Addendum A:
Constant Fermi Level
and
Thermal Equilibrium State

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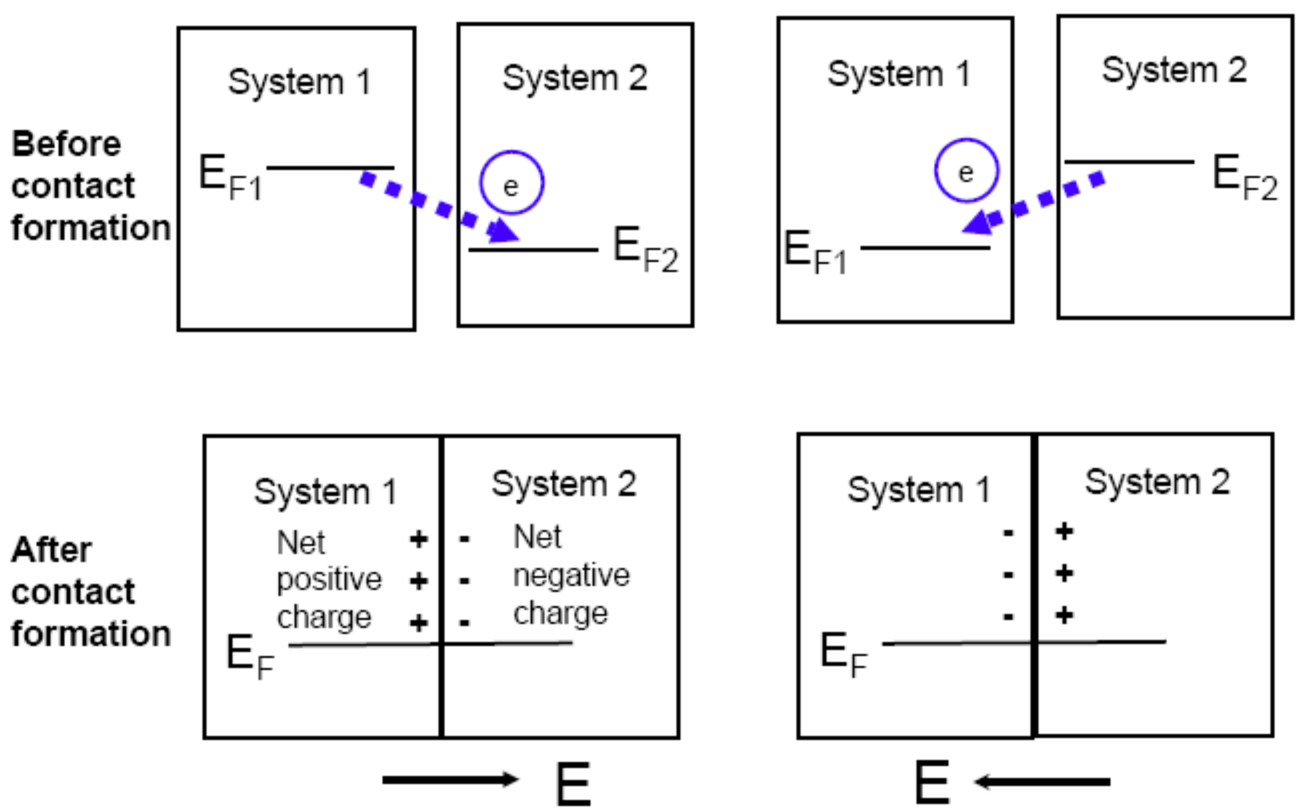
Relevance of the Fermi Level for thermal equilibrium

An important feature of Fermi level is that in thermal equilibrium the Fermi level is constant throughout a system. Consider systems 1 and and 2, for example two metals. The states below E_{F1} and E_{F2} are full with electrons; the electrons states above the Fermi level are mostly empty. If these systems are brought in contact, the electrons in the entire system will tend to seek the lowest possible energy levels. The electrons from 1 with higher Fermi level i.e. $E_{F1} > E_{F2}$ will flow into the lower energy states of system 2, until thermal equilibrium is reached. This equilibrium occurs when the Fermi energy is the same in both materials.

