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Combined theoretical and experimental characterizations of semiconductors for photoelectrocatalytic applications

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15 **Abstract**

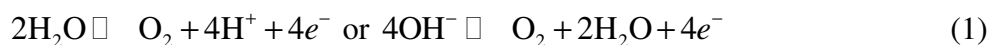
16 Photoelectrocatalysis studies have emerged tremendous knowledge and experience, which has
17 led to discovery of a number of active materials. Due to complexity of the processes involved,
18 however, development of suitable semiconductor and catalyst for the photoelectrocatalysis
19 still requires a try-and-error approach as different parameters are coherently varied to
20 determine overall performance. This contribution provides insight into the key optoelectronic
21 properties of the semiconductors, such as absorption coefficient, dielectric constant, effective
22 masses, exciton binding energy, and band positions. The combined assessment from
23 theoretical and experimental points of view is reviewed, which may help thorough
24 understanding of the semiconductors and the way to reliably characterize them, and in turn to
25 develop improved photoelectrocatalytic materials.

Introduction

The scientific community has devoted much effort to developing efficient photovoltaic devices that can convert sunlight (i.e., photons) into electricity (i.e., electrons and holes in an external circuit). This important topic of research has led scientists to the development of a large variety of photovoltaic materials[1–7] whose photoconversion efficiencies are compared on the frequently updated NREL chart.[8] In parallel to this research activity, the researchers developed the idea that photogenerated electrons and holes can be effectively and directly consumed to perform electrochemical redox reactions.[9,10] Such photoelectrocatalytic reactions can produce valuable molecules with the ability to generate energy on demand or valuable molecules for the chemical industry.[11–19] The two main investigated reactions are CO₂ reduction[20–22] and water splitting.[23–27] Recently, new types of photoelectrocatalytic reactions are being investigated, such as biomass valorization, among which glycerol oxidation seems most promising.[28–31]

Since water splitting is one of the most investigated reactions in photoelectrocatalysis, this manuscript is oriented toward this reaction as an excellent benchmark of the energetically uphill reaction.[32] The main concepts presented herein can be transferred to other photoelectrocatalytic reactions. Water splitting is the combination of two half-electrochemical reactions called oxygen evolution reaction (OER, equation 1) and hydrogen evolution reaction (HER, equation 2). To achieve solar-driven water splitting, multiple device configurations have been proposed.[33,34] The first solar-derived water splitting technology is simply accomplished by connecting a solar panel to an electrolyzer via an external circuit to split water and produce H₂. Another technology consists of solar panels directly immersed in water to perform OER and HER with appropriate surface modifications to make photoelectrodes,[35,36] which might not require wiring.[37] Also, photon absorbers can be

dispersed in water as a powder form with the high surface area, so-called photocatalyst, which has a dual function to absorb the sunlight and to perform the two half-reactions.[38–43]



Multiple articles have addressed the economic viability of these water splitting technologies.[44–47] Several architectures were proposed to estimate their capital cost, assuming several working conditions. As of now, the highest efficiency for producing H_2 from sunlight is to connect two separate devices of a photovoltaic cell and an electrolyzer.[48] It is difficult to rigorously compare these studies because the assumptions made about the properties and architectures of the materials are typically different. However, it seems likely that a direct water splitting technology, using photoelectrochemical and photocatalytic systems, would be more profitable than a solar panel connected to an electrolyzer.[44] Unfortunately, despite the potential economic advantage, efficient photoelectrocatalytic materials have not yet met the requirements for commercialization.

Therefore, for this technology to be considered viable for H_2 production, it is necessary to develop efficient water splitting photoelectrocatalytic materials that are applicable to an integrated photoelectrochemical system or a photocatalyst powder system. Understanding the fundamental phenomena involved in the photocatalytic process should help to improve this efficiency. As we will see in the next section, however, this is a difficult task because of the complex elementary steps involved in the photocatalytic process.[49] This review focuses on characterization of photocatalyst powder materials, but we note that fundamental aspects for optoelectronic properties are very much in common for photoelectrochemical reactions.

Focus on the photocatalysts

Heterogeneous photocatalysts developed for overall water splitting using a single semiconductor typically have the architecture presented in Figure 1.[24,50] The photocatalyst consists of semiconductor particles decorated by cocatalyst nanoparticles to facilitate OER or HER.[51] The fundamental principles of photoelectrochemical OER or HER are generally the same under open circuit conditions. Figure 1 focuses on the respective half-reactions.

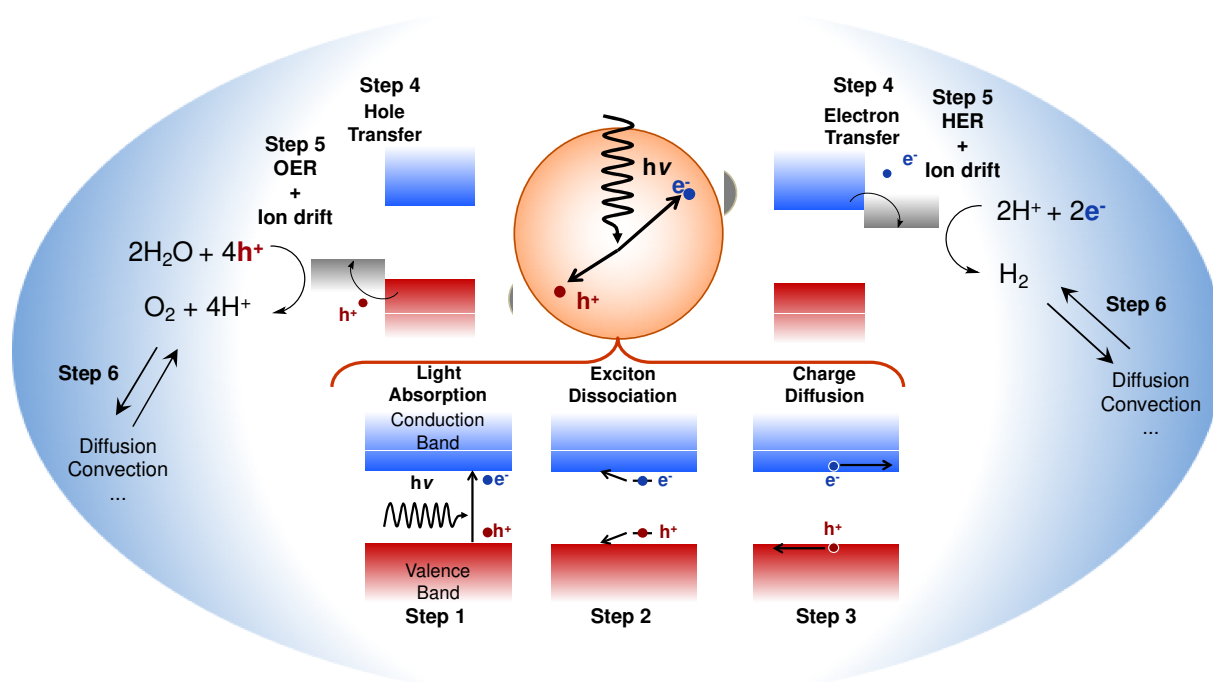


Figure 1. Structure of a photocatalyst with the semiconductor in orange and the cocatalysts in grey. Valence and conduction bands of the semiconductor are in red and blue, respectively.

The photocatalytic reaction can be divided into several sequential processes (Figure 1). The efficiency of these steps is mainly governed by the properties of the semiconductor, the cocatalyst or the interface between the two. Successful photoelectrocatalysis proceeds via the following six steps.

Step 1 corresponds to the light absorption by the semiconductor creating an electron (e^-) and hole (h^+) pair, called exciton.[52] The light absorption is mainly governed by the bandgap (E_g) in a semiconductor that can be seen as the difference in energy between the top

92 of the valence band and the bottom of the conduction band. In short, the bandgap must be low
93 enough to absorb the largest number of photons contained in sunlight and large enough to
94 produce electrons and holes having sufficient energies to perform the two half-reactions. For
95 water splitting reaction, the thermodynamic potential difference is 1.23 eV. In reality, it has
96 been shown that to take into account the unavoidable energy loss due to all the electron
97 transfers and entropic loss,[53,54] the bandgap of the semiconductor is required to be above
98 1.8 eV or, more ideally, between 2.0 and 2.5 eV (to maximize the attainable efficiencies with
99 some variations).[44,55–57] Figure 2(a)-(c) presents the variation of the solar to hydrogen
100 (STH) efficiency as a function of the bandgap of the semiconductor, along with the classical
101 Shockley-Queisser limit of a photovoltaic device based on a p-n junction.[44,58] This
102 simulation includes some models of the energetic losses, including overpotentials for the half-
103 reactions.[44] It is interesting to see the large difference between the theoretical maximum
104 photoconversion efficiencies between a standard p-n junction photovoltaic cell (around 35 %;
105 power efficiency) and the maximum STH efficiency (around 12%; energy efficiency based on
106 bandgap energy and hydrogen product energy) using a single photocatalyst. Because a single
107 semiconductor based photocatalyst has a limited attainable efficiency, multiple semiconductor
108 configurations are considered, such as Z-scheme structures or so-called type-II
109 heterostructure.[59–62] One of the driving forces motivating the development of such
110 architecture is the possibility to achieve, in principle, much higher attainable efficiencies
111 (Figure 2(b)-(d)).[44,56] The maximum attainable STH energy efficiency using two-
112 semiconductor-based materials is ~25% when a tandem configuration is used together with
113 highly efficient electrocatalysts.

