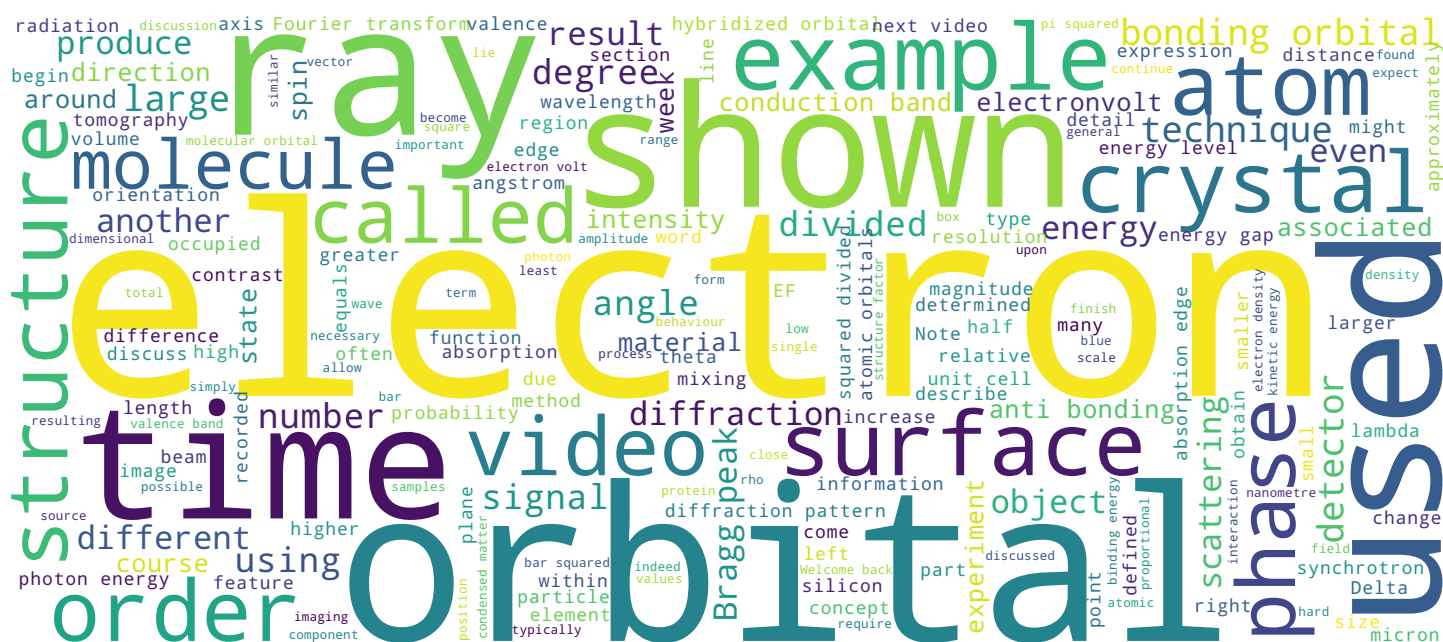


Synchrotrons and x-ray free-electron lasers

Techniques and applications

Prof. Philip Willmott



Search MOOC



Video



Contents and objectives of this video



- Electron orbitals
 - Hydrogen-like atoms
 - Bonding and antibonding molecular orbitals
 - Hybridized orbitals
 - In condensed matter
- The free-electron model and the Fermi energy

Welcome to the second video of week 3 of this course on synchrotrons and x-rays. In this video, we will talk precious little about x-rays or synchrotrons per se, but instead, concentrate on the interaction of electrons with one another in atoms, molecules, and condensed matter including the free electron model and the Fermi energy. The information provided here is a bare minimum to continue with a proper understanding of what is discussed in this and next week's videos and is perforce extremely superficial. For those of you who are entirely unfamiliar with the behaviour of electrons in matter, and their role in bonding, et cetera, I recommend that you do at least a little background reading.

