From Helium to the Periodic Table

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Lecture 27

What Have We Learned?

- The state of a quantum particle is represented by a wave function $\psi(\vec{r}, t)$.
- The probability of finding the particle somewhere at a particular time is proportional to $|\psi(\vec{r}, t)|^2$.
- The variables $\vec{r}$ and $\vec{p}$ cannot be measured simultaneously.
- The time evolution of the state $\psi(\vec{r}, t)$ is governed by the Schroedinger equation

$$i\hbar\frac{\partial \psi(\vec{r}, t)}{\partial t} = H(\vec{r}, \vec{p}, t)\psi(\vec{r}, t),$$

where H is known as the Hamiltonian.

- When the force in the corresponding classical problem is conserved, the Hamiltonian has a simple interpretation as the total energy $E = K + V$, where $K = p^2/2m$ is the kinetic energy and V the potential energy.
- When H is independent of time, the wave function can be separated to be $\psi(\vec{r}, t) = \phi(\vec{r})e^{-iEt/\hbar}$, which satisfies

$$H(\vec{r}, \vec{p})\phi(\vec{r}) = E\phi(\vec{r}).$$

- A particle in a potential trap is only allowed to have discrete energy levels. The particle can absorb light and gain energy or emit light and lose energy.
- Only photons whose energies (colors) match the "jump" in energy levels can be emitted or absorbed.

Outline

- The Pauli Exclusion Principle
- The Helium Atom
- The Periodic Table
- Wave Function Hybridization
- Helium-Neon Laser

The Pauli Exclusion Principle (1925)

- For multiple electrons in the same trap, we must consider the Pauli exclusion principle, named after Wolfgang Pauli.
- The Pauli principle states that no two electrons confined to the same trap can have the same set of values for their quantum numbers.
- In other words, there can be two electrons at most at any energy level; they have opposite spins.
- This principle applies not only to electrons but also to protons and neutrons, all of which have $s = 1/2$; they are known as **Fermions**.

- Consider electrons in an infinite square well with side length L [with $E_{n_1,n_2} = n_1^2 + n_2^2$, in units of $h^2/(8mL^2)$].
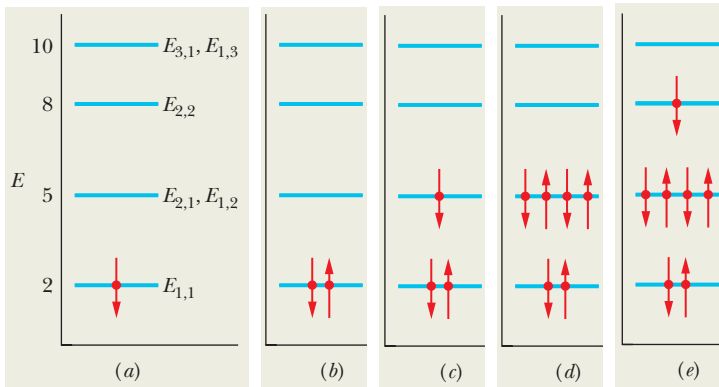
The Helium Atom

- The second simplest atom is the helium atom, which has two 1s electrons (spin up and spin down) in the Coulomb potential of the charge-2e nucleus that obey time-independent Schroedinger's equation of the form

$$(H_1 + H_2 + V_{12}) \Psi(\vec{r}_1, \vec{r}_2) = E\Psi(\vec{r}_1, \vec{r}_2),$$

where

$$H_i = -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{2e^2}{4\pi\epsilon_0 r_i},$$

$$V_{12} = \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|}.$$

- This is already too complex to solve exactly. So trying to solve Schroedinger's equation for a dozen electrons in a large atom is completely insane, unless you have, perhaps, a quantum computer or simulator.
- But this does not intimidate us to extract useful information about atoms from simplified models for qualitative and semi-quantitative understanding.
- An approximation starts from throwing away the interaction term, which we have not learned to deal with, i.e.,

$$(H_1 + H_2) \Psi_0 = E_0 \Psi_0,$$

- The ground state of either H_1 or H_2 has an energy $-4E_R$ and a wave function

$$\psi_{100}(\vec{r}) = \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_B}\right)^{3/2} e^{-2r/a_B}.$$

- One may verify that $\Psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)$ is an exact solution.