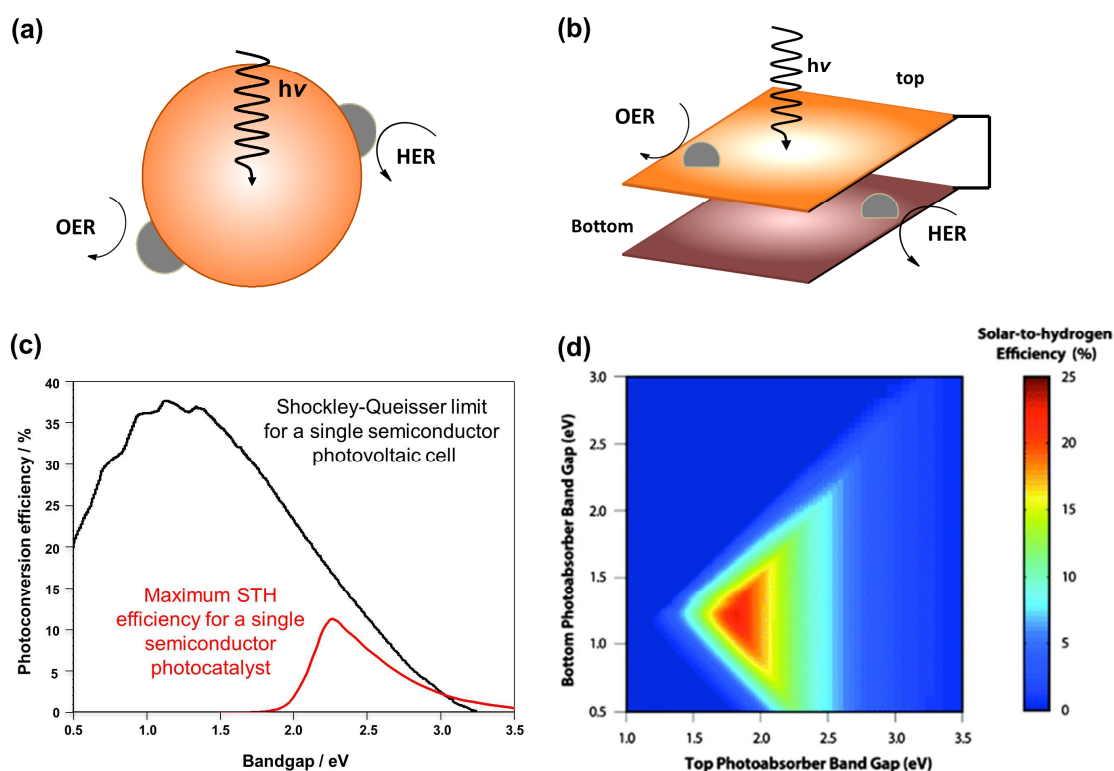


Figure 2. (a) Single semiconductor photocatalyst architecture used for the STH efficiency simulation of (c). (b) Tandem cell architecture used to perform the simulation of the STH efficiency of (d). (c) Comparison between the Shockley-Queisser limit of a photovoltaic cell and the Solar-to-Hydrogen (STH) efficiency of photocatalysts as a function of the bandgap of the semiconductor. (d) STH efficiency of two-junction photocatalysts as a function of the bandgaps of the two semiconductors. Figure reprinted with permission from “B.A. Pinaud et al. Energy Environ. Sci. 2013, 6, 1983” with the permission of the royal society of chemistry.

Step 2: The exciton dissociation. After light absorption, the electron and the hole are bound, creating a particle called an exciton. The electron and the hole must be separated to perform the redox reactions. The exciton ionization energy is called exciton binding energy, noted E_b . To have free charge carriers, this energy should be lower than the thermal energy (~25 meV at room temperature).[63] If the exciton is not dissociated, it will quickly recombine, losing the energy of the photon. The exciton binding energy is mainly governed by the dielectric constant of the material, noted ϵ_r . The dielectric constant represents the

ability of the material to screen charges. The larger the dielectric constant, the easier it will be to dissociate the exciton. In fact, materials frequently used in photovoltaics (e.g., Si, CdTe, GaAs) have a dielectric constant higher than 10, and their E_b is always lower than 25 meV.[64] This value of 10 for ϵ_r can be seen as a target to develop new semiconductors for water splitting.

Step 3: Charge carrier diffusion. Once the exciton is dissociated, electrons and holes diffuse to the surface, according to semiconductors physics.[65] This diffusion is characterized by the diffusion coefficient, D , of the charges related to the charge carrier mobilities, μ , by the Einstein relationship (equation (3)). The mobility is linked to the effective masses, m^* , and the collision time, τ (equation (4)).

$$D = \frac{k_B T}{e} \mu \quad (3)$$

$$\mu = e \frac{\tau}{m^*} \quad (4)$$

There is no fundamental lower limit for the value of the charge carrier mobilities or effective masses. But empirically, by analyzing all semiconductors efficient for photovoltaic applications, it appears that they all have a mobility higher than $10 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ and an effective mass lower than 0.5 electron mass at least in one crystallographic direction. Based on this empirical observation, all semiconductors having an effective mass lower than 0.5 electron mass ($9.1 \times 10^{-31} \text{ kg}$, noted m_0 hereafter) for holes and electrons can be considered as having good charge carrier mobilities.

Step 4: Charge transfer. In practice, the semiconductors developed to efficiently generated charge carriers are not necessarily adapted to catalyze the two-half reactions of water splitting. In other words, the activation energy or the overpotential of the electrocatalytic reactions are generally large on the surface of the semiconductor. This is the reason why the semiconductor surface is often decorated by cocatalysts having better catalytic

activity toward the electrochemical reactions. The electron or hole transfer must be efficient to have a maximum of charges collected by the cocatalysts. This step depends on the quality of the interface between the cocatalyst and the semiconductor.

Step 5: The electrochemical redox reactions. For water splitting, the electrocatalytic reactions are HER and OER, both of which require multiple electrons (see equations (1) and (2)). The potentials used to split water in photocatalysis come from the charge dynamics inside the semiconductor. In other words, photocatalytic water splitting can be seen as electrocatalytic water splitting, in which the applied potential is not chosen by an external electric circuit as in conventional electrolyzer but depends on the efficiency of the semiconductor to generate a charge flow to the surface as a consequence of steps 1–4 (see above). The efficiency of this step is mainly governed by the overpotential (noted η) associated with the cocatalyst. The overpotential corresponds to the extra energy (or the extra potential) needed to perform one half-reaction beyond the thermodynamic limit. We chose photoelectrochemical performance as an example to show how electrocatalytic performance might influence the case of a photoanode for oxygen evolution reaction, as presented in Figure 3.[66]

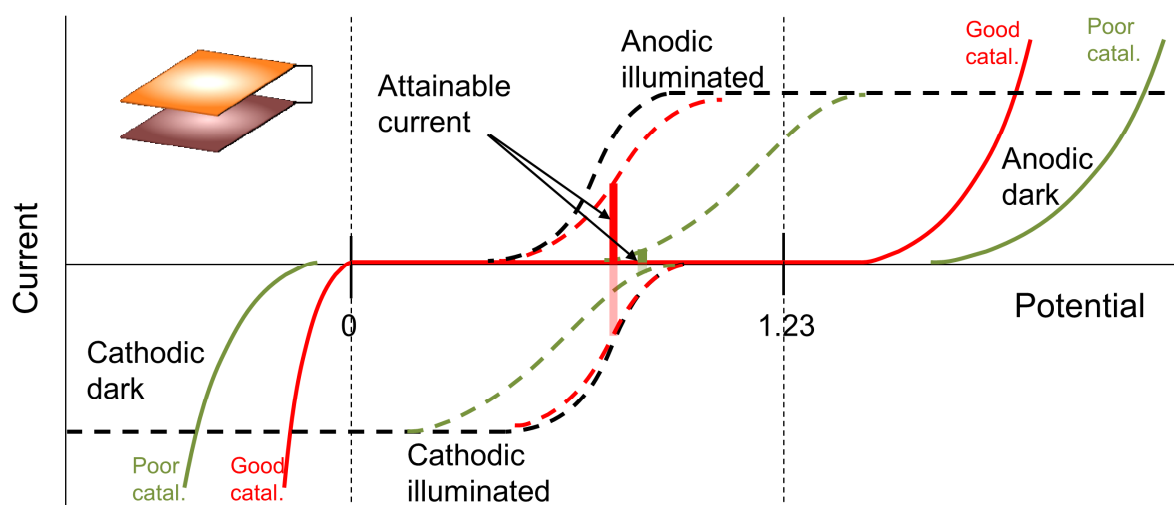


Figure 3. Conceptual schemes representing attainable current as a function of potential in a two-photoelectrode configuration. The same cathodic and anodic currents achieved by the respective photocathode and photoanode will be the total current generated by the entire device. Two types of electrocatalysts (cocatalysts) are arbitrarily chosen to represent their excellent and poor performances. Black dotted lines represent potentially-achievable photoelectrochemical performance from only charge separation, and red and green dotted lines are actual performance obtainable with excellent and poor electrocatalysis.

Step 6: Fluid mechanics and diffusion of ions and molecules. This step presents phenomena happening mainly inside the electrolyte, where the reactions take place.[67] This is an important aspect in the working principle of a water-splitting device, and further improvements of the photocatalytic efficiencies could be obtained by a smart design of the electrolyte. The optimization of the electrolyte at near-neutral pH was reviewed elsewhere.[68]

Development of new semiconductors and photocatalysts (i.e., semiconductor and cocatalyst) fulfilling this list of requirements has been a major source of work for the photoelectrochemistry community, starting from oxides[69–73] but quickly progressing to more sophisticated materials, such as sulfides[70,74–76], oxysulfides[77–80], nitrides[81–84], and oxynitrides.[62,85–87] These new systems are frequently the subject of reviews, highlighting the wealth of new semiconductors designed for photoelectrocatalysis.[16,55,82,88] In parallel, the tools developed by quantum chemists are ever more frequently used to investigate photocatalyst properties,[89–93] mainly based on the Density Functional Theory (DFT).[94] However, rationalizing the differences in activity of these semiconductors is difficult, mainly because of the lack of facile experimental characterization of their optoelectronic properties.

The current review article is dedicated to the characterization of semiconductors, which can be coherently achieved both experimentally and computationally. To make this contribution unique, we focus on the characterizations of optoelectronic properties that can be

198 directly related to the electronic structures of semiconductor solids. We will present the
 199 different techniques available to measure and compute the following key properties, all
 200 directly involved from Step 1 to Step 4 (Figure 1).

