into their cartesian components

$$\hat{\theta} = (\cos \theta \cos \phi) \hat{i} + (\cos \theta \sin \phi) \hat{j} - (\sin \theta) \hat{k} \quad (276)$$

$$\hat{\phi} = -(\sin \phi) \hat{i} + (\cos \phi) \hat{j} \quad (277)$$

Evidently

$$L_x = \frac{\hbar}{i} \left(-\sin \phi \frac{\partial}{\partial \theta} - \cos \phi \cot \theta \frac{\partial}{\partial \phi} \right) \quad (278)$$

$$L_y = \frac{\hbar}{i} \left(+\cos \phi \frac{\partial}{\partial \theta} - \sin \phi \cot \theta \frac{\partial}{\partial \phi} \right) \quad (279)$$

and

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \quad (280)$$

using the raising and lowering operators we find

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (281)$$

conclusion: Spherical harmonics *are* eigenfunctions of L^2 and L_z . When we solved the Schrodinger equation by separation of variables, we were inadvertently constructing simultaneous eigenfunctions of the three commuting operators H , L^2 , and L_z

$$H\psi = E\psi, \quad L^2\psi = \hbar^2 l(l+1)\psi, \quad L_z\psi = \hbar m\psi \quad (282)$$

incidentally, we can use equation 281 to rewrite the Schrodinger equation

$$\frac{1}{2mr^2} \left[-\hbar^2 \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + L^2 \right] \psi + V\psi = E\psi \quad (283)$$

Spin

In classical mechanics, a rigid object admits two kinds of angular momentum: **orbital** ($L = r \times p$), associated with the motion of the center of mass, and **spin** ($S = I\omega$), associated with motion about the center of mass. The *algebraic* theory of spin is a carbon copy of the theory of orbital angular momentum, beginning with the fundamental commutation relations

$$[S_x, S_y] = i\hbar S_z, \quad [S_y, S_z] = i\hbar S_x, \quad [S_z, S_x] = i\hbar S_y \quad (284)$$

it follows that the eigenvectors of S^2 and S_z satisfy

$$S^2|sm\rangle = \hbar^2 s(s+1)|sm\rangle; \quad S_z|sm\rangle = \hbar m|sm\rangle \quad (285)$$

and

$$S_{\pm}|sm\rangle = \hbar\sqrt{s(s+1) - m(m\pm 1)}|s(m\pm 1)\rangle \quad (286)$$

where $S_{\pm} \equiv S_x \pm iS_y$. But this time the eigenfunctions are not spherical harmonics, and there is no *a priori* reason to exclude the half-integer values of s and m :

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots; \quad m = -s, -s+1, \dots, s-1, s. \quad (287)$$

Pi mesons have spin 1/2; photons have spin 1; deltas have spin 3/2; gravitons have spin 2; and so on.

Spin 1/2

By far the most important case is $s = 1/2$, for this is the spin of the particles that make up ordinary matter (protons, neutrons, and electrons), as well as quark and leptons. The general state of a spin-1/2 particle can be expressed as a two-element column matrix (or **spinor**);

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_- \quad (288)$$

with

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (289)$$

representing spin up, and

$$\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (290)$$

for spin down. Meanwhile, the spin operators become 2×2 matrices, which we can work out by noting their effect on χ_+ and χ_- . Equation 285 says

$$\mathbf{S}^2\chi_+ = \frac{3}{4}\hbar^2\chi_+ \quad \text{and} \quad \mathbf{S}^2\chi_- = \frac{3}{4}\hbar^2\chi_- \quad (291)$$

we can write \mathbf{S}^2 in matrix form as

$$\mathbf{S}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (292)$$

Similarly

$$\mathbf{S}_z\chi_+ = \frac{\hbar}{2}\chi_+, \quad \mathbf{S}_z\chi_- = -\frac{\hbar}{2}\chi_- \quad (293)$$

from which it follows that

$$\mathbf{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (294)$$

Meanwhile, equation 286 says

$$\mathbf{S}_+\chi_- = \hbar\chi_+, \quad \mathbf{S}_-\chi_+ = \hbar\chi_-, \quad \mathbf{S}_+\chi_+ = \mathbf{S}_-\chi_- = 0 \quad (295)$$

so

$$\mathbf{S}_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \mathbf{S}_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \quad (296)$$

Now $S_{\pm} = S_x \pm iS_y$, so $S_x = (1/2)(S_+ + S_-)$ and $S_y = (1/2i)(S_+ - S_-)$, and hence

$$\mathbf{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \mathbf{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (297)$$

