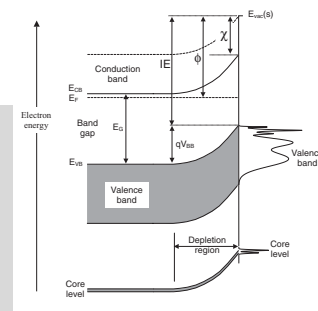


Electron Energetics at Surfaces and Interfaces: Concepts and Experiments**

By David Cahen* and Antoine Kahn*

We present a concise, although admittedly non-exhaustive, but hopefully didactic review and discussion of some of the central and basic concepts related to the energetics of surfaces and interfaces of solids. This is of particular importance for surfaces and interfaces that involve organic molecules and molecular films. It attempts to pull together different views and terminologies used in the solid state, electrochemistry, and electronic device communities, regarding key concepts of local and absolute vacuum level, surface dipole, work function, electron affinity, and ionization energy. Finally, it describes how standard techniques like photoemission spectroscopy can be used to measure such quantities.



1. Introduction

The experimental determination of the work function (ϕ) and related characteristics of a given solid surface, e.g., electron affinity (χ) and ionization energy (IE), have long been recognized as exceedingly important for enabling the prediction and understanding of the energetics of interfaces formed by combining the solid with another solid.^[1–3] For free surfaces, these energetics govern charge carrier emission and other basic mechanisms of electronic and optoelectronic responses of the material. For device interfaces, these energetics govern electronic transport through the device under various stimuli or operating conditions.

Lately, the increasing level of research and device development activity involving a variety of organic, often molecular, interfaces and their modification using organic- and inorganic-induced surface dipoles^[4,5] has tested our fundamental understanding of basic surface energetics, which was developed primarily for well-defined, clean, mostly non-molecular inorganic surfaces and interfaces.^[3] In addition, the nature of developments in what are often called “organic electronics”^[6–8]

and “molecular electronics”,^[9,10] including the behavior of organic molecules on more traditional surfaces,^[11] has tested our ability to make the “classical” understanding available to specialists from areas other than that of surface science. This is important because of the pivotal role that such experts and their expertise do and will play, as their areas of expertise become more and more part of research where these surface and interface boundary regions are crucial. This then defines the purpose of the following, a concise discussion of several of the central concepts used to describe surfaces and interfaces (electronically), and in particular how their electronic characterization can be done with standard techniques such as photoemission spectroscopy.

2. Vacuum Level

The *vacuum level of a finite-size sample* ($E_{\text{vac}}(s)$ in Fig. 1a), as used at times in describing the electron energetics of surfaces in solid state devices, and as discussed in work function measurements, is defined as the energy of an electron at rest just outside the surface of the solid.^[12] In the case of a metal, this distance is also the one where there is no effect of image forces, i.e., where the image potential is essentially zero. This vacuum level is a characteristic of the surface, and depends sensitively, through the electronic surface dipole (see below), on the atomic, chemical, and electronic structures of the outer atomic layers of the solid.

The *vacuum level at infinity* ($E_{\text{vac}}(\infty)$ in Fig. 1a) is defined as the energy of an electron at rest at infinite distance from the surface. That energy level is invariant, but, as will be explained below, this is a reference level that is experimentally not accessible.

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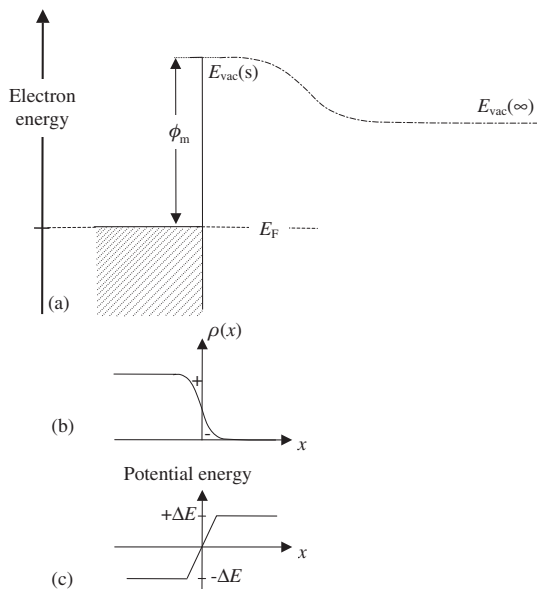


Fig. 1. a) Vacuum level close to the surface $E_{vac}(s)$, work function ϕ_m , and vacuum level at infinity $E_{vac}(\infty)$. The transition between the two levels marks the attenuation of the dipole field. b) Electron distribution density, $\rho(x)$ inside and outside the solid, which creates a dipole layer and contributes to the work function. c) Electron potential energy step, $2\Delta E$, induced by the dipole at the surface.

For a multi-phase system that is electronically in thermodynamic equilibrium, the Fermi level is constant and $E_{vac}(\infty)$ can be viewed as a level at a fixed energy from the Fermi level (at lower electron potential energy; see below). In principle, ab-initio theoretical calculations should be able

to give an exact value of this fixed energy by excluding all electrostatic (including dipolar) contributions to the potential energy.

