Addendum on Metals and Semiconductors

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Metals:

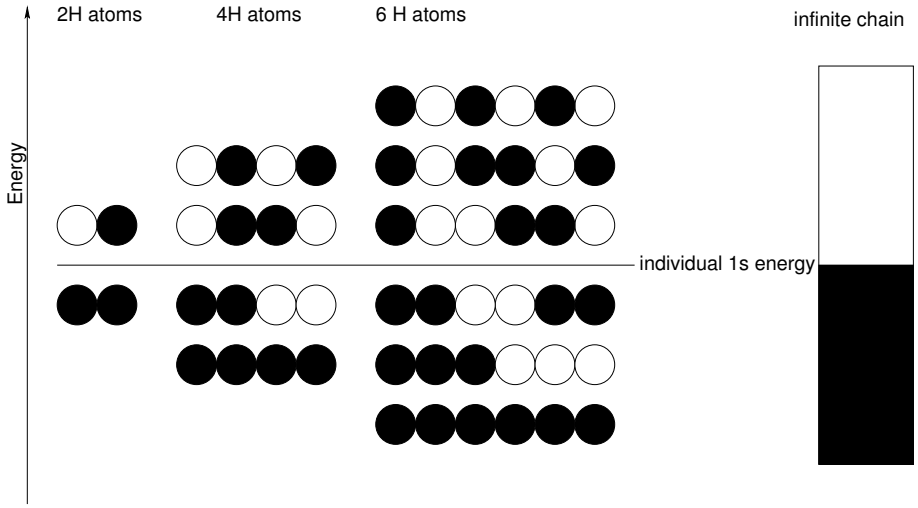
Free electron theory: In the free electron model of a metal, the valence electrons of the constituent atoms conduct by moving around freely over the lattice (crystal). Sodium metal for example, can be thought of as Na^+ cores with the [Ne] configuration, embedded in a crystalline array in a gas (plasma[1]) made up of the 3s valence electrons.

This simple theory allows for an understanding of the electrical conductivity of metals and Ohms law. The thermal conductivity of metals is also explained by the notion that the conduction electrons carrying heat.

If the electrons in the "gas" are subject to the Pauli exclusion principle (as they should be), the resulting model is called the free electron Fermi gas. In this more sophisticated model, other properties of metals such as their heat capacity are also explained rather well.

Typically, the "gas" of electrons is rather dense. At 5 K, it is 2.65×10^{22} electrons/cm^3 for Na; 1.40×10^{22} electrons/cm^3 for K; 1.15×10^{22} electrons/cm^3 for Rb.

Simple band theory: The covalent approach. The simplest form that energy band theory takes is obtained by extending the notion of covalent bonding as formed through linear combinations of atomic orbitals. Just as the H_2 molecule can be described by making linear combinations of the $1s$ orbitals on individual H atoms to form bonding (σ) and antibonding (σ^*) molecular orbitals, so too can energy bands in solids be described as linear combinations of the orbitals in extended systems (chains, planes, 3D *etc.*)