Since \mathbf{S}_x , \mathbf{S}_y , and \mathbf{S}_z all carry a factor of $\hbar/2$, it is tidier to write $\mathbf{S} = (\hbar/2)\sigma$, where

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (298)$$

These are the famous **Pauli spin matrices**. The eigenspinors of \mathbf{S}_z are (of course)

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \left(\text{eigenvalue} + \frac{\hbar}{2} \right) \quad (299)$$

$$\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \left(\text{eigenvalue} - \frac{\hbar}{2} \right) \quad (300)$$

If you measure S_z on a particle in the general state χ (equation 288), you could get $+\hbar/2$, with probability $|a|^2$, or $-\hbar/2$, with probability $|b|^2$. Since they are the only possibilities

$$|a|^2 + |b|^2 = 1 \quad (301)$$

(i.e., the spinor must be *normalized*). But what if instead, you chose to measure S_x ? What are the possible results. According to the generalized statistical interpretation, we need to know the eigenvalues and eigenspinors of \mathbf{S}_x , the characteristic equation is

$$\begin{vmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{vmatrix} = 0 \Rightarrow \lambda^2 = \left(\frac{\hbar}{2}\right)^2 \Rightarrow \lambda \pm \frac{\hbar}{2}$$

Not suprisingly, the possible values for S_x are the same as those for S_z . The normalized eigen-spinors of \mathbf{S}_x are

$$\chi_+^{(x)} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 1 \end{pmatrix}, \left(\text{eigenvalue} + \frac{\hbar}{2} \right) \quad (302)$$

$$\chi_-^{(x)} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -1 \end{pmatrix}, \left(\text{eigenvalue} - \frac{\hbar}{2} \right) \quad (303)$$

As the eigenvectors of a hermitian matrix, they span the space; the generic spinor χ (equation 288) can be expressed as a linear combination of them

$$\chi = \left(\frac{a+b}{\sqrt{2}} \right) \chi_+^{(x)} + \left(\frac{a-b}{\sqrt{2}} \right) \chi_-^{(x)} \quad (304)$$

If you measure S_x , the probability of getting $+\hbar/2$ is $(1/2)|a+b|^2$, and the probability of getting $-\hbar/2$ is $(1/2)|a-b|^2$.

Electron in a Magnetic Field

A spinning charged particle constitutes a magnetic dipole. Its **magnetic dipole moment**, μ , is proportional to its spin angular momentum, \mathbf{S} :

$$\mu = \gamma \mathbf{S} \quad (305)$$

the proportionality constant, γ , is called the **gyromagnetic ratio**. When a magnetic dipole is placed in a magnetic field \mathbf{B} , it experiences a torque, $\mu \times \mathbf{B}$ which tends to line it up parallel to the field. The energy associated with this torque is

$$H = -\mu \cdot \mathbf{B} \quad (306)$$

so the Hamiltonian of a spinning charged particle, at rest in a magnetic field \mathbf{B} is

$$H = -\gamma \mathbf{B} \cdot \mathbf{S} \quad (307)$$

Larmor precession: Imagine a particle of spin $1/2$ at rest in a uniform magnetic field, which points in the z direction

$$\mathbf{B} = B_0 \hat{k} \quad (308)$$

The Hamiltonian, in matrix form, is

$$\mathbf{H} = -\gamma B_0 \mathbf{S}_z = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (309)$$

The eigenstates of \mathbf{H} are the same as those of \mathbf{S}_z

$$\begin{cases} \chi_+, & \text{with energy } E_+ = -(\gamma B_0 \hbar)/2 \\ \chi_-, & \text{with energy } E_- = +(\gamma B_0 \hbar)/2 \end{cases}$$

since the Hamiltonian is time-independent, the general solution to the time-dependent Schrodinger equation is

$$i\hbar \frac{\partial \chi}{\partial t} = \mathbf{H} \chi \quad (310)$$

can be expressed in terms of the stationary states

$$\chi(t) = a\chi_+ e^{-iE_+ t/\hbar} + b\chi_- e^{-iE_- t/\hbar} = \begin{pmatrix} a e^{i\gamma B_0 t/2} \\ b e^{-i\gamma B_0 t/2} \end{pmatrix} \quad (311)$$