The energy difference between these two vacuum levels stems from the contributions of surface dipoles and, in the case of non-metallic surfaces also from extra charges on the solid surface, to the work function. The surface dipole on metals normally raises^[13] the vacuum level, as it is caused by spilling of the electronic charge density out of the surface, leaving a positive charge inside (Fig. 1b). Note that, according to the solid state scale, the total electron energy increases upward^[13,14] in Figures 1–4. As the electron crosses the surface dipole on its way out of the solid, its potential energy is raised by an amount equal to the dipole energy barrier (Fig. 1c). As the electron moves away from the (finite-size) surface, the dipole field and the potential energy decrease, as depicted in Figure 1a.

In that context, there is sometimes confusion as to which vacuum level ($E_{vac}(\infty)$ or $E_{vac}(s)$) is measured with a technique such as photoemission spectroscopy. With this type of measurement, detection (measurement of the kinetic energy of the photoemitted electron) is performed at a distance away from the surface that is large, certainly on the atomic scale and probably on the scale of usual sample dimensions. Therefore, the measurement occurs in a region where the vacuum level has at least partially, and probably completely, converged toward $E_{vac}(\infty)$. We review below two arguments that demonstrate that also here $E_{vac}(s)$, the vacuum level right outside the solid, is the measured quantity.



David Cahen completed his B.Sc. in Chemistry at the Hebrew University of Jerusalem and his Ph.D. in (Materials) Chemistry at Northwestern University, USA (including some XPS and UPS studies). He then returned to Israel to carry out postdoctoral research in (the bioenergetics of) photosynthesis. In 1976 he joined the Weizmann Institute, starting work on photoelectrochemical and other solar cells. This led to work on the materials chemical aspects of electronic materials and devices, and to studying such issues as fundamental solid-state chemical limits to device miniaturization and stability (also part of his current interests, for new solar cells). This has evolved into his work on hybrid molecular/non-molecular materials, which, in turn, led to his present work on understanding how molecules and electronic transport can co-exist, and the limitations and possibilities for fundamentally novel science in this area.



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$E_{\text{vac}}(s)$ differs from the reference level $E_{\text{vac}}(\infty)$, as can be understood by considering different crystallographic faces of a single crystal of metal (W, tungsten, is a good example). Consider the classic gedanken experiment, recently related again by Ishii and coworkers,^[4] in which an electron leaves the crystal through the (111) face. This requires 4.47 eV. We now return it to the bulk of the crystal but via the (110) face. This yields 5.25 eV. The difference in energy (0.78 eV) is due to the difference in the electrostatic potential step across the surface dipoles at the (111) and (110) surfaces. To see that one cannot make a perpetuum mobile from this we need to realize that, when taking an electron out from the Fermi level through the (111) face, we somehow have to get it above the (110) surface, to get it back in through that face, and down to the Fermi level. To bring it to just outside^[12] the (110) face, we spend 4.47 eV to bring the electron from the Fermi level to the vacuum level over the (111) face, then another 0.78 eV to move it over to just above the (110) surface, then recover 5.25 eV when we drop it back to the Fermi level in the solid. So we spend 0.00 eV.

Alternatively, we can bring the electron to infinity. That means that it will reach a reference level that is at an unspecified energy with respect to the vacuum level at the (111) surface. While the exact position of this level is not clear, we can position it qualitatively: as the surface dipole on a metal normally has its negative pole sticking out, it is likely that this reference level is below 4.47 eV (at less than 4.47 eV from the Fermi level of the tungsten). So, we need less energy than in the first case. Let us call this energy E_0 . We then bring the electron over the (110) surface, but at infinity. As we now bring the electron closer to the surface, we need to invest not only 0.78 eV, as in the first case, but also E_0 , to get it just above the (110) face. When we bring it back in, at the Fermi level, we gain 5.25 eV and are left with 0.00 eV energy gain or loss. Experimentally, electrons that were originally at the Fermi level are ejected through the (111) face with a kinetic energy $E_{\text{Kin}} = h\nu - 4.47$ eV. Those ejected through the (110) face come out with $E_{\text{Kin}} = h\nu - 5.25$ eV. The difference in kinetic energy is exactly the opposite of the difference in potential energy due to the differences in work function. So, total energy is conserved. This argument is therefore entirely consistent and independent of the value of E_0 , which is not measurable.

As a preliminary question to the second argument, we ask the following: Can we *experimentally* measure the “absolute” vacuum level $E_{\text{vac}}(\infty)$, in a photoelectron emission experiment?^[15] In order to perform such a measurement, one would need to be able to measure the kinetic energy of the electron with respect to $E_{\text{vac}}(\infty)$. The prob-

lem is that, in such an experiment, the detector is a real one (as opposed to a gedanken detector), made of a solid with its own work function, including surface dipole and, possibly, surface electrostatic field contribution. Thus, the kinetic energy measured by the detector must itself be a function of the detector’s work function.