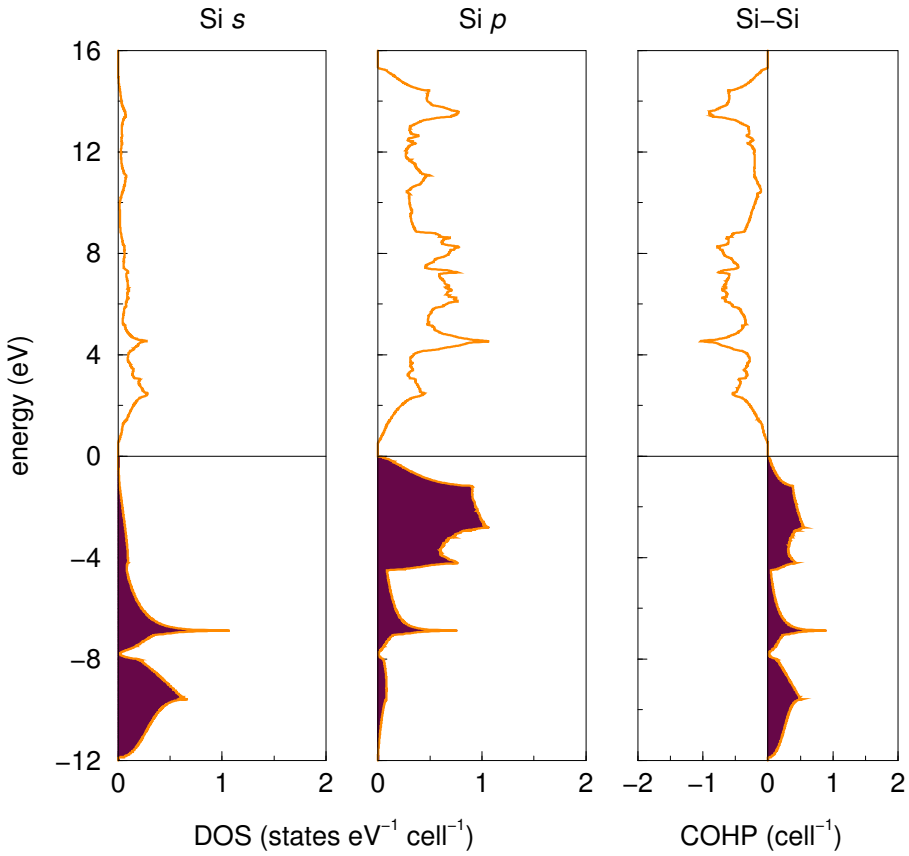


In the illustration displayed above, a chain of s orbitals can be thought as the end result of building molecular orbitals from H atoms forming *linear* H_2, H_4, H_6, and so on. The resulting *band* is half-filled since each s orbital has only one electron. The bottom of the band is most bonding and the top is most antibonding. Such a band would be metallic since it is not fully filled.

This approach allows insulators and semiconductors to be described as well; If the band were fully filled, or if it split into two bands, one filled and and the other unfilled, we would have an insulator or a semiconductor. In the next figure, we show the "real" band diagram of Si in the diamond structure, obtained from performing full quantum-mechanical calculations, using a technique called Density Functional Theory[2] to solve the quantum mechanical problem.

[1] A plasma is a gas of charged particles.

[2] Density Functional Theory arose largely from the work of Professor Walter Kohn and his collaborators in the 1960s. Professor Kohn is in the Physics Department and the KITP, UCSB. He won the Chemistry Nobel Prize in 1988.



The two panels on the left display bands, and the panel on the right displays the nature of the bonding, whether it is net bonding between neighboring Si (positive COHP[3]), or net antibonding (negative COHP).

The pragmatic hybrid picture: Combining the notion of ionic interactions, covalency, as well as metallic bands (the last being the case when bands are partially filled), we can develop an understanding of many different materials:

- For example, in the ionic approach, NaCl is insulating because a filled Cl^- $3p$ band is well-separated from an empty Na^+ $3s$ band.
- In the ionic approach, TiO_2 is insulating because a filled O^{2-} $2p$ band is well-separated from an empty Ti^{4+} $3d$ band.
- In the hybrid approach (ionic + metallic), TiO in the rock-salt structure is metallic because a filled O^{2-} $2p$ band is formed, that is below a a partially filled Ti^{2+} $3d$ band having 2 electrons.
- In the hybrid approach (covalent + metallic), TiC in the rock-salt structure is metallic because it *cannot* be written as a filled C^{4-} $2p$ band separated from an empty Ti^{4+} $3d$ band. Instead, a covalent system is formed which has a Ti-C band which is mostly bonding, that is partially filled.

[3]COHP=Crystal Orbital Hamiltonian Population.