

Today:

I. Last Monday

II. Identical Fermions and the Structure of the Periodic Table

I. Last time

- * Symmetrization in general. Defined the exchange operator and found that it had eigenvalues ± 1 , and also found that commuted with the Hamiltonian, hence symmetrized and anti-symmetrize states are preserved under time evolution.
- * We also introduced the Z particle Hamiltonian for Z electrons in Coulomb interaction with a atomic number Z nucleus and with each other...

I. Two particle wave functions in general

The complete state of an electron puts together both the spatial dependence and the spin of the electron:

$$\psi(\vec{r})\chi.$$

What happens when we put two particles together?

$$\psi(\vec{r}_1, \vec{r}_2)\chi(1,2).$$

The symmetrization (or anti-sym.) axiom of quantum mechanics says that it is the *whole* wave function that has a definite symmetry type; e.g., for a fermion

$$\psi(\vec{r}_1, \vec{r}_2)\chi(1,2) = -\psi(\vec{r}_2, \vec{r}_1)\chi(2,1).$$

This means that we have to consider the full wave function when we are thinking about symmetrization.

The Pauli exclusion principle states that two fermions (e.g. electrons) cannot occupy the same state.

I. Two particle wave functions in general

The **symmetrization axiom** states that not only do identical particles maintain their symmetrization, but they are required to be in such a state: $|(1,2)\rangle = \pm |(2,1)\rangle$.

This is also true for n identical particles, they generally satisfy $|(1,2,\dots,i,\dots,j,\dots,n)\rangle = \pm |(1,2,\dots,j,\dots,i,\dots,n)\rangle$.

I. Atoms

All we'll do today is to write down the Hamiltonian and look at it.:

$$\hat{H} = \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right\} + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^Z \frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

II. Identical Fermions and the Structure of the Periodic Table

Today we're going to study what we can say about the periodic table by looking at the truncated Hamiltonian

$$\hat{H} = \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right\}.$$

This leads us to treat each of the electrons as if it were in a hydrogen state wave function $\psi_{n\ell m}$, where n tells us the energy of the state, ℓ the orbital angular momentum, and m the z -component of the orbital angular momentum. This is a decent approximation. We combine this with the spin state of the electrons; we will treat the electrons two at a time, because Pauli exclusion says that the electrons can't occupy the same total state, but they can occupy the same spatial state as long as they have different spin states. This leads us back to the two particle spin states...

II. Identical Fermions and the Structure of the Periodic Table

This leads us back to the two particle spin states...

$$|0\ 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), \quad \text{singlet state}$$

and

$$|1\ m\rangle = \begin{cases} |\uparrow\uparrow\rangle, m = 1 \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), m = 0, \\ |\downarrow\downarrow\rangle, m = -1 \end{cases} \quad \text{triplet states.}$$

When the electrons are in the singlet state we call it bonding and in the triplet state it's anti-bonding. The hydrogenic wave functions are called orbitals. And their sermonic nature forces us to fill orbitals in an interesting way. What is the degeneracy of a fixed energy level n ?

$$\sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} 1 = \sum_{\ell=0}^{n-1} (2\ell + 1) = 2 \frac{(n-1)n}{2} + n = n^2.$$

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Each of these levels can accept two electrons (we often say one spin up and one spin down, but that's not really true) in a singlet state. So each shell has

$$\begin{cases} n = 1 & 2 \text{ elec.} \\ n = 2 & 8 \text{ elec.} \\ n = 3 & 18 \text{ elec.} \\ \dots & \\ n & 2n^2 \text{ elec.} \end{cases}$$

Nomenclature:

$$\begin{cases} \ell = 0 & \text{"s" for sharp} \\ \ell = 1 & \text{"p" for principle} \\ \ell = 2 & \text{"d" for diffuse} \\ \ell = 3 & \text{"f" for fundamental} \end{cases}$$

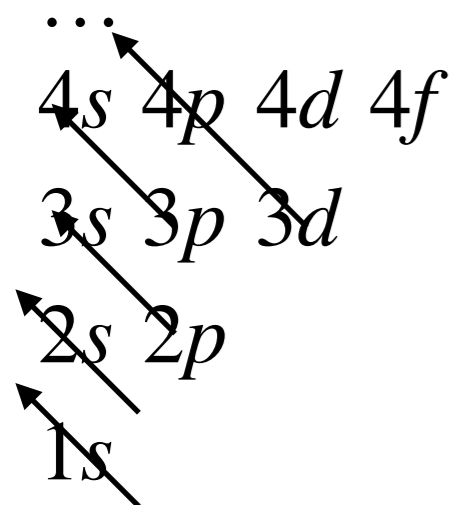
II. Identical Fermions and the Structure of the Periodic Table

Nomenclature:

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from there they go alphabetically (you skip j)

As we noticed the rows of the periodic table don't perfectly correspond to the shells (n). A rule of thumb for filling the orbitals is the so-called Aufbau principle



The 1s state can accept two electrons and we write $\text{He} = (1s)^2$.

II. Identical Fermions and the Structure of the Periodic Table

The $1s$ state can accept two electrons and we write $\text{He} = (1s)^2$. Let's do Carbon, $\text{C} = (1s)^2(2s)^2(2p)^2$. How about Neon?