Figure 2a drives home the point that the vacuum level that is measured in photoemission spectroscopy, e.g., ultraviolet photon spectroscopy (UPS), is $E_{\text{vac}}(s)$, and not $E_{\text{vac}}(\infty)$. Let us assume that the sample under investigation is a metal. The UPS energy distribution spectrum contains primary electrons, whose kinetic energy, as measured *by the detector*, can be as much as $E_{\text{K}}^{\text{max}}$ for electrons originally at the Fermi level. The minimum kinetic energy that can be measured in such an experiment ($E_{\text{K}}^{\text{min}}$), corresponds to those electrons that have just enough energy to escape from the solid, i.e., arrive at an energy at or just above $E_{\text{vac}}(s)$. These electrons are either directly excited from a filled state with an energy $h\nu$ below $E_{\text{vac}}(s)$, or higher energy electrons that have lost energy via scattering on their way toward the surface. These electrons, also called *secondary* electrons, constitute the large majority of slow electrons forming the “secondary tail” in photoelectron emission spectra. Electrons that escape from the solid just above $E_{\text{vac}}(s)$ at the cut-off, have nearly zero kinetic energy. However, the total energy of these electrons is conserved in vacuum. Assuming that the vacuum level of the detector is lower than $E_{\text{vac}}(s)$,^[16] the electrons gain kinetic energy (and lose potential energy) between the sample surface and the entrance of the detector, by an amount equal to the difference in potential energy at these two points. This amount is equivalent to the difference between the work function of the sample and that of the detector. These cut-off electrons are detected with kinetic energy $E_{\text{K}}^{\text{min}}$ (Fig. 2a). $E_{\text{K}}^{\text{min}}$ is unrelated

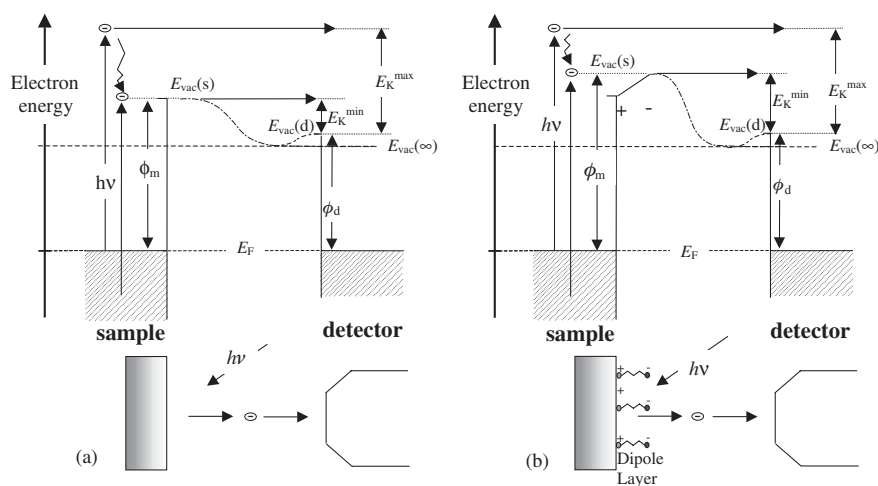


Fig. 2. a) Energy diagram of a metal surface and electron detector in equilibrium. The Fermi level E_{F} is aligned across the system. The vacuum level of the metal surface ($E_{\text{vac}}(s)$), and of the detector, $E_{\text{vac}}(d)$ and their respective work functions, ϕ_{m} and ϕ_{d} , are shown. The vacuum level at infinity $E_{\text{vac}}(\infty)$ is arbitrarily chosen below $E_{\text{vac}}(s)$ and $E_{\text{vac}}(d)$. Also shown are: a primary electron photoexcited from the Fermi level, and detected with kinetic energy $E_{\text{K}}^{\text{max}}$; and a secondary electron escaping the solid just above $E_{\text{vac}}(s)$, and detected with kinetic energy $E_{\text{K}}^{\text{min}}$. b) Same as (a), with an additional molecule-induced surface dipole, which raises the vacuum level of the sample and $E_{\text{K}}^{\text{min}}$.

to $E_{\text{vac}}(\infty)$, and is defined directly by the difference between the vacuum level of the sample $E_{\text{vac}}(\text{s})$ and that of the detector $E_{\text{vac}}(\text{d})$. Assuming that the latter does not change in the course of the experiment, a change in $E_{\text{K}}^{\text{min}}$ indicates a change in $E_{\text{vac}}(\text{s})$ caused, for example, by a surface dipole, as seen in Figure 2b. In this particular case, polar molecules adsorbed on the sample surface induce a dipole, which opposes the escape of electrons by effectively raising the work function of the sample. This change is detected as an increase in kinetic energy $E_{\text{K}}^{\text{min}}$ of the electrons at the photoemission cut-off. Also this argument is entirely independent of $E_{\text{vac}}(\infty)$ and takes into account only the measurable values of the sample and detector vacuum levels, $E_{\text{vac}}(\text{s})$ and $E_{\text{vac}}(\text{d})$.

