Space Charge Transfer in Hybrid Inorganic/Organic Systems

Yong Xu1,*, Oliver T. Hofmann1, Raphael Schlesinger2, Stefanie Winkler3, Johannes Frisch2, Jens Niederhausen2, Antje Vollmer4, Sylke Blumstengel2, Fritz Henneberger2, Norbert Koch2,3, Patrick Rinke1, and Matthias Scheffler1
1Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany
2Humboldt-Universität zu Berlin, Institut für Physik, 12489 Berlin, Germany
3Helmholtz-Zentrum Berlin für Materialien und Energie GmbH-BESSY II, 12489 Berlin, Germany

The adsorption energy \( \Delta E_{q}^{ads} \) of an adsorbate that receives \( q \) electrons from the electron reservoir with an electron chemical potential \( \epsilon_{F} \) can be written as

\[
\Delta E_{q}^{ads}(\epsilon_{F}) = -E_{q}^{surf/mol} + E_{0}^{surf} + E_{0}^{mol} + q\epsilon_{F} + \Delta E_{SC}.
\]  
(1)

\( E_{q}^{surf/mol} \) is the total energy of the adsorbate system computed in a supercell with \( q \) excess electrons. \( E_{0}^{surf} \) and \( E_{0}^{mol} \) are the total energies of the neutral bare substrate and the neutral molecule. This definition is similar to that used in calculations of defects in the bulk or at interfaces [1–3], but differs in the additional term \( \Delta E_{SC} \) that represents the energy correction for describing the space-charge layer.

For the bare substrate, \( E_{0}^{surf} \) is related to \( E_{surf}^{q} \) (the total energy in the charged state) by the definition of the Fermi level \( \epsilon_{F}^{surf}(q) = dE_{surf}/dq \). We thus have

\[
E_{q}^{surf} - E_{0}^{surf} = \int_{0}^{q} dq' [\epsilon_{F}^{surf}(q') - \epsilon_{F}] = q\delta - q\Delta\epsilon_{F},
\]  
(2)

where \( \epsilon_{F} \) can be referenced to energy levels of the bare substrate, for instance, the conduction band minimum \( \epsilon_{CBm} \) for electrons and the valence band maximum \( \epsilon_{VBM} \) for holes.

For electrons,

\[
\Delta\epsilon_{F} = \epsilon_{F} - \epsilon_{CBm},
\]  
(3)

and we obtain

\[
\delta = \frac{\int_{0}^{q} \epsilon_{F}^{surf}(q') - \epsilon_{CBm} E D(E) dE}{\int_{0}^{q} \epsilon_{F}^{surf}(q') - \epsilon_{CBm} D(E) dE},
\]  
(4)

where \( D(E) \) is the density of states (DOS) of the bare substrate.

For holes,

\[
\Delta\epsilon_{F} = \epsilon_{F} - \epsilon_{VBM},
\]  
(5)

and we obtain analogously

\[
\delta = \frac{\int_{0}^{q} \epsilon_{VBM} - \epsilon_{F}^{surf}(q') E D(E) dE}{\int_{0}^{q} \epsilon_{VBM} - \epsilon_{F}^{surf}(q') D(E) dE},
\]  
(6)

In the limit of small \( q \), \( \delta \) becomes zero. Combining Eq. (1) and Eq. (2), the adsorption energy becomes

\[
\Delta E_{q}^{ads}(\epsilon_{F}) = (-E_{q}^{surf/mol} + E_{q}^{surf} + E_{0}^{mol}) + (q\Delta\epsilon_{F} - q\delta) + \Delta E_{SC}.
\]  
(7)

Fermi level as a function of dopant concentration

The Fermi level position \( \Delta\epsilon_{F} = \epsilon_{F} - \epsilon_{CBm} \) of \( n \)-type semiconductors (ZnO here) is related by the bulk dopant concentration \( N_{D} \) by the relation [4]:

\[
\frac{N_{D}}{1 + 2 \exp(-\frac{\Delta\epsilon_{F}}{k_{B}T}) \exp(-\frac{E_{d}}{k_{B}T})} = N_{C} \frac{2}{\sqrt{\pi}} F_{1/2}(\frac{\Delta\epsilon_{F}}{k_{B}T}).
\]  
(8)

\( E_{d} \) is the donor binding energy and \( N_{C} \) the effective density of states in the conduction band, which is given by

\[
N_{C} = 2(\frac{2\pi m^{*}k_{B}T}{h^{2}})^{3/2}.
\]  
(9)

Here \( m^{*} \) is the density of state effective mass for electrons, \( k_{B} \) the Boltzmann constant, \( T \) the temperature and \( h \) the Planck constant. \( F_{1/2} \) is a function defined as

\[
F_{1/2}(\eta_{F}) = \int_{0}^{\infty} \frac{\eta^{1/2} d\eta}{1 + \exp(\eta - \eta_{F})}.
\]  
(10)

For ZnO we used the following parameters: \( E_{d} = 30 \) meV [5], \( m^{*} = 0.27 m_{e} \) (\( m_{e} \): mass of free electron) [4], \( T = 300 \) K.

* yangxu@fhi-berlin.mpg.de