201	I. Bandgaps and absorption coefficient.	12
202	II. Dielectric constant.	25
203	III. Charge transport properties	29
204	IV. Exciton binding energy.	37
205	V. Band positions.	42
206		

I. Bandgaps and absorption coefficient.

The bandgap, E_g , is an essential property of semiconductors, and many publications presenting new semiconductors predominantly focus on reporting E_g to characterize their electronic structures. E_g is an important property since the primary attainable efficiency of a photocatalytic device from photon absorption is directly related to this value (Figure 2). However, the definition of E_g is ambiguous and controversial, sometimes leading to confusion between the optical gap, electronic gap, and HOMO-LUMO gap. A recent article dedicated to the comparison between the different types of bandgaps has been discussed by Breda (Figure 4).[95] Based on this work, we can define the fundamental gap corresponding to the difference in energy between the first ionization potential (IP) and the first electron affinity (EA).

$$E_g(\text{fund}) = \text{EA} - \text{IP} \quad (5)$$

We can also define the optical gap, corresponding to the energy of transition between the ground state (noted S_0) and the first excited state (noted S_1). This fundamental gap is larger than the optical gap, measured by absorption spectroscopy or photoluminescence. The energy difference between these two gaps originates from the formation of an exciton for optical measurements. The exciton formation energy is noted as E_b .

$$E_g(\text{opt}) = \text{EA} - \text{IP} - E_b \quad (6)$$

E_b is generally relatively small for standard covalent semiconductors (few dozens of meV) when compared to the fundamental bandgap (few eV). Thus, in general, $E_g(\text{fund})$ and $E_g(\text{opt})$ are very close.

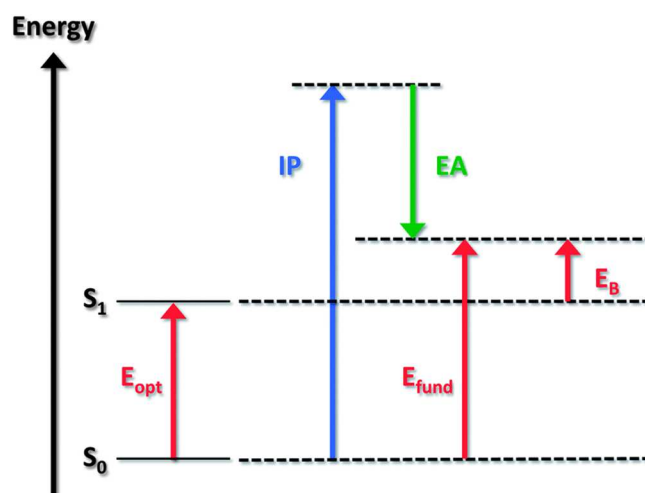


Figure 4. An energetic diagram presenting the different bandgap and their relationships. E_B in this figure corresponds to E_b in the text. Figure reprinted with permission from “J.-L. Breda Mater. Horiz. 2014, 1, 17-19” with the permission of the royal society of chemistry.[95]

Finally, we can define the bandgap corresponding to the energy difference between the top of the valence band (noted ϵ_{VB}) and the bottom of the conduction band (noted ϵ_{CB}). By analogy to molecular calculations, one can call this bandgap the HOMO-LUMO bandgap or the mono-electronic bandgap.

$$E_g(\text{mono}) = \epsilon_{CB} - \epsilon_{VB} \quad (7)$$

These energies are obtained by self-consistently solving the monoelectronic Kohn-Sham equations. Removing or adding an electron to a system, with the associate energies IP and EA, change all the electronic structure of the system because the electrons interact with each other leading to orbital energies variation after the electron addition/removal. Thus, to compute IP and EA, the full electronic structure relaxation induced the change in the number of electrons must be taken into account, that is time consuming to compute or even impossible for periodic system (this aspect is discussed later in the manuscript). In 1934, Koopman demonstrated that under the assumption that if the orbital relaxation is not important under electron addition/removal or in other words if the orbitals does not change in energy and in shape, the orbital energies correspond to IP and EA ($IP \approx -\epsilon_{HOMO}$ and $EA \approx \epsilon_{LUMO}$).[96] This

is called the Koopman's theorem and is the most frequent assumption used to estimate IP and EA of a system. This theorem was demonstrated in the framework of Hartree-Fock theory.[96] An attempt to adapt this theorem to DFT was performed by Janak in 1978.[97] The application area of Janak's theorem is smaller, because this theorem works only for the HOMO orbital (i.e., $IP \approx -\epsilon_{HOMO}$). Nevertheless, the community has taken the habit to apply the Koopman's theorem to DFT allowing to estimate the EA from the LUMO energy or in some scientific fields to use core orbitals to estimate core level energies.

$$E_g(\text{fund}) = EA - IP \approx \epsilon_{CB} - \epsilon_{VB} = E_g(\text{mono}) \quad (8)$$

This assumption is very rough for molecules but works relatively well (for the precision we are looking for) for solids, which will be discussed later.[98] Because the exciton binding energy usually requires only a small correction to go from the fundamental bandgap to the optical bandgap, the monoelectronic bandgap is usually directly compared to the optical bandgap.

Benchmarks of DFT functionals to simulate $E_g(\text{mono})$, thus by using the top of the valence band and the bottom of conduction band energies, have been the subject of numerous works in the literature.[99–108] As a matter of fact, some of us presented a benchmark focused on semiconductors used in photoelectrocatalysis and photovoltaic, using functionals frequently used in solid-state chemistry to computed electronic structures: PBE[109] (GGA), B3LYP (global hybrid, 20% of exact exchange), PBE0[110] (global hybrid, 25% of exact exchange) and HSE06[111,112] (range-separated hybrid). The results of this are presented in Figure 5.[63]

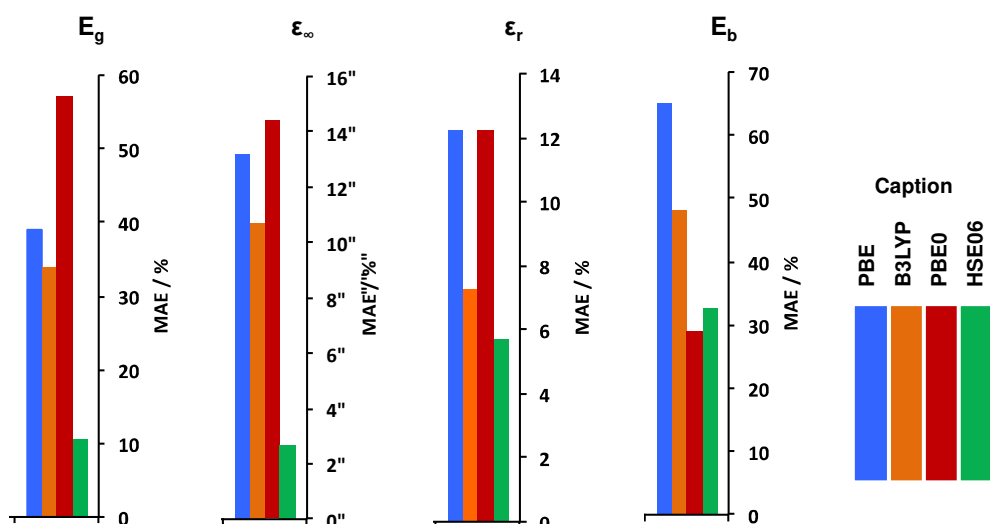


Figure 5. Mean absolute error (MAE) of the four investigated functionals on the selected properties. MAE is obtained by performing the arithmetic average of the absolute error (compared to experiment). Adapted with permission from “Le Bahers, T.; Rérat, M.; Sautet, P. *J. Phys. Chem. C* 2014, *118*, 5997”. Copyright (2018) American Chemical Society.[63]

If we focus on the bandgap calculation, GGA and global hybrids give bandgaps with a relatively large error. Actually, GGA strongly underestimates bandgaps while global hybrids overestimate it.[104] The range-separated hybrid HSE06 gives bandgaps with 10% of error. It is interesting to focus on this functional and attempt to understand its reliability. This is a range-separated hybrid, meaning that the exact exchange (or Hartree-Fock (HF) exchange) depends on the interelectronic distance in the evaluation of the exchange integrals, unlike for global hybrids, such as PBE0 and B3LYP functionals, whose exact exchange is constant (Figure 6). Contrary to the well-known range-separated hybrids, such as cam-B3LYP,[113] designed to increase the HF exchange when increasing the interelectronic distance, the HSE06 functional decreases this fraction (Figure 6). The reason for this behavior is practical rather than physical. Decreasing the HF exchange with the interelectronic distance allows reducing the number of exchange integrals to compute on long-range that save a large amount of computational time in solid-state calculation.[111] The parameters governing the variation of HF exchange were fitted to reproduce the bandgap of several semiconductors.[111] HSE06

works well because it is designed specifically for that purpose. Hybrid functionals are frequently considered to be prohibitive in term of computational time, but their implementation in localized basis set (such as Gaussian basis set) codes offers very accurate performances[114], and they can be easily applied to very large systems (up to several hundreds of atoms).[115,116]

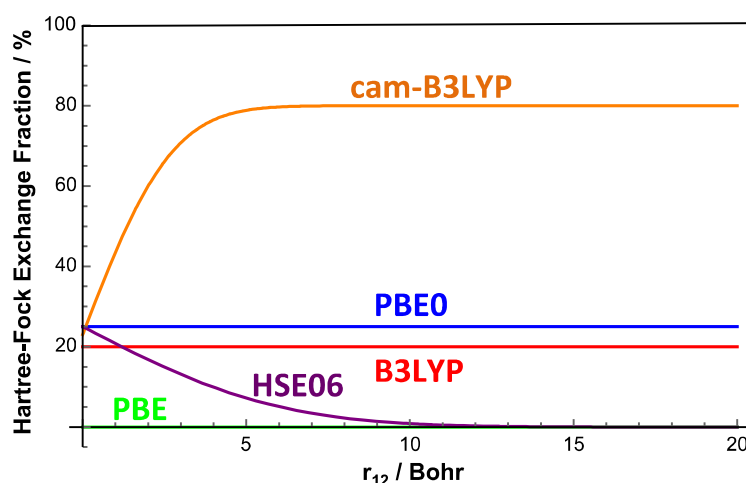


Figure 6. The fraction of exact exchange as a function of the interelectronic distance for several functionals.