- The corresponding energy is

$$E_0 = -8E_R \approx -109 \text{ eV}.$$

- Now, we can assume that it is a good approximation of the helium ground state. We can then treat electron interaction as a correction to the ground state energy.
- The repulsion between the two $1s$ electrons,

$$\iint d\vec{r}_1 d\vec{r}_2 |\psi_{100}(\vec{r}_1)|^2 |\psi_{100}(\vec{r}_2)|^2 V_{12}(\vec{r}_1, \vec{r}_2),$$

can be approximated to be 34 eV; this is known as the Hartree approximation. It is an approximation, because the interaction necessarily changes the ψ_{100} wave function.
- Thus, the ground state energy of the helium atom is approximated to be $E_0 + 34$ eV $= -75$ eV.

- If we knock out one of the two electrons to form an ion, we say we *ionize* the He atom.
- The remaining He^+ ion resembles an hydrogen atom, except that the nucleus now have charge $2e$. So the ground state energy can be obtained from the hydrogenic energy by replacing e^2 by $2e^2$, i.e.,

$$E_0 = -\frac{m(2e^2)^2/(4\pi\epsilon_0)^2}{2\hbar^2} = -4E_R.$$

- Therefore, the first ionization energy (required to create He^+) is $-4E_R - (-75) \approx 21$ eV.

Ionization Energies of the Elements
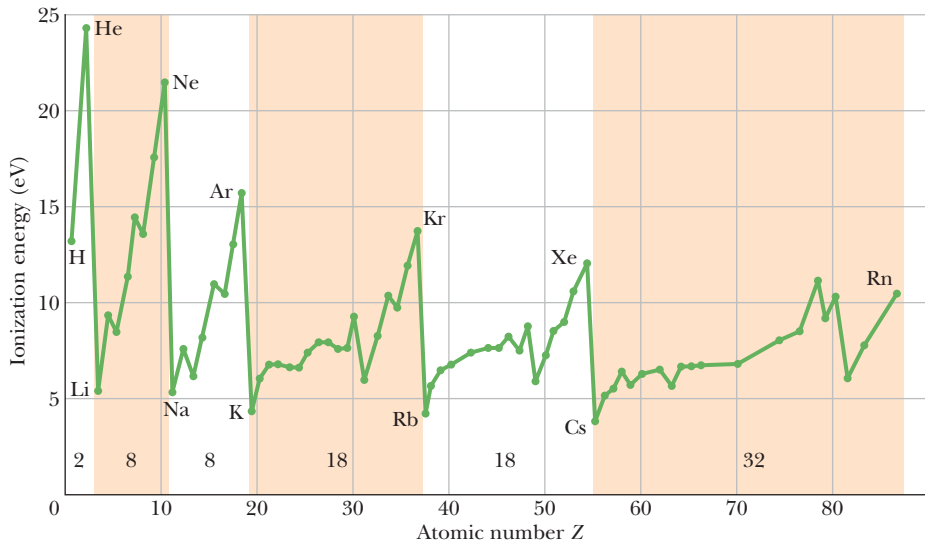
Shells and Subshells

- As we have discussed for the hydrogen atom, four quantum numbers n, ℓ, m_ℓ, and m_s identify the quantum states of individual electrons in a multielectron atom (neglecting relativistic corrections).
  - The wave functions for these states, however, are not the same as the wave functions for the corresponding states of the hydrogen atom, as discussed for the helium atom.
- When we assign electrons to states in a multielectron atom, we must be guided by the Pauli exclusion principle; i.e., no two electrons in an atom can have the same set of the quantum numbers n, ℓ, m_ℓ, and m_s.