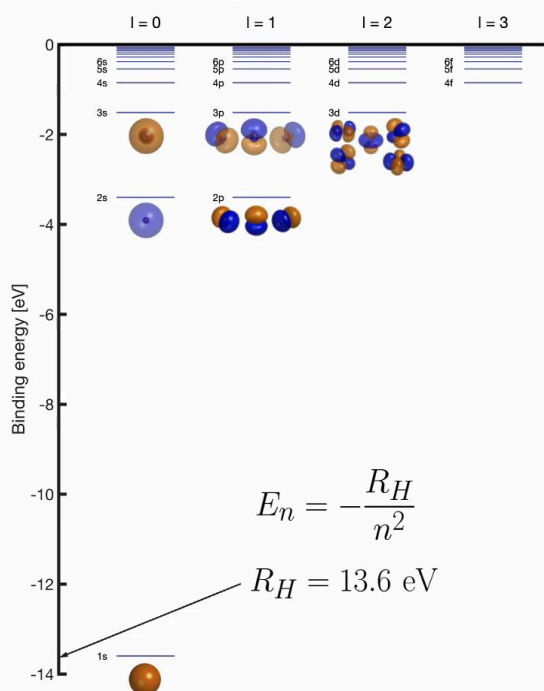
Notes

Summary



0m 05s

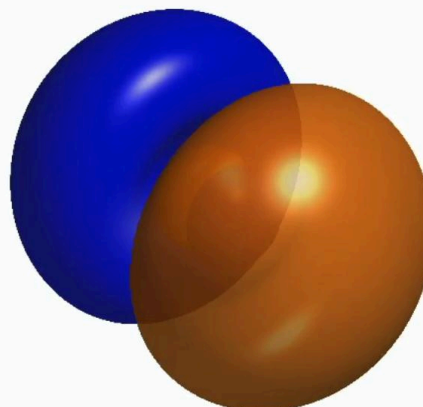
Orbitals – from isolated atoms to condensed matter



$$E_n = -\frac{R_H}{n^2}$$

$$R_H = 13.6 \text{ eV}$$

$$n = 3, l = 1, m = 1$$



Isolated H-atom

See e.g., [P.W. Atkins, "Physical Chemistry"](#)

Hydrogen atoms have only one electron which orbits the nucleus. The behaviour of the electron can be described using wave-like functions known as orbitals. In hydrogen, the first four types of orbitals are called S, P, D, and F. The binding energy of the orbitals is determined by the principal quantum number n , which assumes integer values from one upwards. The energy of the n th orbital is equal to minus R_H divided by n squared, where R_H is the Rydberg constant and is equal to 13.6 electronvolts. The binding energy of the 1s state is therefore 13.6 electronvolts, that of the 2s and 2p orbitals is 3.4 electronvolts, and so on. The orbital angular momentum is determined by l . Which determines whether an orbital is s type, p type, etcetera, etcetera. It can assume values between nought, which is s type and n minus one. Hence, the n equals one orbital can only be s type with l is equal to zero. The s orbital has a spherical shape that surrounds the nucleus. It is the simplest and lowest energy orbital. The p orbitals have a dumbbell shape and come in three orientations, p_x , p_y , and p_z . The d orbitals have a more complex shape, and come in five orientations, d_{xy} , d_{xx} , d_{yy} , d_{z^2} , and $d_{x^2-y^2}$.

