

The Pauli-Exclusion Principle

Disclaimer: These lecture notes are not meant to replace the course textbook. The content may be incomplete. Some topics may be unclear. These notes are only meant to be a study aid and a supplement to your own notes. Please report any inaccuracies to the professor.

Indistinguishability

Objects are distinguished by color, size, shape, mass, etc. But how do you distinguish one electron from another? Each has the same mass and same electric charge. One might have spin up, and another spin down, but all spin-up electrons are *identical*. If you have seen one electron, you have seen them all!

▷ Elementary particles are indistinguishable

Now, Quantum Mechanics tells us that if you *cannot* distinguish between two possibilities, that the probability amplitudes add:

$$\mathbf{y} = \mathbf{y}_1 + \mathbf{y}_2$$

$$P = |\mathbf{y}|^2 = |\mathbf{y}_1 + \mathbf{y}_2|^2 = |\mathbf{y}_1|^2 + |\mathbf{y}_2|^2 + 2\mathbf{y}_1^* \mathbf{y}_2$$

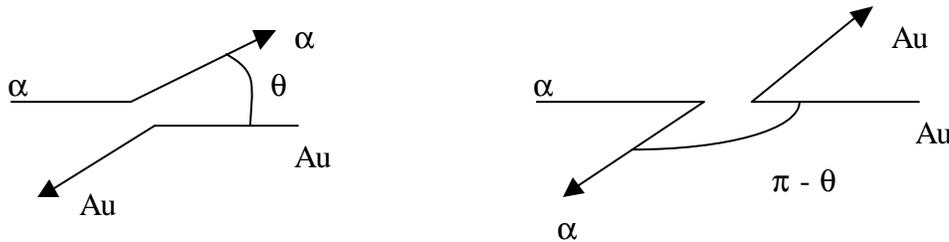
$$P = P_1 + P_2 + \text{interference term}$$

Thus, the overall probability is the sum of the probability of each possibility separately *plus* an interference term. For example, in a double slit experiment, if we cannot distinguish whether a photon (or electron) goes through slit 1 or slit 2, then an interference pattern is observed on a distant screen. But if we put detectors on each slit so that we can observe which path the particle takes, then the interference pattern is lost. That is, when we *can* distinguish between the two possibilities, the combined probability is just the classical expectation:

$$P = P_1 + P_2$$

This bizarre behavior is at the heart of Quantum Mechanics and the uncertainty principle in particular.

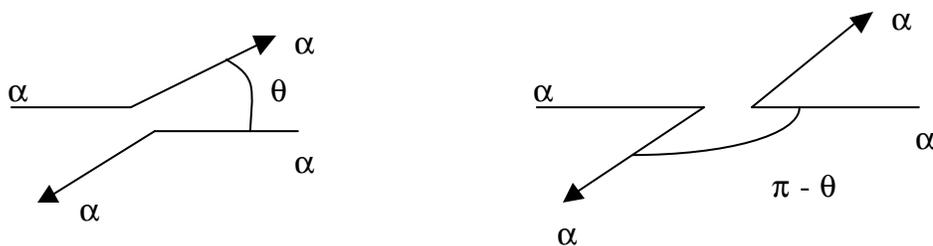
Now let's apply this rule to the scattering of distinguishable and indistinguishable particles. Consider Rutherford scattering of α -particles off gold nuclei.



The two possibilities are easily distinguished from one another because we can tell the difference between an α -particle and a gold nucleus. The scattering rate is given by the Rutherford formula, and it depends on the scattering angle:

$$\text{Rate} \propto |f(\mathbf{q})|^2 \propto \frac{1}{\sin^4 \mathbf{q}/2}$$

But what about the scattering between two α -particles?



All you can detect is the outgoing particles, which are indistinguishable. The uncertainty principle prevents us from knowing what is going on at the collision vertex. If we tried to observe which reaction took place, we would disturb the reaction so that it didn't take place! Another way of saying this is that the wavefunctions overlap at the vertex.

So, we cannot know which possibility took place for the given set of angles. Thus, Quantum Mechanics says that we must add the two scattering amplitudes:

$$\text{Rate} \propto |f(\mathbf{q}) + f(\mathbf{p} - \mathbf{q})|^2 \neq |f(\mathbf{q})|^2$$

In other words, the scattering of identical particles (α - α) gives a different rate (and even a different angular dependence) than for distinguishable particles (α -Au) aside from just the different atomic numbers Z .

This has been confirmed experimentally many times!

It is another example of Quantum Mechanics predicting something different than we expect classically.

