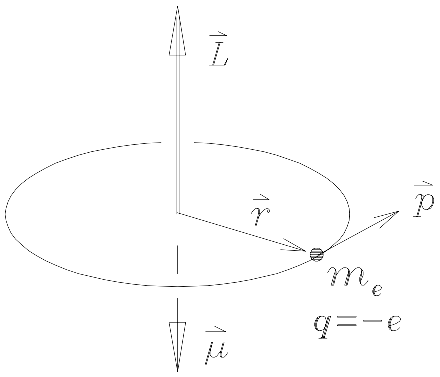
SPIN

One of the most mysterious yet simple aspects of quantum mechanics ($\mathcal{QM}$) is the behaviour of ANGULAR MOMENTUM, both of the familiar "orbital" variety and of the "intrinsic" variety called SPIN. The latter type has a copyright on the term "spin" in the language of Physics; even though in more colloquial usage "spin" is just another name for angular momentum, in Physics it has a special meaning. But before we can make that distinction, we must first remind ourselves of the definition and behaviour of angular momentum and see how it is tied to the MAGNETIC MOMENT of a charged particle.

1 Orbital Angular Momentum



A particle of mass m in a circular orbit of radius r has an angular momentum $\vec{\mathbf{L}} = \vec{\mathbf{r}} \times \vec{\mathbf{p}}$, where $\vec{\mathbf{p}} = m\vec{\mathbf{v}}$ (in the nonrelativistic limit) is the particle's momentum. Although $\vec{\mathbf{r}}$ and $\vec{\mathbf{p}}$ are constantly changing direction, $\vec{\mathbf{L}}$ is a constant in the absence of any *torques* on the system. If the particle happens to carry an *electric charge* as well as a mass (the case shown being an *electron* with mass m_e and charge $-e$) then the circulation of that charge constitutes a *current loop* which in turn generates a MAGNETIC MOMENT $\vec{\mu}$ which is inextricably "locked" to the angular momentum: $\vec{\mu} = -\mu_B \vec{\mathbf{L}}/\hbar$, where $\mu_B \equiv e\hbar/2m_e = 9.2741 \times 10^{-24}\ J/T$ is the BOHR MAGNETON for the case of the electron orbit. Because the potential energy of a magnetic dipole moment $\vec{\mu}$ in a uniform magnetic field $\vec{\mathbf{B}}$ is given by $V_B = -\vec{\mu}\cdot\vec{\mathbf{B}}$, the orientation of the orbit in a magnetic field determines the contribution of its magnetic interaction to the total energy of the state: $E_B = (\mu_B/\hbar)\vec{\mathbf{L}}\cdot\vec{\mathbf{B}}$. This contribution is much smaller than the difference between "shells" with different principle quantum numbers n, and so it is called "FINE STRUCTURE" in atomic spectroscopy.

1.1 Back to Bohr

One of Niels Bohr's main contributions to Physics was his assertion (backed up by experiment) that *angular momentum is quantized* — it can only occur in integer multiples of $\hbar$. Erwin Schrödinger showed why this was true for the wave functions of the hydrogen atom, but by that time Bohr's principle had been elevated to an empirical "law" of Physics that went well beyond the realm of atoms. Schrödinger also showed the peculiar nature of the quantization of $\vec{\mathbf{L}}$: first, its *magnitude* obeys $|\vec{\mathbf{L}}| = \hbar\sqrt{\ell(\ell+1)}$ where ℓ can only have integer values from zero to $(n-1)$, n being the PRINCIPLE QUANTUM NUMBER for which $E_n = -E_\circ/n^2$ in the case of hydrogen; second, its *projection* onto the z axis obeys $L_z = m_\ell \hbar$ where m_ℓ can take on only integer values from $-\ell$ to $+\ell$. Note that Bohr's original prescription for angular momentum quantization (integer multiples of $\hbar$) is actually applicable to the *z component* of $\vec{\mathbf{L}}$ — its projection onto the *z quantization axis*, which is chosen arbitrarily unless there is a magnetic field applied, in which case $\hat{z}$ is always chosen *along the field*, $\vec{\mathbf{B}} = B\hat{z}$.