In the case of a Kelvin probe experiment, the measurement of $E_{\text{vac}}(\text{s})$ is always relative to $E_{\text{vac}}(\text{reference})$, and $E_{\text{vac}}(\infty)$ as such does not come into consideration. In the well-known classical vibrating capacitor mode, the probe is placed within ~ 0.1 mm of the surface.^[17–19] Such a distance is large with respect to the surface dipole dimensions, but small with respect to the surface dimensions (the same is true for the atomic force microscopy (AFM)-based Kelvin probe, where the tip of the cantilever is within a few nanometers of the surface).^[19] Within the picture developed above, the probe clearly “sees” $E_{\text{vac}}(\text{s})$. The measurement yields the difference between $E_{\text{vac}}(\text{s})$ and $E_{\text{vac}}(\text{tip})$, also known as contact potential difference (CPD) between the two surfaces.

3. Work Function and Local Work Function

Turning our attention to the work function, we consider the definition given by Wandelt.^[20] It is useful to consider both the gedanken case of a surface with infinite dimensions, for which the vacuum level far away from the surface, i.e., $E_{\text{vac}}(\infty)$ is the same as that defined above as $E_{\text{vac}}(\text{s})$ and is the relevant vacuum level, and the realistic case of a finite surface for which $E_{\text{vac}}(\text{s})$ is the relevant level.

In the case of the infinite surface, Wandelt defines the work function as the energy difference between two states. In one state the electron is in the highest occupied level of the neutral ground state of the solid, i.e., the Fermi level, and in the other the solid is singly ionized and the electron at infinity in vacuum at rest, at the (absolute) vacuum level $E_{\text{vac}}(\infty)$. (Naturally in all materials but metals or degenerate semiconductors, there are no actual energy levels at the Fermi level and the Fermi level is a statistical concept).^[24]

In the (realistic) case of the finite surface, the second state is that of the singly ionized solid with the electron *at rest* at $E_{\text{vac}}(\text{s})$ just outside the solid. Given that the secondary electron low kinetic energy cut-off ($E_{\text{K}}^{\text{min}}$) in UPS represents (after adding the photon energy) the local vacuum level $E_{\text{vac}}(\text{s})$ of the sample (Fig. 3), UPS gives a direct measure of the work function of the solid, as opposed to the Kelvin probe which gives a value relative to the work function of the probe itself. In the UPS spectrum, ϕ_{m} is therefore the difference between the kinetic energy measured at the detector for electrons at

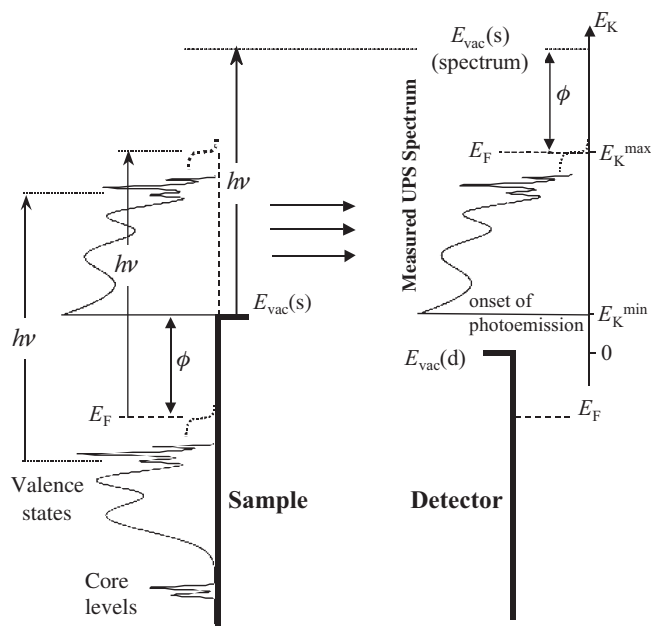


Fig. 3. Photoemission process and UPS spectrum of a semiconducting material. Bottom left: valence band and core levels, vacuum level of the solid, and Fermi level derived from the Fermi step measured on a metal surface electrically connected to the semiconductor. Top left and right: electrons photoexcited above E_{vac} , and detected with kinetic energy E_{K} by the detector. The position of the vacuum level with respect to the UPS spectrum is obtained by translating E_{vac} by one photon energy. E_{Kmin} and E_{Kmax} are the kinetic energies of electrons excited from the Fermi level and escaping the solid just above E_{vac} , respectively. From the figure: $\phi = E_{\text{K}}^{\text{min}} + hv - E_{\text{K}}^{\text{max}}$ (Eq. 1 in text).

the cut-off plus the photon energy, and the energy of the electrons originating from the Fermi level of the sample:

$$\phi_{\text{m}} = E_{\text{K}}^{\text{min}} + hv - E_{\text{K}}^{\text{max}} \quad (1)$$

Wandelt also discusses the notion of a *local work function*,^[20] which includes lateral variations of the surface dipole field on the atomic scale. The local work function (of a metal) includes the electrical effect of surface dipoles and image potential. The lateral variations of the potential over the surface can be probed, for example, via photoemission from core levels of adsorbed Xe. The binding energy of a Xe atomic level depends on the potential at the site of adsorption. Thus photoemission spectroscopy can distinguish between different sites, and therefore point out differences in “local work function” over the surface. This is of course entirely consistent with the fact that photoemission measures the local work function and therefore the local vacuum level, as argued above.^[21]

4. Local Vacuum Level in Device Physics

Strictly speaking, we cannot define a “vacuum level” inside a solid or at an interface, since there is no “vacuum” gap, and since the basic concept of a vacuum level implies the energetics of escape of an electron from the solid through a surface. Alternatively it suffices to note that such a level, if defined under specific conditions and for a specific purpose, is not experimentally accessible but can be conceptually useful.