We run into the same sort of indistinguishable possibilities when we try to describe the wavefunction for the helium atom, which has two electrons bound to the nucleus. The wavefunction should describe the probable locations for electron 1 and electron 2.

$$\mathcal{Y}_{12} = \mathcal{Y}_1(\mathbf{x}_1)\mathcal{Y}_2(\mathbf{x}_2)$$

where $\mathcal{Y}_i = R_{n\ell}(r_i)Y_{\ell m}(\mathbf{q}_i, \mathbf{f}_i)$ assuming hydrogen orbitals for the moment

This wavefunction describes electron 1 at position \mathbf{x}_1 and electron 2 at position \mathbf{x}_2 . But this cannot be distinguished from the case where electron 2 is position \mathbf{x}_1 and electron 1 is at position \mathbf{x}_2 :

$$\mathcal{Y}_{21} = \mathcal{Y}_2(\mathbf{x}_1)\mathcal{Y}_1(\mathbf{x}_2)$$

The two possibilities are drawn schematically below:



Again, if we cannot distinguish between two possibilities, the rule in Quantum Mechanics says that we must “add” both possibilities:

$$\mathcal{Y} = \mathcal{Y}_{12} + \mathcal{Y}_{21}$$

We say that the wavefunction should be symmetric in particle indices. Now, Nature has one more twist in store for us! It turns out that we could also have *subtracted* the two wavefunctions rather than added them. The only thing that would change is the sign of the interference term, but interference would still occur.

It turns out that both cases (adding or subtracting probability amplitudes) occur in Nature, and the rule for selecting which case depends on the particle spin.

Bosons:

If the identical particles involved have integral spin ($s = 0, 1, 2, \dots$), then the rule for adding probability amplitudes is:

$$\begin{aligned} \mathbf{y} &= \mathbf{y}_{12} + \mathbf{y}_{21} \\ P &= |\mathbf{y}|^2 = |\mathbf{y}_{12}|^2 + |\mathbf{y}_{21}|^2 + 2\mathbf{y}_{12}^* \mathbf{y}_{21} \end{aligned}$$

Another way of stating the rule is that the wavefunction must be *symmetric* under particle interchange:

$$\mathbf{y}(\mathbf{x}_1, \mathbf{x}_2) = \mathbf{y}(\mathbf{x}_2, \mathbf{x}_1)$$

The statistics of integral spin particles were studied by Satyendra Nath Bose, and thus such particles are referred to as *bosons*.

Fermions:

If the identical particles involved have half-integral spin ($s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$), then the rule for “adding” probability amplitudes is to subtract them:

$$\begin{aligned} \mathbf{y} &= \mathbf{y}_{12} - \mathbf{y}_{21} \\ P &= |\mathbf{y}|^2 = |\mathbf{y}_{12}|^2 + |\mathbf{y}_{21}|^2 - 2\mathbf{y}_{12}^* \mathbf{y}_{21} \end{aligned}$$

Another way of stating the rule is that the wavefunction must be *anti-symmetric* under particle interchange:

$$\mathbf{y}(\mathbf{x}_1, \mathbf{x}_2) = -\mathbf{y}(\mathbf{x}_2, \mathbf{x}_1)$$

The statistics of half-integral spin particles were studied by Enrico Fermi, and thus such particles are referred to as *fermions*.

Example: Let's consider again helium. We know that electrons have spin 1/2, so they are fermions. The wavefunction describing both electrons must therefore be anti-symmetric. Suppose both electrons have the same spin orientation (say spin-up). Then the spatial part of the wavefunction satisfies: $\mathbf{y}(\mathbf{x}_1, \mathbf{x}_2) = -\mathbf{y}(\mathbf{x}_2, \mathbf{x}_1)$

What happens if $\mathbf{x}_1 = \mathbf{x}_2$? The only solution is $\mathbf{y} = 0$. There is zero probability for two electrons to be in the same location.

Pauli-Exclusion Principle

No two fermions with the same spin may occupy the same position in space. In the context of multi-electron atoms, no two electrons in an atom may have the same set of quantum numbers: n, ℓ, m_ℓ, m_s

If we assume that the electrons are in hydrogen-like orbitals, then the wavefunction is anti-symmetric:

$$\Psi = R_{n\ell}(r_1)Y_{\ell m}(\mathbf{q}_1, \mathbf{f}_1)R_{n'\ell'}(r_2)Y_{\ell' m'}(\mathbf{q}_2, \mathbf{f}_2) - R_{n\ell}(r_2)Y_{\ell m}(\mathbf{q}_2, \mathbf{f}_2)R_{n'\ell'}(r_1)Y_{\ell' m'}(\mathbf{q}_1, \mathbf{f}_1)$$

when both sets of quantum numbers are the same, the overall wavefunction is obviously zero.

This is an important fundamental result, and it comes from a deep connection between identical particles and spin. This principle, as we will see, is responsible for atomic structure (and thus all of chemistry!) and nuclear structure. However, the Pauli-Exclusion Principle only applies to fermions. If the particles are bosons (integral spin) then they are not affected. You can put as many bosons in the same state as you like.

Atomic Structure

The Schrodinger Equation in principle can be used to solve exactly for the wavefunction and energy levels of multi-electron atoms (helium and beyond), something the Bohr model could not do. In practice, the equations cannot be solved exactly. The reason is that this is a *many-body* problem, and the mathematics are very difficult.