1.2 Magnetic Interactions

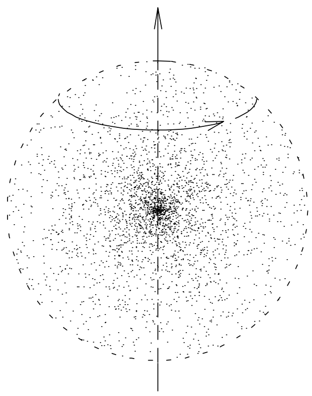
The reason m_ℓ is called the MAGNETIC QUANTUM NUMBER (and the reason m is used for it, rather than some other letter) is that when one imposes a *magnetic field* $\vec{\mathbf{B}}$ on an atom, the energy levels E_n (determined only by n in the absence of $\vec{\mathbf{B}}$) are "*split*" by the ZEEMAN ENERGY $E_B = \mu_B m_\ell B$ due to the interaction potential of the magnetic moment with the field (see above).

In 1925 Goudsmit and Uhlenbeck reported that, in addition to the "splittings" predicted by the quantization of the orbital angular momentum eigenstates of the electrons in an applied magnetic field, there were *additional* splittings of roughly the same magnitude that could only be explained in terms of some "extra" angular momentum associated with *the electrons themselves*. This was relevant to a previous result that had mystified the community:

In 1922, Stern and Gerlach had done an experiment on various neutral atoms passing through a region of large magnetic field *gradient*, the effect of which is to exert on the passing atoms a *net force* that is proportional to the component of their angular momentum along the axis of the gradient. This allowed Stern and Gerlach to experimentally verify that "spin 1" atoms (with $\ell = 1$) did indeed have three and only three possible values of $L_z = m_\ell \hbar$: $m_\ell = +1, 0$ or -1; and similarly for other integer ℓ. However, their experiments on neutral silver atoms revealed *two* possible projections of the angular momentum along the z axis, a range of options incompatible with the rules $\ell = 0, 1, \cdots (n-1)$ and $m_\ell = -\ell, \cdots 0 \cdots \ell$. The discoveries of Goudsmit and Uhlenbeck suggested that the electron itself might have an *intrinsic* angular momentum that was (somehow) *half* as large as the smallest allowable nonzero *orbital* angular momentum — what we now call "spin $\frac{1}{2}$."

2 Intrinsic Angular Momentum

The following description is bogus. That it, this is not "really" what intrinsic angular momentum is all about; but it is possible to understand it in "common sense" terms, so we can use it as a mnemonic technique. Many $\mathcal{QM}$ concepts are introduced *via* this sort of "cheating" until students get comfortable enough with them to define them rigourously. (The truth about SPIN, like much of $\mathcal{QM}$, can never be made to seem sensible; it can only be gotten used to!)



Imagine a big fuzzy ball of mass spinning about an axis. While you're at it, imagine some electric charge sprinkled in, a certain amount of charge for every little bit of mass. (If you like, you can think of a cloud of particles, each of which has the same charge-to-mass ratio, all orbiting about a common axis.) Each little mass element contributes a bit of angular momentum and a proportional bit of magnetic moment, so that $\vec{\mathbf{L}} = \sum \vec{\mathbf{r}} \times \vec{\mathbf{p}}$ (summed over all the mass elements) and, as for a single particle, $\vec{\mu} =(\text{constant})\times\vec{\mathbf{L}}$. If the charge-to-mass ratio happens to be the same as for an *electron*, then $(\text{constant}) = \mu_B$, the Bohr magneton.

Now imagine that, like a figure skater pulling in her/his arms to spin faster, the little bits of charge and mass collapse together, making r smaller everywhere. To conserve angular momentum (which is *always* conserved!) the momentum p has to get bigger — the bits must spin faster. The relationship between L and μ is such that μ also remains constant as this happens.

Eventually the constituents can shrink down to a *point* spinning infinitely fast. Obviously we get into a bit of trouble here with both relativity and quantum mechanics; nevertheless, this is (sort of) how we think (privately) of an *electron*: although we have never been able to find any evidence for "bits" within an electron, we are able to rationalize its possession of an *irreducible, intrinsic angular momentum* (or "SPIN") in this way.

Such *intrinsic* angular momentum is a *property of the particle itself* as well as a dynamical variable that behaves just like orbital angular momentum. It is given a special label ($\vec{\mathbf{S}}$ instead of $\vec{\mathbf{L}}$) just to emphasize its difference. Like $\vec{\mathbf{L}}$, it is *quantized* — *i.e.* it only comes integer multiples of a fundamental quantum of intrinsic angular momentum — but (here comes the weird part!) that quantum can be either $\hbar$, as for $\vec{\mathbf{L}}$, or $\frac{1}{2}\hbar$!