It is interesting to note the high reliability of DFT for bandgap simulation based on band (i.e., orbital) energies. In the molecular case, it is well-documented that to take the HOMO-LUMO gap to simulate the first optical transition is a very bad approximation, with errors of several eV.[117] One reason for this is the large exciton binding energy for molecules because of its very localized nature, unlike the case of the solids. Nevertheless, the HOMO-LUMO gap also fails to reproduce the fundamental gap for molecules. This discrepancy comes from the large orbital relaxation induced by electron addition/removal in molecules, making Koopmans's theorem not applicable. The review proposed by Blase *et al.* on that topic is particularly interesting.[117] For solids, this orbital relaxation is very moderate because of the periodic nature of the system. Adding or removing one electron creates an extra charge (electron or hole) delocalized on several unit cells, thus with a diluted influence on the other electrons of these unit cells leading to a moderate orbital relaxation and

making the Koopmans's theorem more applicable. Interested readers are invited to refer to the work published on that topic by Perdew et al.[98] In addition to the fact that the exciton binding energy is generally a weak correction, the monoelectronic bandgap in solid-state systems is generally close to the fundamental and optical bandgaps.

The development of new functionals for solid-state simulation and, more precisely for semiconductor properties calculations, is still a topic of research. One approach proposed is to use global hybrid functionals, but changing the HF fraction for each semiconductor. A first attempt is to assume that a good HF fraction is equal to $1/\epsilon_{\infty}$. [103,108,118–122] A less empirical approach is to use the Green-Screened Coulomb interaction formalism (better known as GW) and to extract an HF exchange ratio using a screened exchange operator, as proposed by Galli and coworkers, which can also be adapted to build range-separated hybrid functionals.[123,124] The use of tuned hybrid functionals, based on dielectric constant, works relatively well, leading to errors on the bandgaps below 10%, but has the main drawback of requiring a change of functional when going from one semiconductor to another. New functionals are sometimes presented with superior performance than HSE06.[124,125] Meta-GGA functionals, such as the one developed by Becke and Johnson (mBJ)[101,126] and Verna and Truhlar (HLE17)[125], can also lead to errors around or even below 10%. These functionals are pure functionals, meaning that there is no exact exchange calculation. The consequence is faster calculations compared to hybrid functionals, giving an advantage compared to HSE06 for similar reliability. Unfortunately, the SCF convergence of meta-GGA for some systems and surfaces is sometimes difficult.[127–129]

The good performance assessed of density functionals presented above is valid only for semiconductors based on filled (d^{10}) or empty (d^0) d-shells elements. In general, all the density functionals fail to reproduce the bandgap and electronic properties of semiconductors containing partially filled d-orbitals.[130–136] This is particularly true for the third-row

transition metals. The reason is the strong electronic correlations between electrons of d-shells not properly described by DFT. Two approaches can be used to overcome this important difficulty. The first consists of forcing (artificially) the correlation in the DFT Hamiltonian by adding a phenomenological term, called the Hubbard term.[137–140] Once added, the total energy of the system is given by Formula 9, where U is called the Hubbard parameter, J the screened Stoner-like exchange parameter, and ρ^σ is the density matrix.

$$E_{\text{DFT}+U} = E_{\text{DFT}} + \frac{U-J}{2} \sum_{\sigma} \text{Tr}[\rho^{\sigma} - \rho^{\sigma} \rho^{\sigma}] \quad (9)$$

This term promotes the localization of the electrons on d-orbitals inducing a larger correlation. Nevertheless, the strength of this localization is parameterized, corresponding to the U value in Equation 9. This parameter can be adapted, such as reproducing property of the system (bandgap, ionization potential, and atomization energy). As a matter of illustration, Figure 7 presents the influence of the U parameter on the computed bandgap of TiO_2 (anatase and rutile) and compares these values to experimental and HSE06-computed values.[141] The strength of this approach is the speed of calculation, which is close to that of GGA functionals. The weakness is the parameterized character of the approach, making the results parameter dependent. Nevertheless, this approach, due to its easiness of application, is the most used for strongly correlated systems.[130,132,133,137–139,141–143]

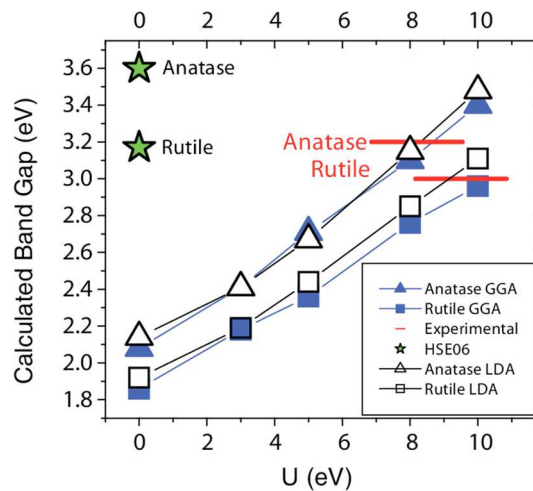


Figure 7. Illustration of the Hubbard Hamiltonian of the bandgap of TiO₂ (anatase and rutile). Figure reprinted with permission from “M.E. Arroyo-de Dompablo *et al. J. Chem. Phys.* 2011, 135, 054503”. Copyright (2018) The American Physical Society.

The most elegant way to improve the description of correlation by DFT is to go beyond the approximations done by DFT in a rigorous manner. Several approaches have been developed in that direction, but the GW approach is mostly used in solid-state chemistry.[99,117,138,144–148] GW is sometimes presented as a “post-DFT” approach. Presenting the full equations of the GW theory goes beyond the topic of this review, and interested readers are invited to look at specific publications.[117,149] The GW method involves two non-local operators called Green’s function (G) and the screened Coulomb repulsion (W). Briefly, the GW approach uses orbitals previously obtained by a DFT calculation and performs either a single point calculation (called G₀W₀) or a self-consistent calculation (called scGW). There are several types of “flavors” of GW calculations depending on the level of self-consistency. Finally, the GW calculation gives new energy levels exactly corresponding to the ones measured experimentally by photoelectron spectroscopy.[117] In other words, the GW bandgap should correspond to $E_g(\text{fund})$ (equation 5). In practice, GW calculations are notably more computational resource demanding than DFT. GW provides very accurate bandgaps for d⁰ and d¹⁰ materials, with the same accuracy as for good DFT functionals (see Figure 8).[99,119,150,151] For partially occupied d-orbitals based-semiconductors, GW leads to much more accurate bandgaps than DFT.[132][135] Interestingly, GW methods are increasingly available in quantum chemistry codes. While these are an improvement compared to DFT calculations, the large computational resources needed to perform such calculations prevents their use in large systems.

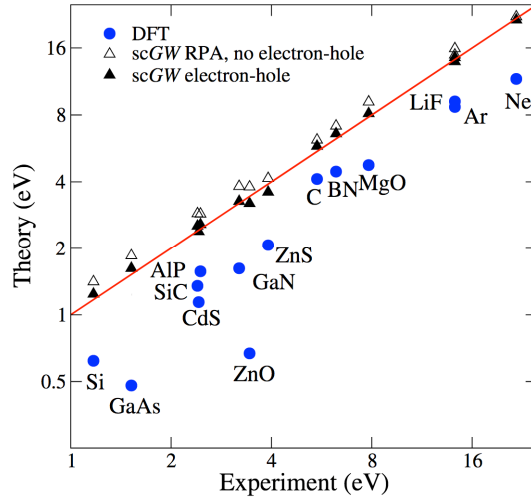


Figure 8. Comparison between DFT (PBE GGA Functional) and GW bandgaps for selected semiconductors. Figure reprinted with permission from [M. Shishkin *et al. Phys. Rev. Lett.* 2007, 99, 246403]. Copyright (2018) The American Physical Society.[95]

From the knowledge of monoelectronic energies and associated orbitals, whether they come from DFT or GW calculations, the imaginary part of the frequency dependent dielectric constant can be computed based on band-to-band transitions using the formula (10)-(12).[152] From this formula, it appears that only the transitions at the same k -point (vertical transition in the band structure) are taken into account. In other words, indirect transitions are not considered by this approach. Finally, the real part of the dielectric constant is computed from the imaginary part, using the Kramers-Kronig transformation (formula (12)) and the absorption coefficient is computed from the real and imaginary part of the dielectric constant (formula (13)-(14)). This approach is now frequently used to evaluate the absorption spectra of semiconductors.[87,152–160] This works fairly well if (i) the methodology used to compute the electronic structure gives a reasonable bandgap and (ii) the monoelectronic approach is a good approximation of the electronic structure.

$$\varepsilon(\omega) = \varepsilon^{(1)}(\omega) + i\varepsilon^{(2)}(\omega) \quad (10)$$

$$\varepsilon_{\alpha\beta}^{(2)}(\omega) = \frac{4\pi e^2}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{v,c,k} 2w_k \delta(\epsilon_{ck} - \epsilon_{vk} - \omega) \langle u_{ck+qe_\alpha} | u_{vk} \rangle \langle u_{vk} | u_{ck+qe_\beta} \rangle \quad (11)$$

$$\epsilon_{\alpha\beta}^{(1)}(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\epsilon_{\alpha\beta}^{(2)}(\omega') \omega'}{\omega'^2 - \omega^2} d\omega' \quad (12)$$

$$\kappa_{\alpha\beta}(\omega) = \sqrt{\frac{\epsilon_{\alpha\beta}^{(1)}(\omega)^2 + \epsilon_{\alpha\beta}^{(2)}(\omega)^2 - \epsilon_{\alpha\beta}^{(1)}(\omega)}{2}} \quad (13)$$

$$\alpha_{\alpha\beta}(\omega) = \frac{4\pi}{\lambda} \kappa_{\alpha\beta}(\omega) \quad (14)$$

The community of computational solid-state chemistry is also working on the implementation of TD-DFT that would give access to a much more accurate simulation of the frequency-dependent dielectric constant, and ultimately a more accurate absorption coefficient (Figure 9).[161–163]

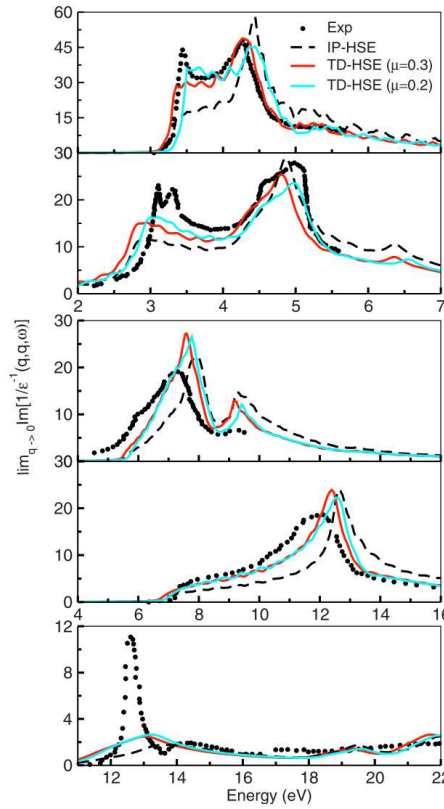


Figure 9. Example of a simulation of the imaginary part of the dielectric constant by TD-DFT for Si, GaAs, SiC, C, and LiF from top to bottom respectively. Figure reprinted with permission from [J. Paier *et al. Phys. Rev.B* 2008, 78, 121201].