The constants a and b are determined by the initial conditions

$$\chi(0) = \begin{pmatrix} a \\ b \end{pmatrix} \quad (312)$$

With no essential loss of generality I will write $a = \cos(\alpha/2)$ and $b = \sin(\alpha/2)$, Thus

$$\chi(t) = \begin{pmatrix} \cos(\alpha/2) e^{i\gamma B_0 t/2} \\ \sin(\alpha/2) e^{-i\gamma B_0 t/2} \end{pmatrix} \quad (313)$$

To get a feel for whats happening here, let's calculate the expectation value of \mathbf{S} , as a function of time

$$\begin{aligned} \langle S_x \rangle &= \chi(t)^\dagger \mathbf{S}_x \chi(t) = (\cos(\alpha/2) e^{-i\gamma B_0 t/2} \quad \sin(\alpha/2) e^{i\gamma B_0 t/2}) \\ &\times \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \cos(\alpha/2) e^{i\gamma B_0 t/2} \\ \sin(\alpha/2) e^{-i\gamma B_0 t/2} \end{pmatrix} \\ &= \frac{\hbar}{2} \sin \alpha \cos(\gamma B_0 t) \end{aligned} \quad (314)$$

similarly,

$$\langle S_y \rangle = \chi(t)^\dagger \mathbf{S}_y \chi(t) = -\frac{\hbar}{2} \sin \alpha \sin(\gamma B_0 t) \quad (315)$$

and

$$\langle S_z \rangle = \chi(t)^\dagger \mathbf{S}_z \chi(t) = \frac{\hbar}{2} \cos \alpha \quad (316)$$

Evidently $\langle \mathbf{S} \rangle$ is tilted at a constant angle α to the z axis, and precesses about the field at the **Larmor frequency**

$$\omega = \gamma B_0 \quad (317)$$

Just as it would classically

Addition of Angular Momenta

Suppose now that we have *two* spin-1/2 particles—for example, the electron and the proton in the ground state of hydrogen. Each can have spin up or spin down so there are four possibilities in all

$$\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow \quad (318)$$

where the first row refers to the electron and the second row to the proton. *Question:* What is the total angular momentum of the atom? Let

$$\mathbf{S} \equiv \mathbf{S}^{(1)} + \mathbf{S}^{(2)} \quad (319)$$

Each of these four composite states is an eigenstate of S_z —the z -components simply add

$$\begin{aligned} S_z \chi_1 \chi_2 &= (S_z^{(1)} + S_z^{(2)}) \chi_1 \chi_2 = (S_z^{(1)} \chi_1) \chi_2 + \chi_1 (S_z^{(2)} \chi_2) \\ &= (\hbar m_1 \chi_1) \chi_2 + \chi_1 (\hbar m_2 \chi_2) = \hbar (m_1 + m_2) \chi_1 \chi_2 \end{aligned} \quad (320)$$

So m (the quantum number of the composite system) is just $m_1 + m_2$

$$\begin{aligned} \uparrow\uparrow: m &= 1; \\ \uparrow\downarrow: m &= 0; \\ \downarrow\uparrow: m &= 0; \\ \downarrow\downarrow: m &= -1 \end{aligned}$$

At first glance, this doesn't look right: m is supposed to advance in integer steps, from $-s$ to $+s$, so it appears that $s = 1$ —but there is an *extra* state with $m = 0$. One way to untangle this problem is to apply the lowering operator, $S_- = S_-^{(1)} + S_-^{(2)}$ to the state $\uparrow\uparrow$, using equation 296

$$S_- (\uparrow\uparrow) = (S_-^{(1)} \uparrow) \uparrow + \uparrow (S_-^{(2)} \uparrow) \quad (321)$$

$$= (\hbar \downarrow) \uparrow + \uparrow (\hbar \downarrow) \quad (322)$$

$$= \hbar (\downarrow\uparrow + \uparrow\downarrow) \quad (323)$$

Evidently the three states with $s = 1$ are (in the notation $|s m\rangle$):

$$\begin{cases} |11\rangle = \uparrow\uparrow \\ |10\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1-1\rangle = \downarrow\downarrow \end{cases} \quad s = 1 \text{ (triplet)}$$

This is called the **triplet** combination, for the obvious reason. Meanwhile, the orthogonal state with $m = 0$ carries $s = 0$;

$$\left\{ |00\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \right\} \quad s = 0 \text{ (singlet)} \quad (324)$$

(if you apply the raising or lowering operator to *this* state, you'll get *zero*)