- All states with the same n form a **shell**, and all states with the same value of n and ℓ form a **subshell**.
- For a given ℓ, there are $2\ell + 1$ possible values of quantum number m_ℓ $(-\ell, -\ell + 1, \ldots, \ell - 1, \ell)$ and, for each m_ℓ, there are two possible values for the quantum number m_s (spin up and spin down). Thus, there are $2(2\ell + 1)$ states in a subshell.
- If we count all the states throughout a given shell with quantum number n $(\ell = 0, 1, 2, \ldots, n - 1)$, we find that the total number in the shell is

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

Periodic Table of the Elements

X Rays and the Ordering of the Elements

- When a solid target, such as solid copper or tungsten, is bombarded with electrons whose kinetic energies are in the kiloelectron-volt range, electromagnetic radiation called **x rays** is emitted.
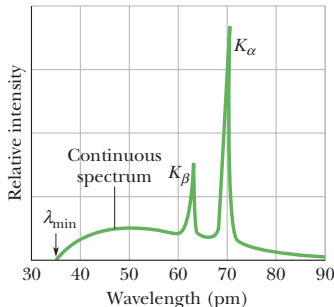
- In general, we observe a broad, continuous spectrum of radiation on which peaks of sharply defined wavelengths are superimposed. The spectrum can teach us about the atoms that absorb or emit them.

The Continuous X-Ray Spectrum

- An electron passing near an atom in the target may generate an X-ray photon, the electron losing part of its energy in the process. The continuous X-ray spectrum arises in this way.

- Independent of the target material, the spectrum has a cutoff wavelength $\lambda_{\min} = hc/K_0$, which corresponds to a collision in which an incident electron loses all its initial kinetic energy K_0 in a single head-on collision with a target atom.
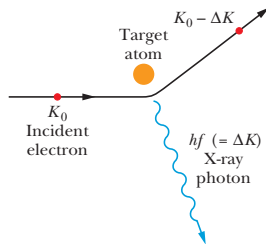
The Characteristic X-Ray Spectrum

The peaks arise in a two-part process.

1. An energetic electron strikes an atom in the target and, while it is being scattered, the incident electron knocks out one of the atom's deep-lying (low n value) electrons, leaving a vacancy, or hole, in this shell.

2. An electron in one of the shells with a higher energy jumps to the K shell, filling the hole in this shell. During this jump, the atom emits a characteristic x-ray photon.

Ordering the Elements
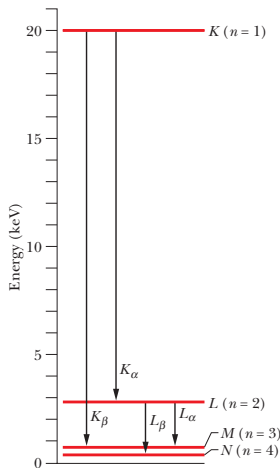
Moseley Plot of Characteristic X-Rays
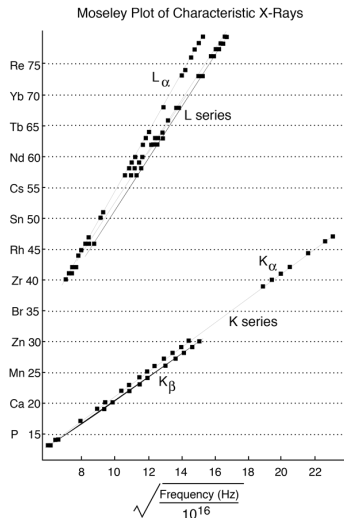
Adapted from Moseley's original data (H. G. J. Moseley, Philos. Mag. (6) 27:703, 1914)

In 1913, British physicist H. G. J. Moseley noted that if, for a given spectral line such as K_a, he plotted for each element the square root of the frequency f against the position of the element (the atomic number) in the periodic table, a straight line resulted.

$$\hbar\omega_{nm} = Z_{\text{eff}}^2 E_R \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

- The value of Z_{eff} of each series depends on how effective the electron(s) in the inner shell(s) shield the nucleus, such that the electron from a certain shell sees an effective nuclear charge of Z_{eff}.