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While bandgap energy is directly associated with the maximum attainable efficiency of the photoelectrocatalysis, the most beneficial property involved in photon absorption is the absorption coefficient as a function of wavelength. UV-visible spectroscopy is a direct method used to determine this property.[164] Based on the Beer-Lambert law, the light intensity $I(x)$ as a function of the point x from the surface to the bulk, which has a dimensionality of power (or photon numbers) per area (e.g., W m^{-2} or photons m^{-2}), is defined as

$$I(x) = I_0 \exp(-\alpha x) \quad (15)$$

where α is the absorption coefficient, which has a dimensionality of inverse length (e.g., cm^{-1}). This exponential decay of light intensity is no longer true if non-linear phenomena happen (multi-photon absorption). At the typical light intensities used to perform the measurement, however, these non-linear phenomena are extremely uncommon and can be ignored in the analysis. Because of this proportionality coefficient, it is convenient to describe the absorption measurement with dimensionless values, such as absorptance, a , and transmittance, T , which are the relative amount of the light being absorbed by, and passing through the sample, respectively, with a thickness, l . In the ideal case where the incident light contributes solely to absorption with the material, the absorptance can be described as;

$$a = \frac{I_{in} - I_{out}}{I_{in}} = 1 - T = 1 - e^{-\alpha l} \quad (16)$$

The reciprocal of absorption coefficient gives absorption depth (i.e., the thickness of the semiconductor requiring sufficient number of photons at a given wavelength). In reality, however, the incident photons might be lost by additional processes, such as specularly reflected (R_s), forward-scattered (S), and back-scattered (R_d), [164] and thus;

$$a + T + R_s + S + R_d = 1 \quad (17)$$

The frequently used dimensionless parameter, the absorbance, A , should not be confused with these values, which is defined as:

$$\alpha = 1 - 10^{-A} \quad (18)$$

For a given semiconductor, it is useful to obtain the absorption coefficient as a function of incident wavelength. A thin-film configuration of the bulk semiconductor that minimizes the contribution of scattering is The measurement becomes more accurate if a thin film with absolute thickness is defined. Swanepoel proposed a useful method to determine film thickness using interference fringes of the transmittance spectrum[165]. In a transmittance mode,[166] the complete light absorption should be avoided to extract the information of α . It is, therefore, necessary to fabricate reliable and sufficiently-thin films that reflect the characteristics of the solid (i.e., the same displacement of atoms as the bulk solid). In practice, it is conducted to measure the absorption coefficient focusing on two measured parameters, which are transmittance, T , and reflectance, R , [167] by minimizing other contributions such as scattering. When the reflectance is small, the absorption coefficient is reported using the following relationship[168].

$$\alpha = -\frac{1}{d} \ln \frac{T}{(1-R)^2} \quad (19)$$

It is important to give extra attention to the type of substrates used in the absorption measurement because it is known to drastically affect the obtained properties.[169]

The common approach to measure absorption characteristics of powder semiconductor materials is diffuse reflectance measurement. Use of an integrating sphere to collect all the scattered light is effective at improving the accuracy of the measurement. The Kubelka-Munk model is based on the measurement assuming scattering and absorption, the relationship of which is given by[170,171];

$$f(R) = \frac{(1-R)^2}{2R} = \frac{\alpha}{s} \quad (20)$$

The Kubelka-Munk function is theoretically proportional to the absorption coefficient, as can be seen in Equation (20). The bandgap is thus obtained using this relationship, even if the scattering coefficient s is unknown. However, Murphy discussed uncertainty to determine bandgap using the Kubelka-Munk function, especially for doped semiconductors[172]. The weak part of the absorption spectrum is frequently overestimated. According to Murphy, the absorption coefficient due to doped electronic state is so weak that the contribution to photoelectrocatalysis using this transition is expected to be minimal[172]. Also, it is important to analyze the data with zero absorption background beyond the bandgaps as this would provide important information about the dopants and defects [173].

Using the obtained absorption coefficient, the bandgap is commonly determined using the Tauc plots. The Tauc relationship[174], which is supported by Davis and Mott[175], provides the following relationship when the reasonable absorption is achieved, typically $\alpha > 10^4 \text{ cm}^{-1}$;

$$\alpha h\nu \propto (h\nu - E_g)^{\frac{1}{n}} \quad (21)$$

where n can take values of 3, 2, 3/2, or 1/2, corresponding to indirect (forbidden), indirect (allowed), direct (forbidden), and direct (allowed) transitions, respectively[164,176,177] The nature of the bandgap (direct, indirect...) is generally obtained from DFT calculations of band structures. Tauc plots, i.e., $(\alpha h\nu)^n$ as a function of $h\nu$ (n is the same as above) give E_g from the intersection of a line tangent to the slope in the linear region of the absorption onset with the baseline (Figure 10). [164,176,177] Bandgaps of many semiconductors are compiled in ref.[64]

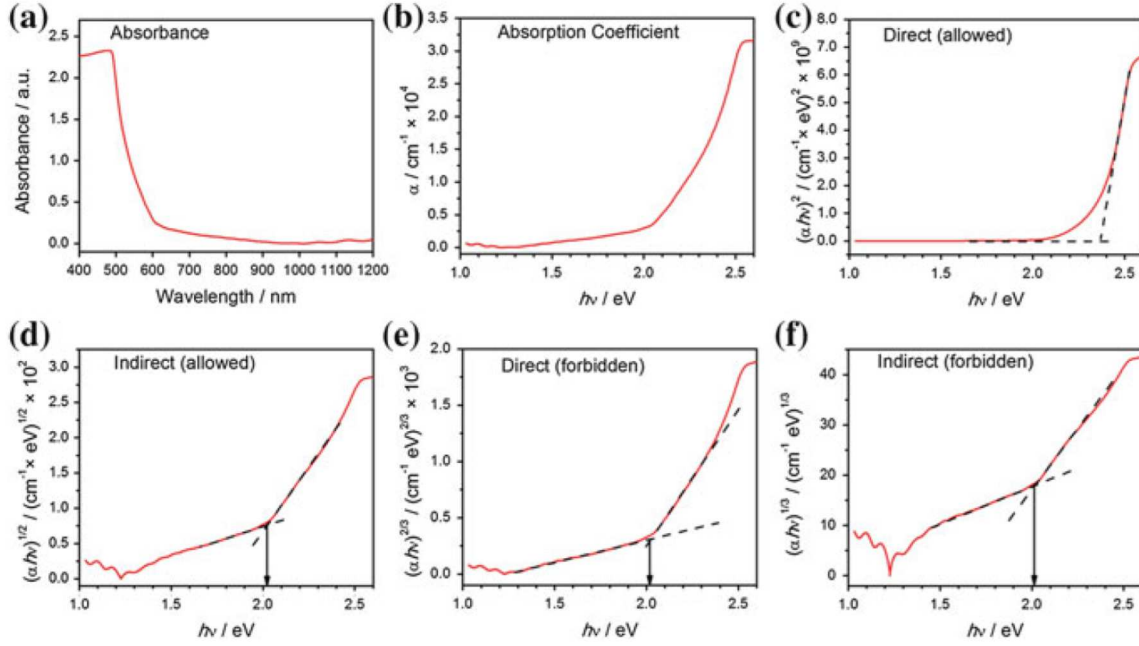


Figure 10. Absorption spectra of Cu₂O (a) along with the related absorption coefficient (b) and several ways to determine the bandgap from the Tauc plot, assuming direct-indirect/allowed-forbidden transitions (c)-(f). Figure reprinted with permission from [Z. Chen et al. Photoelectrochemical Water Splitting, 2013, Springer-Verlag New-York]. Copyright (2018) Springer-Verlag New-York.

Photoluminescence spectroscopy is another experimental method to determine bandgap[178]. In theory, the onset of the luminescence signal should correspond to the bandgap described previously. The intrinsic band structures are reflected by the measurement at low temperatures, avoiding thermal contribution. The bandgap determination by this technique, however, cannot be applied to nonradiative transitions and the samples with indirect bandgap semiconductors. It is also noted that many dopant states appear in the signals and, thus, often lead to ambiguity to determine bandgaps.