I need to prove that the triplet states are eigenvectors of S^2 with eigenvalue $2\hbar^2$, and the singlet is an eigenvector of S^2 with eigenvalue 0. Now,

$$S^2 = (\mathbf{S}^{(1)} + \mathbf{S}^{(2)}) \cdot (\mathbf{S}^{(1)} + \mathbf{S}^{(2)}) \quad (325)$$

$$= (S^{(1)})^2 + (S^{(2)})^2 + 2\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)} \quad (326)$$

Using equations 294 and 297, we have

$$\begin{aligned} \mathbf{S}^{(1)} + \mathbf{S}^{(2)} (\uparrow\downarrow) &= (S_x^{(1)} \uparrow)(S_x^{(2)} \downarrow) \\ &\quad + (S_y^{(1)} \uparrow)(S_y^{(2)} \downarrow) + (S_z^{(1)} \uparrow)(S_z^{(2)} \downarrow) \\ &= \left(\frac{\hbar}{2} \downarrow\right) \left(\frac{\hbar}{2} \uparrow\right) + \left(\frac{i\hbar}{2} \downarrow\right) \left(\frac{-i\hbar}{2} \uparrow\right) \\ &\quad + \left(\frac{\hbar}{2} \uparrow\right) \left(\frac{-\hbar}{2} \downarrow\right) \\ &= \frac{\hbar^2}{4} (2 \downarrow\uparrow - \uparrow\downarrow) \end{aligned} \quad (327)$$

similarly

$$\mathbf{S}^{(1)} + \mathbf{S}^{(2)} (\downarrow\uparrow) = \frac{\hbar^2}{4} (2 \uparrow\downarrow - \downarrow\uparrow) \quad (328)$$

It follows that

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)} |10\rangle = \frac{\hbar^2}{4} \frac{1}{\sqrt{2}} (2 \downarrow\uparrow - \uparrow\downarrow + 2 \uparrow\downarrow - \downarrow\uparrow) = \frac{\hbar^2}{4} |10\rangle \quad (329)$$

and

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)} |00\rangle = \frac{\hbar^2}{4} \frac{1}{\sqrt{2}} (2 \downarrow\uparrow - \uparrow\downarrow - 2 \uparrow\downarrow + \downarrow\uparrow) = -\frac{3\hbar^2}{4} |00\rangle \quad (330)$$

Returning to equation 325-326 (and using equation 291), we conclude that

$$S^2|10\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} + 2\frac{\hbar^2}{4}\right)|10\rangle = 2\hbar^2|10\rangle \quad (331)$$

$$S^2|00\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} - 2\frac{3\hbar^2}{4}\right)|00\rangle = 0 \quad (332)$$

What we have just done (combining spin 1/2 with spin 1/2 to get spin 1 and spin 0) is the simplest example of a larger problem: if you combine spin s_1 with spin s_2 , what total spins s can you get? The answer is that you get every spin from $(s_1 + s_2)$ down to $(s_1 - s_2)$ or $(s_2 - s_1)$, if $s_2 > s_1$ in integer steps

$$s = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), \dots, |s_1 - s_2| \quad (333)$$

The combined state $|sm\rangle$ with total spin s and z -component m will be some linear combination of the composite states $|s_1 m_1\rangle |s_2 m_2\rangle$

$$|sm\rangle = \sum_{m_1+m_2=m} C_{m_1 m_2 m}^{s_1 s_2 s} |s_1 m_1\rangle |s_2 m_2\rangle \quad (334)$$

(because the z components *add*, the only composite states that contribute are those for which $m_1 + m_2 = m$). The triplet combination and the singlet are special cases of this general form, with $s_1 = s_2 = 1/2$ I used the notation $\uparrow = |\frac{1}{2} \frac{1}{2}\rangle$, $\downarrow = |\frac{1}{2} (-\frac{1}{2})\rangle$. The constants $C_{m_1 m_2 m}^{s_1 s_2 s}$ are called **Clebsch-Gordan coefficients**.

