Electrons in atoms and solids

TODAY:

- Lasers and population inversion
- Energy bands in solids
- The Boltzmann factor
- Thermal distribution of electrons

Review: Pauli Exclusion Principle

- No two electrons in the same state.
- That is, one electron for each set of quantum numbers.
- Applies to spin-1/2 particles (fermions) such as electrons, protons, neutrons.
- Does not apply to photons.

Bosons and fermions

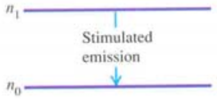
Fermi-Dirac statistics: electrons: *Atoms*

Two particles in the same state is forbidden.

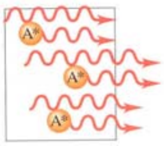
Bose-Einstein statistics: photons: *Lasers*

Two particles in the same state is encouraged.

Stimulated Emission



Light
Amplification by
Stimulated
Emission of
Radiation



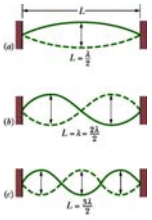
Atom emits a new photon into *exactly the same quantum state* as the original photon. This keeps happening until there is a strong beam of many photons *all in the same quantum state.*

Exactly the opposite of the Pauli Principle.

Review: Problem 40-21

Seven electrons are trapped in a one-dimensional infinite potential well of width L. Find the lowest four energy levels of this system. (Assume the electrons do not interact with each other; do not neglect spin!)

$$\psi(x)$$



First recall the *single-particle energies*, found by analogy with the modes of a vibrating string.

$$\lambda = \frac{2L}{n} \qquad p = \frac{h}{\lambda} = \frac{nh}{2L}$$

$$E_n = \frac{p^2}{2m} = \frac{n^2 h^2}{8mL^2} = n^2 E_0$$

Problem 40-21 (continued)

Seven electrons are trapped in a one-dimensional infinite potential well of width L. Find the lowest four energy levels of this system. (Assume the electrons do not interact with each other; do not neglect spin!)

One electron: $E_n = n^2 E_0 \quad E_0 = \frac{h^2}{8mL^2} \quad n = 1,2,3,\cdots$

If all 7 e's were in the lowest (n=1) single-particle state, then the lowest possible energy for the *system* would be just $7E_0$.

But Pauli forbids that. Only *two electrons* can have energy E_0, one with spin up, and one with spin down.

Problem 40-21 (continued)

Seven electrons are trapped in a one-dimensional infinite potential well of width L. Find the lowest four energy levels of this system.

One electron: $E_n = n^2 E_0 \quad E_0 = \dfrac{h^2}{8mL^2} \quad n = 1,2,3,\cdots$

Make a list of occupied states and energies:

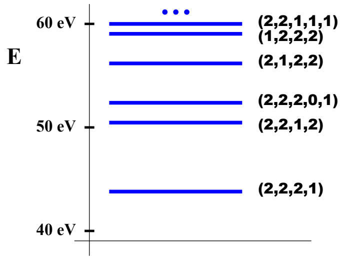
n=1	2	$2E_1 = 2*1E_0 = 2E_0$
n=2	2	$2E_2 = 2*4E_0 = 8E_0$
n=3	2	$2E_3 = 2*9E_0 = 18E_0$
n=4	1	$E_4 = 1*16E_0 = 16E_0$

Total ground state energy: $44E_0$

Problem 40-21 (result)

Seven electrons are trapped in a one-dimensional infinite potential well of width L. Find the lowest four energy levels of this system.

Let's make an energy-level diagram for this system.
Suppose L = 0.62 nm so that E_0 = 1 eV.



Now we can have quantum jumps with emission and absorption of photons!

Q.40-1

Consider again the one-dimensional trap of the previous example, with E_0 = 1 eV.

Suppose we put three electrons in this trap instead of seven. What will now be the ground-state energy?

Enter your answer as a whole number of eV between 1 and 9.

Q.40-1

For 3 electrons in a one-dimensional trap with E_0 = 1 eV, what is the ground state energy (in eV)?

At most 2 electrons can be in each single-particle state.

Single-particle energies are $E_n = n^2 E_0$

So for 2 in the n=1 state, and 1 in the n=2 state,

$$E = 2 \times E_1 + 1 \times E_2 = 2 \times 1\ eV + 1 \times 4\ eV = \boxed{6\ eV}$$

Atomic quantum numbers with spin

Each electron in an atom exists in a quantum state similar to hydrogen. States are labeled by the 3 hydrogen quantum numbers *plus spin.*

$n = 1,2,3,\cdots$ $\qquad E = -E_0 / n^2$

$l = 0,1,\cdots(n-1)$ $\qquad L = \sqrt{l(l+1)}\,\hbar$

$m_l = -l, (-l+1), \cdots, l$ $\qquad L_z = m_l \hbar$

$m_s = \pm 1/2$ $\qquad S_z = m_s \hbar$

s → l=0
p → l=1
d → l=2
etc.

