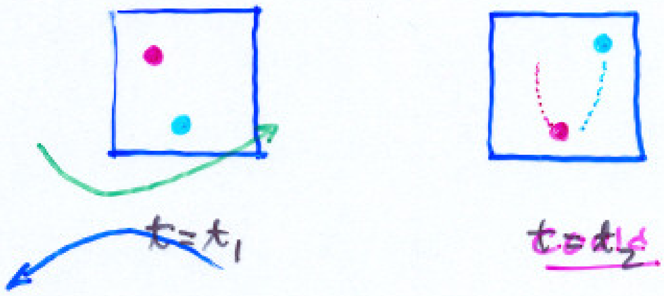
CHAPTER 8 ATOMIC STRUCTURE & PERIODIC TABLE

So, Hydrogen was "easy"... closed form

mathematically clean

How about Helium? – there's a story here.

Imagine a classical box with 2 classical balls.


$t=t_1$

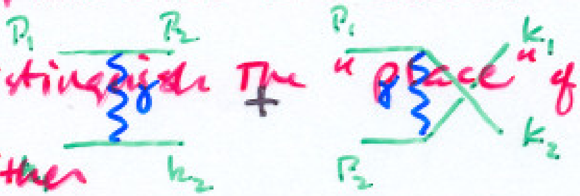
$t=t_2$ can tell the difference classically..

you can easily LABEL and track the trajectories of both through time

suppose they are quantum mechanical objects.

That's a toughy. → their wave functions overlap

⇒ regions where one cannot distinguish the "place" of either



+ all problems of uncertainty princ. & measurement

Remember my definition of an electron?

$m = 0.511\ \mathrm{MeV}/c^2$

$q = -e$

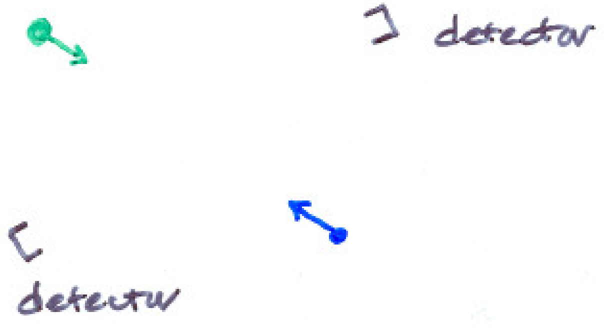
$s = 1/2$

every object with these properties is an electron...

so every electron is absolutely IDENTICAL.

Consider a classical "scattering experiment" between CLASSICAL electrons

can distinguish between them!



"PLACE" becomes really problematic!

→ QM must take INDISTINGUISHABILITY into account.

How about a Schrödinger Equation describing 2 -- say -- electrons?

ψ_T = wavefunction of the whole system of 2 electrons having coordinates $x_1y_1z_1$ & $x_2y_2z_2$

V_T = potential of system

E_T = energy of system.

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_T}{\partial x_1^2}+\frac{\partial^2\psi_T}{\partial y_1^2}+\frac{\partial^2\psi_T}{\partial z_1^2}\right)-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_T}{\partial x_2^2}+\frac{\partial^2\psi_T}{\partial y_2^2}+\frac{\partial^2\psi_T}{\partial z_2^2}\right)$$

$$+\,V_T(x_1y_1z_1x_2y_2z_2) = E_T\psi_T$$

Can separate the variables...

$$\psi_T(x_1y_1z_1x_2y_2z_2) = \phi(x_1y_1z_1)\,\eta(x_2y_2z_2)$$

a function describing particle 1 — wavefunction

function describing particle 2 — wavefunction

Simplify the notation

$$\phi(x_1 y_1 z_1) \longrightarrow \phi(1)$$

$$\eta(x_2 y_2 z_2) \longrightarrow \eta(2)$$

So,

① $\psi_T = \phi(1)\,\eta(2)$ particle 1 in state ϕ

particle 2 in state η

what if particle 1 was in state η &

particle 2 in state ϕ ?