Chapter 5: Identical Particles

Two-Particle System

The state of a two-particle system is a function of the coordinates of particle one (\mathbf{r}_1), the coordinates of particle two (\mathbf{r}_2), and the time

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) \quad (335)$$

Its time evolution is determined (as always) by the Schrodinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad (336)$$

Where H is the Hamiltonian for the whole system

$$H = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t) \quad (337)$$

The statistical interpretation carries over in the obvious way

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 \quad (338)$$

is the probability of finding particle 1 in the volume $d^3\mathbf{r}_1$ and particle 2 in the volume $d^3\mathbf{r}_2$; evidently Ψ must be normalized in such a way that

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 = 1 \quad (339)$$

For time-independent potentials, we obtain a complete set of solutions by separation of variables

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2) e^{-iEt/\hbar} \quad (340)$$

where the spatial wave function (ψ) satisfies the time-independent Schrodinger equation

$$-\frac{\hbar^2}{2m_1} \nabla_1^2 \psi - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi + V\psi = E\psi \quad (341)$$

and E is the total energy of the system

Bosons and Fermions

Suppose particle 1 is in the (one-particle) state $\psi_a(\mathbf{r})$, and particle 2 is in the state $\psi_b(\mathbf{r})$. (ignoring spin at the moment). In that case $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is a simple product

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}) \psi_b(\mathbf{r}) \quad (342)$$

Quantum mechanics neatly accommodates the existence of particles that are *indistinguishable in principle*: We simply construct a wave function that is *non committal* as to which particle is in which state. there are actually two ways to do it

$$\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}) \psi_b(\mathbf{r}) \pm \psi_b(\mathbf{r}) \psi_a(\mathbf{r})] \quad (343)$$

Thus the theory admits to kinds of identical particles: **bosons**, for which we use the plus sign, and **fermions**, for which we use the minus sign. Photons and mesons are bosons; protons and electrons are fermions. It so happens that

- all particles with *integer* spin are bosons, and
- all particles with *half-integer* spin are fermions

It follows, in particular, that *two identical fermions cannot occupy the same state*. For if $\psi_a = \psi_b$, then

$$\psi_-(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r})\psi_b(\mathbf{r}) - \psi_b(\mathbf{r})\psi_a(\mathbf{r})] = 0 \quad (344)$$

This is the famous **Pauli exclusion principle**. I assumed, for the sake of argument, that one particle was in the state ψ_a and the other in state ψ_b , but there is a more general way to formulate the problem. Let us define the **exchange operator**, P , which interchanges the two particles

$$Pf(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1) \quad (345)$$

Clearly $P^2 = 1$, and it follows that the eigenvalues of P are ± 1 . Now, if the two particles are identical, the Hamiltonian must treat them the same: $m_1 = m_2$ and $V(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r}_2, \mathbf{r}_1)$. It follows that P and H are compatible observables,

$$[P, H] = 0 \quad (346)$$

and hence we can find a complete set of functions that are simultaneously eigenstates of both. That is to say, we can find solutions to the Schrodinger equation that are either symmetric (eigenvalue $+1$) or antisymmetric (eigenvalue -1) under exchange

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \pm \psi(\mathbf{r}_2, \mathbf{r}_1) \quad (347)$$

The **symmetrization requirement** states that, for identical particles, the wave function is not merely *allowed*, but *required* to satisfy equation 347. This is the general statement, of which equation 343 is a special case.

Exchange Forces

To give some sense of what the symmetrization requirement does, we can suppose that one particle is in state $\psi_a(x)$, and the other is in state $\psi_b(x)$, and these two states are orthogonal and normalized. If the two particles are distinguishable, and number 1 is in state ψ_a , then the combined wave function is

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2) \quad (348)$$

if they are identical bosons, the composite wave function is

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)] \quad (349)$$

and if they are identical fermions

$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)] \quad (350)$$

Let's calculate the expectation value of the square of the separation distance between the two particles

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle \quad (351)$$

Case 1: Distinguishable particles. For the wave function in equation 348

$$\langle x_1^2 \rangle = \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_a \quad (352)$$

and

$$\langle x_2^2 \rangle = \int |\psi_a(x_1)|^2 dx_1 \int x_2^2 |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_b \quad (353)$$

and

$$\langle x_1 x_2 \rangle = \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 = \langle x \rangle_a \langle x \rangle_b \quad (354)$$

in this case then

$$\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \quad (355)$$

Case 2: Identical particles. For the wave function in equations 349 and 350

$$\begin{aligned} \langle x_1^2 \rangle &= \frac{1}{2} \left(\int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 \right. \\ &\quad \left. + \int x_1^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)|^2 dx_2 \right) \\ &\pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int \psi_b(x_2)^* \psi_a(x_2) dx_2 \\ &\pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int \psi_a(x_2)^* \psi_b(x_2) dx_2 \\ &= \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0] = \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b) \end{aligned} \quad (356)$$

similarly

$$\langle x_2^2 \rangle = \frac{1}{2} (\langle x^2 \rangle_b + \langle x^2 \rangle_a) \quad (357)$$