$\{n, l, m_l, m_s\} \rightarrow$ **Quantum state available for one electron.**

Review: Pauli Exclusion Principle

- **No two electrons in the same state.**
- **That is, one electron for each set of quantum numbers: (n, l, m_l, m_s).**
- **This gives the *periodic table!***
- **Applies to spin-1/2 particles (fermions) such as electrons, protons, neutrons.**
- **Does not apply to photons.**

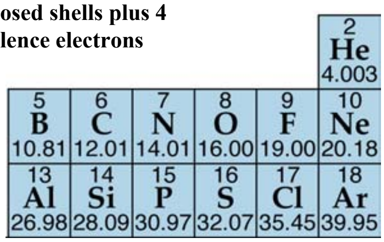
Periodic table

- As we put more and more electrons around a nucleus, the new electrons must go in states not already occupied.
- So for silicon (Z=14) for example:
- 1s subshell; 2 electrons
- 2s subshell; 2 electrons
- 2p subshell; 6 electrons (m_l = -1, 0, +1)
- 3s subshell; 2 electrons
- 3p subshell; 2 electrons, choose any

combination of m_l = 0, ±1, ms = ±1/2.

Review: Carbon and silicon

Closed shells plus 4
valence electrons



					2 He 4.003
5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95

$$C:\quad \underline{1s^2}\,2s^2\,2p^2 \qquad \text{He core}$$

$$Si:\quad \underline{1s^2\,2s^2\,2p^6}\,3s^2\,3p^2 \qquad \text{Ne core}$$

Q.40-2

- The ground configuration of beryllium (atomic number Z=4) is written $1s^2 2s^2$.
- Each possible electron orbital is identified by a set of four quantum numbers (n, l, m_l, m_s).
- If the quantum numbers of three electrons are: (1,0,0,+1/2), (1,0,0,-1/2), (2,0,0,+1/2), what are the quantum numbers of the fourth electron in the ground state of beryllium?

(1)(1,0,0,+1/2) (2)(1,0,0,-1/2) (3)(2,0,0,+1/2) (4)(2,0,0,-1/2)
(5)(2,1,0,+1/2) (6)(2,1,0,-1/2) (7)(2,1,1,+1/2) (8)(2,1,1,-1/2)

Q.40-2

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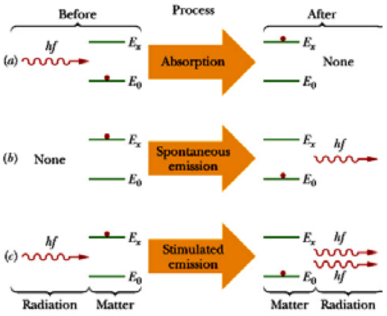
$1s^2 2s^2$ means two e's have n=1, two have n=2, and all have l=0. But both the possible 1s states are taken. So the fourth e must have ***<u>n=2, l=0</u>*** and therefore m_l=0. The ms=+1/2 state is already taken so the fourth e must have ms=-1/2.

(1)(1,0,0,+1/2) (2)(1,0,0,-1/2) (3)(2,0,0,+1/2) $\boxed{\text{(4)(2,0,0,-1/2)}}$
(5)(2,1,0,+1/2) (6)(2,1,0,-1/2) (7)(2,1,1,+1/2) (8)(2,1,1,-1/2)

Photon-Atom Processes



Note if hf = E_x-E_0 we can have ***<u>both</u>*** absorption and stimulated emission. One will dominate depending on the ***<u>populations</u>*** of the two levels.

In thermal equilibrium more atoms are in the lower, so absorption dominates. No laser.

Must have ***<u>population inversion</u>*** to have laser.

Boltzmann's Constant

Review: In an ideal gas, the average kinetic energy of a molecule is $\langle KE \rangle = \frac{3}{2}kT$

Here k is Boltzmann's constant $k = 8.6\times10^{-5}\ eV/K$

And T is the absolute temperature (in kelvins K).

It's useful to remember that at room temperature (300 K) we have $kT \approx \frac{1}{40}\,eV$

Maxwell-Boltzmann Probability Distribution

But the *average* kinetic energy is not the whole story. What about questions like what fraction of molecules have more than twice the average? In other words what is the probability *distribution*?

This is discussed in Chapter 19. The distribution in speeds is *P(v)* given by Equation 19-27 and plotted in Figure 19-7 on page 517.

This equation is messy and not very enlightening. The simpler, more fundamental equation that lies behind it is *not* given!