② $\psi_T = \phi(2)\,\eta(1)$ ... these are different

MEASURABLES...

simplest is just the probability density

① $\psi_T^* \psi_T = \phi^*(1)\,\eta^*(2)\,\phi(1)\,\eta(2)$

② $\psi_T^* \psi_T = \phi^*(2)\,\eta^*(1)\,\phi(2)\,\eta(1)$

crucial point:

If we cannot distinguish between 1 and 2..

then $\psi_T^* \psi_T$ should not be different for switching the labels..

$$\phi^*(1)\,\eta^*(2)\,\phi(1)\,\eta(2) \xrightarrow[2\to 1]{1\to 2} \phi^*(2)\,\eta^*(1)\,\phi(2)\,\eta(1)$$

not the same

eg. $\phi^*(1) \Rightarrow \phi^*(x_1,y_1,z_1)$ a particular function evaluated at $\vec{x}_1$

$\phi^*(2) \Rightarrow \phi^*(x_2,y_2,z_2)$ evaluated at $\vec{x}_2$

There is a way out..

construct wavefunctions such that $\psi_T^* \psi_T$ doesn't change under exchange of particles.

Look at these...

$$\psi_S \equiv \frac{1}{\sqrt{2}}\left[\ \phi(1)\eta(2) + \phi(2)\eta(1)\right]$$ symmetric

$$\psi_A \equiv \frac{1}{\sqrt{2}}\left[\ \phi(1)\eta(2) - \phi(2)\eta(1)\right]$$ antisymmetric

These are linear combinations of

$$\left.\begin{aligned}\psi_T &= \phi(1)\eta(2)\\ \psi_T &= \phi(2)\eta(1)\end{aligned}\right\}\ \text{don't affect } E_T$$

so also solutions to Sch. Eq. @ same E_T

How do ψ_S and ψ_A behave?

$$\psi_S = \frac{1}{\sqrt{2}}\left[\phi(1)\eta(2) + \overset{\eta(1)\,\phi(2)}{\cancel{\phi(2)\eta(1)}}\right] \xrightarrow[\substack{1\to2\\2\to1}]{} \frac{1}{\sqrt{2}}\left[\phi(2)\eta(1) + \phi(1)\eta(2)\right]$$

$$= \psi_S$$

$$\psi_A = \frac{1}{\sqrt{2}}\left[\phi(1)\eta(2) - \overset{\eta(1)\,\phi(2)}{\cancel{\phi(2)\eta(1)}}\right] \xrightarrow[\substack{1\to2\\2\to1}]{} \frac{1}{\sqrt{2}}\left[\phi(2)\eta(1) - \overset{\phi(1)\,\eta(2)}{\cancel{\eta(1)\phi(2)}}\right]$$

$$= -\psi_A$$

$$\psi_S^*\psi_S \xrightarrow[\substack{1\to2\\2\to1}]{} \psi_S^*\psi_S \quad \& \quad \psi_A^*\psi_A \xrightarrow[\substack{1\to2\\2\to1}]{} (-1)^2\,\psi_A^*\psi_A$$

Wolfgang Pauli in 1925

suggested a solution to both an empirical situation and a logical one.

empirical — state of multi-electron spectra .. results

logical — how come all of the electrons in BIG atoms don't collapse into the $n=1$ state?

Pauli Exclusion Principle:

In multi-electron atoms there can be no more than one electron in the same quantum state.

A state: a wave function defined by all quantum numbers so far:

n, ℓ, m_ℓ, m_s

This isn't right, this isn't even wrong

I don't mind your thinking slowly; I mind your publishing faster than you think

If I understand Dirac correctly, his meaning is this: there is no God, and Dirac is his Prophet.

Wolfgang was a typical night bird. He preferred the town, liked to spend evenings in some café, and would thereafter work on his physics with great intensity and great success. To Sommerfeld's dismay he would therefore rarely attend morning lectures and would not turn up until about noon.

It was absolutely marvelous working for Wolfgang Pauli. You could ask him anything. There was no worry that he would think a particular question was stupid, since he thought all questions were stupid.