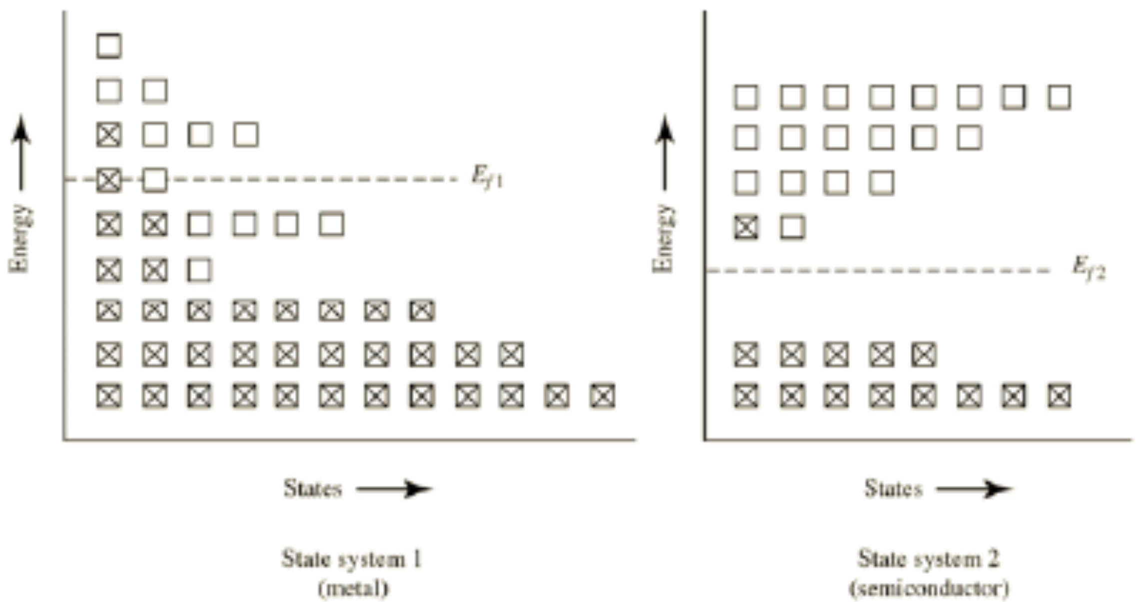
Electron Transfer during contact formation



Mathematical Derivation of the constancy of Fermi level in thermal equilibrium

The filled density for system 1 or 2 is $n_{1,2}$ and the vacant state density is $v_{1,2}$, and $g_{1/2}$ is the density of states and where f_D is the Fermi distribution. Equilibrium is reached when there is no net transfer of electrons at any energy (it does not mean cessation of all processes (every process and its inverse are occurring at the same rate). Equilibrium can be expressed mathematically by noting that that the transfer is proportional to the density of electrons and the vacant density states top which the electron transfers.
The transfer from 1 to 2, will depend on how many electrons are in system 1 and how many empty states are available in system 2 to receive these electrons times some rate of elementary electron transfer rate constant r_e;

Transfer 1→2: $T_{12}=r_e \times n_1 \times v_2$
Transfer 2→1: $T_{21}=r_e \times n_2 \times v_1$ In thermal equilibrium $T_{12}=T_{21}$. We need expressions for filled n and empty v states – see next slide:



Mathematical Derivation of the constancy of Fermi level in thermal equilibrium

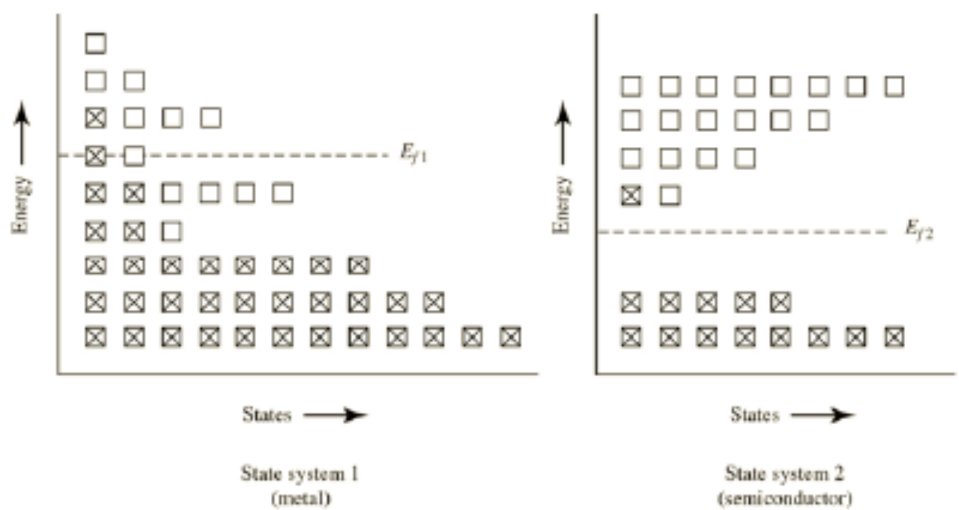
$$n_{1,2} = g_{1/2} \cdot f_{D1,2}$$

$$v_{1,2} = g_{1/2} \cdot (1 - f_{D1,2})$$

$$f_{D1,2} = \frac{1}{1 + \exp[(E - E_{f1,2})/kT]}$$

Fermi distribution for electrons

n - filled states
n - empty states
g - density of states



Therefore $T_{12}=T_{21}$ leads to:

$$n_1 \cdot v_2 = n_2 \cdot v_1$$

$$f_{D1} g_1 (1 - f_{D2}) g_2 = f_{D2} g_2 (1 - f_{D1}) g_1$$

$$f_{D1} g_1 g_2 = f_{D2} g_2 g_1$$

This can be only true if $f_{D1} = f_{D2}$

or $E_{f1}=E_{f2}$ →

constant Fermi energy level