II. Dielectric constant.

When an electric field (\vec{E}) is applied on a dielectric material, an electric displacement field (\vec{D}) appears within it. Both electric fields are linked by the dielectric constant ϵ_r .

$$\vec{D} = \epsilon_0 \epsilon_r \vec{E} \quad (22)$$

This dielectric constant represents the ability of dielectric material to screen the external electric field by the apparition of a polarization. This polarization comes from the reorganization of the electron density or the motion of the ions constituting the material. The dielectric constant induced by the electron density is named ϵ_∞ , and the contribution of the dielectric constant involving the ionic motions is noted ϵ_{vib} . Finally, we have:

$$\epsilon_r = \epsilon_\infty + \epsilon_{vib} \quad (23)$$

A study on dielectric materials itself is an important field. The dielectric constants of various materials are compiled elsewhere.[64,179,180] There are many ways to experimentally measure the dielectric constant of a semiconductor, and one of the common ways is to conduct capacitance measurements with varied frequency after making a disc device with two metal contacts at each side. For example, dielectric properties of TiO_2 powder was measured by making pellets of the sample.[181] For the powder semiconductor, the measurement may give overestimation due to extrinsic microstructural features.[182] Another common technique to measure dielectric properties for powder sample is ellipsometry (Figure 11).[64,183]

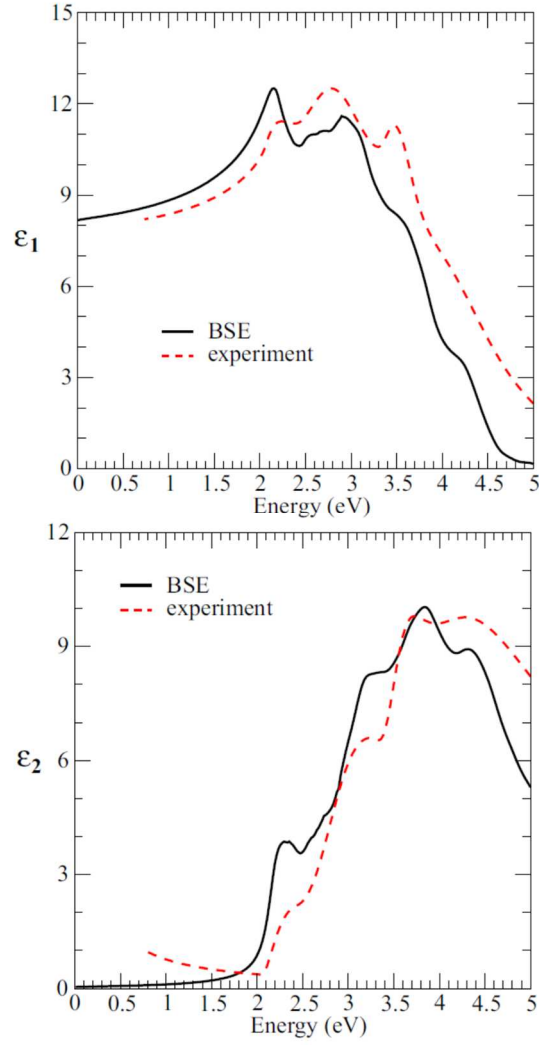


Figure 11. Experimental (obtained by ellipsometry) and computed (GW/BSE) frequency dependent dielectric constant (ϵ_1 real part and ϵ_2 imaginary part) of Ta_3N_5 . Figure reprinted with permission from [J. Morbec *et al. Phys. Rev. B* 2014, 90, 1] Copyright (2018) The American Physical Society.

Computationally, the electronic contribution to the static dielectric tensor can be evaluated through a coupled-perturbed Hartree-Fock/Kohn-Sham (CPHF) scheme adapted to periodic systems[124,162,184–186] or by applying an electric field on the system during the SCF procedure[187]. While more time consuming, determining the total dielectric constant by performing SCF calculations with an electric field considers local field effects because of the self-consistent nature of the calculation. Nevertheless, CPHF and electric field approaches usually lead to similar results, but more sensitive on the choice of the functional (for DFT

calculation) than the way to compute the electronic contribution to the dielectric constant. The reliability of DFT to compute the electronic contribution to the dielectric constant has been assessed in several publications.[63,161,188–190] Results are typically close to experimental data, and the exchange-correlation functional typically has a weaker effect on the dielectric constant than the for the bandgap. In fact, the standard deviation of the DFT for a series of the semiconductor is given in Figure 5. The standard deviation is below 20% for all functionals. It is important to note that the ordering of functionals for the bandgap simulation is the same for ϵ_∞ . Consequently, range-separated functionals are the best for simulating ϵ_∞ . However, as mentioned above, the choice of the function has, in general, not a large impact on the final dielectric constant. Thus, global hybrid or even GGA can reasonably be used to compute that property.

The vibrational contribution is computed from the phonon spectrum, following Formula (24). ν_p is the phonon frequency of mode p, V is the unit cell volume, and Z_p is the mass-weighted mode effective Born vector. The intensity I_p of IR absorbance for a given mode p is proportional to $|Z_p|^2$. [191] From this formula, it appears that the softer the vibrational modes, the more they contribute to the dielectric constant.

$$\epsilon_r = \epsilon_\infty + \epsilon_{vib} = \epsilon_\infty + \frac{4\pi}{V} \sum_p \frac{Z_p^2}{\nu_p^2} \quad (24)$$

The agreement between theory and experiment for the vibrational dielectric constant is also very good, whatever the functional chosen (Figure 5). But this conclusion is no longer available for very large dielectric constants (>100). In these cases, the very soft vibrational modes leading to the large dielectric constant are non-harmonic, thus badly reproduced by DFT in the harmonic approximation. For these difficult systems, DFT results are qualitative informing only on the presence of these soft modes.

III. Charge transport properties

The electron and hole transport is an important phenomenon, not only in photoelectrocatalysis but also for several other applications, including but not limited to photovoltaic and thermoelectric. In some aspect of semiconductor physics, the charge carrier drift due to an electric field of a space charge zone plays a fundamental role (such in a p-n junction), but as pointed out by Grätzel et al. in nanoparticulate materials with a high density of impurities, the space charge zone plays only a marginal role and charge carrier transport are mainly governed by thermal diffusion.[192–195] To quantify the transport at a first guess, the measurement of the conductivity is considered. This property depends on the charge carrier density n (generally in cm^{-3}), the charge of the charge carrier density q (in C) and the mobility of the charge carrier density μ (in $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) as presented in equation (25). In intrinsic (i.e. without any doping) semiconductors in the dark, the conductivity increases with increasing the temperature because of conduction band population with thermal energy (increase of n in equation (25)). But under doping or light exposure, the charge carrier densities (electrons in the conduction band and holes in the valence band) increase from another reason than temperature. This can lead to a different behavior of the conductivity has a function of the temperature. The value of the conductivity is dependent on temperature and purity and synthesis conditions. For that reason, the mobility μ is considered to be a better intrinsic property of the material to quantify the transport of charge carriers.

$$\sigma = nq\mu \quad (25)$$

Furthermore, the conductivity and diffusion coefficient are directly related (see Equation (4)). Two main theories are used to interpret the transport properties in optoelectronic materials. The first theory is called the band-like mechanism and is related to the curvature of the band-structure leading to the quantity called effective mass. This theory works well for delocalized charge carriers. Thus, this theory is adapted for highly covalent d^0 or d^{10} semiconductors. The

band-like model is sometimes called the rigid band-model. This means that, by applying this model, we assume that the bands or, more generally, the electronic structure is almost unaffected by the electron and hole generation. This is a good approximation if the charge carriers are delocalized on several unit cells, thus having a diluted influence on the ions. For systems having the more localized character of their orbitals, the charge carriers can be centered only on few ions, leading to a large perturbation around these atoms. The main consequence is generally a geometrical relaxation around the atoms, stabilizing the system and increasing the localization of the electron and the hole. The term self-trapping is generally used to name this phenomenon. The particle made of the charge carrier and the geometrical relaxation is called a small polaron.[196] The polaronic conductivity is based on a hopping mechanism, well described by the Marcus theory.[197–199] In this theory, the polaron jumps from one site to another, leading to mobility given by Equation (26).[200]

$$\mu = \frac{eR^2n}{k_B T} v e^{-\frac{E_a}{k_B T}} \quad (26)$$

where R is the distance between the two hopping sites and n is density of hopping sites. This mobility is thermally activated, which increases with increasing the temperature, following an Arrhenius behavior, in contrast to the mobility governed by a band-like mechanism, which decreases with the temperature.[201,202] To determine if the transport mechanism is a band-like mechanism or a polaronic mechanism, the measurement of the mobility as a function of the temperature is generally performed. An increase of mobility as a function of the temperature indicates a thermally activated mechanism, and thus a hopping mechanism for the polaron. A decrease of the mobility with the temperature is more in favor of a band-like mechanism of charge transport, affected by phonons generated by increasing the temperature. This is illustrated in the work by Lee *et al.* on a donor-acceptor type thiophene-thiazole copolymer thin film, where the nature of the transport mechanism can change from band-like to polaronic depending on the drain field applied on the film (Figure 12). [63]

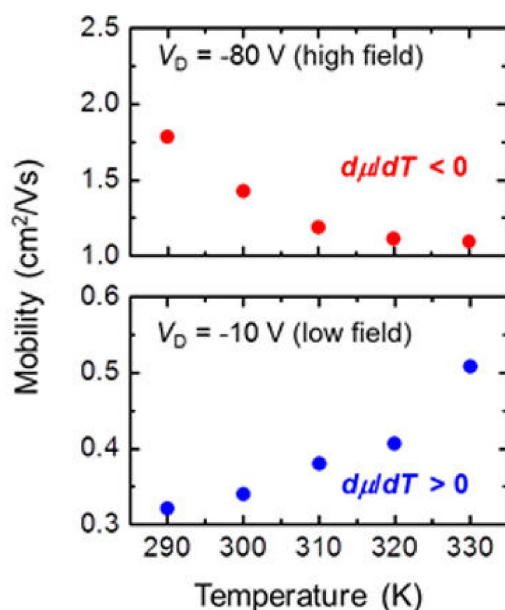


Figure 12. Temperature-dependent mobility as a function of the drain field applied on polymer based on the thiophene-thiazole groups. Adapted with permission from “Lee, J. et al. *J. Am. Chem. Soc.* 2015, 137, 7990”. Copyright (2018) American Chemical Society.[63]

Band-like transport. In the band-like transport theory, the charge carrier mobility is given by the formula (4), including the collision time τ and the effective masses m^* . The concept of effective masses comes from solid-state physics and is related to the curvature of the top of the valence band (for holes) and bottom of the conduction band (for electrons) in the reciprocal space along one direction of the band structure.[39,203–205] The collision time, τ , is extremely experimental dependent and involves all the scattering events (electron-electron, phonon-electron, and electron-impurities) and cannot be easily theoretically evaluated. The effective mass can be obtained by fitting these band extrema by the formula:

$$E(k) = E(k_0) \pm \frac{\hbar^2}{m_{\square}^*} (k_0 - k_{\square})^2 \pm \frac{\hbar^2}{m_{\perp}^*} (k_0 - k_{\perp})^2 \quad (27)$$

The \pm is + for the conduction band and – for the valence band. k_0 is the vector of the reciprocal space where the band is at its extremum. The symbols \square and \perp refer to the longitudinal and perpendicular axes that depend on the structure of the crystal. The effective masses are obtained by fitting the bottom of the conduction band (for the electron effective

mass) and the top of the valence band (for the hole effective mass) with a parabolic function. To calculate the effective mass in that way, the band structure must be computed in several directions. For highly symmetrical crystals, one generally chooses the most symmetric directions. For low symmetry systems, the choice of the crystallographic directions is more difficult and generally arbitrary. Ideally, the effective masses should be computed in a large number of directions to obtain a contour plot allowing to attribute the parallel and perpendicular directions of equation (26), as illustrated in Figure 13 from the work of Feng et al.[206] But, in general, researchers have focused on the simplest directions.