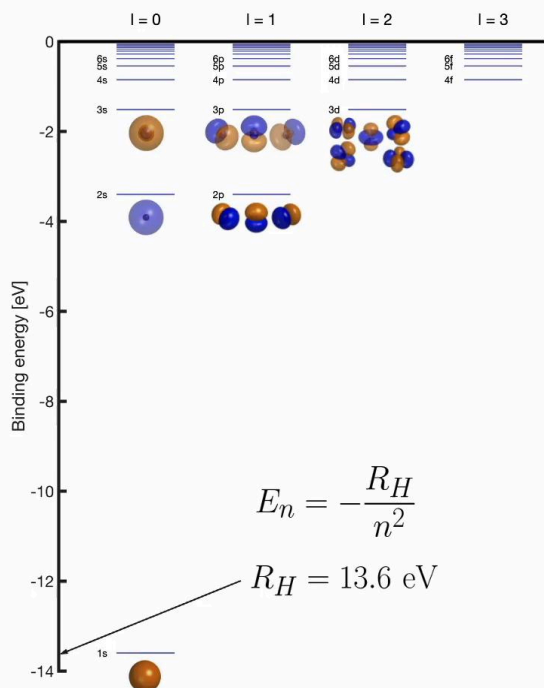
Notes

Summary



0m 56s

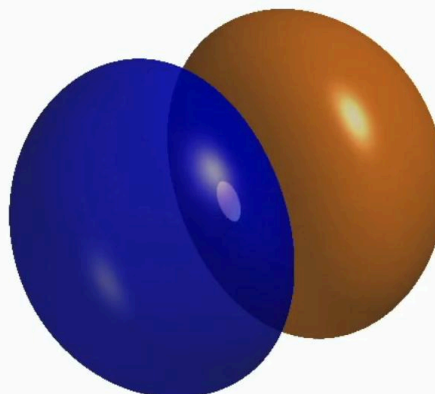
Orbitals – from isolated atoms to condensed matter



$$E_n = -\frac{R_H}{n^2}$$

$$R_H = 13.6 \text{ eV}$$

$$n = 2, l = 1, m = -1$$



Isolated H-atom

See e.g., [P.W. Atkins, "Physical Chemistry"](#)

The f orbitals have even more complex shapes and come in seven orientations. Each orbital can hold up to two electrons which have opposite spins. The electrons fill the orbitals in a specific manner based on their energy levels following the Aufbau principle, Pauli's exclusion principle and Hund's rule. It lies well beyond the brief of this course to go into this in any significant detail. I recommend good undergraduate physical chemistry textbooks if you would like to go into this fundamental aspect of quantum mechanics in greater depth.

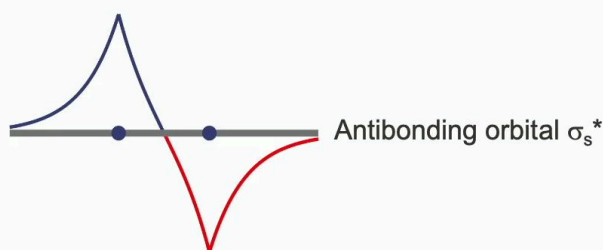
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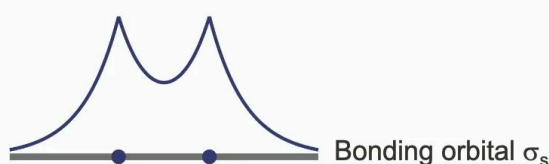


2m 48s

Orbitals – from isolated atoms to bonding



Rule: Number of orbitals must be conserved!!



Bonding and anti-bonding orbitals are concepts used in molecular orbital theory to explain how atoms combine to form molecules. A bonding orbital is formed by the constructive interference of two atomic orbitals with the same phase. This results in a lower-energy molecular orbital, which can be occupied by two electrons with opposite spins. The electrons in the bonding orbital are attracted to both nuclei stabilizing the molecule. The electrons have a high probability of being located between the positive ions. On the other hand, an anti-bonding orbital shown here now is formed by the destructive interference of two atomic orbitals with opposite phases. This results in a higher energy molecular orbital which repels electrons and destabilizes the molecule. The electrons in the anti-bonding orbital are mainly located outside the region between the nuclei. The formation of bonding and anti-bonding orbitals explains why some molecules are stable while others are not. When the number of electrons in the bonding orbital is greater than the number of anti-bonding orbitals, the molecule is stable. However, if the number of electrons in the anti-bonding orbitals is greater, the molecule is unstable and tends to dissociate. The number of orbitals in the combined state compared to those associated with the isolated atoms must be conserved.

Notes

Summary



Orbital hybridization



- Describes the mixing of atomic orbitals to form new hybridized orbitals
- Hybridized orbitals necessary to explain geometry of molecules that cannot be explained by using only the atomic orbitals of the constituent atoms
- Used to describe the bonding properties of molecules

Electron hybridization is a concept in quantum chemistry that describes the mixing of atomic orbitals to form new hybridized orbitals. These new hybridized orbitals are necessary to explain the geometry of molecules that can't be explained by using only the atomic orbitals of the constituent atoms. The process of hybridization involves the mixing of orbitals from the same atom or from different atoms to form new orbitals with different energy levels, shapes, and orientations. The resulting hybridized orbitals are used to describe the bonding properties of molecules. For example, in the case of carbon atoms, the mixing of one s orbital and three p orbitals results in four sp^3 hybridized orbitals, that are used to form the covalent bonds in molecules such as methane. Similarly, the mixing of one s orbital and two p orbitals in carbon, results in three sp^2 hybridized orbitals, that are used to form the pi bonds in molecules such as ethane. We look at this more closely in just a moment. Overall, the concept of electron hybridization is an important tool for understanding the structure and properties of molecules and it plays a critical role in the field of organic chemistry.