(naturally, $\langle x_2^2 \rangle = \langle x_1^2 \rangle$, since you can't tell them apart.) But

$$\begin{aligned}
\langle x_1 x_2 \rangle &= \frac{1}{2} \left(\int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 \right. \\
&\quad \left. + \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)|^2 dx_2 \right. \\
&\quad \left. \pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) dx_2 \right. \\
&\quad \left. \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) dx_2 \right) \\
&= \frac{1}{2} (\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab}) \\
&= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2 \quad (358)
\end{aligned}$$

where

$$|\psi_a(x_1)|^2 dx_1 \int x_2^2 |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_b \quad (359)$$

and

$$\langle x_1 x_2 \rangle = \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 = \langle x \rangle_a \langle x \rangle_b \quad (360)$$

in this case then

$$\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \quad (361)$$

Case 2: Identical particles. For the wave function in equations 349 and 350

$$\begin{aligned}
\langle x_1^2 \rangle &= \frac{1}{2} \left(\int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 \right. \\
&\quad \left. + \int x_1^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)|^2 dx_2 \right. \\
&\quad \left. \pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int \psi_b(x_2)^* \psi_a(x_2) dx_2 \right. \\
&\quad \left. \pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int \psi_a(x_2)^* \psi_b(x_2) dx_2 \right) \\
&= \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0] = \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b) \quad (362)
\end{aligned}$$

similarly

$$\langle x_2^2 \rangle = \frac{1}{2} (\langle x^2 \rangle_b + \langle x^2 \rangle_a) \quad (363)$$

(naturally, $\langle x_2^2 \rangle = \langle x_1^2 \rangle$, since you can't tell them apart.) But

$$\begin{aligned}
\langle x_1 x_2 \rangle &= \frac{1}{2} \left(\int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 \right. \\
&\quad \left. + \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)|^2 dx_2 \right. \\
&\quad \left. \pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) dx_2 \right. \\
&\quad \left. \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) dx_2 \right) \\
&= \frac{1}{2} (\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab}) \\
&= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2 \quad (364)
\end{aligned}$$

where

$$\langle x \rangle_{ab} \equiv \int x \psi_a(x)^* \psi_b(x) dx \quad (365)$$

Evidently

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2 \quad (366)$$

comparing equations 355 and 360, we see that the difference resides in the final term

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2 |\langle x \rangle_{ab}|^2 \quad (367)$$

Atoms

A neutral atom, of atomic number Z , consists of a heavy nucleus, with electric charge Ze , surrounded by Z electrons (mass m and charge $-e$). The Hamiltonian for this system is

$$\begin{aligned}
H &= \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right\} \\
&\quad + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^Z \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|} \quad (368)
\end{aligned}$$

The term in the curly brackets represents the kinetic plus potential of the j_{th} electron, in the electric field of the nucleus; the second sum (which runs over all values of j and k except $j = k$) is the potential associated with the mutual repulsion of the electrons. (the factor of 1/2 in front corresponds that the summation counts each pair twice. The problem is to solve Schrodinger's equation

$$H\psi = E\psi \quad (369)$$

for the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)$. Because electrons are identical fermions, however, not all solutions are acceptable; only those for which the complete state (position and spin)

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z) \chi(\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_Z) \quad (370)$$

is antisymmetric with respect to interchange of any two electrons. In particular, no two electrons can occupy the *same* state

Helium

After hydrogen, the simplest atom is helium ($Z = 2$). The Hamiltonian,

$$H = \left\{ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (371)$$

consists of two *hydrogenic* Hamiltonians (with nuclear charge $2e$), one for each electron 1 and 2, together with the final term describing the repulsion of the two electrons. It is this last term that causes all the trouble. If we simply ignore it, the Schrodinger equation separates, and the solutions can be written as products of *hydrogen* wave functions

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1) \psi_{n'l'm'}(\mathbf{r}_2) \quad (372)$$

only with half the Bohr radius and four times the Bohr energies. The total energy would be

$$E = 4(E_n + E_{n'}) \quad (373)$$

where $E_n = -13.6/n^2$ eV. In particular, the ground state would be

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a} \quad (374)$$

and its energy would be

$$E_0 = 8(-13.6 \text{ eV}) = -109 \text{ eV} \quad (375)$$

Solids

The Free Electron Gas

Suppose the object in question is a rectangular solid, with dimensions l_x, l_y, l_z , and imagine that an electron inside experiences no force at all, except at the impenetrable walls