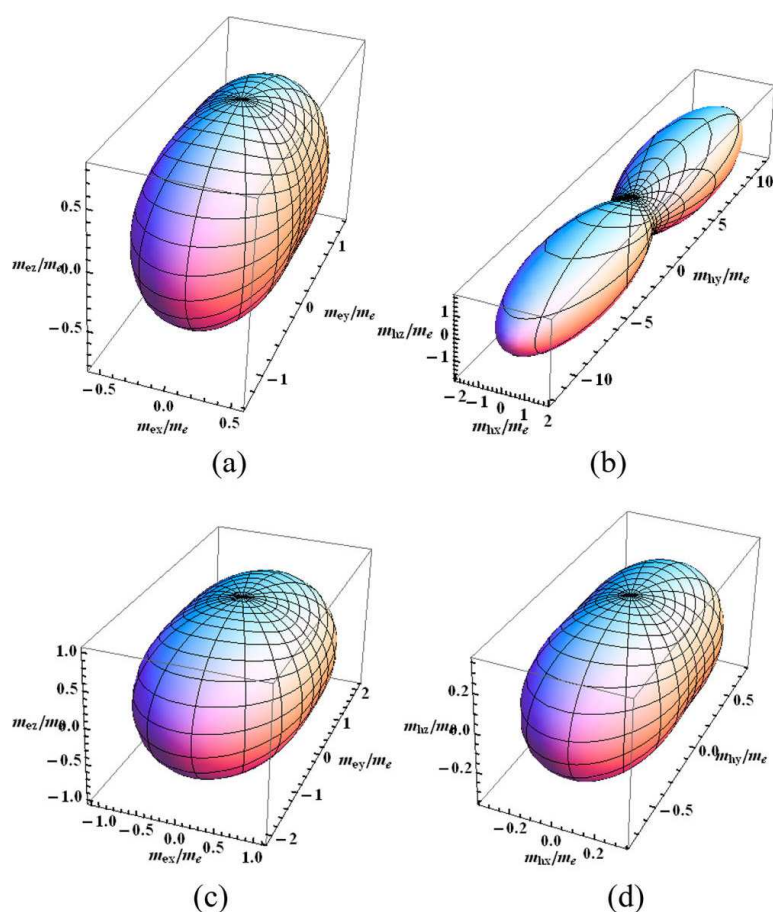


Figure 13. The contour plots of the effective masses of holes and electrons close to the Γ point for $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{I}$ and Br). (a) m_e^* of $\text{CH}_3\text{NH}_3\text{PbI}_3$; (b) m_h^* of $\text{CH}_3\text{NH}_3\text{PbI}_3$; (c) m_e^* of $\text{CH}_3\text{NH}_3\text{PbBr}_3$; (d) m_h^* of $\text{CH}_3\text{NH}_3\text{PbBr}_3$. Figure reprinted with permission from [J. Feng and B. Xiao, J. Phys. Chem. Lett. 2014, 5, 1278-1282]. Copyright (2018) The American Chemical Society.

625 The effective mass calculation from the band-structure is the most frequent approach used by
626 the quantum chemists to characterize the charge carrier
627 mobilities.[63,78,80,154,158,160,207–211] This property can also be used to analyze the
628 excited state entropy of the semiconductor, considered as a source of efficiency decrease, as
629 presented by Osterloh.[53] Assessing the reliability of DFT for that specific property is
630 difficult since we lack experimental data to compare the results. Nevertheless, some classes of
631 semiconductors were deeply characterized leading to the effective mass dataset. Kim *et al.*
632 compared the PBE (GGA), mBJ (meta-GGA), and HSE06 (range-separated hybrid)
633 functionals and found that the non-local nature of the exchange part of HSE06 was necessary
634 to accurately reproduce the effective masses.[212] GW band structures can also be used to
635 evaluate effective masses, typically those close to the masses obtained with hybrid
636 functionals.[150,151,213,214] Beyond the quantitative evaluation of the effective mass, it is
637 important to recall that this property is deeply related to the covalency of the chemical
638 bonds.[204,215,216] Favoring the covalency of the chemical bounds reduces the effective
639 mass and consequently increases the charge carrier mobilities. The covalency can be tuned by
640 changing the chemical nature of the elements or by changing the local geometries, as
641 illustrated by Ha *et al.* for the hole effective mass dominated by the Sn-O interaction in tin
642 oxides (Figure 14).

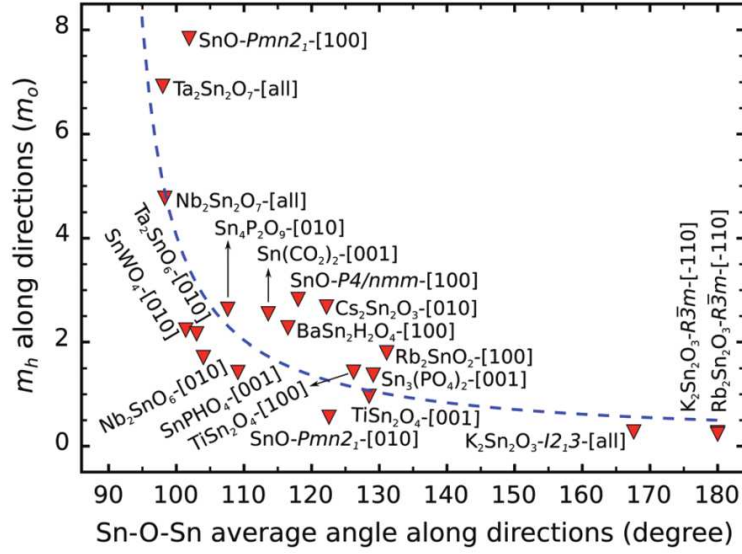


Figure 14. Hole effective mass as a function of the Sn-O-Sn bond in several tin oxides. Figure reprinted with permission from [V.-A. Ha *et al.*, J. Mater. Chem. C. 2017, 5, 5772-5779]. Copyright (2018) The Royal Society of Chemistry.

It is sometimes difficult to find the “good” crystallographic direction for the effective mass calculation, or sometimes, there are several bands extrema close in energy. In these specific cases, the effective masses can be computed using Boltzmann transport theory[217] with the equations (28)-(30), where σ is the conductivity of the material and τ is the collision time. This corresponds to an effective mass averaged on the density of state of the conduction band and the valence band parameterized by the scattering time τ . Using that approach, the calculation of the effective mass is a post-treatment of a full band structure. Several codes now offer the possibility to perform such analysis.[116,217–219]

$$\sigma_{\alpha\beta} = -e^2\tau \sum_i v_{\alpha}(i,k) v_{\beta}(i,k) \frac{\partial}{\partial E} f(E(i,k), \mu, T) \frac{dk^3}{4\pi^3} \quad (28)$$

$$v_{\alpha}(i,k) = \frac{1}{\hbar} \frac{\partial E(i,k)}{\partial k_{\alpha}} \quad (29)$$

$$m^* = \frac{\sigma}{e^2\tau} \quad (30)$$

Experimentally, the determination of effective mass is not an easy task. This is mainly based on the measurement of the cyclotron frequency (Equation 31). The sample is placed in a static

magnetic field, B . From a classical point of view, free charge carriers start to have a helicoidal motion with an angular frequency equal to the cyclotron frequency noted ω_c . From a quantum point of view, their energy levels are quantified and separated by a constant energy $\hbar\omega_c$. [220] Transitions between these states are possible under radio-frequency radiations, leading to the measurement of the cyclotron frequency and the determination of the effective mass. [220–225]

$$\omega_c = \frac{eB}{m^*} \quad (31)$$

To have a measurable cyclotron resonance, the mean free path of charge carriers must be large. Considering a charge carrier scattering time τ , it is assumed that the product $\omega_c\tau$ must be larger than 1 to lead to well-defined cyclotron resonance. In other words, the crystal must be as pure as possible and cool down below 100 K. Thus, this type of experiment is rather difficult for semiconductors synthesized as a powder with a large number of impurities; making the experimental determination of effective mass difficult to find for weakly investigated semiconductors.

Another approach has been proposed in 1966 by Zhitinskaya et al. to determine the effective mass of the charge carriers at the Fermi level from the experimental measurement of the Hall (R_H), Seebeck (α), conductivity (σ) and Nernst (Q) coefficients using the following formula (where q , \hbar , k_B and T are the charge of the particle, the reduced Planck constant, the Boltzmann constant and the temperature respectively): [226,227]

$$m^* = \left(\frac{3}{|R_H|q\pi} \right)^{\frac{2}{3}} \frac{q\hbar^2}{k_B^2 T} \left(\alpha - \frac{Q}{|R_H|\sigma} \right) \quad (32)$$

The demonstration of the equation presented above is based on the Boltzmann transport theory, thus the effective mass obtained in that way is a density averaged effective mass. This method to estimate the effective mass is sometimes called “the method of four coefficients” because it involves the knowledge of the four coefficients presented above. Because the

measurement of the Hall, Seebeck and conductivity coefficients is a kind of routine work in the field of thin solid films, the determination of effective mass using the equation (32) has been mainly employed by scientists in that field.[228–230] This experimental way to determine the effective mass can be applied to materials being less pure than the one used by the cyclotron resonance experiment, but the result is an averaged effective mass while the cyclotron resonance gives access to hole and electron effective mass in several crystallographic directions.