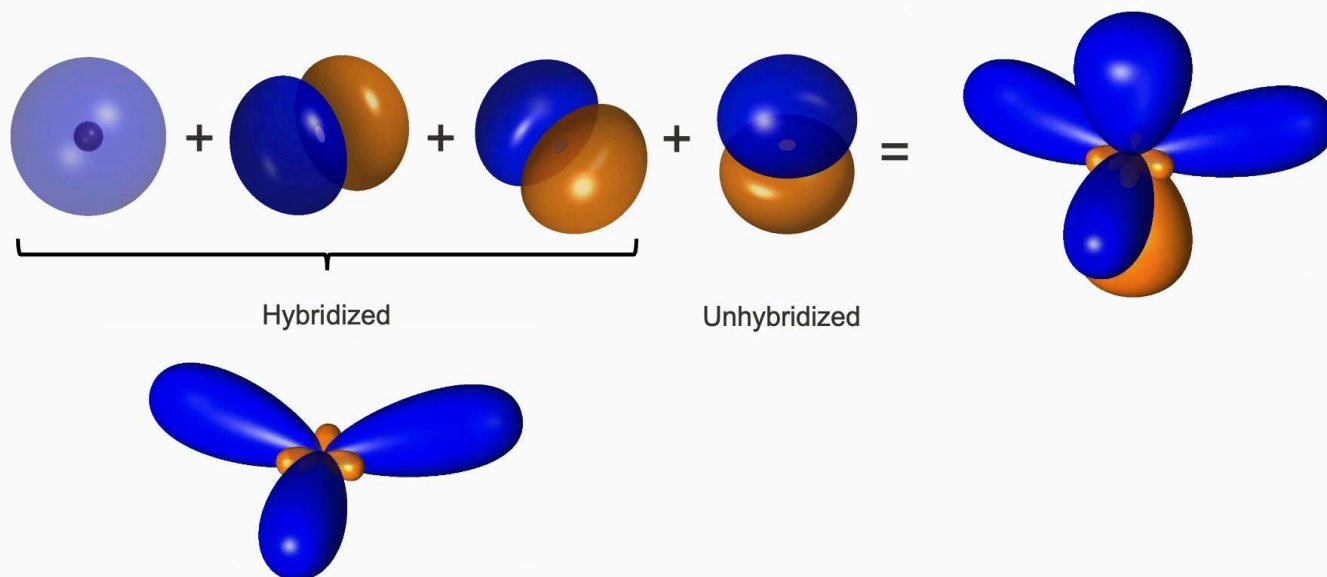
Notes

Summary



5m 06s

Hybridization of s- and p-orbitals: sp^2



We now look at three examples of s and p hybridization, that is the combination of a spherical s orbital with one or more dumbbell-shaped p orbitals to produce hybridized orbitals with shapes and angles we immediately recognize as being necessary to form bonds in some familiar compounds. The first orbital is the sp orbital, combining one each of the atomic s and p orbitals. Note that the s orbital is symmetric while the p orbital is anti-symmetric. In other words, the orbital amplitudes at r and $-r$ are opposite. This is shown by the blue and orange colours. Hybridization of these orbitals produces a symmetric but dumbbell-shaped sp orbital. Combining this with two other unhybridized p orbitals produces the electron probability which is shown on the right. This is used in the bonding of C_2H_2 or acetylene. The two hybridized sp orbitals form an on-axis sigma bond, while the unhybridized p orbitals produce the other two pi orbitals. In total, this results in the triple CC bond of acetylene. sp^2 orbitals combine as can be guessed by their name, one s orbital, and two p orbitals. To produce a helicopter rotor-like hybridized structure with threefold symmetry.