  - For the K_α line ($n = 1$ and $m = 2$), $Z_{\text{eff}} = Z - 1$.

  - For the L_α line ($n = 2$ and $m = 3$), $Z_{\text{eff}} = Z - 7.4$.

- The significance of the plot is that *the nuclear charge (i.e., atomic number Z), not atomic mass, is the real basis for ordering the elements*.

Carbon

- A carbon atom has a nucleus of 6 protons and 6 neutrons with a total charge of $6e$.
- The lowest level ($1s$) contains 2 electrons, one spin up and one spin down. There are 4 electrons on the outer shell [$2s$ (lower in energy) and $2p$].
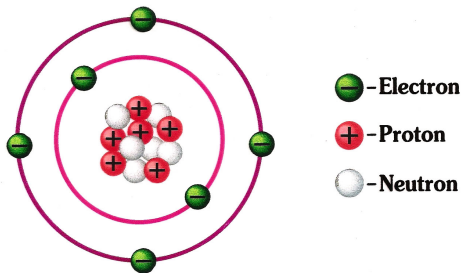
- Recall that we can write down 2s and 2p wave functions more explicitly as

$$
\begin{aligned}
s &: \ f(r) \\
p_x &: \ g(r)x = \tilde{g}(r)\sin\theta\cos\phi \\
p_y &: \ g(r)y = \tilde{g}(r)\sin\theta\sin\phi \\
p_z &: \ g(r)z = \tilde{g}(r)\cos\theta
\end{aligned}
$$

  where $f(r)$ and $g(r)$ are the corresponding radial wave functions for $n = 2$, up to a normalization constant.
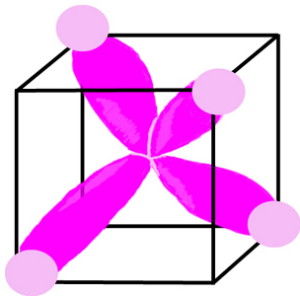
Menthane (CH_4): sp^3 Hybridization

- Hybridization is the idea that atomic orbitals fuse to form newly hybridized orbitals, which in turn, influences molecular geometry and bonding properties.
- In CH_4, the carbon $2s$ and $2p$ orbitals are hybridized.

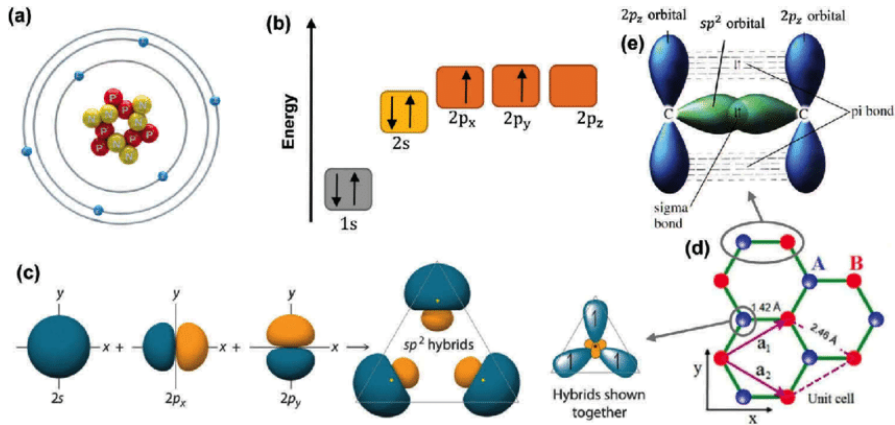$$\phi_1 = \frac{1}{2}s + \frac{1}{2}p_x + \frac{1}{2}p_y + \frac{1}{2}p_z$$

