Physics 228

Today:

Stern-Gerlach Experiment
Electron Spin
Zeeman Effect for Spins
Many Electron Atoms
Pauli Exclusion Principle
Periodic Table
Bonding
If the magnetic field is not constant, there will be a force on the atom \( F = -\nabla U = -m_l\mu_B(dB/dz) \).

An atom beam will separate into \( 2l+1 \) separate bunches if there is a \( B \) field with enough spatial variation.

This shows the quantization of the \( z \)-component of the magnetic moment, and by inference, the quantization of \( L_z \).
The Stern-Gerlach Experiment

- The number of "bunches" should be $2l+1$, therefore odd.
- This is observed for some atoms.
- However, in other cases an even number is seen.
- If we interpret this as angular momentum quantization, we require half-integer angular momentum quantum numbers $j = 1/2, 3/2, \text{etc.}$
- The number of sublevels $2j+1$ is then even.
Electron Spin

• This half-integral angular momentum also shows up in the Zeeman effect.
• Half-integral angular momentum is now understood as “spin” of the electron.
• Spin is an intrinsic angular momentum that the electrons always have, irrespective of orbital motion.
• For electrons, the magnitude of the spin angular momentum is
  \[ S = \sqrt{s(s + 1)}\hbar \] with \( s = \frac{1}{2} \) (spin quantum number).
• The z-component of the spin angular momentum is
  \[ S_z = m_s\hbar \] with \( m_s = \pm \frac{1}{2} \) (spin magnetic quantum number).
• For many particles (electrons, protons, neutrons, ...) \( s = \frac{1}{2} \). Such particles are called fermions.
• Other particles have integral spin (\( s = 0 \) for the Higgs boson, \( s = 1 \) for the photon). Such particles are called bosons.
Electron Spin Magnetic Moment

• For a classical spinning body of charge \(-e\) and mass \(m\) (assuming equal charge and mass distribution), we would expect a magnetic moment of \(\mu = (-e/2m)L\), where \(L\) would be replaced by the spin angular momentum \(S\).

• However, the electron is not a classical spinning body. Its magnetic moment is actually larger than expected classically:

\[
\mu = g(e/2m)S
\]

• The “quantum mechanics” factor \(g\) is called the “g-factor” (duh).

• Classical mechanics predicts \(g = -1\).

• Experimentally, \(g = -2.002319304361\) (the most precisely known fundamental constant in physics!!)

• Nonrelativistic QM (Schroedinger equation) makes no prediction at all. Spin has to be added in an ad-hoc manner (without derivation).

• Relativistic QM (Dirac equation) predicts \(g = -2\) (exactly).

• Another refinement of relativistic QM (quantum electrodynamics) predicts \(g = -2.002319304361\) (The most accurate theoretical prediction in physics!!)
As a result of spin, in each of the H-atom energy levels the electron can be "spin up" or "spin down". Thus, even for s-orbitals, the spin gives rise to a two-fold Zeeman splitting in a magnetic field.
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What is the magnitude of the spin angular momentum of an electron?

a) 0
b) $\hbar$
c) $\hbar/2$
d) $+\hbar/2$ or $-\hbar/2$, depending on whether spin is “up” or “down”
e) $\sqrt{\frac{3}{4}} \hbar$
Many Electron Atoms

In heavier atoms, the nucleus has charge $Ze$.

The electrons in orbit about the nucleus repel each other.

This leads to “screening” of outer electrons by inner electrons: The potential is no longer $1/r$.

As a consequence, the energy levels of different $l$ quantum numbers (same $n$) are no longer degenerate.

Accurate calculations are much more complicated than for hydrogen (“Coulomb correlations”).

On average, the $2s$ electron is considerably farther from the nucleus than the $1s$ electrons. Therefore, it experiences a net nuclear charge of approximately $+3e - 2e = +e$ (rather than $+3e$).
Pauli Exclusion Principle

- The Pauli exclusion principle states that each single-particle state (characterized by the four quantum numbers \( n, l, m_l, m_s \)) can accommodate no more than one electron.

- As a consequence, as we add electrons to an atom, the inner shells “fill up” first, then the more weakly bound shells will be populated. ("Aufbau principle").

- The Pauli exclusion principle applies to all half-integer spin particles, i.e., fermions (incl. protons and neutrons).

- There is no such principle for bosons. For example, a large number of photons may occupy the same quantum state in a laser.
Aufbau Principle

Periodic Table of the Elements
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<table>
<thead>
<tr>
<th>Period</th>
<th>Group</th>
<th>Elements</th>
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</thead>
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<tr>
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</tr>
</tbody>
</table>

- **s orbitals**: fill s orbitals (except He)
- **p orbitals**: fill p orbitals (except He)
- **d orbitals**: fill d orbitals
- **f orbitals**: fill f orbitals

Note: The subgroup numbers 1-18 were adopted in 1984 by the International Union of Pure and Applied Chemistry. The names of elements 112-118 are the Latin equivalents of their numbers.
According to the Pauli Exclusion Principle,

a) Any two elementary particles cannot be in the same quantum state.

b) Two electrons in an atom cannot have all the same quantum numbers.

c) Two photons cannot have the same quantum numbers.

d) Two electrons cannot be in the same energy level.

e) Two p-electrons cannot have the same magnetic quantum number.
According to the Aufbau principle, in which order do atomic levels become populated as we go to higher atomic numbers?

a) 3d 4s 4p
b) 4s 3d 4p
c) 4s 4p 3d
d) 3d 4p 4s
e) 4p 4s 3d
Bonding: Molecules and Crystals

Except for the noble gases, or at high temperatures, most atoms in nature are not found alone, but instead are bound into molecules, liquids, or solids.
Ionic Bonds

- Ionic bonds occur when an electron transfers from one atom to another. This takes energy, but the Coulomb attraction between the two charged atoms reduce the total energy to form a stable bond.

- For example, an atom with one more electron than a noble gas (filled shell) may donate its outermost electron to another atom with one electron less than a noble gas.

- In this way, we typically form a transparent, insulating crystal.
Covalent Bonds

In covalent bonds there is a hybrid electron orbital that results from the combined, separated charges of the two atomic nuclei.

Because of delocalization (uncertainty principle!) the molecular orbital has lower kinetic energy than the separated atomic orbitals would, resulting in bonding.

Hydrogen molecule $H_2$

Methane $CH_4$
Polar Molecules

- In many covalent molecules, the electron probability density is such that there is excess positive charge near one end, and negative charge near the other, forming an electric dipole.
- A good example is the water molecule.

- Whether a molecule is polar or not is determined by symmetry. For example, a molecule with inversion symmetry (such as ethane) cannot be polar, despite the individual bonds having polar character.
Van der Waals Forces

- At large separation, molecules (or atoms) exert a weak attractive force on each other.
- These “Van der Waals forces” come from orbiting electrons leading to fluctuating dipole moments, which, by dipole-dipole interactions, induce correlated dipoles in adjacent molecules.
- This may lead to weak bonds between molecules, typically with energies about 0.1 eV (rather than a few eV for covalent or ionic bonds).
- The vdW interaction is characterized by a long-range attractive potential that decays as $1/r^6$ with distance.

The graphene sheets in graphite are held together by vdW forces.
Which of the following is not correct:

a) In a covalent bond, some electrons are shared between atoms.
b) in an ionic bond, electrons are attracted to the nucleus of greater charge.
c) Van der Waals force is typically weak compared to ionic or covalent forces.
d) In an ionic bond, the bonding force is electrostatic in nature.
e) In a covalent bond, energy lowering is due to delocalization.