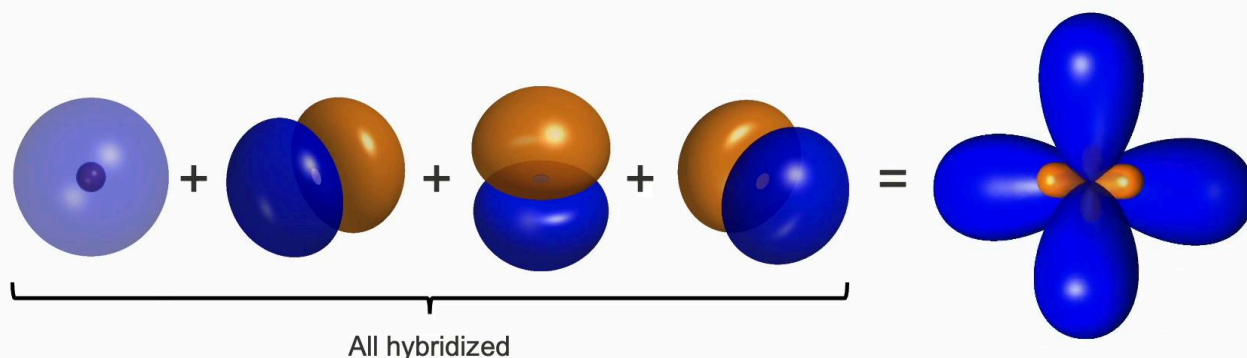
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Summary

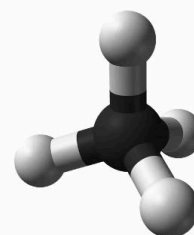


6m 39s

Hybridization of s- and p-orbitals: sp^3



sp^3 : e.g. methane:



Combining this with one p orbital with its axis out of plane relative to the hybridized orbital produces a configuration that can be used to produce a double bond as in C_2H_4 or ethane. Note that the bond angles in ethane, are 120 degrees, as we would expect from the three-fold symmetry of the sp^2 orbitals. Finally, sp^3 orbitals are tetrahedral structures such as found in diamond or methane produced by the hybridization of one s and all three p orbitals.

Notes

Summary



Orbitals – from isolated atoms to condensed matter

- Metals: Valence band only partially filled (@ 0K)

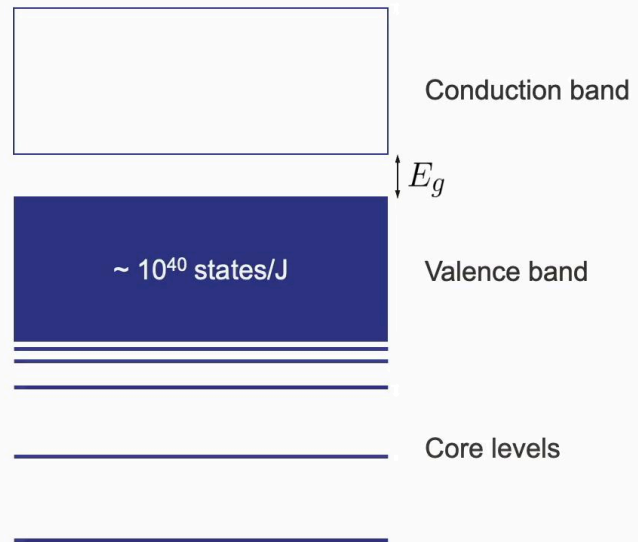
- Semiconductors: Valence band full, conduction band empty

- Band gap E_g for Si is 1.1 eV, for Ge is 0.7 eV, and for GaAs is 1.4 eV

- Insulators: Valence band full, conduction band empty, $E_g > 3$ eV

- e.g. diamond $E_g = 5.5$ eV

- N.B. $k_B T$ @ 300 K = 0.025 eV



At the start of this video, we showed the production of bonding and anti-bonding orbitals as two isolated atoms converge and their electrons interact. Two isolated valence orbitals combined to produce one bonding and one anti-bonding orbital. In the case of condensed matter, there may be of the order of Avagadro's number, in other words, six times 10 to the 23 atoms, which will interact with one another to a greater or lesser extent. This causes the combined orbitals to generate two sets of orbitals that are extremely densely packed so that they form continuous bands. The lower energy one is the valence band, and the upper energy one is the conduction band. They are in general separated by an energy gap E_g , which depends on how strongly the electrons interact with one another.