$$\phi_2 = \frac{1}{2}s - \frac{1}{2}p_x - \frac{1}{2}p_y + \frac{1}{2}p_z$$

$$\phi_3 = \frac{1}{2}s + \frac{1}{2}p_x - \frac{1}{2}p_y - \frac{1}{2}p_z$$

$$\phi_4 = \frac{1}{2}s - \frac{1}{2}p_x + \frac{1}{2}p_y - \frac{1}{2}p_z$$

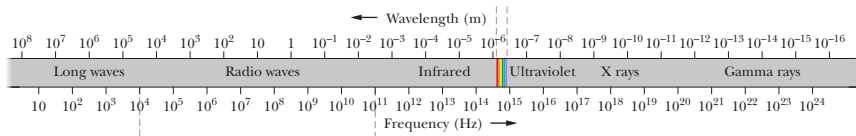# Graphene: sp^2 Hybridization

Interaction of Light and Matter

- X-ray: Compton scattering and photoionization
- Ultraviolet (UV): Photoionization (at higher energy) and sunburn (electron transitions due to near-UV radiation)
- Visible: Absorption in atomic electron transitions

- Infrared: Molecular vibration (absorption causes heating) and lattice vibration
- Microwave: Molecular rotation and torsion

- Remember that each electron is only allowed to have certain energies in an atom. Electron can absorb light and gain energy or emit light and lose energy.
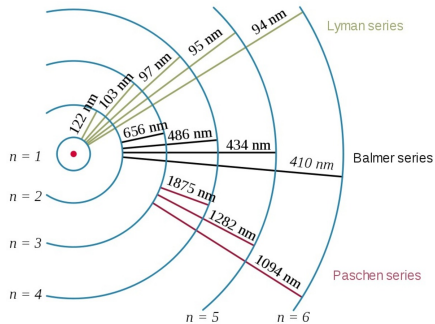
- Only photons whose energies (colors) match the "jump" in electron energy levels can be emitted or absorbed.
- In particular, an excited level will decay to a lower one (spontaneous emission), but the reverse spontaneous absorption does not occur.

Spontaneous and Stimulated Emission
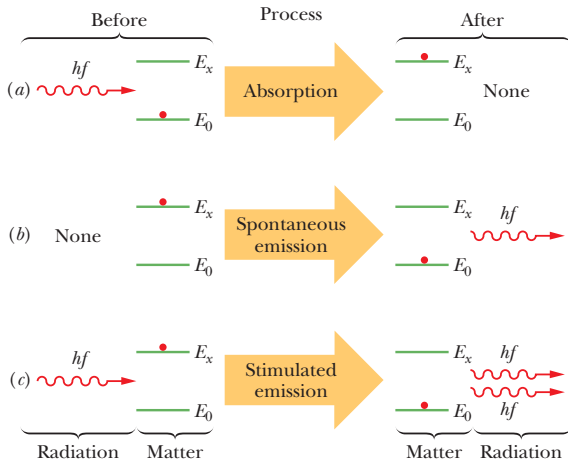
Einstein showed that the probabilities per atom for absorption and stimulated emission are identical. In stimulated emission, the emitted photon is in every way identical (same energy, phase, polarization, and direction of travel) to the stimulating photon; they are bosons.

Population Inversion

- In thermal equilibrium at temperature T, most atoms (N_0) in a sample are in their ground states. The occupation of an excited state is given, according to Boltzmann, by

$$N_x = N_0 e^{-(E_x - E_0)/k_B T}.$$
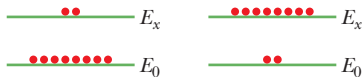
- To produce coherent laser light, we must engineer a **population inversion**, such that stimulated emission dominates.