To illustrate the point, consider helium. The potential energy can be written:

$$V = \frac{-Ze^2}{4\pi\epsilon_0 r_1} + \frac{-Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|}$$

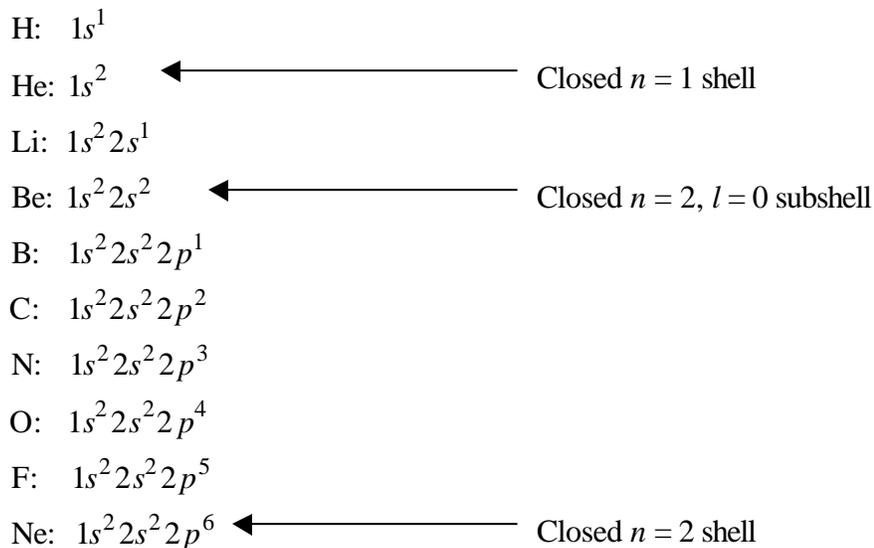
The last term from the Coulomb repulsion of the two electrons makes the separation of variables technique to solve the Schrodinger Equation impossible. However, if we could neglect this term, then the solutions are already known! They are just the hydrogen orbitals (one for each electron). The overall solution would just be the anti-symmetric combination of hydrogen orbitals.

Thus, we can obtain an approximate solution and learn a lot about atomic structure if we just neglect electron repulsion compared to the nuclear attraction. The ground state solution is approximated by filling hydrogen orbitals with electrons starting with the lowest available, but taking into consideration the Pauli-Exclusion principle.

So for **helium** ($Z = 2$), if you want both electrons in the ground state ($n = 1, \ell = 0$), one electron must have spin-up and the other spin-down.

For **lithium** ($Z = 3$), the third electron must go into the first excited state of the hydrogen atom ($n = 2, \ell = 0$)

Continuing on in this way, we find the following atomic structure:



Atoms with closed subshells tend to be more tightly bound (and more chemically inert) than atoms with valence electrons (electrons in outer subshell). In fact, those atoms with similar chemical properties have the same valence structure. Thus, we can derive the organization of the Periodic Table (first written down by Dmitri Mendeleev in 1869) based on the solution to the Schrodinger Equation coupled with the Pauli-Exclusion principle.

Groups:

- Similar chemical properties, same valence structure:
- inert gases (closed subshell),
- alkalis (one outer valence electron),
- halogens (lack one electron from closed subshell)

Periods:

Filling of subshells

Group

Period

PERIODIC TABLE OF THE ELEMENTS																			
1 IA																	18 VIII		
1 H Hydrogen 1.00794	2 He Helium 4.002602																		
3 Li Lithium 6.941	4 Be Beryllium 9.012182	5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797											17 Cl Chlorine 35.4527	18 Ar Argon 39.948
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050	13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosph. 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948											17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge German. 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80		
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybd. 95.94	43 Tc Technet. 97.907215	44 Ru Ruthen. 101.07	45 Rh Rhenium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29		
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (208.982415)	85 At Astatine (209.987131)	86 Rn Radon (222.017570)		
87 Fr Francium (223.019731)	88 Ra Radium (226.025402)	89-103 Actinides	104 Rf Rutherford. (261.1089)	105 Db Dubnium (262.1144)	106 Sg Seaborg. (263.1186)	107 Bh Bohrium (262.1231)	108 Hs Hassium (265.1306)	109 Mt Meitner. (266.1378)	110	111 (272)	112 (277)	114 (289)	116 (289)			118 (293)			
Lanthanide series		57 La Lanthan. 138.9055	58 Ce Cerium 140.116	59 Pr Praseodym. 140.90765	60 Nd Neodym. 144.24	61 Pm Prometh. (144.912745)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolin. 157.25	65 Tb Terbium 158.92534	66 Dy Dyspros. 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967			
Actinide series		89 Ac Actinium (227.027747)	90 Th Thorium 232.0381	91 Pa Protactin. 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237.048166)	94 Pu Plutonium (244.064197)	95 Am Americ. (243.061372)	96 Cm Curium (247.070346)	97 Bk Berkelium (247.070298)	98 Cf Californ. (251.079579)	99 Es Einstein. (252.08297)	100 Fm Fermium (257.095096)	101 Md Mendelev. (258.098427)	102 No Nobelium (259.1011)	103 Lr Lawrenc. (262.1098)			