Notes

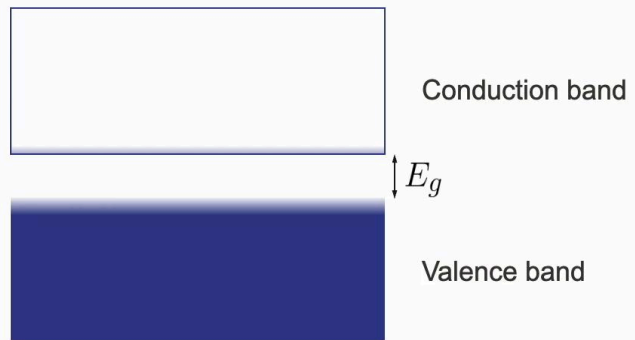
Summary



Orbitals – from isolated atoms to condensed matter

- Metals: Valence band only partially filled (@ 0K)
- Semi-metals: $E_g \leq 0$
 - e.g. arsenic, bismuth, and antimony
- **Semiconductors:** $E_g \sim 1 - 3 \text{ eV}$
 - e.g. $E_g = 1.1 \text{ eV}$ for Si, 0.67 eV for Ge, and 1.43 eV for GaAs
- Insulators: $E_g \gtrsim 4 \text{ eV}$
 - e.g. diamond $E_g = 5.5 \text{ eV}$

- N.B. $k_B T$ @ 300 K = 0.025 eV



We now consider different scenarios of occupation in the valence and conduction bands and the impact of their energy gap separation given by EG. Metals are defined as having valence bands, which are only partially filled, even at zero degrees Kelvin. It is therefore possible for electrons to jump from an occupied to an unoccupied state within the same band if they receive some energy. Note that the thermal energy of a particle is approximately k_B times T or more accurately, each degree of freedom has an average energy of $k_B T$ Divided by two. Here, k_B is the Boltzmann constant, which is 1.38×10^{-23} joules per kelvin, and T is the absolute temperature. Semi metals are different in that there is an overlap between the valence and conduction band, which allows the promotion of electrons to a higher level. Examples of semi metals include arsenic, bismuth, and antimony. Semiconductors are characterized by having an energy gap, typically between one and three electronvolts. Although the probability of a given electron within a thermally distributed ensemble of around 10^{23} electrons at room temperature, the probability that it will have enough energy to be promoted to the conduction band is extremely small, a sufficient number will indeed be promoted to allow conduction.

Notes

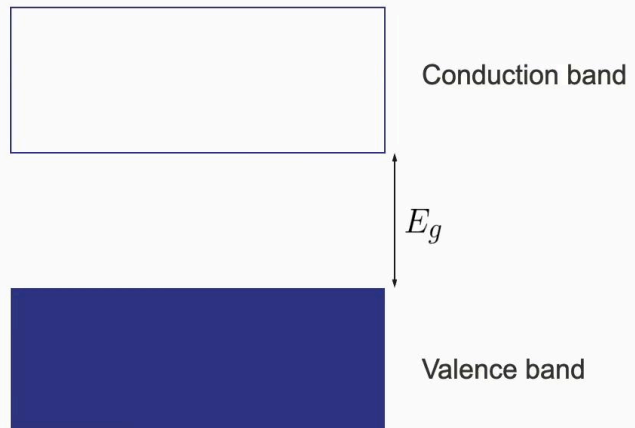
Summary



Orbitals – from isolated atoms to condensed matter

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- N.B. $k_B T @ 300 \text{ K} = 0.025 \text{ eV}$



Conductivity thus increases with the sample temperature. Note incidentally, that the intrinsic density of conduction electrons in undoped silicon is around 1.45×10^{10} per cubic centimeter. The density of atoms in silicon is about 5×10^{22} per cubic centimeter. Hence, only about one in 3×10^{10} silicon atoms will have an electron that is in the conduction band. Doping the silicon with trivalent or pentavalent atoms such as boron or phosphorus radically increases the conductivity by adding dopant bands that extend the valence band upwards and the conduction band downwards, thus reducing the energy gap. Insulators are characterized by having a band gap that is so large that no significant number of electrons can be thermally excited from the valence to conduction band. A good example is diamond with a band gap of 5.5 electronvolts.