Helium-Neon Laser
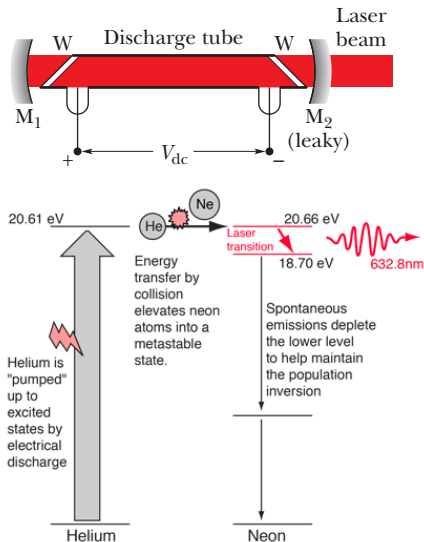
- One of the excited levels of helium at 20.61 eV (Do you know which one this is?) is very close to a level in neon at 20.66 eV, so close in fact that upon collision of a helium and a neon atom, the energy can be transferred from the helium to the neon atom.
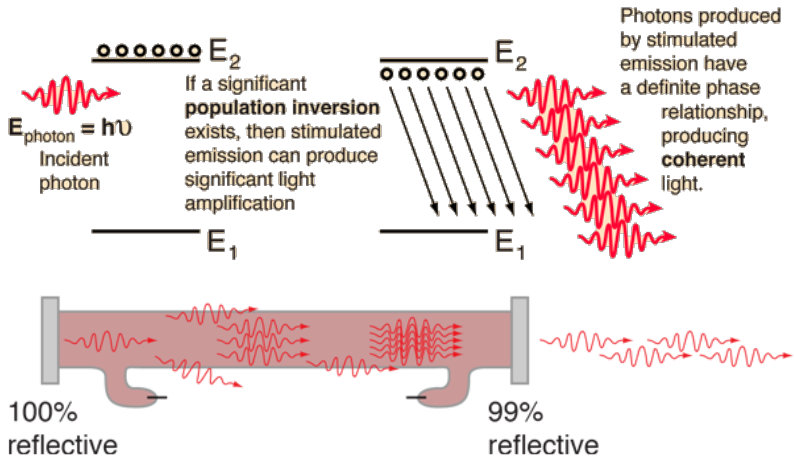
- Laser light is coherent, monochromatic, and collimated.

Summary

- Understand the helium spectrum and the distinction of singlet and triplet.
- Understand the Pauli exclusion principle and how to antisymmetrize wave functions for two electrons.
- Understand how atoms are ordered and how the periodic table is structured.
- Understand the basic principles of laser.

Reading

Halliday, Resnick & Krane:

- Chapter 48: Properties of Atoms

Appendix 27A: More on Helium

- Recall that we have two electrons in the $1s$ orbital in the helium atom, one spin up and another spin down. The wave functions for individual electrons are $\psi_{100}(\vec{r})\ket{\uparrow}$ and $\psi_{100}(\vec{r})\ket{\downarrow}$, where $\uparrow$ and $\downarrow$ represent spin magnetic quantum number $m_s = \pm 1/2$.

- Our earlier treatment of the helium atom assumes a ground state wave function $\psi_{100}(\vec{r_1})\psi_{100}(\vec{r_2})\ket{\uparrow}_1\ket{\downarrow}_2$, where the subscripts 1,2 label the two electrons.

- However, this implies $\psi_{100}(\vec{r_1})\psi_{100}(\vec{r_2})\ket{\downarrow}_1\ket{\uparrow}_2$ would be a different but degenerate (same energy) state.

- In fact, there is no intrinsic difference among particles, so we must symmetrize or antisymmetrized the two states as

$$\Psi_\sigma = \frac{1}{\sqrt{2}} \psi_{100}(\vec{r_1}) \psi_{100}(\vec{r_2}) \left(\left| \uparrow \right\rangle_1 \left| \downarrow \right\rangle_2 + \left| \downarrow \right\rangle_1 \left| \uparrow \right\rangle_2 \right)$$

and

$$\Psi_\alpha = \frac{1}{\sqrt{2}} \psi_{100}(\vec{r_1}) \psi_{100}(\vec{r_2}) \left(\left| \uparrow \right\rangle_1 \left| \downarrow \right\rangle_2 - \left| \downarrow \right\rangle_1 \left| \uparrow \right\rangle_2 \right)$$

- The exchange of the two particles does nothing to Ψ_σ, but adds a phase π to Ψ_α. However, such a phase is irrelevant in the probability interpretation.