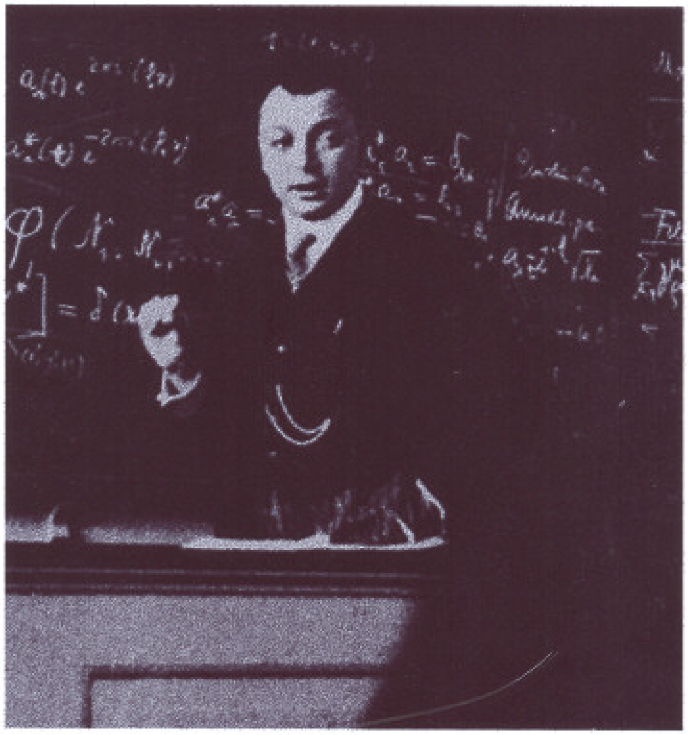
At the moment physics is again terribly confused. ...I wish I had been a movie comedian or something of the sort and had never heard of physics.

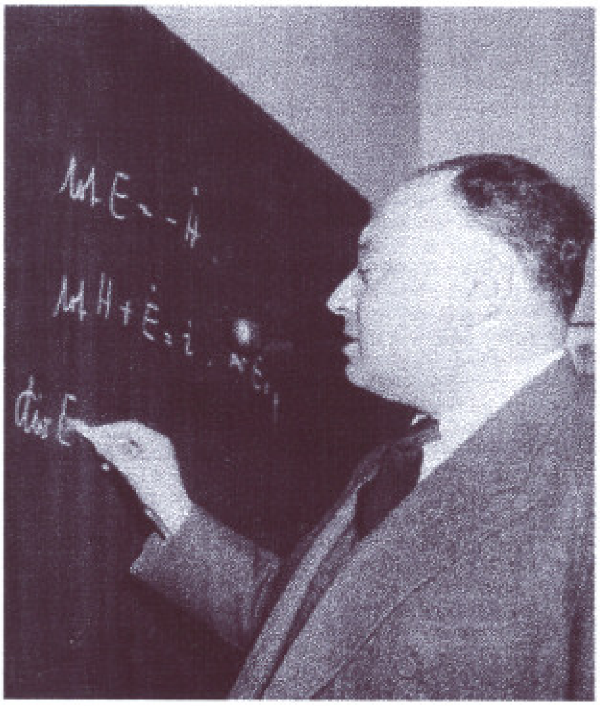
For quite a while I have set for myself the rule if a theoretician says 'universal' it just means pure nonsense.

You know, what Einstein has just said isn't so stupid.

Einstein wrote, "No one studying this mature, grandly conceived work would believe that the author is a man of twenty-one. One wonders what to admire most, the psychological understanding for the development of the ideas, the sureness of mathematical deduction, the profound physical insight, the capacity for lucid, systematic presentation, the knowledge of the literature, the complete treatment of the subject matter, or the sureness of critical appraisal.

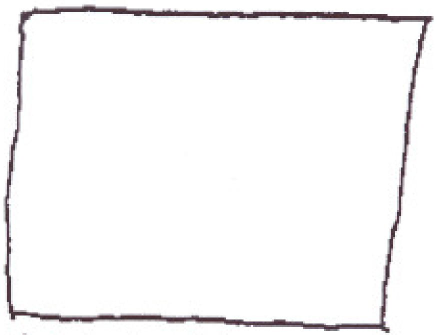
I have done a terrible thing, I have postulated a particle that cannot be detected.




$\mathrm{rot}\,E = -\dot{H}$
$\mathrm{rot}\,H + \dot{E} = i$
$\mathrm{div}\,E$

Comment on Heisenberg's radio advertisement:

"This is to show the world, that I can paint like Titian:"



Only technical details are missing.