Notes

Summary



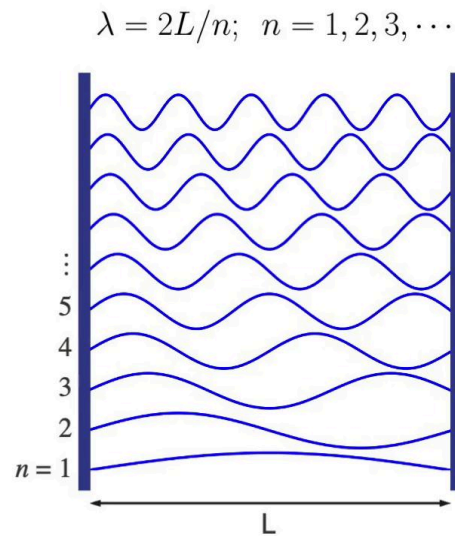
The Fermi gas

- Describes free electrons in a metal
- 1D box, electrons trapped inside
 - EM-theory demands zero E-field at boundary $\Rightarrow \lambda = 2L/n$
 - Energy level given by λ (or $k = 2\pi/\lambda$)

$$E = \frac{p^2}{2m_e} = \frac{\hbar^2 k^2}{2m_e} = \frac{\hbar^2 n^2 \pi^2}{2m_e L^2}$$

- Pauli exclusion principle allows maximum 2 electrons per energy level (spin up and spin down)
- N electrons. Highest energy = E_F @ 0K

$$E_F^{(1D)} = \frac{\hbar^2 \pi^2}{2m_e L^2} \left(\frac{N}{2} \right)^2$$



See also Supplementary material "The Fermi gas and the Fermi level"

We now turn to the behaviour of electrons in a metal. The Fermi gas model starts off by assuming that the conduction electrons are completely free to move as they please without influence from the ionic cores of the atoms, or indeed without any interaction with one another. Let's consider a one dimensional case corresponding to a single line of regularly separated metal atoms of length L. Electromagnetic theory demands that the electric field at the boundaries to the box be zero resulting in standing waves emerging from electrons with periodicity 2L divided by N. But the momentum of the electron is p is equal to h upon lambda, which is equal to h bar k. The electron kinetic energy is thus p squared upon 2m_e, which is equal to h bar squared, k squared divided by 2m_e. Using our expression for lambda, we then get E is equal to h bar squared n squared pi squared divided by 2m_e L squared. The Pauli exclusion principle allows a maximum of only two electrons per energy level, one with spin up, the other spin down. If we say there are large N electrons in total, there will be large N divided by two energy levels, each occupied by two electrons. The highest energy, called the Fermi energy, is therefore equal to h bar squared pi squared divided by 2m_e L squared times N upon two squared.

Notes

Summary



The Fermi gas in 3D

- In 3D

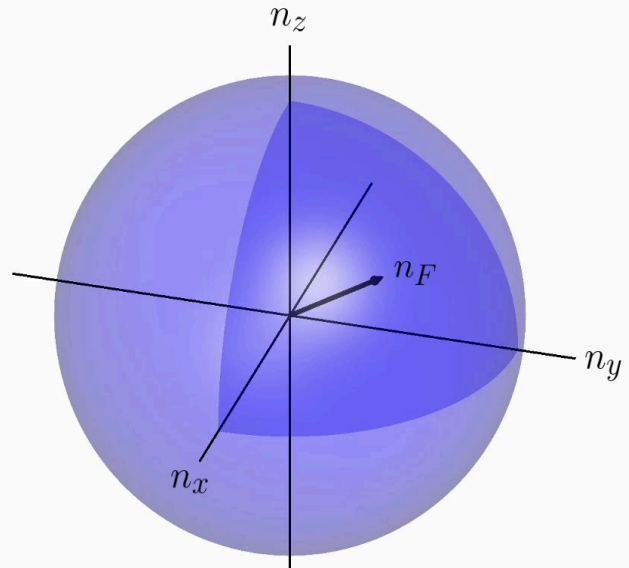
$$E^{(3D)} = \frac{\hbar^2 \pi^2}{2m_e L} (n_x^2 + n_y^2 + n_z^2)$$