- It turns out that electrons, as well as protons and neutrons, are identical and can only have antisymmetric wave functions in respect to exchanging the arguments corresponding to any two particles. They are known as **fermions** and have half-integer spins.
- We see, immediately, the Pauli exclusion principle follows, because the wave function of two electrons with identical quantum numbers would necessarily have $\Psi_\alpha = 0$.
- On the other hand, particles like photons have symmetric wave functions in respect to exchanging the arguments corresponding to any two particles. They are known as **bosons** and have integer spins.

Singlet and Triplet

- In general, if the spatial coordinates and the spin are not coupled, the two-electron wave function must be either

$$\Psi(\vec{r}_1, m_1, \vec{r}_2, m_2) = \Phi_{\mathrm{sym}}(\vec{r}_1, \vec{r}_2)\chi_{\mathrm{as}}(m_1, m_2)$$

or

$$\Psi(\vec{r}_1, m_1, \vec{r}_2, m_2) = \Phi_{\mathrm{as}}(\vec{r}_1, \vec{r}_2)\chi_{\mathrm{sym}}(m_1, m_2).$$

- The spin part of the two-electron wave function can have two forms.
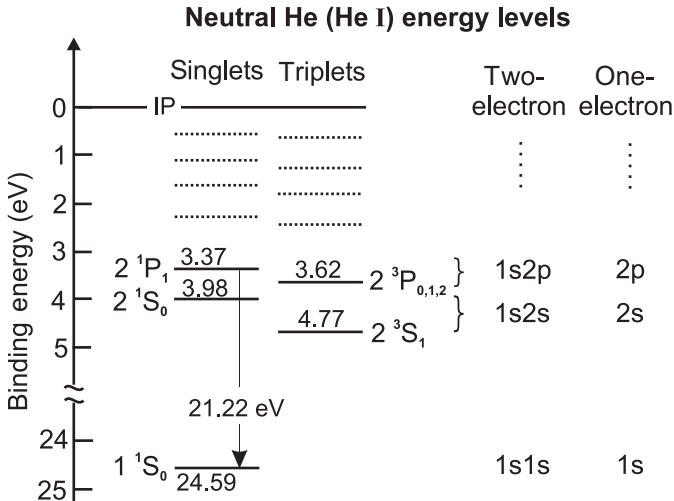   - A singlet, whose total spin is 0.

$$\chi_{\text{as}}(m_1, m_2) = \frac{1}{\sqrt{2}}(\left|\uparrow\right\rangle \left|\downarrow\right\rangle - \left|\downarrow\right\rangle \left|\uparrow\right\rangle)$$

    - A triplet, whose total spin is 1.

$$\chi_{\text{sym}}(m_1, m_2) = \begin{cases} \left|\uparrow\right\rangle \left|\uparrow\right\rangle \\ \frac{1}{\sqrt{2}}(\left|\uparrow\right\rangle \left|\downarrow\right\rangle + \left|\downarrow\right\rangle \left|\uparrow\right\rangle) \\ \left|\downarrow\right\rangle \left|\downarrow\right\rangle \end{cases}$$

    S_z of the total spin is $+1$, 0, -1, respectively.

