Class 27

this is one of the most true things in text

spin-statistics thm: (result in relativistic quantum field theory)

Consider the wavefunction that involves N identical particles

if fermions (spin = 1/2, 3/2, 5/2, ... "half integer")

then wavefunction odd under coordinate exchange

ie $\psi(1,2,3,\cdots,N) = -\psi(2,1,3,\cdots N)$

this refers to all space/spin coordinates of particle 1

Above I exchange just 1 & 2 – but applies to exchange of any pair.

if boson (spin = 0, 1, 2, ... "integer spin") then wavefunction is even under coordinate exchange

ie $\psi(1,2,3,\cdots N) = +\psi(2,1,3,\cdots N)$

Eg – the function: $x_1 x_2 x_3$ is totally symmetric

Eg - for any functions f, g, h the following is antisymmetric

$$f(x_1)g(x_2)h(x_3) + g(x_1)h(x_2)f(x_3) + h(x_1)f(x_2)g(x_3)$$
$$- f(x_1)g(x_3)h(x_2) - g(x_1)h(x_3)f(x_2) - h(x_1)f(x_3)g(x_2)$$

the following is neither symmetric or antisymmetric

$$x_1(x_2^2 - x_3^2)$$

Remark. this is the grown up version of the Pauli Exclusion Principle – that "you can't put two electrons into exactly the same state"

Pedagogical Problem 1: real examples of this them involve 3d locations (ie $\vec{r}$ not x) & lots of particles - it quickly exceeds what one can do at the blackboard. We will mostly deal in $N=2$ particles in just one dimension - x_1 & x_2 - eg 2 particles in an infinite well

Pedagogical Problem 2: the problems you can solve typically have been cases of non-interacting particles - cases where $H = H_1 + H_2$ where H_1 & H_2 are identical (cuz the particles are identical) and each involves just the coordinates of one particle. Under these conditions you can find the eigenfunctions/values $H_1 \psi_a = E_a \psi_a$ where "a" could run over all the ~~eigenfunctions/values~~. The entire Hamiltonian would have eigenfunctions/values $\to E_a + E_b$ &

$\psi_a(1)\,\psi_b(2)$ ← represents all space/spin coordinates of particle 2

it doesn't matter if we symmetrize or antisymmetrize we get the same set of energies (except for the case of fermions where $E_a + E_a$ & $\psi_a(1)\,\psi_a(2)$ would be ruled out) so it doesn't seem like a big deal. Real problems have interactions between the identical particles and those interactions result in different energies depending on fermion or boson. But the techniques to deal with interactions is in the following chapter - we are left with some hand waving at present.

Remarks In the case of non interacting identical particles

$$H = \sum_i H_i \qquad \text{eigenfunctions/values:} \quad H_i \psi_a = E_a \psi_a$$

you can make an antisymmetric wave function with energy $= \underbrace{E_a + E_b + E_c + \cdots}$ with the Slater

a, b, c... distinct energies - one for each particle

determinant:

$$\psi(1,2,3,\dots N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(1) & \psi_b(1) & \psi_c(1) & \cdots \\ \psi_a(2) & \psi_b(2) & \psi_c(2) & \cdots \\ \psi_a(3) & \psi_b(3) & \psi_c(3) & \cdots \\ & & & \end{vmatrix}$$

To make a totally symmetric wavefunction just replace every $-$ in the determinant with $+$

$$\text{eg:} \quad \psi(1,2) = \begin{vmatrix} f(x_1) & g(x_1) \\ f(x_2) & g(x_2) \end{vmatrix} = f(x_1) g(x_2) - f(x_2) g(x_1)$$

On page 209 the text says:

"Identical bosons tend to be somewhat closer together and identical fermions somewhat farther apart than distinguishable particles in the same two states"

The evidence is eq 5.22:

bosons: closer together

$$\Delta x^2_{\pm} = \Delta x^2_d \mp 2 \left| \langle x \rangle_{ab} \right|^2$$

typical distance apart if distinguishable

fermions: more distance apart

This statement is then used to argue that if (as is the case with electron-electron repulsion) particles resist being put together (ie there is a positive interaction P.E. that increases if particles are close together) then wavefunctions with antisymmetric spacial states will have lower energy than wavefunctions with symmetric spacial states.