- But

$$N = 2 \times \frac{1}{8} \times \frac{4}{3} \pi n_F^3$$

$$\Rightarrow n_F = \left(\frac{3N}{\pi} \right)^{1/3}$$

$$\Rightarrow E_F = \frac{\hbar^2 \pi^2}{2m_e L^2} \left(\frac{3N}{\pi} \right)^{2/3}$$



See also Supplementary material "The Fermi gas and the Fermi level"

Extension of the above argument to a three-dimensional box is fairly straightforward. The energy depends independently on n_x , n_y and n_z corresponding to the three orthogonal axes of the box. We only consider positive N , therefore, the total number of electrons, large N is equal to two times the volume of an octant of a sphere of radius n_F or two times one eighth times four thirds πn_F^3 , which is equal to πn_F^3 divided by three. From this, we can say that n_F is equal to $(3N/\pi)^{1/3}$ and therefore, that E_F is equal to $\hbar^2 \pi^2 / (2m_e L^2) (3N/\pi)^{2/3}$, whereby V is equal to L^3 , the volume of the box.

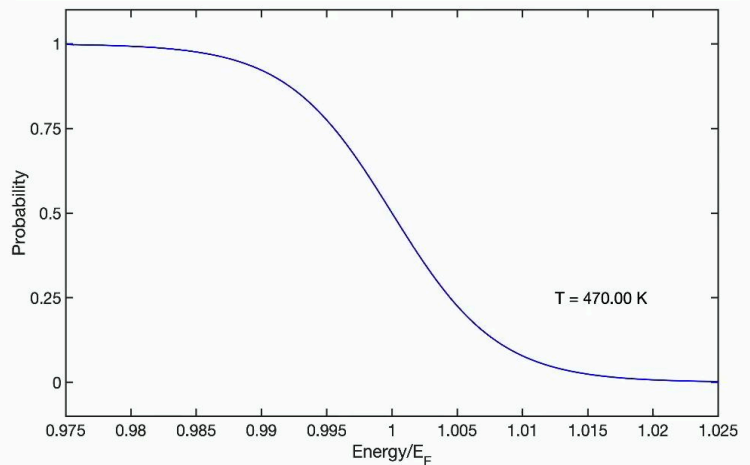
Notes

Summary



The Fermi energy and Fermi-Dirac statistics

- At absolute zero, all valence-band states filled up to E_F , all states are unoccupied above E_F
- Above 0K, some electrons can be thermally promoted to unoccupied states above E_F
- Probability of occupation @ $E_F = 0.5$
- Magnitude of E_F ?
 - $N/V \sim 10^{28} - 10^{29}/\text{m}^3$
 - e.g. Na has $2.5 \times 10^{28}/\text{m}^3$
 - $E_F \sim 2 - 10 \text{ eV}$



$$p(E) = \frac{1}{\exp[(E - E_F)/k_B T] + 1}$$

The probability of occupation of electrons in the free electron model follows the Fermi Dirac distribution shown here. At absolute zero temperature, none of the electrons have sufficient energy to access a state above E_F . All states below E_F are occupied, and all above are empty. Above zero degrees Kelvin, some electrons can be thermally promoted to unoccupied states above E_F . The probability of occupation exactly at E_F is equal to 0.5. What can we expect as a magnitude for E_F ? In other words, the energy of the highest energy electron at absolute 0 compared to that of the lowest energy electron. The number of electrons per unit volume is typically around 10 to the 22 or 10 to 23 per cubic centimeter. Hence, we can expect E_F to be around three to 10 electron volts.

Notes

Summary



15m 28s

In the next video...



In the next video, we continue with some more basic theoretical concepts that are absolutely required for spectroscopy, namely dipole transitions and associated selection rules, followed by Fermi's Golden rule.

Notes

Summary



16m 28s