In the following, s is the "spin quantum number" analogous to the "orbital quantum number" ℓ such that the spin angular momentum $\vec{\mathbf{S}}$ has a magnitude $|\vec{\mathbf{S}}| = \hbar\sqrt{s(s+1)}$ and a z component $S_z = m_s\hbar$ where $\hat{z}$ is the chosen spin quantization axis. The magnetic quantum number for spin $\frac{1}{2}$ has only two possible values, spin "up" ($m_s = +\frac{1}{2}$) and spin "down" ($m_s = -\frac{1}{2}$). This is the explanation of the Stern-Gerlach result for silver atoms: with no orbital angular momentum at all, the Ag atoms have a single "extra" electron whose spin determines their overall angular momentum and magnetic moment.

3 Identical Particles: the Platonic Ideal lives!

Plato taught something along these lines: every "real" chair is merely an "imprint" of (or an imperfect approximation to) a single "ideal" chair. Similarly for tables, glasses and certainly for the wine in the glass!

As things turned out, when it came to elementary particles Plato didn't go quite far enough. When physicists talk of "*The* electron..." or "*The* neutron..." they are not referring to one particular electron or neutron; they are expressing their (experimentally verified) belief that *every electron is exactly identical* to every other electron! Not just very similar, but *indistinguishable even in principle*. That is, every electron is a *perfect* "imprint" of the "ideal" electron — it *is*, in fact, the ideal electron! This is true of *all* elementary particles, and in QUANTUM FIELD THEORY reaches its ultimate expression: the *number* of (*e.g.*) electrons in existence is just another "quantum number" of the unique and solitary "electron *field*." All evidence suggests that this description is "true" — *i.e.* it predicts what is observed, and its negation would predict things that are not observed.

3.1 Spin and Statistics

What are some of these predictions? Probably the most unambiguous example is the dramatic effect of the indistinguishable nature of the particles on *scattering probabilities*. However, another example was historically more important and is more obviously essential to the qualitative properties of our universe. This has to do with ATOMIC PHYSICS and the PAULI EXCLUSION PRINCIPLE for electrons. Said principle was actually surmised from atomic physics data in the first place, and was later proved mathematically. We will simply state it.

3.1.1 BOSONS

All elementary particles with *integer spin* ($s = 0, 1, 2, 3, \cdots$) are called BOSONS because they obey BOSE-EINSTEIN STATISTICS — namely, *an unlimited number of identical bosons can be in exactly the same state*. (Here "state" means that *all* properties are *fully specified*.) Examples of bosons are photons, ^{4}He atoms, pions, ...

3.1.2 FERMIONS

All elementary particles with *half-integer spin* ($s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$) are called FERMIONS because they obey FERMI-DIRAC STATISTICS — namely, *no two identical fermions can be in exactly the same quantum state*. (This rule includes the PAULI EXCLUSION PRINCIPLE, but it carries over into many other branches of physics.) Examples of fermions are electrons, protons, neutrons, muons, quarks, ...

The name FERMION honours Enrico Fermi, who (with Paul A.M. Dirac) described the special properties of this type of particles.

4 Chemistry and The Periodic Table

Let us consider the consequences of the PAULI EXCLUSION PRINCIPLE for the chemical properties of atoms: for each allowed wave funtion (or "orbital") of an electron in the Coulomb potential, fully specified by the quantum numbers (n, ℓ, m_ℓ), there are *two* (and *only* two) possible *spin* states for the electron: spin "up" ($m_s = +\frac{1}{2}$) and spin "down" ($m_s = -\frac{1}{2}$). Since the Pauli principle only excludes occupation of *exactly* the same state by two electrons, this means that *each orbital* may be occupied by at most *two* electrons; and if both electrons are present in that orbital, their spins are necessarily "paired" — equal and opposite in direction, thus perfectly cancelling each other and contributing nothing to the net angular momentum or magnetic moment.