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < l_x, 0 < y < l_y, \text{ and } 0 < z < l_z \\ \infty, & \text{otherwise} \end{cases}$$

The Schrodinger equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi \quad (376)$$

separates, in cartesian coordinates: $\psi(x, y, z) = X(x)Y(y)Z(z)$, with

$$-\frac{\hbar^2}{2m} \frac{dX^2}{dx^2} = E_x X \quad (377)$$

$$-\frac{\hbar^2}{2m} \frac{dY^2}{dy^2} = E_y Y \quad (378)$$

$$-\frac{\hbar^2}{2m} \frac{dZ^2}{dz^2} = E_z Z \quad (379)$$

and $E = E_x + E_y + E_z$. Letting

$$k_x \equiv \frac{\sqrt{2mE_x}}{\hbar}, \quad k_y \equiv \frac{\sqrt{2mE_y}}{\hbar}, \quad k_z \equiv \frac{\sqrt{2mE_z}}{\hbar} \quad (380)$$

we obtain the general solutions

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x) \quad (381)$$

$$Y(y) = A_y \sin(k_y y) + B_y \cos(k_y y) \quad (382)$$

$$Z(z) = A_z \sin(k_z z) + B_z \cos(k_z z) \quad (383)$$

$$(384)$$

The boundary conditions require $X(0) = Y(0) = Z(0) = 0$, so $B_x = B_y = B_z = 0$, and $X(l_x) = Y(l_y) = Z(l_z) = 0$, so that

$$k_x l_x = n_x \pi, \quad k_y l_y = n_y \pi, \quad k_z l_z = n_z \pi \quad (385)$$

where each n is a positive integer

$$n_x = 1, 2, 3, \dots, \quad n_y = 1, 2, 3, \dots, \quad n_z = 1, 2, 3, \dots \quad (386)$$

The normalized wave functions are

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right) \quad (387)$$

$$\langle x \rangle_{ab} \equiv \int x \psi_a(x)^* \psi_b(x) dx \quad (388)$$

Evidently

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2 \quad (389)$$

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The term in the curly brackets represents the kinetic plus potential of the j_{th} electron, in the electric field of the nucleus; the secon sum (which runs over all values of j and k except $j = k$) is the potential associated with the mutual repulsion of the electrons. (the factor of 1/2 in front corresponds that the summation counts each pair twice. The problem is to solve Schrodinger's equation

$$H\psi = E\psi \quad (392)$$

for the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)$. Because electrons are identical fermions, however, not all solutions are acceptable; only those for which the complete state (position and spin)

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z) \chi(\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_Z) \quad (393)$$

is antisymmetric with respect to interchange of any two electrons. In particular, no two electrons can occupy the *same* state

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$$H = \left\{ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (394)$$

consists of two *hydrogenic* Hamiltonians (with nuclear charge $2e$), one for each electron 1 and 2, together with the final term describing the repulsion of the two electrons. It is this last term that causes all the the trouble. If we simply ignore it, the Schrodinger equation sperates, and the solutions can be written as products of *hydrogen* wave functions

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1) \psi_{n'l'm'}(\mathbf{r}_2) \quad (395)$$

only with half the Bohr radius and four times the Bohr energies. The total energy would be

$$E = 4(E_n + E_{n'}) \quad (396)$$

where $E_n = -13.6/n^2$ eV. In particular, the ground state would be

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$$E_0 = 8(-13.6 \text{ eV}) = -109 \text{ eV} \quad (398)$$

Solids

The Free Electron Gas

Suppose the object in question is a rectangular solid, with dimensions l_x, l_y, l_z , and imagine that an electron inside experiences no force at all, except at the impenetrable walls

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < l_x, 0 < y < l_y, \text{ and } 0 < z < l_z \\ \infty, & \text{otherwise} \end{cases}$$