That is the Boltzmann factor:

$$\boxed{P(E) \propto e^{-E/kT}}$$

The Boltzmann Factor

Given any system in thermodynamic equilibrium at temperature T. The probability of finding this system in a state of energy E is given by

$$P(E) = Ce^{-E/kT}$$

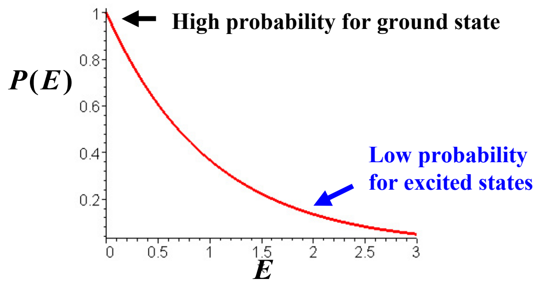
That is, the relative probability of any two states is

$$\frac{P(E_2)}{P(E_1)} = e^{-(E_2 - E_1)/kT} = e^{-\Delta E/kT}$$

So if $\Delta E > kT$ then $P(E_2) << P(E_1)$

For example in a gas the number of atoms in an excited state is smaller than the number in the ground state.

Boltzmann Factor $P(E) = e^{-E/kT}$



High probability for ground state

Low probability for excited states

Population Inversion

So for a laser we cannot have a source in thermal equilibrium at temperature T. We must have some kind of *trick* to arrange things so that there are more atoms in the excited state than in the ground state. This requires two things.

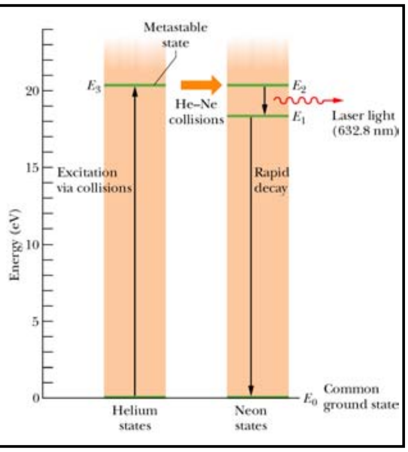
We must *pump* the system into the excited state.

That state must be *metastable* (low probability for spontaneous decay.)

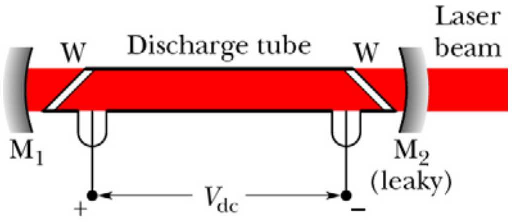
He-Ne Laser

Key to any laser is finding a metastable state which can be pumped (populated) somehow.

Get population inversion (cheat the Boltzmann factor).



Laser Construction



End of old ch40 part 2.

Electrons in Solids

Atoms combine to form solids

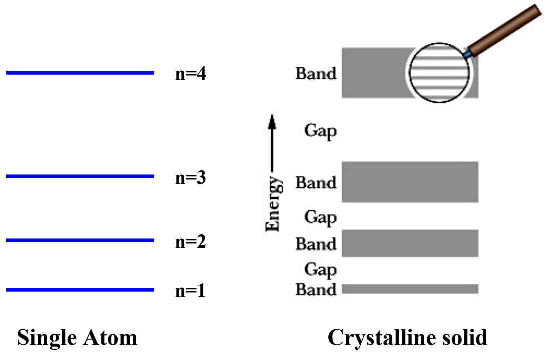
The discrete energy ***levels*** of the atom merge to form energy ***bands*** in the solid.

We have roughly Avagadro's number of atoms

$$N_A = 6\times10^{23}$$

So if there are 2 electrons in the n=1 subshell of a single atom, the number of electrons in the lowest energy band of the solid is of order 10^{24}

Energy Bands



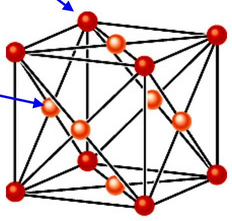
Crystal structures

- Different crystal structures result in different energy bands and band gaps
- Sodium Chloride: insulator
- Copper: Conductor
- Silicon: Semiconductor
- Carbon:
  - Diamond is insulator
  - Graphite is conductor

Ionic bonding

$Na^+ = 1s^2\ 2s^2 2p^6$

$Cl^- = 1s^2\ 2s^2 2p^6\ 3s^2 3p^6$



Ions have closed-shell inert-gas-like cores.

Atoms kept separate. No shared electrons.

Coulomb attraction balanced by Pauli.

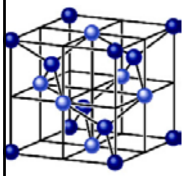
Good insulator.

Face-centered cubic.

