NOTES IN ATOMIC SPECTRA

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INTRODUCTION

The 20th century was the century we discovered that the world ~~was~~ is Quantum Mechanical (QM).
We also discovered that there are 4-Dimensions: we live in a 4-D space-time!

During the early 1900's most physicists believed that these discoveries are mostly academic, without clear applications.

Today? Q.M. has led to

Computers, Electronics, Lasers, Nanotechnology, Internet, MRI scanners (medical physics), ...
And who knows? In the future
Quantum Teleportation, Quantum Computers .....
Space travel, ...

Intro - 2

Beyond Applications

- However, Einstein's dream is ..still a dream:

  Have NOT unity Gravity with QM
  ⇒ (we haven't unified the known forces).

- We have even greater problems

  Universe Energy (Measurements) → Visible matter 4%
  Universe Energy (Measurements) → Dark matter 25%
  Universe Energy (Measurements) → Dark Energy 71%

  What is DM, DE? ⇒ Large Hadron Collider may tell us? (DM)

- Why there is mass? Where is it coming from?

- Maybe the biggest question:

  THE COSMOLOGICAL CONSTANT PROBLEM

Universe appears flat. It means it has energy density very close to 0.

It means that the empty space

, the vacuum, does NOT gravitate.

This seems in conflict with QM:

In QM the vacuum is filled with energy ... But from Einstein:

$$\boxed{m = \frac{E}{c^2}}$$

So, the vacuum should gravitate. What cancels this energy? (need $\sim 10^{40}$!!! cancellation!).

The quest to answering these questions has started since the years of Aristotle and Democritos (who coined the term "atom" for elementary constituent).

Understanding of the Atomic Structure was the first breakthrough in 1900's.

Now we know about quarks and gluons but our original questions are still there!

Intro - 4

Having now entered in the 21st Century, we have two main streams of QM + Gravity unification:

(1) String theory: here we live in 11 dimensions!

(2) Quantum (loop) Gravity: we still live in 4-Dimensions but these (the spacetime) are not fundamental.

Nobody knows what the right theory is (the above could both be wrong)!

However it is amusing that (2) is based on a fundamental particle property called "spin". In (2) "spin" could create spacetime!

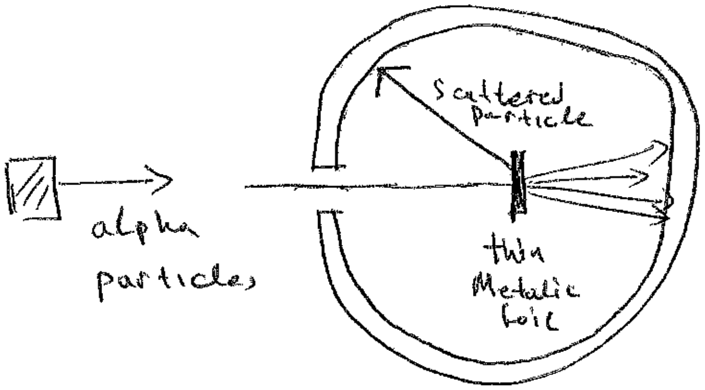
Angular Momentum (Spin) is the main topic of this module. As we will see, it is responsible for the observed structure of the periodic table.

HISTORY : THE BIRTH OF ATOMS

Atom : from the Greek "Ά-τομο"
translation: "No - Division"

- It is something that cannot be divided

1911: Geiger and Marsden perform the "Rutherford" experiment



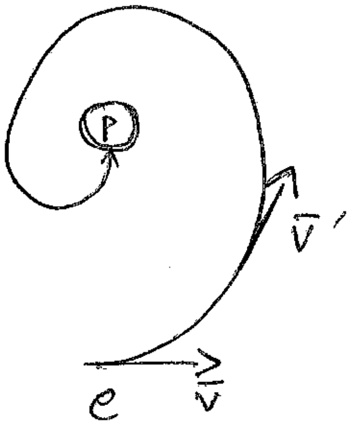
G&M found that Alpha particles with mass $\simeq 8000 \times m_{electron}$ and $V = 2 . 10^7$ m/s were occasionally back-scattered.

In 1911 Rutherford introduced the "nuclear" model of the atom: there is a heavy nucleus in the center with the electrons orbiting like planets orbiting the sun!

Hist 2

PROBLEMS with Classical Physics

Rutherford's model had a major problem. EM tells us that an accelerating electric charge radiates energy:



So, an electron should plunge onto the nucleus because the $\vec{v}$ velocity vector is changing (so it should radiate energy)

However, atoms are stable (see Hydrogen).

Problem 2 : Emission + Absorption line spectra of elements

- While "white" light from the sun through a prism reveals a rainbow (continuous)
  Light from excited Hydrogen through a prism showed characteristic wavelength lines!
- Similarly when the same element was used as an absorption medium, only certain wavelengths of the light spectrum would be absorbed!

Hist - 3

What was even stranger was that some of the "lines" were thicker than others!

1885: J. J. Balmer found a formula to explain these lines

$$\frac{1}{\lambda} = R_y\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad n = 3, 4, 5, \ldots$$

$\hookrightarrow 1.097 \cdot 10^7 \, m^{-1}$ Rydberg constant

Others followed but finally:

1913 Bohr (Nobel 1922) put forward his model, with two postulates:

① An electron can have only certain (specific) energy levels in an atom. This means electrons move in orbits restricted by the requirement that the angular momentum L is an integral multiple of $\hbar$: $\boxed{L = n\hbar}$

② Transitions between energy levels can take place be emitting/absorbing a photon of the appropriate frequency!

Bohr wrote the following equation for the energy levels

$$E_n = -2.178 \cdot 10^{-18} \cdot \frac{Z^2}{n^2} \quad , n = 1, 2, 3, \ldots$$

where Z = atomic number.

Note that $\boxed{-2.178 \cdot 10^{-18}\,J = R_y \cdot h}$

Thus a transition from $n_{initial}$ to n_{final}: gives an energy of

$$\Delta E = E_f - E_i = -2.178 \cdot 10^{-18} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{ Joul}$$

BUT PROBLEMS REMAIN!

- How can particles follow these orbits without collapsing?
- Spectral line thickness?
- Wave-like nature of electrons?
- What is an electron? Particle or Wave?

$\Longrightarrow$ NEED A THEORY $\Rightarrow$ QUANTUM MECHANICS

SYMMETRY IN QUANTUM MECHANICS

According to H. Weyl, a thing is Symmetrical if there is something we can do to it so that after we have done it, it looks the same as it did before.

So, if we do an operation on a physical system under which certain physical phenomena remain invariant, then this is a symmetry Operation.

Examples of Symmetry Operations:

- Translation is space
- Translation in time
- Rotation about an axis
- Reversal of time
- Reflection of space ..

CONSERVATION LAWS:

When we come to Q.M. the situation gets interesting:

For every symmetry operation $\Longrightarrow$ there is a corresponding conservation law.

SYM-2

Symmetry under translation in space $\Rightarrow$

$\Rightarrow$ Momentum conservation

Symmetry under translation in space

$\Rightarrow$ Energy conservation.

As we know in QM the wavefunction

$\psi(x)$ is a probability amplitude:

$|\psi(x)|^2$ = the probability to find a particle at x, or better

$|\psi(x)|^2 \cdot dx$ = prob. to find partice in dx

Since Ψ is complex, in general, we can apply a "phase rotation":

$\Psi \longrightarrow e^{i\Delta} \cdot \Psi$ which would lead to the same probability:

$$|\Psi|^2 = |e^{i\Delta}\Psi|^2 = |\Psi|^2 \cdot \underbrace{|e^{i\Delta}|^2}_{\to 1} \qquad (1)$$

Thus, (1) is a symmetry operation ($\psi \rightarrow e^{i\Delta}\psi = U \cdot \psi$) which leaves the probability invariant.

$\Rightarrow$ The conservation law connected with this invariance (Q.M. phase $\Delta \in \mathbb{R}$) is the <u>conservation of electric charge</u>!

$$\boxed{\frac{dQ}{dt} = 0}$$ Charge is conserved

It is beyond the scope of the module to prove this, however the whole discussion hints to the fact that the presence of charge (or particles with charge) requires the presence of complex wave-functions.

For real wave-functions, $\Psi \in \mathbb{R}$ the only way (1) would work is for $\Delta = 0$ and this corresponds to a neutral particle.

SYM-4

QUANTUM LABELS

Quantum states are usually labelled by quantum labels or numbers.
For example, a free (non-interacting) particle could be labelled as:

$\boxed{\Psi_{E,P}}$, where E, P its energy & momentum.

The particle could be in a potential and its energy labelling be very specific.
For example in the Harmonic Oscillator case:

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega \quad , n = 0, 1, \ldots$$

As we will see in this module, the electron in a central potential like in the Hydrogen atom $(V = V(R))$ has also a particular labelling:

$$\boxed{\begin{array}{c} E_n = \dfrac{-13.6\,\text{eV}}{n^2} \\ n = 1, 2, \ldots \end{array}}$$

ARE THERE MORE LABELS
(other than E and P)?

Energy and Momentum

As we said the origin of mass is one of the big questions in Physics.

Einstein wanted to remove mass from the fundamental equations of physics so he wrote his famous equation

$$E = mc^2 \Longrightarrow \boxed{m = \frac{E}{c^2}}$$

I.e mass is energy.

Constant "c", the speed of light is just a constant that changes the units with which we measure energy!

Note: if we set $c = 1$, then

mass is measured in units of Energy!

$$m \rightarrow [eV]$$

$$E \rightarrow [eV]$$

EM-2

Moving in QM, De Broglie's relations are:

$$\boxed{\begin{aligned} E &= \hbar \omega \\ p &= \hbar K \end{aligned}}$$

⇒ Energy **is** angular frequency

⇒ Momentum **is** wavenumber

These relations connect "particle" properties (E, p) to "wave" properties (ω, k)

Reminder:

f = "frequency" $\quad \frac{\text{cycles}}{\text{second}}$

ω = angular frequency $= 2\pi f \quad \frac{\text{rad}}{\text{second}}$

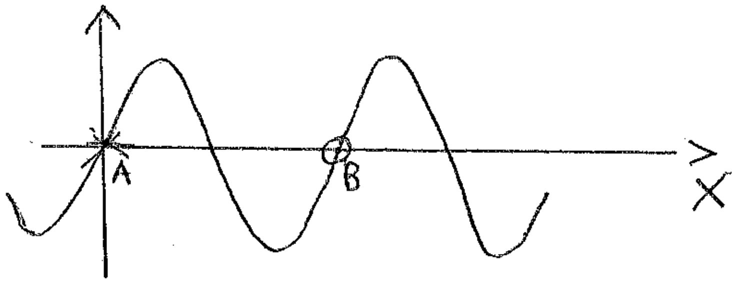
λ = "Wave ~~number~~ length" = distance travelled per cycle

c = "speed of wave" $= \lambda \cdot f \quad \frac{\text{distance}}{\text{second}}$

$K = \frac{2\pi}{\lambda}$ = "Wave number" in $\frac{\text{rad}}{\text{distance}}$

EM-3

- For a plane wave: $\sin(kx - \omega t)$



At point A we assume the position of a point on our wave at $\boxed{X = 0,\ t = 0}$

After time $= t$, our wave moves in X, at

$$X = \frac{\omega}{k} t = \frac{\lambda}{T} \cdot t = V_{ph} \cdot t$$

↳ "phase velocity"

For example it takes time T to go from A to B for a distance equal to λ (wavelength).

$$\Rightarrow \boxed{U_{ph} = \frac{\omega}{K}}$$

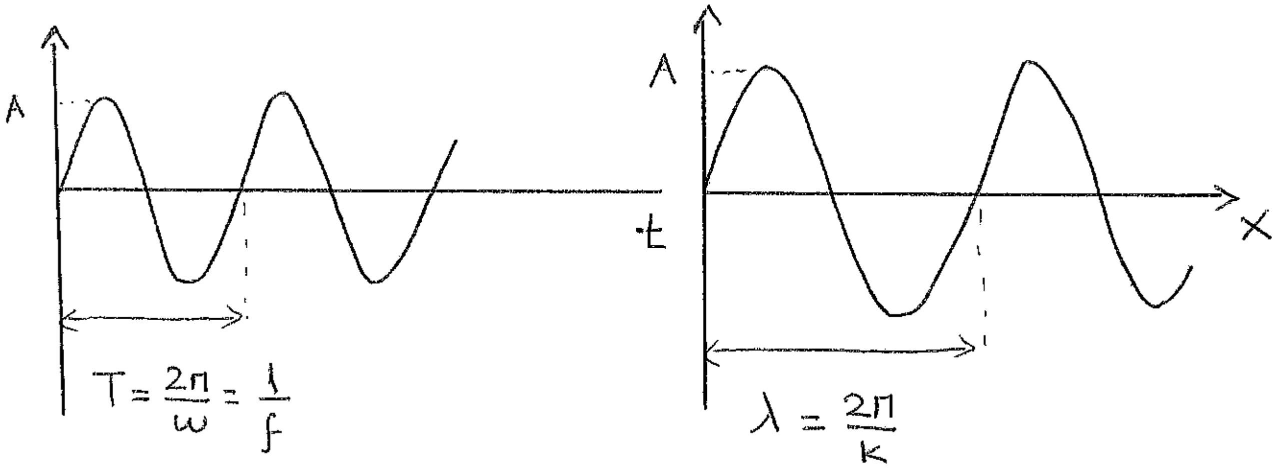
Phase velocity is NOT a measurable quantity. It does not appear in any $\phi^* \psi$ observable probability density.

Particles like an electron in H-atom, are described by wave-packets which are Fourier sums of

$A \sin(\cancel{uk}x - \omega t)$. Example:

$$\Psi(x,t) = \int A(k,\omega) \cdot \sin(kx - \omega t)\, dk\, d\omega$$

EM-4



- What is the relationship between frequency and wavelength?
OR, ang. frequency and wavenumber?