W. Pauli

How about an ANTISYMMETRIC wave function where 1 and 2 are in the same state ... say ϕ ?

$$\psi_A = \frac{1}{\sqrt{2}}\left[\, \phi(1)\,\phi(2) - \overset{\phi(2)\,\phi(1)}{\cancel{\phi(1)}} \,\right] = 0$$

This insures it.

A system containing several electrons must be in a totally antisymmetric state.

another statement of
Pauli E.P.

now... Helium.

Ignore the fact (for a minute) that the 2 electrons repel one another

$$\psi_A = \frac{1}{\sqrt{2}}\left[\, \phi(1)\,\eta(2) - \eta(1)\,\phi(2) \,\right]$$

ϕ and η include both the n, l, m_l characterizations → functions of $x, y, \& z$

also some characterization of the spins. not x, y, z.

total wavefunction = (space wavefunction) × (spin w.f.)
for any particle

↓

ψ_A or ψ_S

Spin is different. not a function of x, y, z but something that depends on $m_s = \pm 1/2$

Often use little cartoons...

$m_s = +1/2$ ↑ spin "up"
$m_s = -1/2$ ↓ spin "down"

The total spin state of the 2-electron system

$$\vec{S} = \vec{S}_1 + \vec{S}_2$$

length: $S =$ ~~[illegible]~~ $\hbar\sqrt{s(s+1)}$

projection: $S_z = m_s \hbar$

possible values: $m_s = -s \ldots +s$

what's s? a combination of s_1 and s_2

$s_1 = \uparrow$ or $\downarrow$

$s_2 = \uparrow$ or $\downarrow$

can combine like

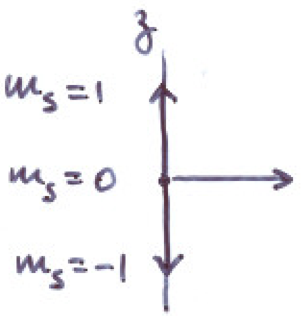
$$\begin{matrix} s_2 & \uparrow \\ s_1 & \uparrow \end{matrix} \quad \text{or} \quad \begin{matrix} s_1 & \uparrow \\ s_2 & \uparrow \end{matrix} \quad \Rightarrow \quad \Big\uparrow \Big\} = 1$$

or

$$s_1 \uparrow\downarrow s_2 \quad \text{or} \quad s_2 \uparrow\downarrow s_1 \quad \Rightarrow \quad \cdot \,\} = 0$$

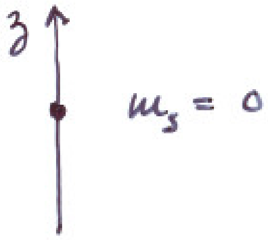
So, s can be either 0 or 1

when $s = 1$



s_1, s_2: $\begin{matrix} \uparrow \frac{1}{2} \\ \uparrow \frac{1}{2} \end{matrix}$

when $s = 0$



s_1, s_2 $\frac{1}{2} \downarrow \uparrow \frac{1}{2}$

forget continuous functions of x, y, z .. can still write SPIN WAVEFUNCTIONS

$$\Sigma = \underbrace{(\uparrow,\downarrow)}_{\substack{m_{s_1} = 1/2 \\ m_{s_2} = -1/2}} \qquad (m_{s_1}, m_{s_2})$$

Can also form A & S

$$\Sigma_S = \cancel{\tfrac{1}{\sqrt{2}}} \left[(\uparrow,\uparrow) \right]$$

$$\Sigma_S = \tfrac{1}{\sqrt{2}} \left[(\uparrow,\downarrow) + (\downarrow,\uparrow) \right]$$

$$\Sigma_S = \left[(\downarrow,\downarrow) \right]$$

a "triplet"

three symmetric states

symmetric in the exchange of $m_{s_1} \to m_{s_2}$

$m_{s_2} \to m_{s_1}$

and:

$$\Sigma_A = \tfrac{1}{\sqrt{2}} \left[(\uparrow,\downarrow) - (\downarrow,\uparrow) \right]$$

a singlet

one antisymmetric state