The Schrodinger equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi \quad (399)$$

separates, in cartesian coordinates: $\psi(x, y, z) = X(x)Y(y)Z(z)$, with

$$-\frac{\hbar^2}{2m} \frac{dX^2}{dx^2} = E_x X \quad (400)$$

$$-\frac{\hbar^2}{2m} \frac{dY^2}{dy^2} = E_y Y \quad (401)$$

$$-\frac{\hbar^2}{2m} \frac{dZ^2}{dz^2} = E_z Z \quad (402)$$

and $E = E_x + E_y + E_z$. Letting

$$k_x \equiv \frac{\sqrt{2mE_x}}{\hbar}, \quad k_y \equiv \frac{\sqrt{2mE_y}}{\hbar}, \quad k_z \equiv \frac{\sqrt{2mE_z}}{\hbar} \quad (403)$$

we obtain the general solutions

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x) \quad (404)$$

$$Y(y) = A_y \sin(k_y y) + B_y \cos(k_y y) \quad (405)$$

$$Z(z) = A_z \sin(k_z z) + B_z \cos(k_z z) \quad (406)$$

The boundary conditions require $X(0) = Y(0) = Z(0) = 0$, so $B_x = B_y = B_z = 0$, and $X(l_x) = Y(l_y) = Z(l_z) = 0$, so that

$$k_x l_x = n_x \pi, \quad k_y l_y = n_y \pi, \quad k_z l_z = n_z \pi \quad (407)$$

where each n is a positive integer

$$n_x = 1, 2, 3, \dots, \quad n_y = 1, 2, 3, \dots, \quad n_z = 1, 2, 3, \dots \quad (408)$$

The normalized wave functions are

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right) \quad (409)$$

and the allowed energies are

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) = \frac{\hbar^2 k^2}{2m} \quad (410)$$

where k is the magnitude of the **wave vector**, $\mathbf{k} \equiv (k_x, k_y, k_z)$.

If you imagine a three-dimensional space, with axes k_x, k_y, k_z , and planes drawn in at $k_x = (\pi/l_x), (2\pi/l_x), (3\pi/l_x), \dots$, at $k_y = (\pi/l_y), (2\pi/l_y), (3\pi/l_y), \dots$ and at $k_z = (\pi/l_z), (2\pi/l_z), (3\pi/l_z), \dots$. Each block in this grid, and hence each state, occupies a volume

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V} \quad (411)$$

of ' k -space,' where $V = l_x l_y l_z$ is the volume of the object itself. Suppose the sample contains N atoms, and each contribute q electrons. They will fill up one octant of a *sphere* in k -space, whose radius k_F is determined by the fact that each pair of electrons require a volume π^3/V

$$\frac{1}{8} \left(\frac{4}{3} \pi k_F^3 \right) = \frac{Nq}{2} \left(\frac{\pi^3}{V} \right) \quad (412)$$

thus

$$k_F = (3\rho\pi^2)^{1/3} \quad (413)$$

where

$$\rho \equiv \frac{Nq}{V} \quad (414)$$

is the *free electron density* (the number of free electrons per unit volume)

The boundary separating occupied and unoccupied states, in k -space, is called the **Fermi surface**. The corresponding energy is called the **Fermi energy**, E_F ; for a free electron gas,

$$E_F = \frac{\hbar^2}{2m} (3\rho\pi^2)^{2/3} \quad (415)$$

The *total* energy of the electron gas can be calculated as follows; Each of these states carries an energy $\hbar^2 k^2 / 2m$, so the energy of the shell is

$$dE = \frac{\hbar^2 k^2}{2m} \frac{V}{\pi^2} k^2 dk \quad (416)$$

and hence the total energy is

$$\begin{aligned} E_{tot} &= \frac{\hbar^2 V}{2m\pi^2} \int_0^{k_F} k^4 dk = \frac{\hbar^2 k_F^5 V}{10\pi^2 m} \\ &= \frac{\hbar^2 (3\pi^2 Nq)^{5/3}}{10\pi^2 m} V^{-2/3} \end{aligned} \quad (417)$$

This quantum mechanical energy plays a role rather analogous to the internal thermal energy (U) of an ordinary gas. In particular, it exerts a *pressure* on the walls, for if the box expands by an amount dV , the total energy decreases

$$\begin{aligned} dE_{tot} &= -\frac{2}{3} \frac{\hbar^2 (3\pi^2 Nq)^{5/3}}{10\pi^2 m} V^{-5/3} dV \\ &= -\frac{2}{3} E_{tot} \frac{dV}{V} \end{aligned} \quad (418)$$

and this shows up as work done on the outside ($dW = PdV$) by the quantum pressure P . Evidently

$$P = \frac{2}{3} \frac{E_{tot}}{V} = \frac{2}{3} \frac{\hbar^2 k_F^5}{10\pi^2 m} = \frac{(3\pi^2)^{2/3} \hbar^2}{5m} \rho^{5/3} \quad (419)$$

this is sometimes called **degeneracy pressure** strictly due to quantum effects.