- For a slow non-relativistic particle (like an electron in H-atom):

$$E = \frac{p^2}{2m} \Rightarrow \hbar\omega = \frac{(\hbar k)^2}{2m} \Rightarrow \boxed{\omega = \frac{\hbar k^2}{2m}}$$

- In general one has to use Einstein's formula

$$E^2 = m_0^2 c^4 + p^2 \cdot c^2 \Rightarrow \quad (m_0 : \text{rest mass})$$

$$\Rightarrow \underset{\downarrow \atop (\hbar\omega)^2}{E^2} = m_0^2 \cdot c^4 + \underset{\downarrow \atop (\hbar k)^2}{p^2} c^2 \Rightarrow$$

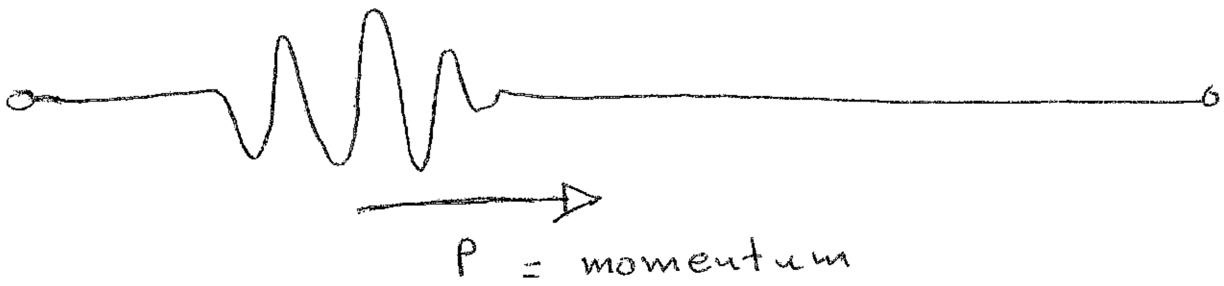
$$\boxed{\omega^2 = \frac{m^2 c^4}{\hbar^2} + k^2 \cdot c^2}$$

"Dispersion Relation"
$\omega = \omega(k)$

EM-5

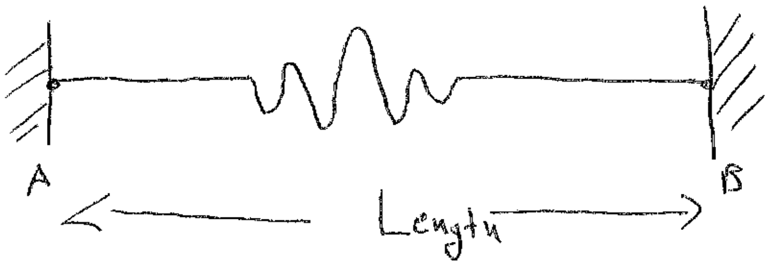
Quantization of Momentum

In QM we are talking about <u>Wave</u>functions, and about quantum states or elementary particles (like an electron) described by a "WAVE" ⇒ an excitation of some sort of medium like a string:



Note this is moving in 1-D space from $-\infty$ to $+\infty$.

To get rid of the infinity one could put a boundary condition.

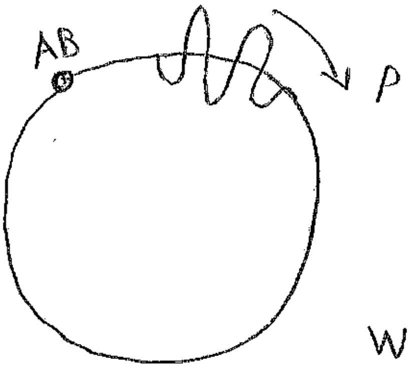


Length $= \ell$

However this would violate conservation of momentum!

EM-6

The solution is to connect points A and B introducing a periodicity



$\Longrightarrow$ Still a 1-D motion now on a Circle. When our wave reaches point "AB" it just continues!

No violation of P-conservation

For a circle radius $R \rightarrow \infty$ notice that we are recovering the original "infite" line.

The circumference of our circle is ℓ.

Notice that the wavelength λ can only be:

$$\boxed{\lambda = \frac{\ell}{N}}\ , \quad N = \text{integer}$$

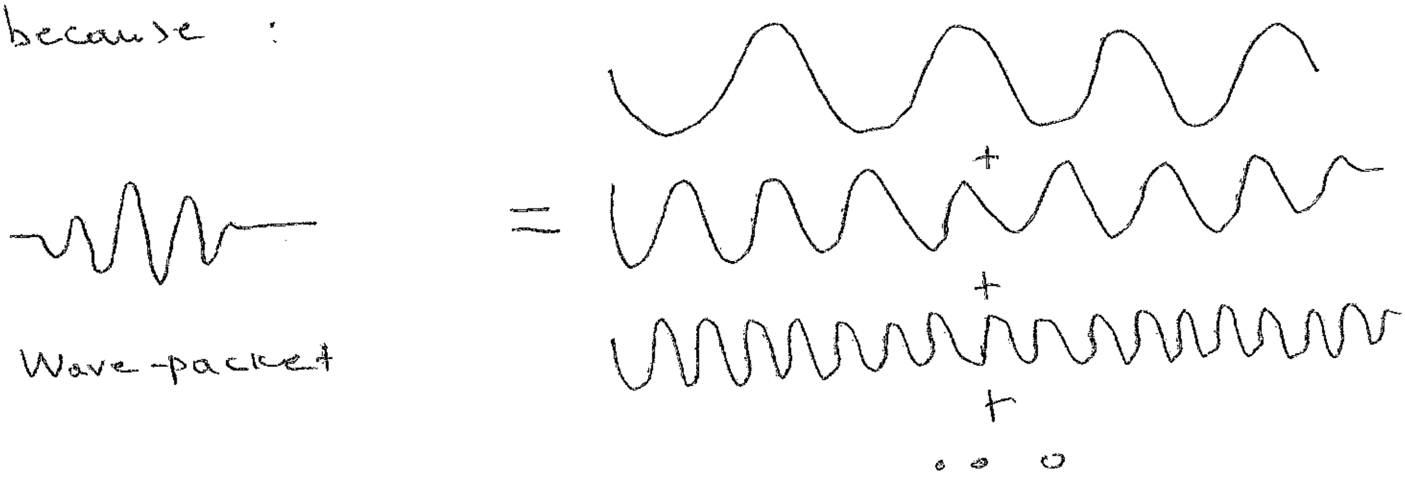
Otherwise our wave wouldn't fit in the circle. So only certain "modes" are allowed, due to the boundary condition.

The De Broglie relations give:

$$p = \hbar k = \frac{\hbar}{\lambda/2\pi} \Rightarrow p = 2\pi\frac{N}{\ell}\cdot\hbar$$

$$\Rightarrow \boxed{p = \frac{2\pi N}{\ell}\cdot\hbar}$$ Momentum is Quantized! (1)

Note that this is also true for a wave-packet because :



it is a sum of plane waves ("Fourier series").

Extend equation (1) in the case of a true circular orbit (electron in H atom).

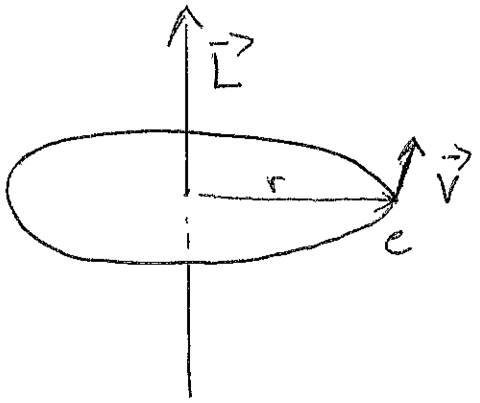
$$p = \frac{2\pi N}{2\pi R}\cdot\hbar \Rightarrow P\cdot R = N\hbar \Rightarrow$$

$$\Rightarrow \boxed{L = N \cdot \hbar}$$

N = integer

Quantization of (orbital) Angular Momentum L

ORBITAL ANGULAR MOMENTUM



$$\vec{L} = \vec{r} \times \vec{p}$$

The OAM is a vector produced by the $\vec{r}$ and $\vec{p}$ vectors. This is done via a "cross-product".

$$L_x = yP_z - zP_y \, , \; L_y = zP_x - xP_z \, , \; L_z = xP_y - yP_x$$

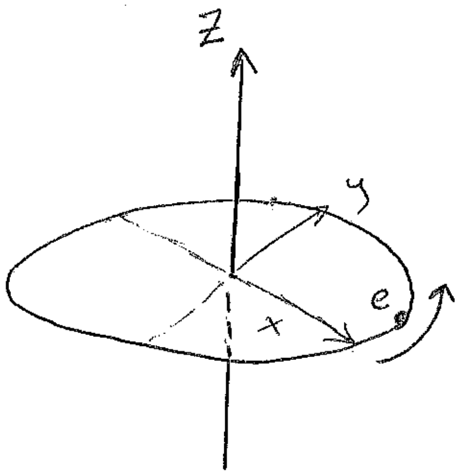
Here we distinguish between OAM and "spin": we are interested only about a particle moving about an axis in space. The "centre of mass" of the particle is moving about the rotation axis.

Classicaly, $\vec{L}$ points along the rotation axis (see figure).

Assume this axis is $Z \Rightarrow \vec{L} = L_z \cdot \vec{k}$ where $\vec{k}$ the unit vector along Z-axis.

Hence:

$$L_x = 0 \;,\; L_y = 0 \;,\; L_z = x \cdot p_y - y p_x$$



Hence, in this case

$P_Z = 0$ and $Z = 0$

for our electron which is orbiting on the xr plane.

$\Rightarrow$ However in Quantum Mechanics this situation CANNOT occur:

$$[x, \hat{P}_x] = [y, \hat{P}_y] = [z, \hat{P}_z] = i\hbar \neq 0$$

So, Z and P_Z cannot be simultaneously zero because of the uncertainty principle:

$$\boxed{\Delta x \cdot \Delta p \geqslant \frac{\hbar}{2}}$$

To find out what happens in the quantum case for $\hat{\vec{L}} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$ we have to study the commutation relations of these operators.

From our Bohr discussion we had concluded that L_z is quantized in integer units of $\hbar$, $\boxed{L_z = n\hbar}$.

This was based on "wave-mechanical" argumets.

— What does formal QM tell us about OAM?

Commutations of $\hat{\vec{x}}$ and $\hat{\vec{P}}$ operators:

$$[x, y] = [y, z] = [z, x] = [P_x, P_y] = [P_y, P_z] = [P_z, P_x] = 0$$

So

$$\left.\begin{array}{l}[i, j] = [P_i, P_j] = 0 \\ [i, P_j] = 0\end{array}\right\}, \quad \text{for } i \neq j,\ i, j = (x, y, z)$$

And as we said:

$$\boxed{[x, P_x] = [y, P_y] = [z, P_z] = i\hbar} \qquad (1)$$

(*) Here we remove the hats "$\overset{\wedge}{P_x}$" over the operators.

If you look at eq. (1), it's not surprising that the ang. momentum is measured in units of $\hbar$!

$\Delta x \cdot \Delta p \geqslant \frac{\hbar}{2}$, i.e $\hbar$ has units of angul momentum

How about the commutation relations for $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$?

$$[L_x, L_y] = [yP_z - zP_y, zP_x - xP_z] =$$

$$= [yP_z, zP_x] - [yP_z, xP_z] -$$

$$[zP_y, zP_x] + [zP_y, xP_z]$$

$$= y \cdot P_x [P_z, z] - y \cdot x \cancelto{0}{[P_z, P_z]} -$$

$$P_y \cdot P_x \cancelto{0}{[z, z]} + xP_y [z, P_z]$$

$$= -i\hbar \cdot yP_x + i\hbar \cdot xP_y =$$

$$= i\hbar \cdot (xP_y - yP_x) = i\hbar L_z$$

In Summary:

$$\left.\begin{aligned}[L_x, L_y] &= i\hbar L_z \\ [L_y, L_z] &= i\hbar L_x \\ [L_z, L_x] &= i\hbar L_y\end{aligned}\right\} \qquad (2)$$

Note there is nothing particular about the XYZ frame of reference above. The same relations (2) holds for an X'Y'Z' rotated with respect to XYZ.

How about $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$, or $\hat{L}$?

Define the useful operators:

$$L_\pm = L_x \pm i L_y \quad , \qquad (3)$$

These give

$$[L_\pm, L_z] = [L_x \pm i L_y, L_z] = \mp L_\pm \qquad (4)$$

This comes out using equations (2)

Now, notice that $\hat{L}^2$ commutes with any of the $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$ (prove as a homework!)

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0$$

$\Rightarrow$ This means that we can measure the OAM and at least one component simultaneously!

We can measure:

$$(\underset{\substack{\downarrow \\ \text{magnitude of OAM}}}{L^2}, L_x) \text{ OR } (L^2, L_y) \text{ OR } (L^2, L_z)$$

But we <u>cannot measure</u> L, L_x, L_y, L_z

So, to complete the study of OAM, we need the eigenvalues/eigenfunctions of one of the pairs above:

$$\boxed{\begin{aligned} \hat{L}^2 \, Y_{\lambda m} &= \lambda \hbar^2 Y_{\lambda m} \qquad (*) \\ \hat{L}_z \, Y_{\lambda m} &= m \hbar Y_{\lambda m} \end{aligned}} \quad (5)$$

λ = unknown eigenvalue of $\hat{L}^2$

m = unknown eigenvalue of $\hat{L}_z$

Here $Y_{\lambda m}$ are the unknown eigen-functions of $\hat{L}^2$ and $\hat{L}_z$. (*) I will drop $\hbar$ for the remainder!

Can we find what λ and m are?

To do so we need the help of the L_+, L_- operators we defined earlier.

<u>Remember</u> $[L_z, L_+] = L_+$

$$[L_z, L_-] = -L_-$$

So,

$$L_z \cdot Y_{\lambda m} = m Y_{\lambda m} \Longrightarrow$$

$$(L_z \cdot L_\pm) Y_{\lambda m} = (\pm L_\pm + L_\pm L_z) \cdot Y_{\lambda m}$$

$$= \pm L_\pm \cdot Y_{\lambda m} + L_\pm \cdot m Y_{\lambda m}$$

$$= (m \pm 1) L_\pm Y_{\lambda m}$$

In words:

$(L_+ Y_{\lambda m})$ is now an eigenfunction of L_z with eigenvalue $(m+1)$

$L_- Y_{\lambda m}$ is also an eigenfunction of L_z with eigenvalue $(m-1)$

How about L^2 ?

$$\underbrace{L^2 \cdot L_\pm}_{\text{they commute!}} Y_{\lambda m} = L_\pm \left(L^2 \cdot Y_{\lambda m} \right) = \lambda \cdot L_\pm Y_{\lambda m}$$

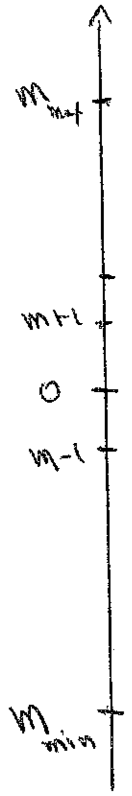
So, the $L_\pm$ does not change λ but only m.