$\text{Ne} = \text{He}(2s)^2(2p)^6$. What about Calcium? $\text{Ca} = \text{Ar}(4s)^2$. If we wanted to keep studying this structure in more detail we would go towards Hund's rules, which tell us the lowest energy way to fill the shells with electrons. There is another piece of spectroscopic notation that you should study before taking the Physics GRE:

$$^{2S+1}L_J.$$

Further structure of periodic table: 0

Entanglement (in general: 3, EPR paradox: 3)

Density Matrices: 2

II. G&S Problem 4.47

The Hamiltonian is

$$\hat{H}(r, \theta, \phi) = -\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}m\omega^2 r^2 \quad (\text{isotropic oscillator}).$$

Working in spherical coordinates

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell}^m(\theta, \phi).$$

The radial wave equation is

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{1}{2}m\omega^2 r^2 + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} \right] u = Eu,$$

where $u = rR(r)$. This is the equation we want to solve. We can attempt a power series solution. First make it homogeneous, next find unitless variables to make as clean as possible, finally strip off the asymptotic behavior. This would allow us to write

$$u(r) = f_{a1}f_{a2}v(r).$$

II. G&S Problem 4.47

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[\frac{1}{2} m \omega^2 r^2 + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} - E \right] u = 0$$

Unitless variables: $\xi = \sqrt{\frac{m\omega}{\hbar}} r = \sqrt{\frac{m\omega^2 r^2}{\omega\hbar}}$ and $r^2 = \frac{\hbar}{m\omega} \xi^2$. The

chain rule gives

$$\frac{du}{dr} = \frac{du}{d\xi} \frac{d\xi}{dr} = \sqrt{\frac{m\omega}{\hbar}} \frac{du}{d\xi},$$

$$\frac{d^2 u}{dr^2} = \frac{m\omega}{\hbar} \frac{d^2 u}{d\xi^2},$$

So finally

$$-\frac{\hbar^2}{2m} \frac{m\omega}{\hbar} \frac{d^2 u}{d\xi^2} + \left[\frac{1}{2} m \omega^2 \frac{\hbar}{m\omega} \xi^2 + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{\frac{\hbar}{m\omega} \xi^2} - E \right] u = 0$$

II. G&S Problem 4.47

So finally

$$-\frac{d^2u}{d\xi^2} + \left[\xi^2 + \frac{\ell(\ell+1)}{\xi^2} - K \right] u = 0, \text{ where } K = \frac{2E}{\hbar\omega}. \text{ We're going to}$$

try and use the power series method of solution. To find the

asymptotic behavior we consider the limits $\xi \rightarrow 0$ and $\xi \rightarrow \infty$. In the

$\xi \rightarrow 0$ case

$$\frac{d^2u}{d\xi^2} = \frac{\ell(\ell+1)}{\xi^2}u, \quad \text{with solution } u \sim \xi^{\ell+1}. \text{ In the other limit we have}$$

$$\frac{d^2u}{d\xi^2} = \xi^2u, \quad \text{with solution } u \sim e^{-\xi^2/2}. \text{ Now we've found the asymptotic}$$

behavior and can write $u(\xi) = \xi^{\ell+1}e^{-\xi^2/2}v(\xi)$. Good exercise

$$\frac{d^2v}{d\xi^2} + 2\frac{dv}{d\xi} \left(\frac{\ell+1}{\xi} - \xi \right) + (K - 2\ell - 3)v = 0. \text{ What's next? Guess}$$

that $v(\xi)$ has the form $v(\xi) = \sum_{j=0}^{\infty} a_j \xi^j$. Next compute derivatives of...

II. G&S Problem 4.47

Good exercise

$$\frac{d^2v}{d\xi^2} + 2\frac{dv}{d\xi} \left(\frac{\ell + 1}{\xi} - \xi \right) + (K - 2\ell - 3)v = 0. \text{ What's next? Guess}$$

that $v(\xi)$ has the form $v(\xi) = \sum_{j=0}^{\infty} a_j \xi^j$. Next compute derivatives of v :

$$v' = \sum_{j=0}^{\infty} j a_j \xi^{j-1} \quad \text{and} \quad v'' = \sum_{j=0}^{\infty} j(j-1) a_j \xi^{j-2}. \text{ Then our equation}$$

becomes

$$\sum_{j=0}^{\infty} j(j-1) a_j \xi^{j-2} + 2(\ell + 1) \sum_{j=0}^{\infty} j a_j \xi^{j-2} - 2 \sum_{j=0}^{\infty} j a_j \xi^j + (K - 2\ell - 3) \sum_{j=0}^{\infty} a_j \xi^j = 0$$

Or upon re-indexing

$$\sum_{j=0}^{\infty} (j+2)(j+1) a_{j+2} \xi^j + 2(\ell + 1) \sum_{j=0}^{\infty} (j+2) a_{j+2} \xi^j - 2 \sum_{j=0}^{\infty} j a_j \xi^j + (K - 2\ell - 3) \sum_{j=0}^{\infty} a_j \xi^j = 0$$

To make my indexing of the 2nd sum correct, I force $a_1 = 0$.