The Spectrum of Neutral Helium

Neutral He (He I) energy levels

Excited States

- Consider states with one $1s$ electron being excited to an excited state with quantum numbers nlm. We can have the singlet excited state (S)

$$\frac{1}{\sqrt{2}}[\psi_{100}(\vec{r}_1)\psi_{nlm}(\vec{r}_2) + \psi_{100}(\vec{r}_2)\psi_{nlm}(\vec{r}_1)]\chi_{\mathrm{as}}(m_1, m_2)$$

or the triplet excited state (T)

$$\frac{1}{\sqrt{2}}[\psi_{100}(\vec{r}_1)\psi_{nlm}(\vec{r}_2) - \psi_{100}(\vec{r}_2)\psi_{nlm}(\vec{r}_1)]\chi_{\mathrm{sym}}(m_1, m_2).$$

- The singlet and triplet states have an energy splitting $E^T - E^S = -2J$ (the **exchange energy**), where J is called the **exchange integral**.
- The exchange interaction arises from the Coulomb interaction between electrons and the symmetrization postulate (the dipole-dipole interaction between two spins is much smaller).
- The symmetrization postulate leads to either parallel or antiparallel spins.
  - If J is positive, the spins point into the same direction and are aligned parallel.
  - If J is negative, the spins are antiparallel.

Appendix 27B: Structure of the Periodic Table

- Recall that an electron in an atomic orbital can be labeled by four quantum numbers, $|n, l, m_l, m_s\rangle$, where

$$n = 1, 2, \ldots, \quad l = 0, 1, \ldots, n-1$$

$$m_l = -l, \ldots, l, \quad m_s = \pm 1/2$$

- All states with the same n form a **shell**, and all states with the same value of n and l form a **subshell**.
- Recall that the angular momentum subshells with $l = 0, 1, 2, 3, \ldots$ are sometimes known as s, p, d, f, $\ldots$ respectively in atomic language.

- **Aufbau Principle**: Subshells should be filled starting with the lowest available energy state. An entire subshell is filled before another subshell is started.
- **Madelung's Rule**: The energy ordering is from the lowest value of $n + l$ to the largest; and when two subshells have the same value of $n + l$, fill the smaller n first.
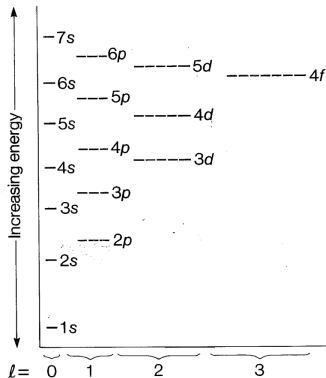

Figure 1: Ordering of filling orbitals: $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, \ldots$.

- There are $2(2l + 1)$ states in a subshell. These orbitals can accommodate 2, 6, 10, 14, ... electrons respectively including both spin states.
- Therefore, elements are arranged in the periodic table in seven horizontal periods.
- The numbers of elements in the first six complete periods are 2, 8 ($= 2 + 6$), 8, 18 ($= 2 + 10 + 6$), 18, and 32 ($= 2 + 14 + 10 + 6$). Do you understand why I order the numbers this way?
- Note that there are a few atoms that violate Madelung's rule. One example is copper which typically fills the $3d$ shell by "borrowing" an electron from the $4s$ shell.

Hund's Rules

In cases when shells are partially filled:

1. Electrons try to align their spins.
2. Electrons try to maximize their total orbital angular momentum, consistent with Hund's first rule.

$$l_z = \quad -3 \quad -2 \quad -1 \quad 0 \quad 1 \quad 2 \quad 3$$

The two rules are results of the Coulomb interaction between electrons (and between the electrons and the nucleus) — the Coulomb energy is lower when the electron spins align.

3. Given Hund's first and second rules, the orbital and spin angular momentum either align or antialign, so that the total angular momentum is $J = |L \pm S|$ with the sign being determined by whether the shell of orbitals is more than half filled $(+)$ or less than half filled $(-)$.

The third rule is the result of spin-orbit coupling.

- Example: Praseodymium (Pr) has three $4f$ electrons.

$$S = 3/2, \ L = 6, \ J = |6 - 3/2| = 9/2.$$