From the above we can see that:

$$\boxed{L_\pm Y_{\lambda, m} = Y_{\lambda, m \pm 1}}$$

$L_\pm$ increases (decreases) the eigenvalue m by 1 unit!

So the eigenvalues of L_z form a "ladder" of values $\ldots, m-3, m-2, m-1, m, m+1, m+2, \ldots$



There must be an m_{max} and an m_{min}, simply because $L_z \leqslant |\vec{L}|$, bounded by $|\vec{L}|$.

So

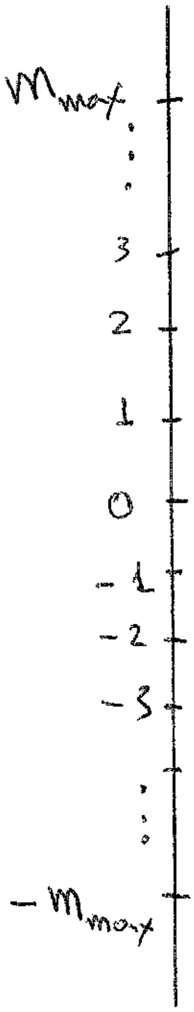
$$L_+ \cdot Y_{\lambda, m_{max}} = 0$$

$$L_- \, Y_{\lambda, m_{min}} = 0$$

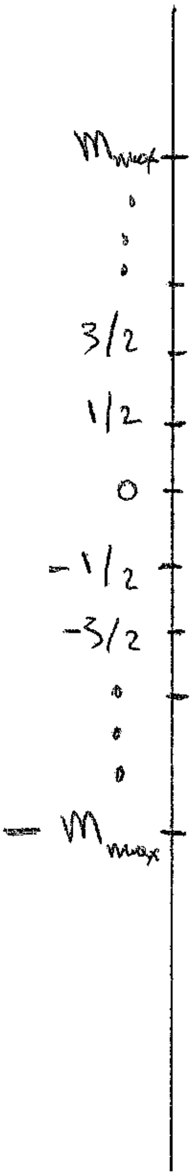
Note that $m_{max} = |m_{min}|$ from rotational invariance.

So the spectrum must be symmetric about 0, with some m_{max} and m_{min}.

There are ONLY two possibilities:



m = integer



m= half-integer

However, we already know that the OAM Cannot ~~be~~ have L_z quantized in half-integer units of $\hbar$. Hence for OAM:

$$L_z = m\hbar \quad , \quad \begin{array}{l} m = -m_{max}, \dots, m_{max} \\ \text{(integer)} \end{array}$$

$$\hat{L}_z \cdot Y_{\lambda m} = m\hbar \, Y_{\lambda m}$$

One would think that $m_{max} = \lambda$, or its square-root.

To check this we write:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

but

$$\hat{L}_- \hat{L}_+ = (\hat{L}_x - i\hat{L}_y)(\hat{L}_x + i\hat{L}_y) = \hat{L}_x^2 + \hat{L}_y^2 + i[\hat{L}_x, \hat{L}_y]$$

$$= \hat{L}_x^2 + \hat{L}_y^2 - \hbar \hat{L}_z$$

So

$$\boxed{\hat{L}^2 = \hat{L}_- \hat{L}_+ + \hbar \hat{L}_z + \hat{L}_z^2} \quad (6)$$

All we need to do is to apply (6) to $Y_{\lambda\, m_{max}}$:

$$\hat{L}^2 \cdot Y_{\lambda, m_{max}} = \left(\hat{L}_- \hat{L}_+ + \hbar \hat{L}_z + \hat{L}_z^2\right) Y_{\lambda, m_{max}}$$

$$= \cancelto{0}{\hat{L}_- \hat{L}_+ Y_{\lambda, m_{max}}} + \hbar \hat{L}_z Y_{\lambda, m_{max}} + \hat{L}_z^2 Y_{\lambda, m_{max}}$$

$$= \hbar \cdot (m_{max} \cdot \hbar) Y_{\lambda, m_{max}} + m_{max}^2 \cdot \hbar^2 Y_{\lambda, m_{max}}$$

$\Rightarrow$

$$\boxed{\hat{L}^2 Y_{\lambda, m_{max}} = m_{max}(m_{max}+1)\hbar^2 \cdot Y_{\lambda, m_{max}}}$$

So, the maximum (integer) m_{max} defines the constant eigenvalue of $\hat{L}^2$: we called it λ

$$\lambda = m_{max}(m_{max}+1)\hbar^2 .$$

Conventionally we call $\boxed{m_{max} = l}$

SUMMARY

We found the following eigenvalues for the OAM operators $\hat{L}^2$, $\hat{L}_z$

$$\boxed{\begin{aligned} \hat{L}^2 \, Y_{lm} &= l(l+1)\hbar^2 \cdot Y_{lm} \\ \hat{L}_z \, Y_{lm} &= m \hbar \, Y_{lm} \end{aligned}} \qquad (7)$$

(note that we use $Y_{l,m}$ instead of $Y_{\lambda,m}$ to avoid writing $Y_{l(l+1),m}$ ...)

In (7) $m = -l, -l+1, \ldots, 0, 1, \ldots, l$ is an integer.

So we say that a particle has an Orbital Angular $l = 1$ ("OAM one") which means that the possible states of that particle are

$$l = 1, \quad m = 1 \quad \Rightarrow L^2 = \sqrt{2}\,\hbar^2, \quad L_z = \hbar$$

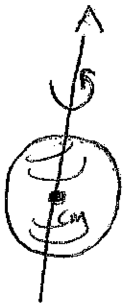
$$l = 1, \quad m = 0 \quad \Rightarrow L^2 = \sqrt{2}\,\hbar^2, \quad L_z = 0$$

$$l = 1, \quad m = -1 \quad \Rightarrow L^2 = \sqrt{2}\,\hbar^2, \quad L_z = -\hbar$$

SPIN ANGULAR MOMENTUM

Classically, besides the angular momentum due to a particle's orbital motion (OAM), we have spin.

By "spin" we mean whatever AM is left when the centre of mass of the particle (or object) is stationary.



Centre of mass **not** moving

But object rotating about an axis through the centre of mass.

However here we are interested in (elementary) particles, like an electron.

By "elementary" we mean a particle that cannot be further divided.

Experimentally $\boxed{\text{Radius of } e < 10^{-18}\ \text{m}}$

Let's try to put into rotation an object and ask the question how much energy we would need if this object is tiny as the electron ($R_e < 10^{-18}$ m !).

The kinetic energy of a rotating body is:

$$E_{KIN} = \frac{1}{2} m v^2 = \frac{1}{2} m (\omega r)^2$$

but this body has an angular momentum

$$L = m.v.r = m \omega r^2 \Rightarrow (\omega r)^2 = \frac{L^2}{m^2 r^2}$$

So

$$\boxed{E_{KIN} = \frac{L^2}{2 m r^2}} \quad (1)$$

This is equivalent to the familiar

$$E_{KIN} = \frac{p^2}{2m}$$

The quantity "mr^2" is normally called <u>moment of inertia</u>. It depends on the geometry of the rigid body but in general:

$$I = I(r^2)$$

Thus in order to put a body into rotation with an AM $\mathcal{L}$ we need an amount of energy proportional to $\sim \frac{L^2}{mr^2}$.

$\Rightarrow$ The smaller the body, the larger the energy!

The smaller the mass, the larger the energy.

QUESTION: We know that particles like the electron are of such a small size that we need QM for their description.

IF "angular momentum" is quantized, is there a quantized equivalent of the classical spin?

IF an electron has a "quantum spin" about its centre of mass axis, is this a rotation?

What are the possible values of S_z? (the third component of the Spin Angular Momentum).

Before we answer these questions let's remind ourselves that "elementary particles" are considered "point like".

Even if one argues that this is unphysical and the minimum we can go is the so-called "planck length" : $R \simeq 10^{-35}$ m, one can immediately see that it should require an enormous energy ($\frac{1}{R^2} \sim 10^{70}$) to set an elementary particle into rotation.

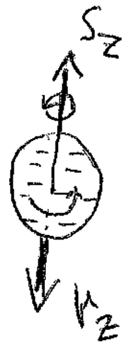
$\Rightarrow$ So it doesn't make sense to talk in terms of "spinning electrons".

Even for $R_e \simeq 3$ fm the surface of this electron would have to be spinning with a speed of $\sim 2 \cdot 10^{11}$ m/s, i.e FASTER than the speed of light!

However the existence of spin could be tested experimentally.

One just need the use of a magnetic field:

a "spinning" charged object is like a little magnet:



For a charge q the magnetic moment is

$$\mu_z = \frac{q}{2m} \cdot L$$

and if $q = -e$

$$\boxed{\mu_z = -\frac{q}{2m} S_z} \quad (2)$$

So if electrons (or other ~~charged~~ particles) have $S_z \neq 0$, then they should have

S-G

Some magnetic moment, i.e. they must be small magnets that can be deflected if thrown in an inhomogeneous magnetic field $\vec{B}$.

Here

$$E_{mag} = -\vec{\mu}\cdot\vec{B} \qquad \text{energy of "magnet" in field } \vec{B}$$

$$\Rightarrow \quad E_{mag} = -|\vec{\mu}|\cdot B_z\cdot\cos\vartheta$$

$$= -\mu_z\cdot B_z \quad , \text{ for } \vec{B} = (0,0,B_z)$$

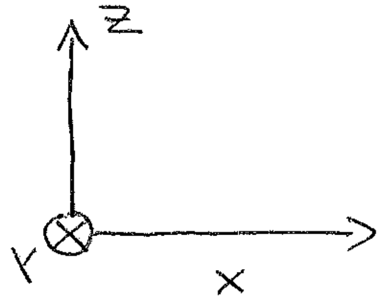
$$\vec{\mu} = (\mu_x, \mu_y, \mu_z)$$

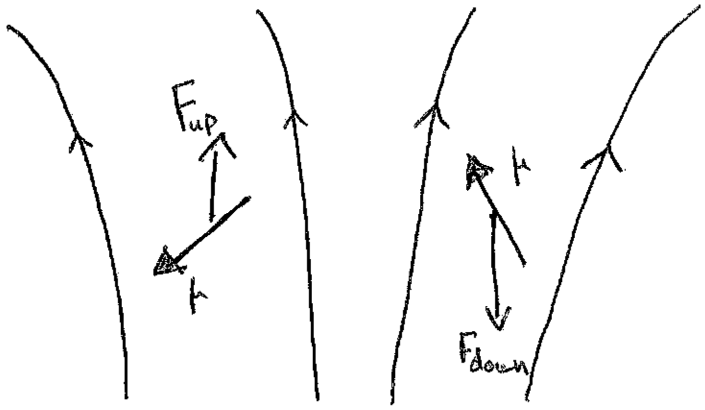
This means that if we throw a number of randomly orientated magnets in the field, then their possible energy spectrum should be continuous:

$$E_{max} = \left[-|\vec{\mu}|\cdot B, \ldots, 0, \ldots, |\vec{\mu}|\cdot B\right]$$

When we throw such a classical magnet in a magnetic field $(0,0,B_z)$ the force on the magnet is:

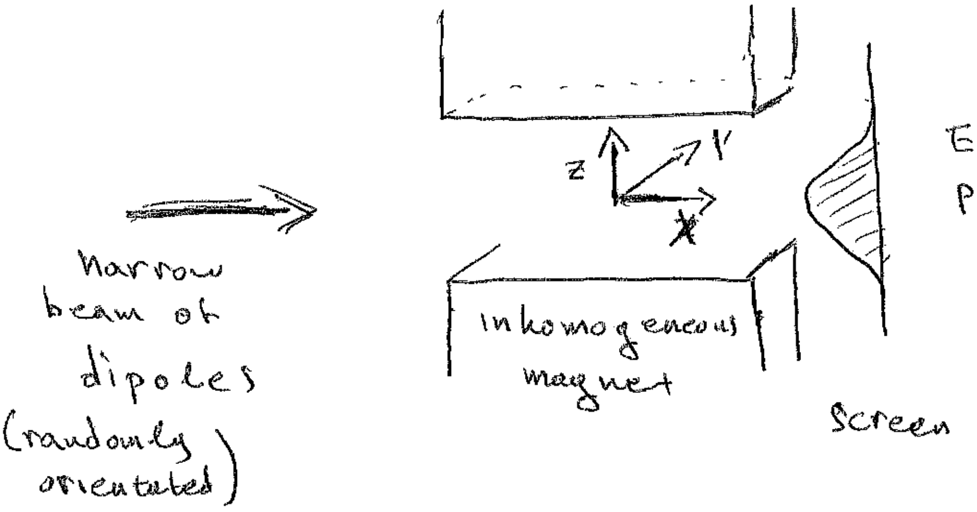
$$F_{mag} = - \frac{\partial E_{mag}}{\partial z} = \mu_z \cdot \frac{\partial B}{\partial z}$$





So, depending on the orientation of $\vec{\mu}$ with respect to $B_z \vec{k}$, the dipole will be forced to go UP or DOWN.

IF $\vec{\mu}$ on the XY plane ⇒ Force = zero!