Determining the chemical properties of the elements thus becomes a simple matter of *counting states*: for each "shell" (n) we see how many different orbitals there are with different values of ℓ and m_ℓ and then multiply by two for the two m_s possibilities to get the total number of electrons that will "fit" into that shell. Of course, this simple picture contains some crude approximations that we must expect to break down before things get very complicated, and they do. We assume, for example, that for a positive charge of $+Ze$ on the nucleus, each time we "add another electron" it goes into the lowest available (unfilled) energy state and effectively reduces the effective charge of the nucleus by one. That is, the first electron "sees" a positive charge of $+Ze$ but the second electron "sees" a positive charge of $+(Z-1)e$, and so on. This is not true, of course, for electrons in the same n shell; they all pretty much see the same apparent charge on the "core" of the atom (and see each others' charges as well). One important effect of such "screening" is that states of higher ℓ (whose wavefunctions do not penetrate as deeply into the core) "see" on average a lower effective charge on the core and therefore are slightly less bound (higher energy) than their low-ℓ neighbours. This provides the rule that (up to a point) lower ℓ states are filled first. A collection of states with the same n and ℓ is called a "subshell."

If we want to do this *right* for an arbitrary many-electron atom, we have several very difficult problems to solve: first, for large Z the innermost electrons have kinetic energies comparable to their rest mass energy; thus our nonrelativistic Schrödinger equation is inadequate and one must resort to more advanced descriptions. Second, the approximation that one shell simply "screens" part of the nucleus' charge from the next shell is not that great, especially for wavefunctions that have a significant probability density near the nucleus; moreover, electrons in the *same* shell definitely "see" each other and are affected by that interaction. One way of approaching this problem is to start with an *initial guess* based upon this approximation and then recalculate each electron wavefunction including the effects of the other electrons in their wavefunctions; then go back and correct again with the new guess as a starting point. Eventually this "Hartree-Fock" method should converge on the *actual* wavefunctions for all the electrons.... Finally, the coupling of orbital and spin angular momentum contributions can follow several possible scenarios, depending upon which couplings are the strongest; the final result must always be a single overall net angular momentum (and magnetic moment) for the atom as a whole; but for large atoms it is very difficult to predict even its magnitude; the only thing we can be sure of is that if there are an even number of electrons, protons and neutrons making up the atom, it will be a BOSON.

Having issued these *caveats*, we can go back to our "state counting":

- For each "shell" characterized by an energy E_n (starting at $n = 1$, where n is the PRINCIPLE QUANTUM NUMBER) we have n possible values of ℓ, ranging from $\ell = 0$ to $\ell = (n - 1)$.
- For each ORBITAL QUANTUM NUMBER ℓ, we have $2\ell + 1$ possible values of the MAGNETIC QUANTUM NUMBER m_ℓ, ranging from $m_\ell = -\ell$ to $m_\ell = +\ell$.
- For each orbital specified by (n, ℓ, m_ℓ), there are two possible values of m_s: spin up ($m_s = +\frac{1}{2}$) and spin down ($m_s = -\frac{1}{2}$).

Thus there are a total of $N_n = \sum_{\ell=0}^{n-1} 2(2\ell + 1)$ possible fully-specified states for electrons in the n^{th} energy shell. For the first shell, $N_1 = 2$; for the second shell, $N_2 = 8$.

Since (at least for small n) it is a long way (in energy) between shells, a "closed shell" is especially stable — it "likes" neither to give up an electron nor to acquire an extra one from another atom; it has "zero valence." This means an atom with $N_1 = 2$ electrons [helium] is very unreactive chemically, and so is one with $N_1 + N_2 = 10$ electrons [neon]. This goes on until the breakdown of our assumption that all the electrons for one shell are filled in before any electrons from the *next* shell. This breakdown comes at the $n = 3, \ell = 2$ subshell. Section 9.1 of the text provides all the details you need to explore the periodic table on your own; it also offers at least a qualitative explanation for the fact that the $n = 4, \ell = 0$ subshell is actually *lower* in energy than the $n = 3, \ell = 2$ subshell and therefore fills first, despite having a higher n. This is the point at which our simple qualitative rules break down and we must rely on empirical information to further understand the chemical properties of the elements.

4.1 Chemical Reactions

Two atoms can "react" chemically in either of two ways. In the IONIC reaction, one can give up an electron (becoming a positive ion or *cation* [so called because it is attracted to an electric *cat*hode]) to the other, which becomes a negative ion or *anion* [because it is attracted to an electric *an*ode]; the two oppositely charged ions are then attracted to each other by the Coulomb interaction but do not have to stay together — sort of like today's high school dances. When the two atoms can't decide which would rather be the donor or the receptor of electrons, they can form the ambiguous or COVALENT bond, in which they *share* one or more electrons; in this case everyone stays electrically neutral but no drifting away from one's partner is allowed.