This is the case of the vacuum level that is often used in electron energy diagrams for electronic devices (Fig. 4). The local vacuum level concept has been explained by Marshak^[22] and recently by Kronik and Shapira, in their review of surface photovoltage phenomena.^[19] It is a concept that can be found already in the early semiconductor literature.^[1,23] That level is described as following the bands, whose energies are given by the sum of the standard chemical potential of the electron (i.e., the chemical potential,^[24] excluding density/activity effects, μ_e^0) and the electrostatic potential (ψ):

$$E_{CB} = \mu_e^0 + q\psi \quad (2)$$

$$E_{VB} = \mu_e^0 + q\psi - E_G \quad (2a)$$

where q is the electron charge and E_G the semiconductor bandgap. This local vacuum level, E_{vac}^{loc} is given by

$$E_{vac}^{loc} = a + q\psi \quad (3)$$

where the constant a can be taken as the energy difference between the Fermi level^[24] and the absolute vacuum level $E_{vac}(\infty)$. As such it follows only the variation in electrostatic potential ψ , which is continuous. It does NOT include any differences in standard chemical potential of the electrons, which can be expressed as spikes and cliffs in the bands.

Only in this way can the difference between the local and absolute vacuum levels be given by the electrostatic potential in the gedanken figures (Fig. 4) where both are drawn *all through* a given device or experimental structure. A reference level is then defined that essentially is parallel to the absolute vacuum level $E_{vac}(\infty)$. Since $E_{vac}(\infty)$ is also not defined inside a structure, it is simplest to define this reference level as being

equidistant (in energy) from the Fermi level of the system under consideration, at an energy b :

$$E_{REF} = E_F + b \quad (4)$$

This then fits perfectly with the UPS experimental situation where all data are referred to the Fermi level^[24] of the electron energy analyzer, which should be in electronic equilibrium with the sample that is being investigated.^[14,25–31]

Returning to the surface, we note that in the case of a semiconductor the work function can also contain a contribution from band bending (V_{BB}), in addition to contributions of the chemical potential, the surface dipole, and image potential. As band bending is the result of an electrostatic field, which raises or lowers the potential of the surface with respect to the bulk, all surface electronic levels, from core levels to filled valence levels, empty conduction levels, and $E_{vac}(s)$ follow the band bending (Fig. 5). As a consequence, and everything else being equal, the work function of the semiconductor follows the change in band bending. The relative magnitude of the image potential contribution depends on the free carrier density of the semiconductor. At low carrier densities, there still is a local polarization contribution, but no image potential contribution as known from metal physics.

5. Electron Affinity and Ionization Potential

In the usual description of the physicist, the *electron affinity* (χ) at a semiconductor surface is defined as the energy required to excite an electron from the bottom of the conduction band minimum (E_{CB}) *at the surface* to the local vacuum level (Fig. 5). Similarly, the *ionization energy* (IE) is defined as the energy needed to excite an electron from the top of the valence band maximum (E_{VB}) *at the surface* to the local vacuum level. As the bandgap collapses to zero and the semiconductor becomes a metal, both χ and IE converge toward the work function defined above.

The chemical definition of χ , used for molecules, is the energy gained by an originally neutral molecule when an electron is added to the lowest-unoccupied molecular orbital (LUMO) of the neutral molecule. This definition is, in principle, equivalent to the previous one, although one should be aware of issues that are specific to molecular solids. In particular one should keep in mind when performing photoelectron spectroscopies that molecules are relatively small N -electron systems, which are significantly perturbed by the addition ($N \rightarrow N+1$) or removal ($N \rightarrow N-1$) of an electron. Unlike in non-molecular