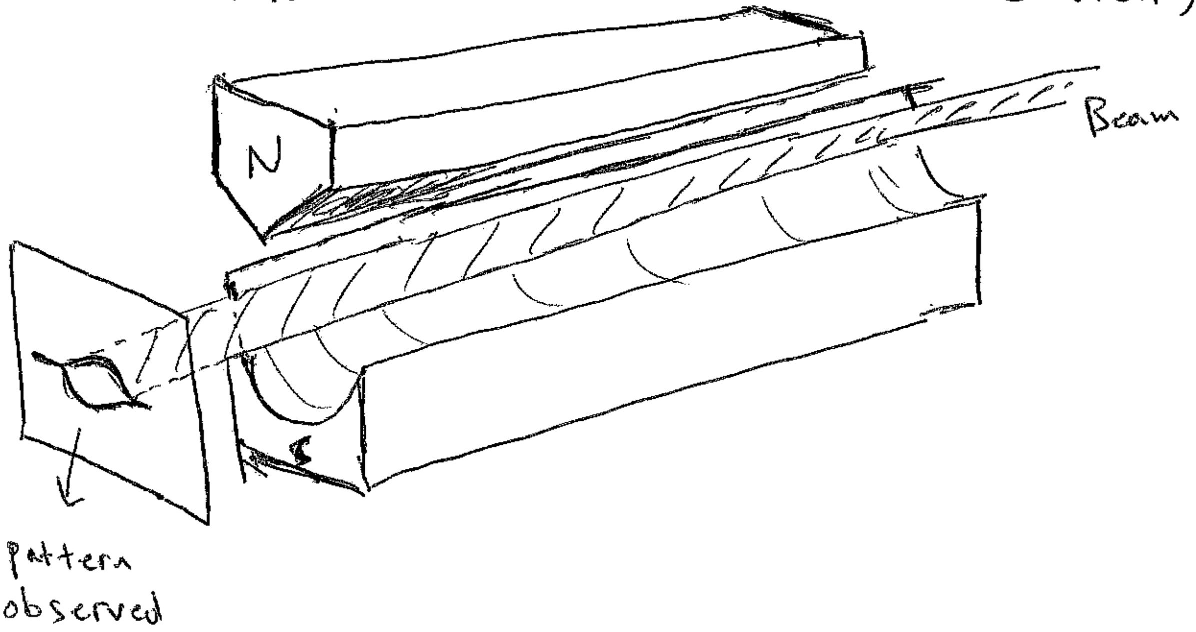


Expected dipole positions on screen.

S-8

Stern - Gerlach Experiment (1922)

Stern and Gerlach directed a beam of neutral Silver ~~p~~ atoms from an oven through a set of collimating slits into an inhomogeneous magnetic field. A photographic plate recorded the configuration of the beam after its passage through the field. The magnetic moment of a Si atom is due to the magnetic moment of one of its electrons (it has one outer electron).



The beam was split into two parts showing a two-valued magnetic moment!

Since from our OAM discussion we know that angular momentum takes only integer values (the third component L_z is a multiple integer of $\hbar$), here we seem to have a form of angular momentum that IS NOT orbital (nothing orbits) that we call "SPIN".

Spin $\vec{S}$ is a type of angular momentum and can take both INTEGER and HALF-INTEG values:

$$\left.\begin{aligned} \hat{S}^2 \cdot \chi_{s m_s} &= s(s+1)\hbar^2 \chi_{s m_s} \\ \hat{S}_z \cdot \chi_{s m_s} &= m_s \hbar \chi_{s m_s} \end{aligned}\right\} \begin{array}{c}\text{In}\\ \text{Analogy}\\ \text{to}\\ \text{OAM}\end{array}$$

but

$$\boxed{\begin{array}{l} S = \ldots, +\frac{3}{2}, +1, +\frac{1}{2}, 0 \\ \hline m_s = -s, -s+1, \ldots, s-1, s \end{array}}$$

S-10

Note that the magnetic moment of the electron is given by

$$\mu_z^{(spin)} = -2 \cdot \frac{e}{2m_e} S_z = -2 \frac{e\hbar}{2m_e} m_s \qquad (1)$$

while for an orbiting electron we have

$$\mu_z^{(orbital)} = -\frac{e}{2m_e} L_z = -\frac{e\hbar}{2m_e} m_\ell \qquad (2)$$

Notice the factor 2 in eq. (1).

This factor (sometimes called the gyromagnetic ratio g) is a purely QM factor that can be calculated by Dirac's theory of spin-$\frac{1}{2}$ electrons!

This factor has been measured to 12 decimal places!!!

$$g_e = 2{,}00231930436 17(15)$$

Note that QM can predict this number to the 9th decimal!!!
(this is the best theoretical prediction of any measurement today).

Bohr magneton:

In Eq. (1) the quantity

$$\mu_B = \frac{e\hbar}{2m_e} = 9{,}274 \cdot 10^{-24} \frac{J}{T}$$

is a constant called the "Bohr Magneton μ_B".

$$\Rightarrow \quad \mu_z = -g \cdot \mu_B \cdot m_s \simeq -\mu_B \quad \Big\{ \text{For Electrons!}$$

For Protons / Neutrons

$$\left.\begin{aligned} \mu_z^{(\text{Proton})} &= 2.79 \, \frac{e\hbar}{2m_p} \cdot m_s \\ \mu_z^{(\text{Neutron})} &= -1{,}95 \, \frac{e\hbar}{2m_p} \cdot m_s \end{aligned}\right\} \quad \mu_N = \frac{e\hbar}{2m_p} = 5.05 \cdot 10^{-27} \frac{J}{T}$$

"Nuclear Magneton"

QUESTION: What exactly is spin? If the electron is NOT spinning and not orbiting, where is this extra degree of freedom coming from?

As we said in the introduction, particles are "labelled" by Quantum Numbers:

$$\psi = \psi_{E,p}$$

E = quantized energy
p = -//- momentum

In general there may be more labels:

$$\psi = \psi_{E,p,s,\ldots}$$

Spin S is one of them:

$$\Psi = \psi_{E,p} \otimes \chi_s$$

our wave function has 2 parts: a spatial part and a spin part

For electrons $S = \frac{1}{2}$ (the spin quantum number)

$$\left(\text{or } \hat{\vec{S}}\, \chi_s = \sqrt{s(s+1)} \cdot \hbar\, \chi_s \right)$$

↳ spin wave function

We usually write for spin $\frac{1}{2}$ particles:

$\chi_{\uparrow}$ or $\chi_{+\frac{1}{2}}$ $\Rightarrow$ "spin up"

$\chi_{\downarrow}$ or $\chi_{-\frac{1}{2}}$ $\Rightarrow$ "spin down"

A spin wave function χ ~~[illegible]~~ lives in a 2 dimensional $\mathbb{C}$ space:

$$\chi = c_1 \chi_{\uparrow} + c_2 \chi_{\downarrow}$$

So, an electron can be ~~in~~ observed <u>ONLY</u> in spin UP or spin DOWN states!

S - 14

All elementary particles have some spin :

Spin = 0 ⇒ Scalars ⇒ Higgs Boson

Spin = $\frac{1}{2}$ ⇒ Fermions ⇒ $e, \mu, \nu, \ldots$

Spin = 1 ⇒ (Vector) Bosons ⇒ photon

Spin = $3/2$ ⇒ $\frac{3}{2}$ Fermions ⇒ ? (gravitino)

Spin = 2 ⇒ (tensor) Bosons ⇒ Graviton

⋮

However today we only know of the existence of $s = \frac{1}{2}$ and $s = 1$ elementary particles!

S - 15

Spin maybe a type of an "internal" Space (somewhat "mysterious") however the spin of a particle is related to symmetry under space rotations!

"Symmetry" means: after some rotation in space particle "looks" the same!

Particle	SYMMETRY
Scalars	Sphrically symmetric (look the same from all angles)
$s = \frac{1}{2}$	Need 4π rotation "about" the electron to came back to its original state!!!
$s = 1$ (photon)	Need 2π rotation
$S = 2$	Need $180^\circ = \pi$ rotation

Why is that? How can a 4π rotation (and not a 2π) get our electron back to its original state?

Sketchy Answer:

When we rotate our electron by R

$$R \cdot \psi_{elec} = R \cdot \left(\psi_{E,p} \otimes \chi_s \right)$$

then we ~~do~~ not only rotate the spatial part $\psi_{E,p}$ but also the 2-Dimensional Complex vector χ !!! Rotations in this $\mathbb{C}$ space need $360^\circ \times 2 = 720^\circ$ in order to get χ back to itself!

(Look for "Dirac's Belt trick" for a visual example!).

ADDITION OF ANGULAR MOMENTA

A particle can have OAM L and spin S. The total angular momentum is usually denoted by J and is the "product" of the two spaces.

Here we will give some simple examples using the quantum numbers of angular momenta.

Example 1:

An electron has OAM (quantum number) ℓ.
Its $s + \ell = j$ angular momentum is:

$$\boxed{j = s+\ell \,,\, s+\ell-1 \,,\, \dots \,,\, |s-\ell|}$$

So, there are a number of possible j's.

Take $\ell = 1$ and $s = \frac{1}{2}$

$$1 + \frac{1}{2} = 1 + \frac{1}{2} \,,\, \dots \,,\, \left|1 - \frac{1}{2}\right| = \frac{3}{2} \text{ OR } \frac{1}{2}$$

Take $l = 0$, $s = \frac{1}{2}$ (H - ground state)

$$j = 0 + \frac{1}{2}, \ldots, \left|0 - \frac{1}{2}\right| = \frac{1}{2}$$

only one possibility.

Example 2:

A particle has $j_1 = 1$ and a second particle has $j_2 = 2$. The total AM of the 2-particle system is

$$J = 1+2, \ldots, |1-2| = 3, 2, 1$$

So, the total AM can be $j = 3$, $j = 2$ or $j = 1$

Note: it is common to use capital J, S, L for the combined angular momenta.

H - 1

Quantum mechanics of a particle in a central potential

The quantum states of a particle in a central potential are described by a wave function $\Psi(r,\theta,\phi,t)$. We shall focus on quantum states with sharply defined energy E which, according to Section 4.3, have wave functions of the form

$$\Psi(r,\theta,\phi,t) = \psi(r,\theta,\phi)\,\mathrm{e}^{-iEt/\hbar}, \tag{9.4}$$

where $\psi(r,\theta,\phi)$ is an energy eigenfuction satisfying the eigenvalue equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi = E\psi. \tag{9.5}$$

This partial differential equation in three independent variables r,θ and ϕ may be greatly simplified if we assume that the quantum state has, in addition to definite energy E, definite angular momentum properties of the type described in Chapter 8. In particular, if we assume that the magnitude of the orbital angular momentum is $L = \sqrt{l(l+1)}\hbar$ and its z-component is $L_z = m_l\hbar$, where l and m_l are quantum numbers which could take on the values $l = 0, 1, 2 \ldots$ and $m_l = -l, \ldots, l$, the eigenfunctions have the form

$$\psi(r,\theta,\phi) = R(r)Y_{l,m_l}(\theta,\phi). \tag{9.6}$$

In this equation, $Y_{l,m_l}(\theta,\phi)$ is a simultaneous eigenfunction of $\hat{L}^2$ and $\hat{L}_z$ satisfying Eq. (8.23) and $R(r)$ is an unknown function of r. If we substitute Eq. (9.6) into Eq. (9.5), use the identities

$$\nabla^2\psi = \frac{1}{r}\frac{\partial^2(r\psi)}{\partial r^2} + \frac{1}{r^2}\left[\frac{\partial^2\psi}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial\psi}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$$

and

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right),$$

and also use Eq. (8.23), we obtain the following ordinary differential equation for $R(r)$:

$$-\frac{\hbar^2}{2mr}\frac{\mathrm{d}^2(rR)}{\mathrm{d}r^2} + \left[\frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right]R = ER. \tag{9.7}$$

By introducing a radial function $u(r)$, defined by

$$R(r) \equiv \frac{u(r)}{r}, \tag{9.8}$$

we obtain

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u}{\mathrm{d}r^2} + \left[\frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right]u = Eu. \tag{9.9}$$

This important equation is called the *radial Schrödinger equation*. It describes a particle with angular momentum $L = \sqrt{l(l+1)}\hbar$ which behaves like a particle in a one-dimensional effective potential of the form

$$V_e(r) = \frac{l(l+1)\hbar^2}{2mr^2} + V(r). \tag{9.10}$$

If we compare this potential with the analogous effective potential in classical mechanics given in Eq. (9.3), we see that the first term, $l(l+1)\hbar^2/2mr^2$, can either be thought of as a kinetic energy associated with transverse motion or as a centrifugal potential that arises from the orbital angular momentum of the particle.

When solutions of the radial Schrödinger equation (9.9) are sought, the boundary condition

$$u(r) = 0 \quad \text{at} \quad r = 0$$

must be imposed to ensure that the function $R(r) = u(r)/r$, and hence the actual three-dimensional eigenfunction given by Eq. (9.6), is finite at the origin. In addition, bound state solutions, which describe a particle that cannot escape to infinity, must also satisfy the boundary condition

$$u(r) \to 0 \quad \text{as} \quad r \to \infty.$$

Bound states only exist if the effective potential $V_e(r)$, Eq. (9.10), is sufficiently attractive. We shall label these states by a quantum number $n_r = 0, 1, 2, \ldots$ which will be shown to be equal to the number nodes of the radial eigenfunction $u(r)$ between $r = 0$ and $r = \infty$. This means a bound state of a particle in a central potential can always be specified by three quantum numbers n_r, l and m_l and that the eigenfunction has the form

$$\psi_{n_r,l,m_l}(r,\theta,\phi) = \frac{u_{n_r,l}(r)}{r}\,Y_{l,m_l}(\theta,\phi). \tag{9.11}$$

H-9

By using the normalization condition (8.25) for spherical harmonics, we can easily show that the eigenfunction $\psi_{n_r,l,m_l}(r,\theta,\phi)$ is normalized if the radial eigenfunction $u_{n_r,l}(r)$ obeys the condition

$$\int_0^\infty |u_{n_r,l}|^2 \, \mathrm{d}r = 1. \tag{9.12}$$

The energy of these bound states will be denoted $E_{n_r,l}$. By thinking of this energy as the sum of three terms, the average radial kinetic energy, the average transverse kinetic energy and the average Coulomb energy, we can see that states with higher l and higher n_r have higher energies. The energy $E_{n_r,l}$ increases with l because the average transverse kinetic energy is given by

$$\int_0^\infty u^*_{n_r,l}(r)\left(\frac{l(l+1)\hbar^2}{2mr^2}\right) u_{n_r,l}(r)\,\mathrm{d}r;$$

and the energy $E_{n_r,l}$ also increases with n_r because the average radial kinetic energy, which is given by

$$\int_0^\infty u^*_{n_r,l}(r)\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2}\right)u_{n_r,l}(r)\,\mathrm{d}r,$$

increases as the number of radial nodes increases.[1]

Before considering the explicit expressions for the energy levels and eigenfunctions of a particle in a Coulomb potential, we pause and reconsider how we obtained the radial Schrödinger equation Eq. (9.9). The crucial step was to seek a quantum state with definite E, L and L_z for a particle in a central potential. Such states must exist because this step has had a successful outcome: it has led to Eq. (9.9) which can be solved to give sensible energy eigenvalues and eigenfunctions. Readers who have studied compatible observables in Chapter 7 should not be surprised by this success. In general, E, L and L_z can be taken as three compatible observables which uniquely define a quantum state of a particle in a central potential.