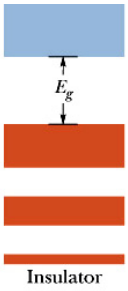
For example, NaCl.

Insulators such as diamond

Covalent bonds. Electrons are shared between neighboring atoms. Atomic levels become energy bands.



Diamond lattice



- All bands either full or empty.
- Band gap is large.
- Diamond:

$$E_g = 5.5\ eV$$

Excellent insulator

Band gaps

Why is diamond an insulator?

Why is 5.5 eV a “large” band gap?

Electrons in filled bands cannot move because of Pauli exclusion principle.

Must move up to conduction band.

Boltzmann factor doesn’t let this happen: $\boxed{E_g >> kT}$

Room temperature kT is about .025 eV.

$$P(E) = e^{-E/kT} = e^{-5.5/.025} = e^{-220} = 3\times 10^{-96}$$

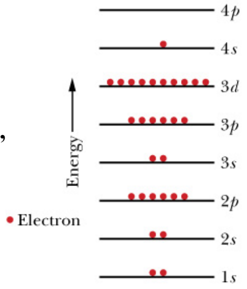
Also 5.5eV is larger than energy of photon of visible light. So diamond is transparent, photons are not absorbed. Shining light on a diamond doesn’t make it a conductor.

Electrons in a metal atom

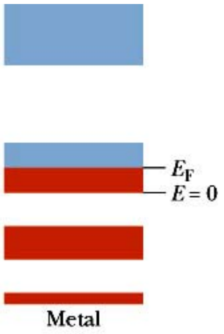
Electrons in copper, *Z*=29. Filled shells n=1,2,3, hold 28.

Outer 4s subshell is half filled.

When Cu atoms form a crystal, these 4s subshells merge to form the conduction band.



Electrons in a solid metal



Atomic core states are full.

Conduction band is half full.

Fermi energy E_F shows highest filled state.

Easy for electron to jump to slightly higher energy state, and then move through solid.

Good conductor.

Density of states and electrons

A crucial quantity for electronic properties of a solid is the *density of states.* We will not try to learn how to calculate it. Its meaning is straightworward:

N(E) dE = Number of *quantum states* with energy in the range E to E+dE.

Multiply by P(E) = probability of finding an electron in a state with energy E to get number of *electrons* with energy in range dE.

If e’s were not *fermions,* this would be $P(E) = e^{-E/kT}$

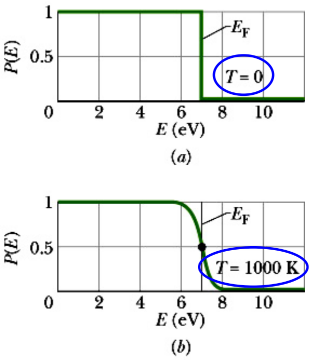
But because e’s are fermions, they obey the Fermi-Dirac probability distribution function instead.

Fermi-Dirac Distribution Function

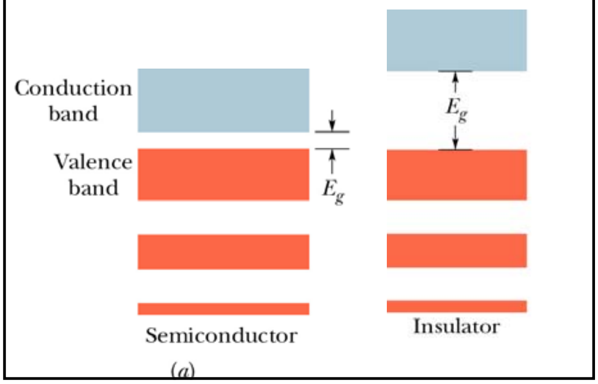
At T=0, states are filled just up to Fermi energy.

At T>0, some electrons have gotten a thermal boost.

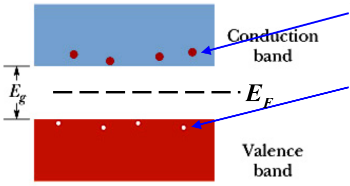
$$\boxed{P(E) = \frac{1}{e^{(E-E_F)/kT}+1}}$$



Semiconductors



Charge carriers in semiconductor



Electrons in conduction band

Holes in valence band

For example $E_g = 1\,eV$ $E_F = 0.5\,eV$

$$P(E_{conduction}) = \frac{1}{e^{(E_g - E_F)/kT} + 1} = \frac{1}{e^{(.5)/.025} + 1}$$

$$= \frac{1}{e^{20} + 1} = e^{-20} = \underline{2\times10^{-9}}$$

Multiply by Avagadro's number to get rough estimate of charge carriers per mole: $6\times10^{23}\times2\times10^{-9} = 10^{15}$