The context here is we will have a product wave function $\psi(1,2) = (\text{function of space})\left(\begin{smallmatrix}\text{function}\\ \text{of spin}\end{smallmatrix}\right)$

like $g(\vec{r}_1, \vec{r}_2)\left(\frac{\uparrow\downarrow - \downarrow\uparrow}{\sqrt{2}}\right)$

In a long mathematics calculation we looked a 2 particles in an infinite well $0 \to a$

For a single particle we had normalized eigenfunctions

$$u_n(x) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi}{a}x\right)$$

we focused on 2 particle wave functions

$$\psi_1 = u_n(x_1)\,u_\ell(x_2) \quad \text{with} \quad n=2 \ \&\ \ell=3$$ ← distinguishable

$$\psi_2 = \frac{1}{\sqrt{2}}\left(u_n(x_1)u_\ell(x_2) + u_\ell(x_1)\,u_n(x_2)\right)$$ ← symmetric

$$\psi_3 = \frac{1}{\sqrt{2}}\left(u_n(x_1)\,u_\ell(x_2) - u_\ell(x_1)\,u_n(x_2)\right)$$ ← antisymmetric

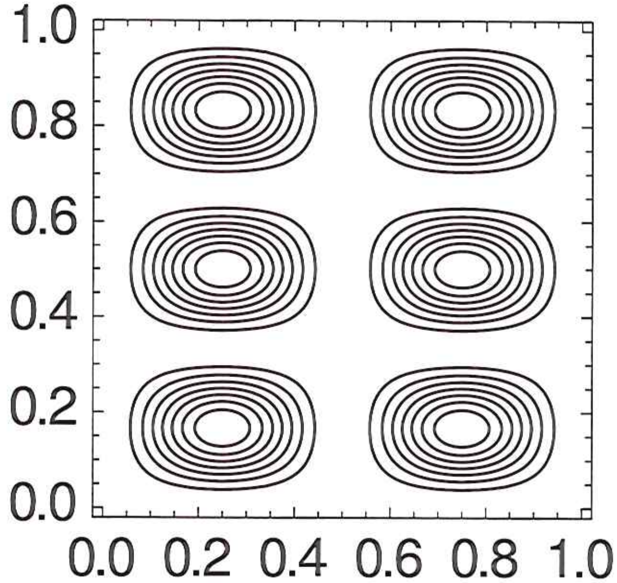
we calculated $\langle (x_1-x_2)^2\rangle$ ie the rms distance between the two particles

$$\langle \psi_1 (x_1-x_2)^2 \psi_1\rangle = .148\,a^2$$

$$\langle \psi_2 (x_1-x_2)^2 \psi_2\rangle = .073\,a^2$$ ← symmetric ⇒ closer together

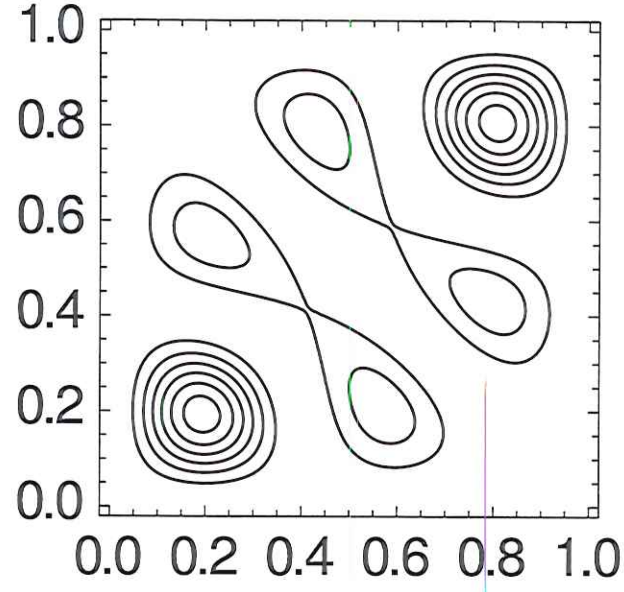
$$\langle \psi_3 (x_1-x_2)^2 \psi_3\rangle = .224\,a^2$$ ← antisymmetric ⇒ further apart