In addition, a quantum state of a particle with definite energy in a central potential has another observable property with a definite value. It is called *parity*. Eigenfunctions with the property

$$\psi(-\mathbf{r}) = +\psi(\mathbf{r}), \tag{9.13}$$

are said to have even parity, and eigenfunctions with the property

$$\psi(-\mathbf{r}) = -\psi(\mathbf{r}) \tag{9.14}$$

are said to have odd parity. By using Table 8.1, we can easily show that an eigenfunction with definite orbital angular momentum given by Eq. (9.6), i.e. by

$$\psi(r,\theta,\phi) = R(r)Y_{l,m_l}(\theta,\phi),$$

has even parity when $l = 0$ and $l = 2$ and odd parity when $l = 1$. It can be shown that, in general, the parity of a particle in a central potential is even when l is even and odd when l is odd.

Parity is one of the simplest observables in quantum mechanics, but, because it is an observable with no classical analogue, it is often perceived as mysterious. Energy and parity are compatible observables whenever the Hamiltonian is unchanged when the coordinates undergo a reflection through the origin. Because this is true for all Hamiltonians which do not involve the weak nuclear interaction, parity has an important role in classifying quantum states in atomic, nuclear and particle physics.

9.2 QUANTUM MECHANICS OF THE HYDROGEN ATOM

In this section we shall give a brief description of the hydrogen atom using the quantum mechanical concepts introduced in the last section.

Because the hydrogen atom is essentially an electron in a Coulomb potential and the Coulomb potential is a central potential, bound states of atomic hydrogen may be taken to have definite orbital angular momentum properties given by $L = \sqrt{l(l+1)}\hbar$ and $L_z = m_l\hbar$. These states have wave functions of the form

$$\Psi_{n_r,l,m_l}(r,\theta,\phi,t) = \psi_{n_r,l,m_l}(r,\theta,\phi)\exp(-iE_{n_r,l}t/\hbar)$$

with

$$\psi_{n_r,l,m_l}(r,\theta,\phi) = \frac{u_{n_r,l}(r)}{r}Y_{l,m_l}(\theta,\phi),$$

where $u_{n_r,l}(r)$ is an eigenfunction given by the radial Schrödinger equation (9.9) for an electron in a Coulomb potential

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

---

[1] We encountered a similar behaviour when we considered the energy levels of one-dimensional potential wells in Chapters 4, 5 and 6. In general, more nodes in a wave function means higher energy in quantum mechanics, just as more nodes in a classical normal mode means higher frequency.

H-3

Specifically, the radial eigenfunction $u_{n_r,l}(r)$ is a solution of the differential equation

$$\frac{\hbar^2}{2m_e}\frac{\mathrm{d}^2 u_{n_r,l}}{\mathrm{d}r^2} + \left[\frac{l(l+1)\hbar^2}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r}\right] u_{n_r,l} = E_{n_r,l}u_{n_r,l}, \qquad (9.15)$$

which satisfies the boundary conditions

$$u_{n_r,l}(r) = 0 \quad \text{at} \quad r = 0 \quad \text{and at} \quad r = \infty. \qquad (9.16)$$

The qualitative features of the energy levels given by the eigenvalue problem defined by Eqs. (9.15) and (9.16) may be deduced by considering the effective potential that occurs in Eq. (9.15),

$$V_e(r) = \frac{l(l+1)\hbar^2}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r}. \qquad (9.17)$$

The shape of this potential for electrons with different values for the orbital angular momentum quantum number l are shown in Fig. 9.2. We see that, for non-zero values of l, the effective potential is attractive at large r and repulsive at small r. By setting $\mathrm{d}V_e/\mathrm{d}r$ to zero, we can easily show that $V_e(r)$ has a minimum value of

$$V_e(r) = -\frac{E_R}{l(l+1)} \quad \text{at} \quad r = l(l+1)a_0, \qquad (9.18)$$

where a_0 and E_R are the natural units of length and energy in atomic physics, defined as follows: the Bohr radius

$$a_0 = \left[\frac{4\pi\epsilon_0}{e^2}\right]\frac{\hbar^2}{m_e} = 0.529 \times 10^{-10}\ \mathrm{m} \qquad (9.19)$$

and the Rydberg energy

$$E_R = \frac{e^2}{8\pi\epsilon_0 a_0} = 13.6\ \mathrm{eV}. \qquad (9.20)$$

The minimum given by Eq. (9.18) implies that bound states with angular momentum $L = \sqrt{l(l+1)}\hbar$ have energies somewhere between $E = -E_R/l(l+1)$ and $E = 0$. It also implies that the spatial extent of bound state eigenfunctions with low angular momentum is of the order of a_0 and that the eigenfunctions extend to larger distances when the angular momentum increases. When the angular momentum greatly exceeds $\hbar$, we expect many bound states with closely spaced energy levels that correspond to the circular and elliptic orbits of classical mechanics.

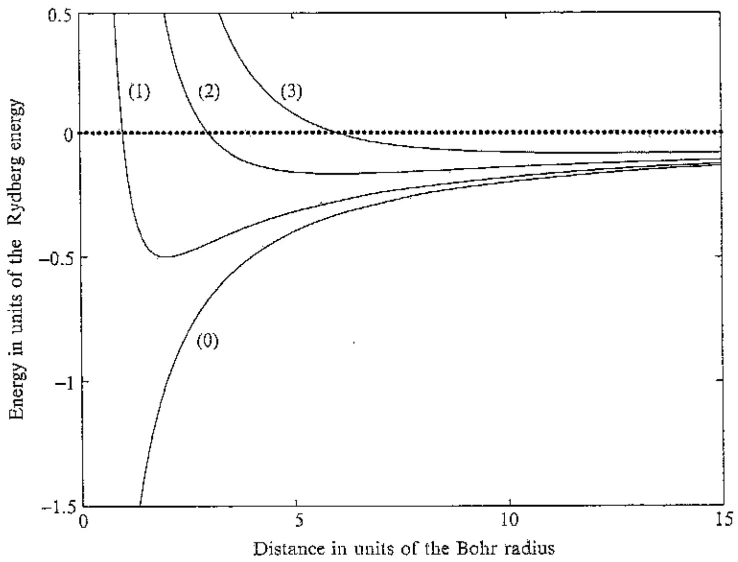


Fig. 9.2 The effective potential energy $V_e(r)$ for an electron in a hydrogen atom with orbital angular momentum quantum numbers $l = 0, 1, 2$ and 3. The unit of distance is the Bohr radius a_0, defined in Eq. (9.19), and the unit of energy is the Rydberg energy E_R, defined in Eq. (9.20). The effective potential for an electron with quantum number l has a minimum value of $-E_R/l(l+1)$ at $r = l(l+1)a_0$ which, in classical physics, corresponds to the energy and radius of a circular orbit of an electron with angular momentum $L = \sqrt{l(l+1)}\hbar$.

We also see from Fig. 9.2 that the effective potential is purely attractive for an electron with zero angular momentum. In classical mechanics, such an electron simply plunges towards the proton and there are no stable bound states. But there are stable bound states with zero angular momentum in quantum mechanics, whose existence can be understood by using the uncertainty principle.

The uncertainty principle implies that an electron localized in a region of size r has an uncertain momentum of the order of $\hbar/r$ and an average kinetic energy which is at least of the order of $\hbar^2/2m_e r^2$. This means that the least energy of an electron with zero orbital angular momentum in a region of size r near a proton is roughly given by

$$E \approx \frac{\hbar^2}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r}.$$

H-4

As the region of localization decreases, this energy decreases because the potential energy decreases, but eventually the kinetic energy of localization, $\hbar^2/2m_e r^2$, increases more rapidly. As a result the total energy has a minimum value of about

$$E \approx -E_R \quad \text{at} \quad r \approx a_0.$$

This minimum provides an estimate of the lowest possible energy of an electron with zero angular momentum in a Coulomb potential and suggests that there are quantum bound states with energies in the range $E \approx -E_R$ and $E = 0$.

Energy levels and eigenfunctions

The energy levels and eigenfunctions for an electron bound in a Coulomb potential are found by solving the eigenvalue problem defined by Eqs.(9.15) and (9.16). In order to focus on the physical properties of the hydrogen atom, we shall consider the results of this mathematical problem before describing how these results are obtained in Section 9.7.

We shall show in Section 9.7 that an electron with angular momentum $L = \sqrt{l(l+1)}\hbar$ in a Coulomb potential has an infinite number of bound states with energies given by

$$E_{n_r,l} = -\frac{E_R}{(n_r + l + 1)^2} \quad \text{with} \quad n_r = 0, 1, 2, 3, \ldots \tag{9.21}$$

The quantum number n_r is called the *radial quantum number*. These energy levels are illustrated in Fig. 9.3.

As expected, there are bound states with zero and non-zero angular momentum. Also the energy levels are very closely spaced if the angular momentum is very large, indicating a correspondence with a continuum of classical bound-state energies.

Unexpectedly, many of the energy levels in Fig. 9.3, those with the same value for $n_r + l$, have the same energy. Because of this degeneracy, the energy levels of the hydrogen atom are usually given as

$$E_n = -\frac{E_R}{n^2} \tag{9.22}$$

where E_R is the Rydberg energy and n is a quantum number defined by

$$n = n_r + l + 1. \tag{9.23}$$

This quantum number is called the *principal quantum number* and can take on the values $n = 1, 2, 3, \ldots$

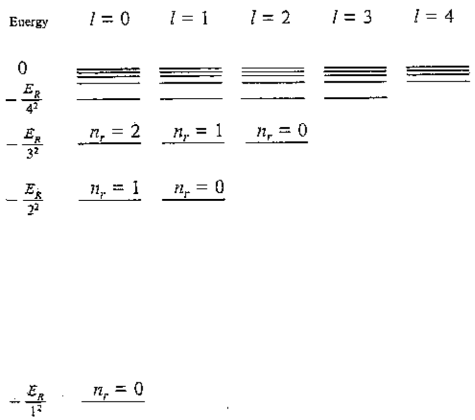


Fig. 9.3 The energy levels given by Eq. (9.21) for the bound states of an electron in a hydrogen atom. For each value of the orbital angular momentum quantum number $l = 0, 1, 2,$, there is an infinite stack of energies $E_{n_r,l}$ with radial quantum number $n_r = 0, 1, 2, \ldots$. Note that, because bound states with the same value for $n_r + l$ have the same energy, these energy levels are often given as $E_n = -E_R/n^2$ where E_R is the Rydberg energy and n is defined by $n = n_r + l + 1$; the quantum number n is called the *principal quantum number* and can take on the values $n = 1, 2, 3, \ldots$. There is also a continuum of unbound or ionized states with positive energy.

We shall also show in Section 9.7 that the radial eigenfunction $u_{n_r,l}(r)$ belonging to the energy eigenvalue $E_{n_r,l}$ has three characteristics:

(1) In Section 5.1 we found that the eigenfunction of a particle in a one-dimensional square well with binding energy $\epsilon = \hbar^2\alpha^2/2m$ falls off exponentially like $e^{-\alpha x}$. In a similar way, the radial eigenfunction of an electron in a Coulomb potential with binding energy

$$\epsilon = \frac{E_R}{n^2} = \frac{\hbar^2}{2m_e}\frac{1}{n^2 a_0^2}$$

falls off exponentially at large r like

$$u_{n_r,l}(r) \propto e^{-r/na_0}.$$

(2) Because of the singular nature at $r = 0$ of the centrifugal potential $l(l+1)\hbar^2/2m_e r^2$, the behaviour of the eigenfunction at small r is governed by the orbital angular momentum and is given by

$$u_{n_r,l}(r) \propto r^{l+1}.$$

(3) Finally, because the radial quantum number n_r denotes the number of nodes between $r = 0$ and $r = \infty$, the eigenfunction $u_{n_r,l}(r)$ is proportional to a polynomial with n_r zeros. If this polynomial is denoted by $p_{n_r,l}(r)$, we have

H-5

$$u_{n_r,l}(r) \propto p_{n_r,l}(r).$$

By combining these three characteristics, we arrive at a radial eigenfunction of the form

$$u_{n_r,l}(r) = Np_{n_r,l}(r) r^{l+1}\,\mathrm{e}^{-r/na_0}, \tag{9.24}$$

where N is a constant which ensures that the normalization condition (9.12) is satisfied.

Explicit expressions for the radial eigenfunctions with low values for the angular momentum quantum number l and low values for the radial quantum number n_r are given in Table 9.1, and some of these eigenfunctions are illustrated in Fig. 9.4. To conform with the conventions of atomic physics these eigenfunctions are labelled using spectroscopic notation. This notation employs the principal quantum number $n = n_r + l + 1$ and a letter to designate the value of l; the letter s is used for $l = 0$, p for $l = 1$, d for $l = 2$, and f for $l = 3$. The historical origin of this notation dates back to the early days of atomic physics when spectral lines were labelled s for sharp, p for principal, d for diffuse and f for fundamental.