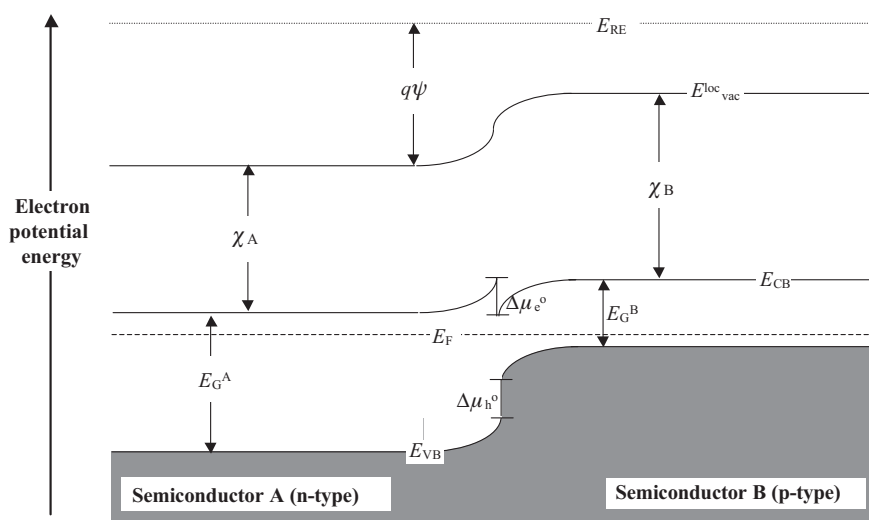


Fig. 4. Illustration of the use of the concept of local vacuum level in energy band diagrams of electronic device structures [1,19,22]. q : electron charge, ψ : electrostatic potential, E_{CB} : the bottom of the conduction band, E_{VB} : top of valence band, $\Delta\mu_e^0$: the difference in standard chemical potentials of the electron (excluding density/activity effects) between the two types of semiconductors, χ : electron affinity, E_G : bandgap.

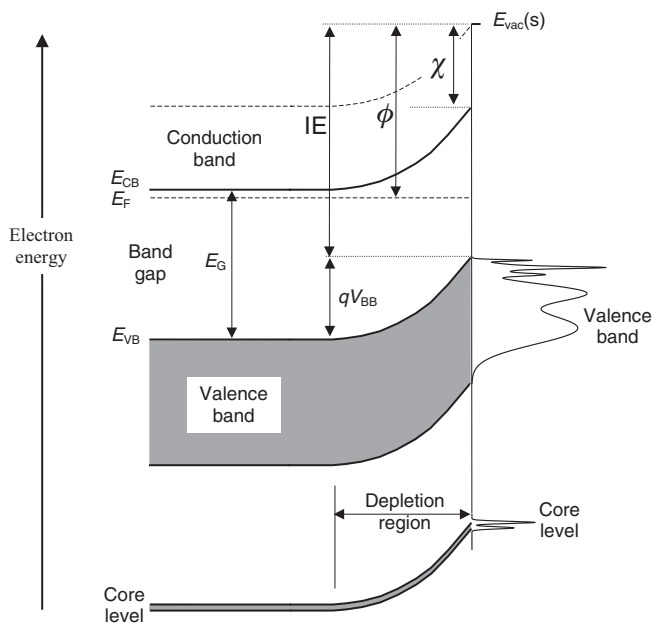


Fig. 5. Energy band diagram of a semiconductor near its surface, showing the band bending (qV_{BB}) and the evolution of all the energy levels within the depletion region. The work function ϕ depends directly on qV_{BB} . IE: ionization energy; χ : Electron affinity; E_G : Bandgap.

electronic solids, where electrons and holes in the conduction and valence bands are highly delocalized and the addition or removal of a charge does not significantly alter the electronic levels, in small molecules large (0.5–1.0 eV) electronic and atomic relaxations occur upon formation of the molecular ion. χ can be calculated as the differences in total electronic energy between the neutral molecule and the radical anion. For some systems, such calculations can be done for identical geometry systems, while for others, the relaxed conformation of the radical anion must be included. Similar issues exist for calculations of the IE of molecules, where the radical cation is used.

The issue of how to calculate the IE and χ of molecules is highly relevant experimentally, as methods to determine these quantities will provide different answers. We give here the example of direct and inverse photoemission spectroscopy (PES/IPES)^[32–34] and two-photon photoemission spectroscopy (2PPES).^[35,36]

PES and 2PPES measure the same IE, as in both cases an electron is ejected from the highest occupied molecular orbital (HOMO) of the neutral molecule and a radical cation is left. The kinetic energy measured reflects the (fast) change in polarization due to electronic relaxation upon formation of the radical cation. It does not reflect the small effect of the (slow) lattice relaxation, and may or may not (depending on the time scale involved) reflect effects of molecular relaxation.^[34] In that regard, the UPS experiment generates photoemitted electrons that are slow enough to carry away with them the relaxation energies, e.g., electronic polarization and structural relaxation energy of the molecular ion.^[34] Koopmans' theorem cannot, therefore, be assumed to be valid. In contrast, XPS measurements generally involve much larger

electron kinetic energies. The timescales involved in XPS are short enough so that some energies, such as that of the structural relaxation, are not normally included.