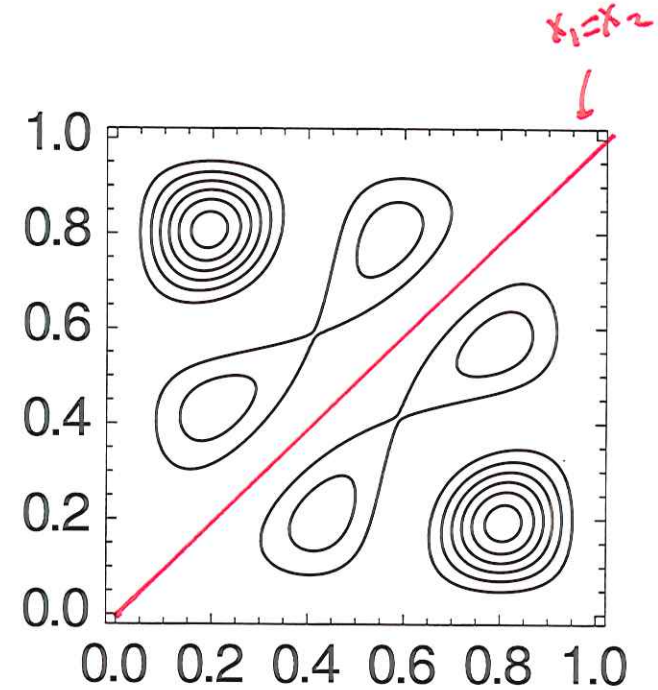
Contour Plot of $n=2$ $l=3$ two particles in infinite square well $a=1$



distinguished particles pay no attention to $x_1=x_2$ line — the locations are independent

symmetric state — bosons pile up on the $x_1=x_2$ line — likely to be together





antisymmetric — fermions have <u>zero</u> chance of having $x_1=x_2$ — likely to be far apart

Claim (to be justified in next chapter)

We can estimate the effect of interaction between identical particles by finding $\langle \Psi | V_{int} | \Psi \rangle$

For electrons in atom $V_{int} = \dfrac{+e^2}{4\pi\varepsilon_0 \underbrace{|\vec{r}_1 - \vec{r}_2|}_{\text{the actual 3d separation between particles}}}$

repulsive so +

Case of Z electrons, one nucleus with Z protons

eg He (but also H^-, Li^+, Be^{++}, etc)

$$H = \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_1}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{1}{r_2}\right) + \left(\frac{1}{Z}\frac{1}{|\vec{r}_1 - \vec{r}_2|}\right)$$

Note: this is in dimensionless coordinates where length is in terms of $\frac{\text{Bohr radius}}{Z}$ & energy

Z^2 $\underbrace{\text{hartree}}_{27.2\,eV}$

if we ignore the interaction term the energy is $E = -\frac{1}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$ with wave function

$$\Psi_{n_1 l_1 m_1}(\vec{r}_1)\,\Psi_{n_2 l_2 m_2}(\vec{r}_2)$$

(note that the energy does not depend on l & m)

we consider excited states of the form: 1s2s
1s2p

ie one electron remains in ground state
the other electron is in one of the n=2 states.