TABLE 9.1 Normalized radial eigenfunctions for low-lying states of the hydrogen atom

Spectroscopic notation	Radial eigenfunction $u_{n_r,l}(r)$
1s	$u_{0,0}(r) = \dfrac{2}{\sqrt{a_0}}\left(\dfrac{r}{a_0}\right)\mathrm{e}^{-r/a_0}$
2s	$u_{1,0}(r) = \dfrac{1}{\sqrt{2a_0}}\left[1 - \dfrac{1}{2}\left(\dfrac{r}{a_0}\right)\right]\left(\dfrac{r}{a_0}\right)\mathrm{e}^{-r/2a_0}$
3s	$u_{2,0}(r) = \dfrac{2}{3\sqrt{3a_0}}\left[1 - \dfrac{2}{3}\left(\dfrac{r}{a_0}\right) + \dfrac{2}{27}\left(\dfrac{r}{a_0}\right)^2\right]\left(\dfrac{r}{a_0}\right)\mathrm{e}^{-r/3a_0}$
4s	$u_{3,0}(r) = \dfrac{1}{4\sqrt{a_0}}\left[1 - \dfrac{3}{4}\left(\dfrac{r}{a_0}\right) + \dfrac{1}{8}\left(\dfrac{r}{a_0}\right)^2 - \dfrac{1}{192}\left(\dfrac{r}{a_0}\right)^3\right]\left(\dfrac{r}{a_0}\right)\mathrm{e}^{-r/4a_0}$
2p	$u_{0,1}(r) = \dfrac{1}{2\sqrt{6a_0}}\left(\dfrac{r}{a_0}\right)^2\mathrm{e}^{-r/2a_0}$
3p	$u_{1,1}(r) = \dfrac{8}{27\sqrt{6a_0}}\left[1 - \dfrac{1}{6}\left(\dfrac{r}{a_0}\right)\right]\left(\dfrac{r}{a_0}\right)^2\mathrm{e}^{-r/3a_0}$
4p	$u_{2,1}(r) = \dfrac{1}{16}\sqrt{\dfrac{5}{3a_0}}\left[1 - \dfrac{1}{4}\left(\dfrac{r}{a_0}\right) + \dfrac{1}{80}\left(\dfrac{r}{a_0}\right)^2\right]\left(\dfrac{r}{a_0}\right)^2\mathrm{e}^{-r/4a_0}$
3d	$u_{0,2}(r) = \dfrac{4}{81\sqrt{30a_0}}\left(\dfrac{r}{a_0}\right)^3\mathrm{e}^{-r/3a_0}$
4d	$u_{1,2}(r) = \dfrac{1}{64\sqrt{5a_0}}\left[1 - \dfrac{1}{12}\left(\dfrac{r}{a_0}\right)\right]\left(\dfrac{r}{a_0}\right)^3\mathrm{e}^{-r/4a_0}$

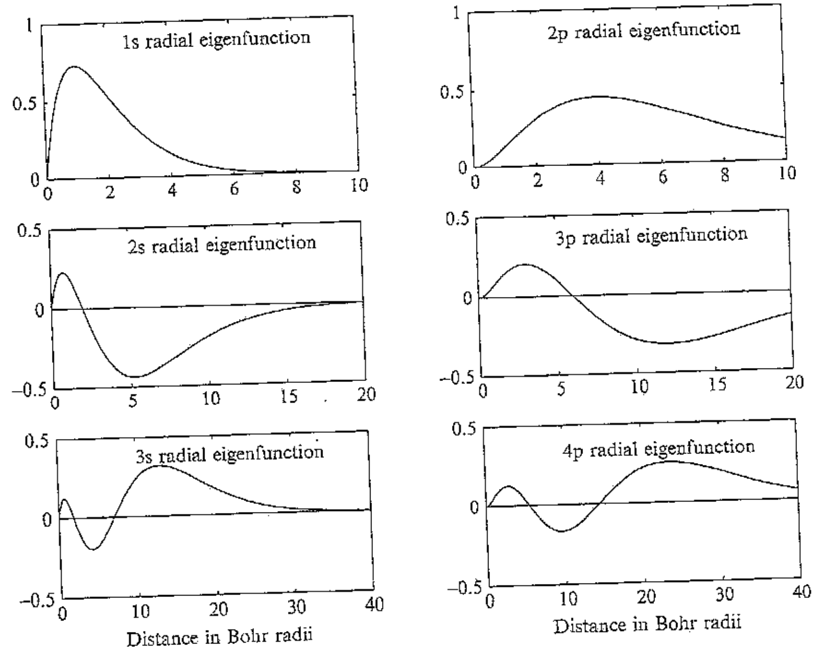


Fig. 9.4 Radial eigenfunctions $u_{n_r,l}(r)$ for an electron in the hydrogen atom with radial quantum numbers $n_r = 0$, 1, and 2 and with angular momentum quantum numbers $l = 0$ and 1. The eigenfunctions have been labelled using spectroscopic notation ns and np, where n is the principal quantum number $n = n_r + 1 + l$ and s denotes $l = 0$ and p denotes $l = 1$. Note that the unit of distance is the Bohr radius a_0 and that different scales are used for eigenfunctions with different values of n_r.

9.3 SIZES AND SHAPES

The size and shape of a quantum state of atomic hydrogen can be determined by considering the most probable locations of the electron in the atom. For a state with eigenfunction $\psi_{n_r,l,m_l}(r,\theta,\phi)$, the probability of finding the electron with coordinates (r,θ,ϕ) in a volume element $\mathrm{d}^3\mathbf{r}$ is

$$|\psi_{n_r,l,m_l}(r,\theta,\phi)|^2\,\mathrm{d}^3\mathbf{r}.$$

We can easily find the radial probability distribution for the electron. To do so, we use $\mathrm{d}^3\mathbf{r} = r^2\,\mathrm{d}r\,\mathrm{d}\Omega$, where $\mathrm{d}\Omega = \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$ is an element of solid angle, and express the eigenfunction as

H-6

$$\psi_{n_r,l,m_l}(r,\theta,\phi) = \frac{u_{n_r,l}(r)}{r} Y_{l,m_l}(\theta,\phi),$$

where $Y_{l,m_l}(\theta,\phi)$ is a spherical harmonic which obeys the normalization condition Eq. (8.25). The probability of finding the electron at a distance between r and $r + dr$ from the nucleus is then given by

$$\left|\frac{u_{n_r,l}(r)}{r}\right|^2 r^2\, dr \int |Y_{l,m_l}(\theta,\phi)|^2\, d\Omega = |u_{n_r,l}(r)|^2\, dr.$$

Thus, the radial shape of the quantum state is described by a radial probability density $|u_{n_r,l}(r)|^2$.

Radial probability densities for states with $n_r = 0, 1$ and 2 and with $l = 0$ and 1 are shown in Fig. 9.5. We note that the radial extent increases as n_r increases and as l increases. This may be confirmed by considering the mean radius of a state with quantum numbers n_r and l which is given by

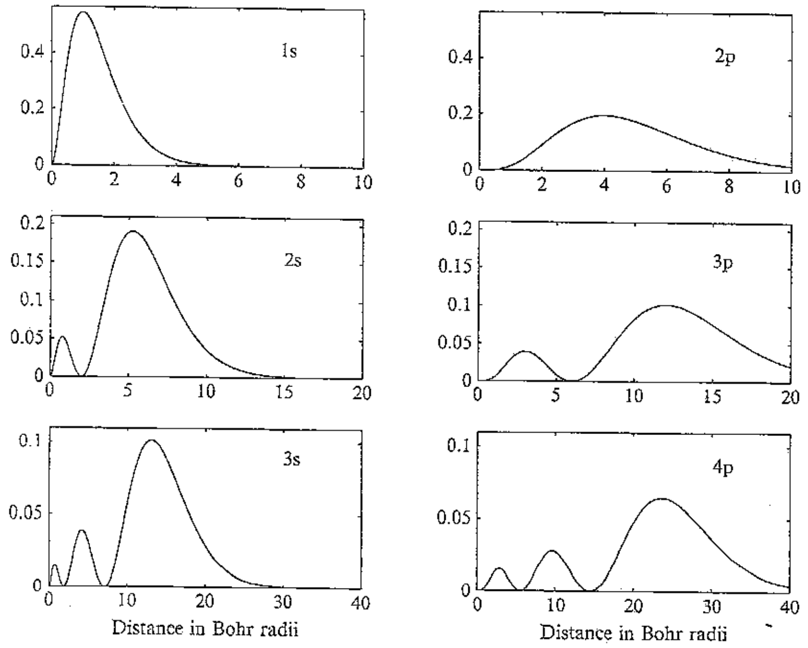


Fig. 9.5 Radial probability densities for the 1s, 2s, 3s, 2p, 3p and 4p states of the hydrogen atom. Note that the unit of distance is the Bohr radius a_0 and that a different scale is used for states with a different number of radial nodes.

$$\langle r\rangle_{n_r,l} = \int_0^\infty r|u_{n_r,l}(r)|^2\, dr.$$

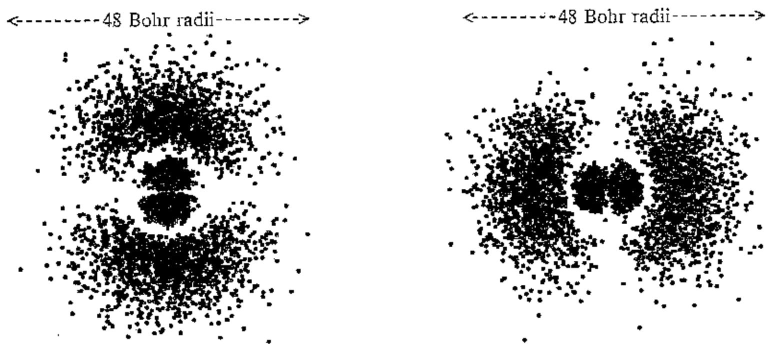
This integral may be evaluated by using the mathematical properties of the eigenfunctions $u_{n_r,l}(r)$ to give an expression,

$$\langle r\rangle_{n_r,l} = \tfrac{1}{2}[3n_r^2 + 6n_r(l+1) + (l+1)(2l+3)]a_0, \tag{9.25}$$

which explicitly shows how the radial extent increases with n_r and l.

By using explicit forms for $u_{n_r,l}(r)$ and $Y_{l,m_l}(\theta,\phi)$ we can evaluate the probability density $|\psi_{n_r,l,m_l}(r,\theta,\phi)|^2$ and explore both the radial and angular shapes of a hydrogen atom state with quantum numbers n_r, l, m_l. First, we note that the angular shape does not depend on the azimuthal angle ϕ because, as indicated by Eq. (8.26), the spherical harmonic $Y_{l,m_l}(\theta,\phi)$ has the ϕ dependence $e^{im_l\phi}$. Thus, the probability density of the state does not change if it is rotated about the z axis. This means that the size and shape of the state may be fully specified by showing the most likely positions of the electron on any vertical plane that passes through the z axis, as demonstrated in Figs. 9.6 and 9.7.

In Figs. 9.6 and 9.7 we show the sizes and shapes of the 3p and 3d states of atomic hydrogen. The 3p states in Fig. 9.6 have one radial node and an angular dependence given by $|Y_{1,m_l}(\theta,\phi)|^2$ with $m_l = 1, 0$ and -1. The 3d states in Fig. 9.7 have no radial nodes and the angular shape of a state with $l = 2$.

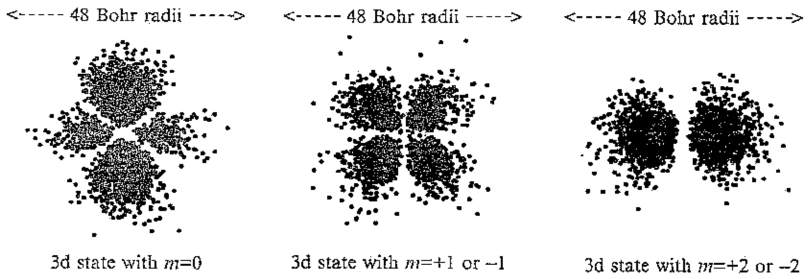


3p state with $m = 0$

3p state with $m = +1$ or -1

Fig. 9.6 The size and shape of the 3p states of the hydrogen atom with a z component of orbital angular momentum equal to $m\hbar$. These states have rotational symmetry about the z axis. The density of dots is proportional to the probability of finding an electron on a vertical plane passing through the z axis. These pictures were produced by selecting a point on the plane at random and deciding to plot or not to plot in accordance with the value of $|\psi_{n_r,l,m_l}(r,\theta,\phi)|^2$ at that point.

H-7



3d state with m=0 3d state with m=+1 or −1 3d state with m=+2 or −2

Fig. 9.7 The size and shape of the 3d states of the hydrogen atom with a z component of orbital angular momentum equal to $m\hbar$.

9.4 RADIATIVE TRANSITIONS

When a hydrogen atom interacts with an electromagnetic field, quantum states with quantum numbers n, l and m_l are, in general, no longer stationary states with definite energy, and radiative transitions between these states may take place in which electromagnetic energy is either absorbed or emitted.

The most probable radiative transitions are called *electric dipole transitions*. They are caused by an interaction of the electric field component **E** of the electromagnetic field with the operator describing the electric dipole moment of the electron–nucleus system. The electric dipole operator is $\mathbf{d} = -e\mathbf{r}$, where **r** is the vector position operator for the electron in the atom, and the interaction is given by

$$\hat{H}_I = -\mathbf{d}\cdot\mathbf{E}. \tag{9.26}$$

In the presence of this interaction, the probability for a transition between states with quantum numbers n_i, l_i, m_{l_i} and n_f, l_f, m_{l_f} is proportional to

$$\left| \int \psi^*_{n_f,l_f,m_{l_f}}(\mathbf{r})\, \hat{H}_I\, \psi_{n_i,l_i,m_{l_i}}(\mathbf{r})\, d^3\mathbf{r}\, \right|^2. \tag{9.27}$$

We can easily prove that electric dipole transitions always involve a change in parity by showing that the integral in Eq. (9.27) is zero if the initial and final states have the same parity. We show this by considering the effect of changing the integration variable from **r** to −**r**. The interaction $\hat{H}_I = -\mathbf{d}\cdot\mathbf{E}$ changes sign, but the sign of the eigenfunction, $\psi_{n_i,l_i,m_{l_i}}(\mathbf{r})$ or $\psi_{n_f,l_f,m_{l_f}}(\mathbf{r})$, is unchanged if the eigenfunction has even parity and it is changed if the eigenfunction has odd parity, as shown by Eqs. (9.13) and (9.14). Thus, when both eigenfunctions have the same parity, the integrand in Eq. (9.27) changes sign when the integration variable **r** is changed to −**r** and this implies that the integral must be zero.

It can also be shown, by noting that the angular dependence of the eigenfunctions $\psi_{n_f,l_f,m_{l_f}}(\mathbf{r})$ and $\psi_{n_i,l_i,m_{l_i}}(\mathbf{r})$ are given by spherical harmonics, that the integral in Eq. (9.27), and hence the probability of transition, is zero unless the difference $\Delta l = l_f - l_i$ is +1 or −1. This means that all electric dipole transitions in the hydrogen atom also obey the *selection rule*

$$\Delta l = \pm 1. \tag{9.28}$$

The electric dipole transitions between low-lying states of the hydrogen atom are shown as dotted lines in Fig. 9.8, where spectroscopic notation, 1s, 2s, 2p, etc. has been used to label the levels corresponding to states with different values for the principal quantum number n and orbital angular momentum quantum number l; for example, 2s corresponds to $n = 2$ and $l = 0$ and 2p corresponds to $n = 2$ and $l = 1$.