In 2PPES^[35,36] (Fig. 6), χ is derived from the measurement of the HOMO–LUMO gap of the neutral molecule, followed by the photoemission of the electron that populates the

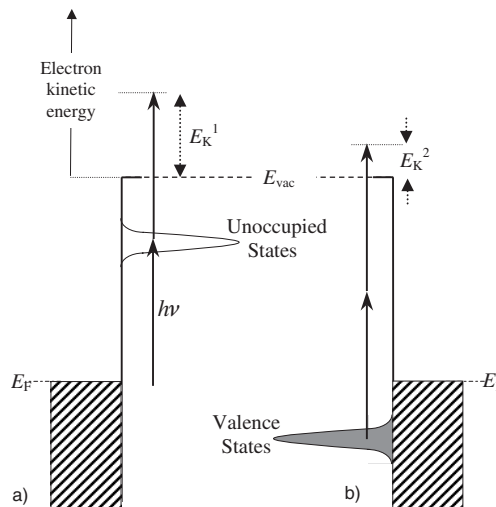


Fig. 6. Schematic illustration of principles of use of two-photon photoemission spectroscopy for the determination of a) empty states, e.g., LUMO, and b) filled states, e.g., HOMO levels [35]. E_K^1 : kinetic energy of electron, excited by two one-photon processes; E_K^2 , kinetic energy of electron excited by 2-photon process.

LUMO. The final state is a molecular *cation*, like in PES, with the hole in the HOMO. So, polarization and relaxation corresponding to the molecular cation are included.

In IPES, however, it is the radical *anion* that is probed to find the LUMO energy and calculate the χ . There is thus a *double polarization difference* between the two χ determinations. This hardly affects the χ determination in inorganic semiconductors, in which polarization energies are generally below experimental noise for samples best described electronically by band theory (with delocalized valence electrons), rather than by localized bonding of the valence electrons. However, polarization energies are of the order of 1 eV in molecular systems, and thus should be carefully considered when doing spectroscopy.^[37]

Finally, in 2PPES the HOMO–LUMO gap that is derived from the measurement is the optical one, i.e., the gap for on-site excitation of the neutral molecule (as it is determined from the photon energy that fits that gap). In PES/IPES, however, it is the cation–anion gap, i.e. the energy difference between the LUMO of the negative molecular ion occupied by an electron (IPES), and the HOMO of the positive molecular ion occupied by a hole (PES), that is measured. It is this latter gap, also known as transport gap^[33,34] or single-particle gap that is relevant for charge transfer from substrate to molecules, or transport measurements through organics. On the other hand for MO molecule–surface state interactions^[5,38,39] the relevant LUMO is the one from 2PPES.

6. Summary

While no attempt has been made here to present a complete review of the abundant literature on vacuum level, work function, electron affinity, and ionization energy at solid surfaces, we hope to have clarified some of the basic concepts. These include the difference between surface and absolute vacuum levels, and the possibilities of determining some of these using experimental measurement techniques such as photoemission spectroscopy. Without pretending to give a thorough treatment of these issues, we have aimed at providing a clear basis for a community for which different concepts and terminologies must more than ever be brought together to understand the interplay between interface chemistry, energetics and charge carrier transport.