In the end we consider 4 excited states

- spacially symmetric states (to be paired with antisymmetric spin states) — singlet

$1s(r_1)2s(r_2) + 1s(r_2)2s(r_1)$ → singlet s

$1s(r_1)2p(r_2) + 1s(r_2)2p(r_1)$ → singlet p

- specially antisymmetric states (to be paired with symmetric spin states) — triplet

$1s(r_1)2s(r_2) - 1s(r_2)2s(r_1)$ → triplet s

$1s(r_1)2p(r_2) - 1s(r_2)2p(r_1)$ → triplet p

the integrals ($\langle\psi| \frac{1}{|\vec{r}_1 - \vec{r}_2|} |\psi\rangle$) are hard to do

see H.06.html & H.07.html .. Results

$-.495$ —— 1s2p

$-.509$ —— 1s2s

singlet 1s2p —— $-.512$

~~triplet~~

1s2s —— $-.531$

triplet

Those results are not super accurate. Generally the splittings are about 2x too big & order incorrect: singlet 1s2s below triplet 1s2p

On this too slim basis we proclaim Hunds Rule #1: the state with max spin (here triplet) has lower energy ... Reason: max spin symmetry ⇒ lots of antisymmetry in space ⇒ $|\vec{r}_1 - \vec{r}_2|$ big ⇒ small electron-electron interaction

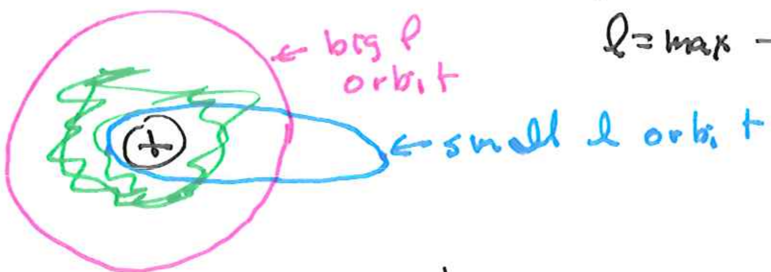
For a 1 electron atom (eg H, He^+, Li^{++}, ...)
the energy depends only on n (not l m)

$$E = -\frac{13.6\,eV\,Z^2}{n^2} = -\frac{1}{2}\frac{Z^2}{n^2}\ \text{hartree}$$

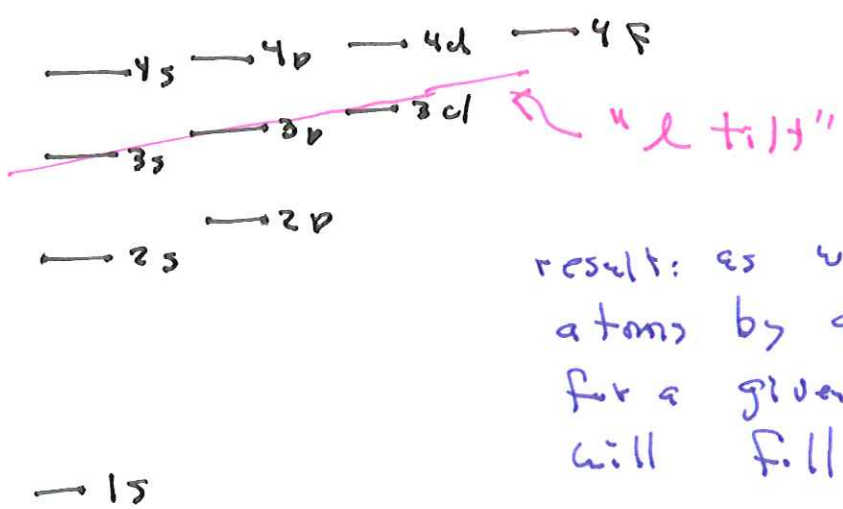
In a multi electron atom an outer electron
sees

The effective charge it sees is reduced.

Now classically $n \to$ semi major axis
$l \to$ angular momentum
$l=0 \to$ in-out comet orbits
$l = \max \to$ circular orbits



These two orbits have same semi major axis (n)
but small l orbit "see thru" the electron
cloud to experience the full pull of nucleus
$\to$ result: given same n, small l is lower energy



result: as we build up ("Aufbau")
atoms by adding electrons
for a given n, small l
will fill first.