The transitions shown in Fig. 9.8 may be *induced* or *spontaneous*. Induced transitions between states with energy E_{n_i} and E_{n_f} occur strongly when the atom interacts with an external electromagnetic field which oscillates with an angular frequency ω which satisfies the resonant condition

$$\hbar\omega = |E_{n_f} - E_{n_i}|;$$

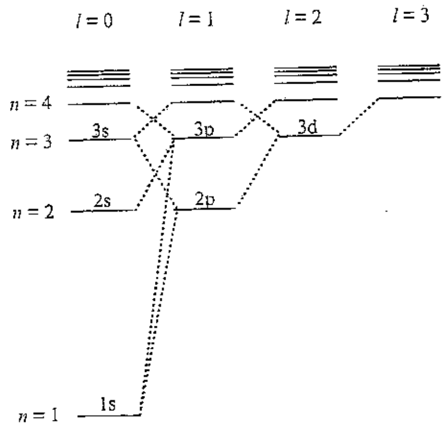


Fig. 9.8 Electric dipole radiative transitions between low-lying energy levels of the hydrogen atom with different values for the quantum numbers n and l. Spectroscopic notation, 1s, 2s, 2p, etc. has been used to label the energy levels; for example, 2s corresponds to $n = 2$ and $l = 0$ and 2p corresponds to $n = 2$ and $l = 1$. We note that the electric dipole transitions shown by the dotted lines obey the $\Delta l = \pm 1$ selection rule given in Eq. (9.28).

7.3 THE EXCLUSION PRINCIPLE

In the normal configuration of a hydrogen atom, the electron is in its lowest quantum state. What are the normal configurations of more complex atoms? Are all 92 electrons of a uranium atom in the same quantum state, to be envisioned perhaps as circling the nucleus crowded together in a single Bohr orbit? Many lines of evidence make this hypothesis unlikely. One example is the great difference in chemical behavior exhibited by certain elements whose atomic structures differ by just one electron: for instance, the elements having atomic numbers 9, 10, and 11 are respectively the halogen gas fluorine, the inert gas neon, and the alkali metal sodium. Since the electronic structure of an atom controls its interactions with other atoms, it is hard to understand why the chemical properties of the elements should change so abruptly with a small change in atomic number if all the electrons in an atom exist together in the same quantum state.

In 1925 Wolfgang Pauli discovered the fundamental principle that governs the electronic configurations of atoms having more than one electron. His *exclusion principle* states that **no two electrons in an atom can exist in the same quantum state.** Each electron in an atom must have a different set of quantum numbers n, l, m_l, m_s.

Pauli was led to the exclusion principle by a study of atomic spectra. It is possible to determine the various states of an atom from its spectrum, and the quantum numbers of these states can be inferred. In the spectra of every element but hydrogen a number of lines are *missing* that correspond to transitions to and from states having certain combinations of quantum numbers. Thus no transitions are observed in helium to or from the ground-state configuration in which the spins of both electrons are in the same direction to give a total spin of 1, although transitions *are* observed to and from the other ground-state configuration, in which the spins are in opposite directions to give a total spin of 0. In the absent state the quantum numbers of *both* electrons would be $n = 1$, $l = 0$, $m_l = 0$, $m_s = \frac{1}{2}$, while in the state known to exist one of the electrons has $m_s = \frac{1}{2}$ and the other $m_s = -\frac{1}{2}$. Pauli showed that every unobserved atomic state involves two or more electrons with identical quantum numbers, and the exclusion principle is a statement of this empirical finding.

Before we explore the role of the exclusion principle in determining atomic structures, let us look into its quantum-mechanical implications. We saw in the previous chapter that the complete wave function ψ of the electron in a hydrogen atom can be expressed as the product of three separate wave functions, each describing that part of ψ which is a function of one of the three coordinates r, θ, ϕ. It is possible to show in an analogous way that the complete wave function $\psi(1, 2, 3, \ldots, n)$ of a system of n particles can be approximately expressed as the product of the wave functions $\psi(1), \psi(2), \psi(3), \ldots, \psi(n)$ of the individual particles. That is,

$$\psi(1, 2, 3, \ldots, n) = \psi(1)\,\psi(2)\,\psi(3)\ldots\psi(n) \tag{7.9}$$

We shall use this result to investigate the kinds of wave functions that can be used to describe a system of two identical particles.

Let us suppose that one of the particles is in quantum state a and the other in state b. Because the particles are identical, it should make no difference in the probability density $|\psi|^2$ of the system if the particles are exchanged, with the one in state a replacing the one in state b and vice versa. Symbolically, we require that

$$|\psi|^2(1,2) = |\psi|^2(2,1) \tag{7.10}$$

Hence the wave function $\psi(2,1)$, representing the exchanged particles, can be given by either

$$\psi(2,1) = \psi(1,2) \qquad \textbf{Symmetric} \tag{7.11}$$

or

$$\psi(2,1) = -\psi(1,2) \qquad \textbf{Antisymmetric} \tag{7.12}$$

and still fulfill Eq. 7.10. The wave function of the system is not itself a measurable quantity, and so it can be altered in sign by the exchange of the particles. Wave functions that are unaffected by an exchange of particles are said to be *symmetric,* while those that reverse sign upon such an exchange are said to be *antisymmetric.*

If particle 1 is in state a and particle 2 is in state b, the wave function of the system is, according to Eq. 7.9,

$$\psi_{\mathrm{I}} = \psi_a(1)\,\psi_b(2) \tag{7.13a}$$

while if particle 2 is in state a and particle 1 is in state b, the wave function is

$$\psi_{\mathrm{II}} = \psi_a(2)\,\psi_b(1) \tag{7.13b}$$

Because the two particles are in fact indistinguishable, we have no way of knowing at any moment whether ψ_{I} or ψ_{II} describes the system. The likelihood that ψ_{I} is correct at any moment is the same as the likelihood that ψ_{II} is correct. Equivalently, we can say that the system spends half the time in the configuration whose wave function is ψ_{I} and the other half in the configuration whose wave function is ψ_{II}. Therefore a linear combination of ψ_{I} and ψ_{II} is the proper description of the system. There are two such combinations possible—

the symmetric one

$$\psi_S = \frac{1}{\sqrt{2}}[\psi_a(1)\,\psi_b(2) + \psi_a(2)\,\psi_b(1)] \tag{7.14}$$

and the antisymmetric one

$$\psi_A = \frac{1}{\sqrt{2}}[\psi_a(1)\,\psi_b(2) - \psi_a(2)\,\psi_b(1)] \tag{7.15}$$

The factor $1/\sqrt{2}$ is required to normalize ψ_S and ψ_A. Exchanging particles 1 and 2 leaves ψ_S unaffected, while it reverses the sign of ψ_A. Both ψ_S and ψ_A obey Eq. 7.10.

There are a number of important distinctions between the behavior of particles in systems whose wave functions are symmetric and that of particles in systems whose wave functions are antisymmetric. The most obvious is that, in the former case, both particles 1 and 2 can simultaneously exist in the same state, with $a = b$, while in the latter case, if we set $a = b$, we find that $\psi_A = 0$: the two particles *cannot* be in the same quantum state. Comparing this conclusion with Pauli's empirical exclusion principle, which states that no two electrons in an atom can be in the same quantum state, we conclude that systems of electrons are described by wave functions that reverse sign upon the exchange of any pair of them.

The results of various experiments show that *all* particles which have a spin of ½ have wave functions that are antisymmetric to an exchange of any pair of them. Such particles, which include protons and neutrons as well as electrons, obey the exclusion principle when they are in the same system; that is, when they move in a common force field, each member of the system must be in a different quantum state. Particles of spin ½ are often referred to as *Fermi particles* or *fermions* because, as we shall learn in Chap. 9, the behavior of aggregates of them is governed by a statistical distribution law discovered by Fermi and Dirac.

Particles whose spins are 0 or an integer have wave functions that are symmetric to an exchange of any pair of them. These particles do not obey the exclusion principle. Particles of 0 or integral spin are often referred to as *Bose particles* or *bosons* because the statistical distribution law that describes aggregates of them was discovered by Bose and Einstein. Photons, alpha particles, and helium atoms are Bose particles.

There are other important consequences of the symmetry or antisymmetry of particle wave functions besides that expressed in the exclusion principle. It is these consequences that make it useful to classify particles according to the nature of their wave functions rather than simply according to whether or not they obey the exclusion principle.

7.4 ELECTRON CONFIGURATIONS

Two basic rules determine the electron structures of many-electron atoms:

1. A system of particles is stable when its total energy is a minimum.
2. Only one electron can exist in any particular quantum state in an atom.

Before we apply these rules to actual atoms, let us examine the variation of electron energy with quantum state.

While the various electrons in a complex atom certainly interact directly with one another, much about atomic structure can be understood by simply considering each electron as though it exists in a constant mean force field. For a given electron this field is approximately the electric field of the nuclear charge Ze decreased by the partial shielding of those other electrons that are closer to the nucleus. All the electrons that have the same total quantum number n are, on the average, roughly the same distance from the nucleus. These electrons therefore interact with virtually the same electric field and have similar energies. It is conventional to speak of such electrons as occupying the same atomic *shell*. Shells are denoted by capital letters according to the following scheme:

$$\begin{array}{llllll} n = 1 & 2 & 3 & 4 & 5 \ldots \\ \quad K & L & M & N & O \ldots \end{array} \qquad \text{Atomic shells}$$

The energy of an electron in a particular shell also depends to a certain extent upon its orbital quantum number l, though this dependence is not so great as that upon n. In a complex atom the degree to which the full nuclear charge is shielded from a given electron by intervening shells of other electrons varies with its probability-density distribution. An electron of small l is more likely to be found near the nucleus (where it is poorly shielded by the other electrons) than one of higher l (see Fig. 6-11), which results in a lower total energy (that is, higher binding energy) for it. The electrons in each shell accordingly increase in energy with increasing l. This effect is illustrated in Fig. 7-5, which is a plot of the binding energies of various atomic electrons as a function of atomic number.

Electrons that share a certain value of l in a shell are said to occupy the same *subshell*. All the electrons in a subshell have almost identical energies, since the dependence of electron energy upon m_l and m_s is comparatively minor.

The occupancy of the various subshells in an atom is usually expressed with the help of the notation introduced in the previous chapter for the various quantum states of the hydrogen atom. As indicated in Table 6.2, each subshell is identified by its total quantum number n followed by the letter corresponding to its orbital quantum number l. A superscript after the letter indicates the

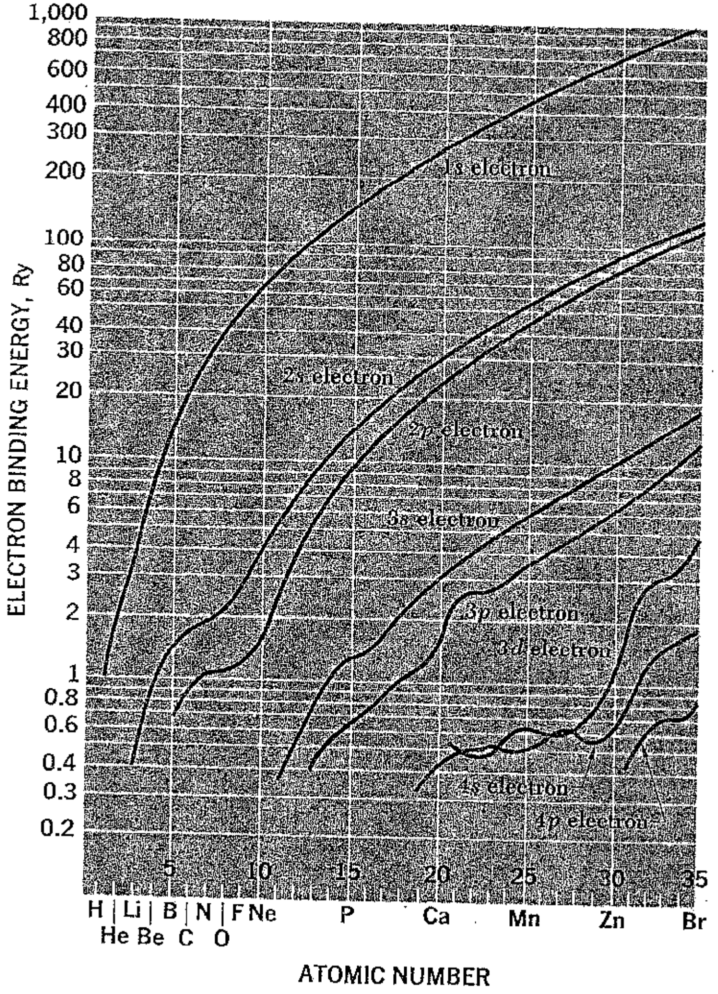


FIGURE 7-5 The binding energies of atomic electrons in Ry. (1 Ry = 1 Rydberg = 13.6 eV = ground-state energy of H atom.)

number of electrons in that subshell. For example, the electron configuration of sodium is written

$$1s^22s^22p^63s^1$$

which means that the 1s ($n = 1$, $l = 0$) and 2s ($n = 2$, $l = 0$) subshells contain two electrons each, the 2p ($n = 2$, $l = 1$) subshell contains six electrons, and the 3s ($n = 3$, $l = 0$) subshell contains one electron.

7.5 THE PERIODIC TABLE

When the elements are listed in order of atomic number, elements with similar chemical and physical properties recur at regular intervals. This empirical observation, known as the *periodic law*, was first formulated by Dmitri Mendeleev about a century ago. A tabular arrangement of the elements exhibiting this recurrence of properties is called a *periodic table*. Table 7.1 is perhaps the simplest form of periodic table; though more elaborate periodic tables have been devised to exhibit the periodic law in finer detail, Table 7.1 is adequate for our purposes.

Elements with similar properties form the *groups* shown as vertical columns in Table 7.1. Thus group I consists of hydrogen plus the alkali metals, all of which are extremely active chemically and all of which have valences of +1. Group VII consists of the halogens, volatile, active nonmetals that have valences of −1 and form diatomic molecules in the gaseous state. Group VIII consists of the inert gases, elements so inactive that not only do they almost never form compounds with other elements, but their atoms do not join together into molecules like the atoms of other gases.

The horizontal rows in Table 7.1 are called *periods*. Across each period is a more or less steady transition from an active metal through less active metals and weakly active nonmetals to highly active nonmetals and finally to an inert gas. Within each column there are also regular changes in properties, but they are far less conspicuous than those in each period. For example, increasing atomic number in the alkali metals is accompanied by greater chemical activity, while the reverse is true in the halogens.

A series of *transition elements* appears in each period after the third between the group II and group III elements. The transition elements are metals with a considerable chemical resemblance to one another but no pronounced resemblance to the elements in the major groups. Fifteen of the transition elements in period 6 are virtually indistinguishable in their properties, and are known as the *lanthanide* elements (or *rare earths*). A similar group of closely related metals, the *actinide* elements, is found in period 7.