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- [1] A. G. Milnes, D. L. Feucht, *Heterojunctions and Metal-Semiconductor Junctions*, Academic, New York **1972**.
- [2] W. Mönch, *Semiconductors surfaces and interfaces*, 2nd ed., Springer, Berlin **1995**.
- [3] H. Lüth, *Surfaces and Interfaces of Solid Materials*, 3rd ed., Springer, Heidelberg **1998**.
- [4] H. Ishii, K. Sugiyama, E. Ito, K. Seki, *Adv. Mater.* **1999**, *11*, 605.
- [5] G. Ashkenasy, D. Cahen, R. Cohen, A. Shanzer, A. Vilan, *Acc. Chem. Res.* **2002**, *35*, 121.
- [6] C. D. Dimitrakopoulos, D. J. Mascaro, *IBM J. Res. Dev.* **2001**, *45*, 11.
- [7] S. Forrest, P. Burrows, M. Thompson, *IEEE Spectrum* **2000**, *37*, 29.
- [8] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlung, W. R. Salaneck, *Nature* **1999**, *397*, 121.
- [9] J. Jortner, M. Ratner, *Molecular Electronics*, Blackwell Science, Oxford **1997**.
- [10] D. Cahen, G. Hodes, *Adv. Mater.* **2002**, *14*, 789.
- [11] S. Seker, K. Meeker, T. F. Keuch, A. B. Ellis, *Chem. Rev.* **2000**, *100*, 2505.
- [12] We recall here that “just outside” the solid means that the distance between the electron and the surface is larger than the interatomic distance but smaller than the size of the crystal surface.
- [13] All energies here are given on the so-called solid-state scale; to convert them to the electrochemical scale the values need to be multiplied by -1 (as the solid state scale is for electrons and the electrochemical one for positive unit charges) and $4.5\text{--}4.75$ eV subtracted [14]. The uncertainty is due to the uncertainty in the value of the standard hydrogen electrode’s potential on the solid-state scale.
- [14] E. M. Stuve, A. Krasnopoler, D. E. Sauer, *Surf. Sci.* **1995**, *335*, 177.
- [15] We consider here the following methods: ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), and two photon photoemission spectroscopy (2PPES).
- [16] This is the normal case in photoelectron emission experiments where the detector is biased negatively with respect to the sample to assure this situation.
- [17] K. Besocke, S. Berger, *Rev. Sci. Instrum.* **1976**, *47*, 840.
- [18] N. A. Surplice, R. J. D’Arcy, *J. Phys. E: Sci. Instrum.* **1970**, *3*, 477.
- [19] L. Kronik, Y. Shapira, *Surf. Sci. Rep.* **1999**, *37*, 1.
- [20] K. Wandelt, *Appl. Surf. Sci.* **1997**, *111*, 1.
- [21] Scanning Kelvin microscopy also provides laterally resolved work function data, but not on an atomic scale.
- [22] A. H. Marshak, *IEEE Trans. Electron Devices* **1989**, *ED-36*, 1764.
- [23] A. R. Plummer, in *The Electrochemistry of Semiconductors* (Ed: P. J. Holmes), Academic, London **1962**.
- [24] At 0 K the energy of the Fermi level equals the chemical potential of the electron (μ_e). As the temperature dependence of μ_e is generally very small, at least for metals, the two terms are often used interchangeably at finite temperature. Following the customary definition of the Fermi energy as the energy which separates the filled from the empty energy levels, no single Fermi level can be defined for intrinsic (and most extrinsic) semiconductors. In such a case, whenever the term Fermi level or Fermi energy is used, chemical potential of electron (electrochemical, if there is an electrostatic potential contribution to the electron partial free energy) is meant. For further details, see for example, N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Saunders, Philadelphia, PA **1976**.
- [25] Similar concepts exist in electrochemistry, where electrode potentials are relative values with respect to a reference and there has been a long quest to determine “absolute” electrode potentials experimentally (cf. Samec et al., [26]; Stuve et al., [14]) and to understand it conceptually. The issue has been discussed often (cf. Trasatti [28,29], and recently, for a solid state electrochemical system, by Tsiplakides and Vayenas [27]). Trasatti also compares the use of an absolute vacuum level at infinity to that of a local one. In general we reach a similar conclusion to him. However, while he states that the absolute vacuum level at infinity is in principle measurable, we claim that this level is NOT amenable to experimental determination. The importance of the comparison with concepts from electrochemistry for the “organic electronics” community lies in the frequent use of electrochemical experiments, mostly in a solvent, such as cyclic voltammetry, to judge suitability of a material or compare between materials (cf. for example, Brabec et al. [30]). A. lucid didactic discussion can be found in the book of Bockris and Reddy [31], Vol. 2, Ch. 7.2. In electrochemistry the outer (or Volta or psi, ψ) potential of a solid electrode is defined as the work done to bring a unit (positive) test charge from infinity to a point just outside the range of the image forces of the electrode (i.e., to what we call here the local vacuum level). The surface (or dipole or χ) potential is defined for a condensed phase, with no extra electric charge but surrounded by a dipole layer, as the work done to bring the test charge from infinity to a point just across the dipole layer into the condensed phase. In our definitions here this potential is part of the work function and electron affinity of the condensed phase. The combination of both is called the inner (or Galvani or ϕ) potential. Bockris and Reddy argue that of these only the outer potential and its differences can be measured. For the others, only changes are experimentally accessible.
- [26] Z. Samec, B. W. Johnson, K. Doblhofer, *Surf. Sci.* **1992**, *264*, 440.
- [27] D. Tsiplakides, C. G. Vayenas, *J. Electrochem. Soc.* **2001**, *148*, E189.
- [28] S. Trasatti, *Electrochim. Acta* **1990**, *35*, 269.
- [29] S. Trasatti, *Electrochim. Acta* **1991**, *36*, 1659.
- [30] C. J. Brabec, A. Cravino, D. Meissner, N. S. Saricifci, T. Fromherz, M. T. Rispens, L. Sanchez, J. C. Hummelen, *Adv. Funct. Mater.* **2001**, *11*, 374.
- [31] J. O’M. Bockris, K. N. Reddy, *Modern Electrochemistry*, Vol. 2, Plenum, New York **1970**.
- [32] J. H. Weaver, D. M. Poirier, in *Solid State Physics* (Eds: H. Ehrenreich, F. Spaepen), Vol. 48, Academic, New York **1994**.
- [33] C. I. Wu, Y. Hirose, H. Sirringhaus, A. Kahn, *Chem. Phys. Lett.* **1997**, *272*, 43.
- [34] I. G. Hill, A. Kahn, Z. G. Soos, R. A. Pascal, *Chem. Phys. Lett.* **2000**, *327*, 181.
- [35] X. Y. Zhu, *Ann. Rev. Phys. Chem.* **2002**, *53*, 221.
- [36] See also <http://www.fkp.uni-erlangen.de/methoden/2ppetutor/start.html>
- [37] P. A. Cox, *The Electronic Structure and Chemistry of Solids*, Oxford University Press, Oxford **1987**.
- [38] R. Hoffman, *Solids and Surfaces*, VCH, Weinheim **1988**.
- [39] R. Cohen, S. Bastide, D. Cahen, J. Libman, A. Shanzer, Y. Rosenwaks, *Adv. Mater.* **1997**, *9*, 746.