The notion of electron shells and subshells fits perfectly into the pattern of the periodic table, which is just a mirror of the atomic structures of the elements. Let us see how this pattern arises.

The exclusion principle places definite limits on the number of electrons that can occupy a given subshell. A subshell is characterized by a certain total quantum number n and orbital quantum number l, where

$$l = 0, 1, 2, \ldots, (n - 1)$$

There are $2l + 1$ different values of the magnetic quantum number m_l for any

Table 7.1.

THE PERIODIC TABLE OF THE ELEMENTS. The number above the symbol of each element is its atomic number, and that below is its atomic mass in u. The elements whose atomic masses are given in parentheses do not occur in nature, but have been prepared artificially in nuclear reactions. The atomic mass in such a case is the mass number of the most long-lived radioactive isotope of the element.

Period	Group I	Group II											Group III	Group IV	Group V	Group VI	Group VII	Group VIII
1	1 H 1.00																	2 He 4.00
2	3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.98	16 S 32.07	17 Cl 35.46	18 Ar 39.94
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.8
5	37 Rb 85.47	38 Sr 87.66	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (99)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
6	55 Cs 132.91	56 Ba 137.34	57–71 *	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 197.0	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (210)	85 At (210)	86 Rn 222
7	87 Fr (223)	88 Ra 226.05	89–103 **															

* Rare earths	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 152.0	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.92	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
** Actinides	89 Ac 227	90 Th 232.04	91 Pa 231	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)

l, since

$$m_l = 0, \pm 1, \pm 2, \ldots, \pm l$$

and two possible values of the spin magnetic quantum number m_s ($+\frac{1}{2}$ and $-\frac{1}{2}$) for any m_l. Hence each subshell can contain a maximum of $2(2l + 1)$ electrons and each shell a maximum of

$$\sum_{l=0}^{l=n-1} 2(2l + 1) = 2[1 + 3 + 5 + \cdots + 2(n - 1) + 1]$$
$$= 2[1 + 3 + 5 + \cdots + 2n - 1]$$

The quantity in the brackets contains n terms whose average value is $\frac{1}{2}[1 + (2n - 1)]$, so that the maximum number of electrons in the nth shell is

$$2 \times \frac{n}{2}[1 + (2n - 1)] = 2n^2$$

An atomic shell or subshell that contains its full quota of electrons is said to be *closed*. A closed s subshell ($l = 0$) holds two electrons, a closed p subshell ($l = 1$) six electrons, a closed d subshell ($l = 2$) ten electrons, and so on.

The total orbital and spin angular momenta of the electrons in a closed subshell are zero, and their effective charge distributions are perfectly symmetrical (see Prob. 8 of Chap. 6). The electrons in a closed shell are all very tightly bound, since the positive nuclear charge is large relative to the negative charge of the inner shielding electrons (Fig. 7-6). Since an atom containing only closed shells has no dipole moment, it does not attract other electrons, and its electrons cannot be readily detached. Such atoms we expect to be passive chemically, like the inert gases—and the inert gases all turn out to have closed-shell electron configurations or their equivalents.

Those atoms with but a single electron in their outermost shells tend to lose this electron, which is relatively far from the nucleus and is shielded by the inner electrons from all but an effective nuclear charge of $+e$. Hydrogen and the alkali metals are in this category and accordingly have valences of +1. Atoms whose outer shells lack a single electron of being closed tend to acquire such an electron through the attraction of the imperfectly shielded strong nuclear charge, which accounts for the chemical behavior of the halogens. In this manner the similarities of the members of the various groups of the periodic table may be accounted for.

Table 7.2 shows the electron configurations of the elements. The origin of the transition elements evidently lies in the tighter binding of s electrons than d or f electrons in complex atoms, discussed in the previous section. The first element to exhibit this effect is potassium, whose outermost electron is in a 4s

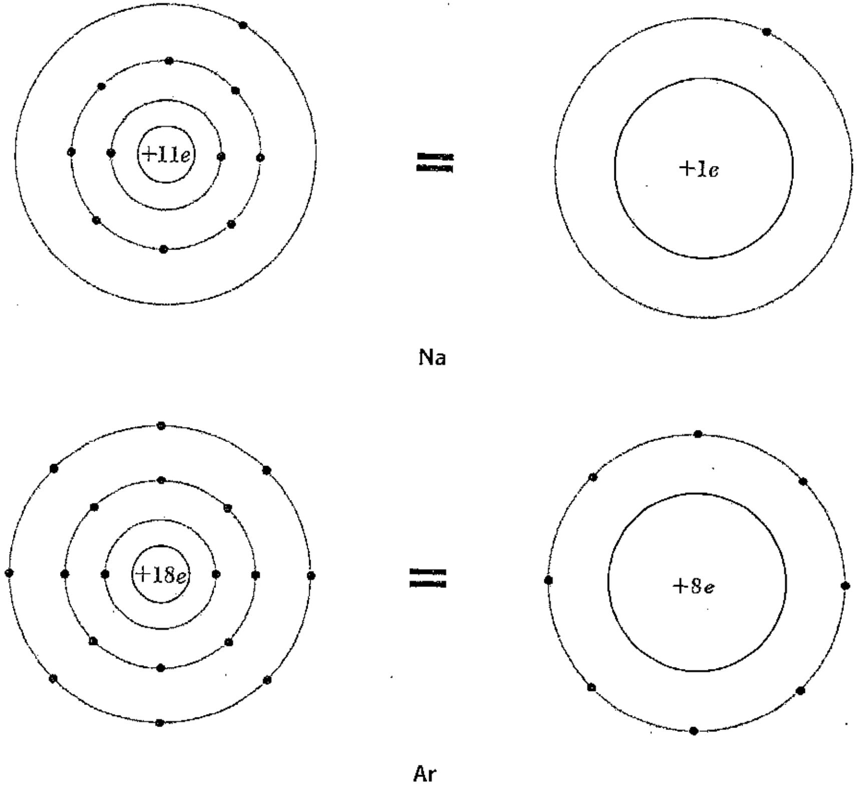


FIGURE 7-6 Electron shielding in sodium and argon. Each outer electron in an Ar atom is acted upon by an effective nuclear charge 8 times greater than that acting upon the outer electron in a Na atom, even though the outer electrons in both cases are in the $M(n = 3)$ shell.

instead of a $3d$ substate. The difference in binding energy between $3d$ and $4s$ electrons is not very great, as can be seen in the configurations of chromium and copper. In both of these elements an additional $3d$ electron is present at the expense of a vacancy in the $4s$ subshell. In this connection another glance at Fig. 7.5 will be instructive.

The order in which electron subshells are filled in atoms is

$$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 6d$$

as we can see from Table 7.2 and Fig. 7-7. The remarkable similarities in chemical behavior among the lanthanides and actinides are easy to understand on the basis of this sequence. All of the lanthanides have the same $5s^2 5p^6 6s^2$ configurations but have incomplete $4f$ subshells. The addition of $4f$ electrons has virtually no effect on the chemical properties of the lanthanide elements,

Table 7.2.

ELECTRON CONFIGURATIONS OF THE ELEMENTS.

	K	*L*		*M*			*N*				*O*				*P*			*Q*
	$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	$4p$	$4d$	$4f$	$5s$	$5p$	$5d$	$5f$	$6s$	$6p$	$6d$	$7s$
1 H	1																	
2 He	2																	
3 Li	2	1																
4 Be	2	2																
5 B	2	2	1															
6 C	2	2	2															
7 N	2	2	3															
8 O	2	2	4															
9 F	2	2	5															
10 Ne	2	2	6															
11 Na	2	2	6	1														
12 Mg	2	2	6	2														
13 Al	2	2	6	2	1													
14 Si	2	2	6	2	2													
15 P	2	2	6	2	3													
16 S	2	2	6	2	4													
17 Cl	2	2	6	2	5													
18 A	2	2	6	2	6													
19 K	2	2	6	2	6		1											
20 Ca	2	2	6	2	6		2											
21 Sc	2	2	6	2	6	1	2											
22 Ti	2	2	6	2	6	2	2											
23 V	2	2	6	2	6	3	2											
24 Cr	2	2	6	2	6	5	1											
25 Mn	2	2	6	2	6	5	2											
26 Fe	2	2	6	2	6	6	2											
27 Co	2	2	6	2	6	7	2											
28 Ni	2	2	6	2	6	8	2											
29 Cu	2	2	6	2	6	10	1											
30 Zn	2	2	6	2	6	10	2											
31 Ga	2	2	6	2	6	10	2	1										
32 Ge	2	2	6	2	6	10	2	2										
33 As	2	2	6	2	6	10	2	3										
34 Se	2	2	6	2	6	10	2	4										
35 Br	2	2	6	2	6	10	2	5										
36 Kr	2	2	6	2	6	10	2	6										
37 Rb	2	2	6	2	6	10	2	6			1							
38 Sr	2	2	6	2	6	10	2	6			2							
39 Y	2	2	6	2	6	10	2	6	1		2							
40 Zr	2	2	6	2	6	10	2	6	2		2							
41 Nb	2	2	6	2	6	10	2	6	4		1							
42 Mo	2	2	6	2	6	10	2	6	5		1							
43 Tc	2	2	6	2	6	10	2	6	5		2							
44 Ru	2	2	6	2	6	10	2	6	7		1							
45 Rh	2	2	6	2	6	10	2	6	8		1							
46 Pd	2	2	6	2	6	10	2	6	10									
47 Ag	2	2	6	2	6	10	2	6	10		1							
48 Cd	2	2	6	2	6	10	2	6	10		2							
49 In	2	2	6	2	6	10	2	6	10		2	1						
50 Sn	2	2	6	2	6	10	2	6	10		2	2						
51 Sb	2	2	6	2	6	10	2	6	10		2	3						

Table 7.2 (Continued)

	K	L		M			N				O				P			Q
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
52 Te	2	2	6	2	6	10	2	6	10		2	4						
53 I	2	2	6	2	6	10	2	6	10		2	5						
54 Xe	2	2	6	2	6	10	2	6	10		2	6						
55 Cs	2	2	6	2	6	10	2	6	10		2	6			1			
56 Ba	2	2	6	2	6	10	2	6	10		2	6			2			
57 La	2	2	6	2	6	10	2	6	10		2	6	1		2			
58 Ce	2	2	6	2	6	10	2	6	10	2	2	6			2			
59 Pr	2	2	6	2	6	10	2	6	10	3	2	6			2			
60 Nd	2	2	6	2	6	10	2	6	10	4	2	6			2			
61 Pm	2	2	6	2	6	10	2	6	10	5	2	6			2			
62 Sm	2	2	6	2	6	10	2	6	10	6	2	6			2			
63 Eu	2	2	6	2	6	10	2	6	10	7	2	6			2			
64 Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
65 Tb	2	2	6	2	6	10	2	6	10	9	2	6			2			
66 Dy	2	2	6	2	6	10	2	6	10	10	2	6			2			
67 Ho	2	2	6	2	6	10	2	6	10	11	2	6			2			
68 Er	2	2	6	2	6	10	2	6	10	12	2	6			2			
69 Tm	2	2	6	2	6	10	2	6	10	13	2	6			2			
70 Yb	2	2	6	2	6	10	2	6	10	14	2	6			2			
71 Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
72 Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
73 Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
74 W	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
75 Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
76 Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
77 Ir	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
78 Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
79 Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
80 Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
81 Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
82 Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
83 Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
84 Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
85 At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
86 Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
87 Fr	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
88 Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
89 Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
90 Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
91 Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
92 U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
93 Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
94 Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6	1	2
95 Am	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	1	2
96 Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
97 Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
98 Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
99 E	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
100 Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
101 Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
102 No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2
103 Lw	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2

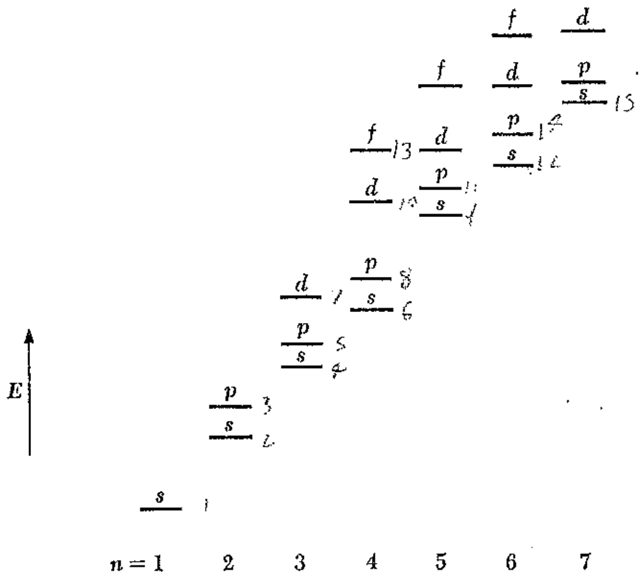


FIGURE 7-7 The sequence of quantum states in an atom. Not to scale.

which are determined by the outer electrons. Similarly, all of the actinides have $6s^2 6p^6 7s^2$ configurations, and differ only in the numbers of their $5f$ and $6d$ electrons.

These irregularities in the binding energies of atomic electrons are also responsible for the lack of completely full outer shells in the heavier inert gases. Helium ($Z = 2$) and neon ($Z = 10$) contain closed K and L shells respectively, but argon ($Z = 18$) has only 8 electrons in its M shell, corresponding to closed $3s$ and $3p$ subshells. The reason the $3d$ subshell is not filled next is simply that $4s$ electrons have higher binding energies than $3d$ electrons, as we have said, and so the $4s$ subshell is filled first in potassium and calcium. As the $3d$ subshell is filled in successively heavier transition elements, there are still one or two outer $4s$ electrons that make possible chemical activity. Not until krypton ($Z = 36$) is another inert gas reached, and here a similarly incomplete outer shell occurs with only the $4s$ and $4p$ subshells filled. Following krypton is rubidium ($Z = 37$), which skips both the $4d$ and $4f$ subshells to have a $5s$ electron. The next inert gas is xenon ($Z = 54$), which has filled $4d$, $5s$, and $5p$ subshells, but now even the inner $4f$ subshell is empty as well as the $5d$ and $5f$ subshells. The same pattern recurs with the remainder of the inert gases.

While we have sketched the origins of only a few of the chemical and physical properties of the elements in terms of their electron configurations, many more can be quantitatively understood by similar reasoning.