Polaron. In terms of computational chemistry, the investigation of polaron conductivity is not easy in periodic systems. A charged system must be created to address the problem of treating such systems in periodic boundary conditions.[231–233] Then the charge must be localized, that is usually done first by distorting the geometry around the central atom and by adding a +U parameter on this atom. Next, the energy of the system is computed along several directions for the charge transfer (i.e., the hopping) to find the highest energy and define the activation energy. Because of all these steps, the simulation of hopping is difficult. Furthermore, this type of simulation is methodology dependent because of the charge compensation, because of the +U parameter and the initial distortion artificially imposed to localize the charge. Nevertheless, some examples are proposed in the literature for Ta₃N₅[200] (Figure 15), TiO₂[234], Fe₂O₃[235] or BiVO₄[236]. The main information extracted from this type of simulation is the influence of the crystallographic direction on the polaron diffusion and the activation energy for the thermal activation of the diffusion (Equation 25).

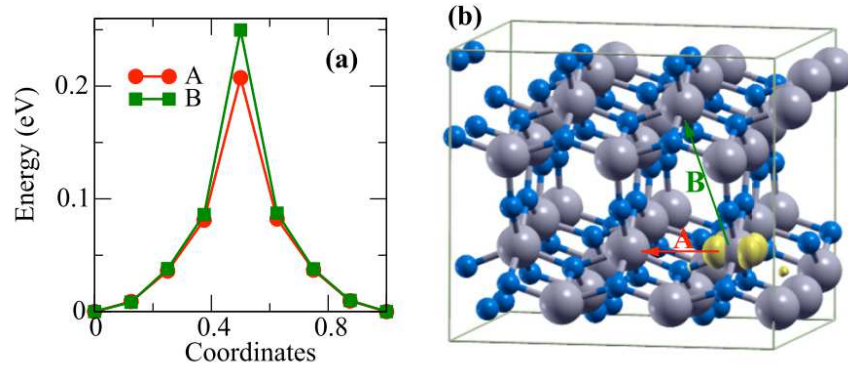


Figure 15. Simulation of the potential energy surface for the electron polaron hopping in two different directions (green and red curves) in Ta_3N_5 . Figure reprinted with permission from [J. M. Morbec and G. Galli *Phys. Rev. B* 2016, 93, 035201].

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Some works solve some of the drawbacks of using periodic boundary conditions by extracting a cluster from the crystal structure and performing post-Hartree-Fock calculations (such as CASSCF).[237] The advantages of this approach are to avoid the problem of the electric charge in periodic boundary conditions and to use a more accurate method than DFT to investigate correlated materials. The drawback of the cluster approach is the removal of the Madelung potential of the infinite crystal that is known to have an important effect on charge-transfer states.

The activation energy of polaron hopping can be obtained experimentally by performing an Arrhenius analysis of charge carrier mobilities or conductivity.[238–241] The main difficulty is to attribute the activation energy to a specific mechanism since several mechanisms can be active for the conduction.

IV. Exciton binding energy.

The exciton is a quasi-particle developed in solid-state physics to describe the bound state between an electron and a hole. The formation of the exciton upon light absorption leads to a decrease of the fundamental gap energy, by an amount called exciton binding energy,

E_b ,[242] explaining why the fundamental bandgap is larger than the optical one (Figure 4, equation 6). Excitons are generally classified in two categories depending on their delocalization: (i) The Mott-Wannier exciton delocalized on several unit cells and having a radius as high as several hundred of Å and generally having a relative low exciton binding energy (few meV). This is the exciton found in silicon. (ii) The Frenkel exciton, more localized (a radius of few Å) and generally having a large exciton binding energy (up to several eV). Other types of excitons can sometimes be defined in specific materials. The exciton plays an important role in photoelectrocatalysis since it must be dissociated to obtain free charge carriers that will be able to transport toward the surface of the semiconductor. To be dissociated efficiently at room temperature, the exciton must have a binding energy of the order of magnitude of the room thermal energy ($k_B T \sim 25$ meV) or lower. If E_b is notably larger, like in polymer semiconductors, the exciton cannot dissociate in the bulk material and must diffuse toward an interface to dissociate at this interface. This type of architecture is called bulk-heterojunction has been developed by the organic photovoltaic community.[243]

The most classical way to determine the exciton binding energy is by absorption or photoluminescence spectroscopy.[244] If the exciton is a Mott-Wannier one (i.e., delocalized on several unit-cells), researchers frequently compare it to a hydrogen atom, namely a positive (the hole) and a negative (the electron) charges interacting through the Coulomb potential, because the Hamiltonian of this exciton is the same as the one of the hydrogen atom. The hydrogen-like exciton has the same wavefunctions and energies as the hydrogen atom, adapted to the dielectric constant of the material and the hole mass (lighter than a proton). Due to the hydrogen-like nature of the exciton, it is sometimes possible to observe, in the absorption spectra of the semiconductor, energetic levels inside the fundamental bandgap associated with the hydrogen-like levels of the exciton. As a matter of illustration, we can

show the remarkable exciton spectroscopy measured in the Cu_2O crystal by Kazimierczuk et al. (Figure 16) confirming the hydrogen-like nature of excitons.[245]

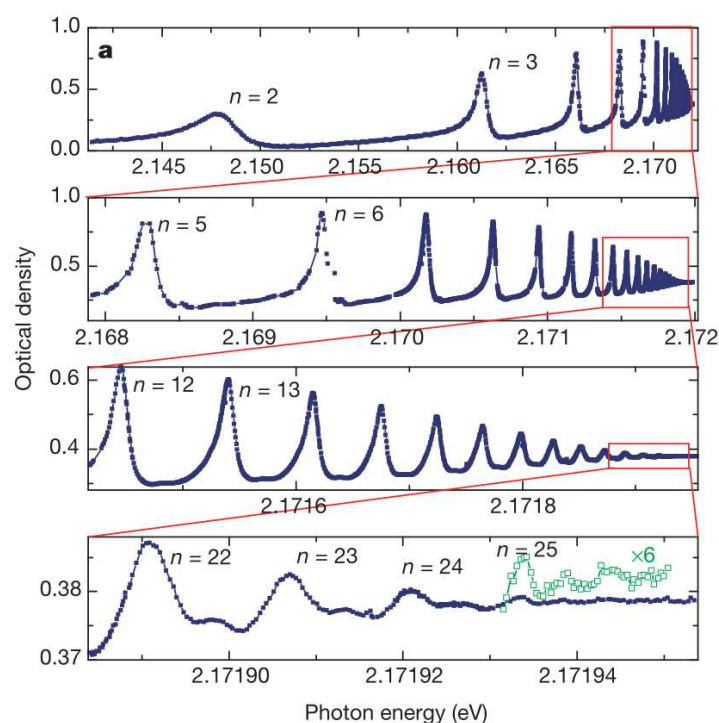


Figure 16. The high-resolution absorption spectrum of an exciton in Cu_2O measured at 1.2 K. The peak labeling “n” corresponds to the quantum number of the hydrogen-like levels of the exciton. Figure adapted with permission from [Kazimierczuk et al. *Nature* 2014, 514, 343]. Copyright (2018) Springer.

Some other less usual approaches can be used to determine exciton binding energies, such as STM spectroscopy[246] or UV-Vis spectroscopy under strong magnetic field (up to 65 T)[221,222]. In general, it is rather difficult to experimentally access exciton binding energies because of the good purity of the sample required and the very accurate spectroscopic measurements needed.

Due to the excited state nature of excitons, standard DFT, developed for ground state systems, is unable to treat them. Consequently, only theories developed to investigate excited states can perform a reliable analysis of exciton properties. These theories have been briefly presented in the discussion on bandgap simulations and are GW/BSE and TD-DFT methods. The BSE procedure (from Bethe-Salpeter Equations) is a post-treatment of the GW quasi-

particle calculation to get access to the exciton binding energy. The computation time of the BSE procedure is similar to the TD-DFT one.[247] The efficiency of TD-DFT and GW/BSE are not frequently compared in solid-state physics since TD-DFT is marginally used in that field. Their comparison is more documented for molecular systems.[247–250] The recent review of Blase *et al.* shows that hybrid functional generally gives optical gaps close to the ones of GW/BSE.[117] In term of computational time, these approaches are now quite similar, and because the large improvement performed in the recent years in the speed of GW/BSE calculations, we can expect that in the near future, such calculations will be performed in a daily manner.

If the exciton belongs to the Mott-Wannier category (i.e., delocalized on several unit cells), it can be treated as a hydrogen atom (the hole being the proton) offering an analytical formula for the binding energy.³⁷ In that model, the absolute value of the 1S state energy of the exciton is its binding energy, E_b , and it can be computed with the formula:

$$E_b = -E_H \frac{\mu}{\epsilon_r^2} \quad (33)$$

E_H is the energy of the 1s orbital of hydrogen (−13.6 eV), and μ is the reduced mass of the exciton.

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \quad (34)$$

Consequently, if the dielectric constant and the effective masses of the semiconductor were already computed, the exciton binding energy can be easily estimated through Formula 33. The strength of this simple model is to highlight the dominant effect of the dielectric constant, representing the ability of the material to screen charges, confirmed by more sophisticated calculations.[251] The Mott-Wannier model has been used to compute the exciton binding energy used to build Figure 5. As expected, hybrid functionals (global or range-separated) lead the best agreement with the experiment, but with a standard deviation of around 30%.

This error is relatively large, but considering the simplicity of Formula (33), it is an excellent ratio precision/time. Of course, this model fails to predict Frenkel exciton binding energy. GW/BSE simulation of exciton binding energies has been compared to Mott-Wannier ones for C₃N₄ based-semiconductors (Figure 17).[252] The very large exciton binding energies were in agreement with the known Frenkel exciton character of this semiconductor. The error between the scGW/BSE exciton binding energy and the Mott-Wannier energy can reach 100%. But interestingly, while quantitatively wrong, the Mott-Wannier model succeed to predict the very large values of the exciton binding energy of this system, confirming that this approach could be used at least qualitatively.

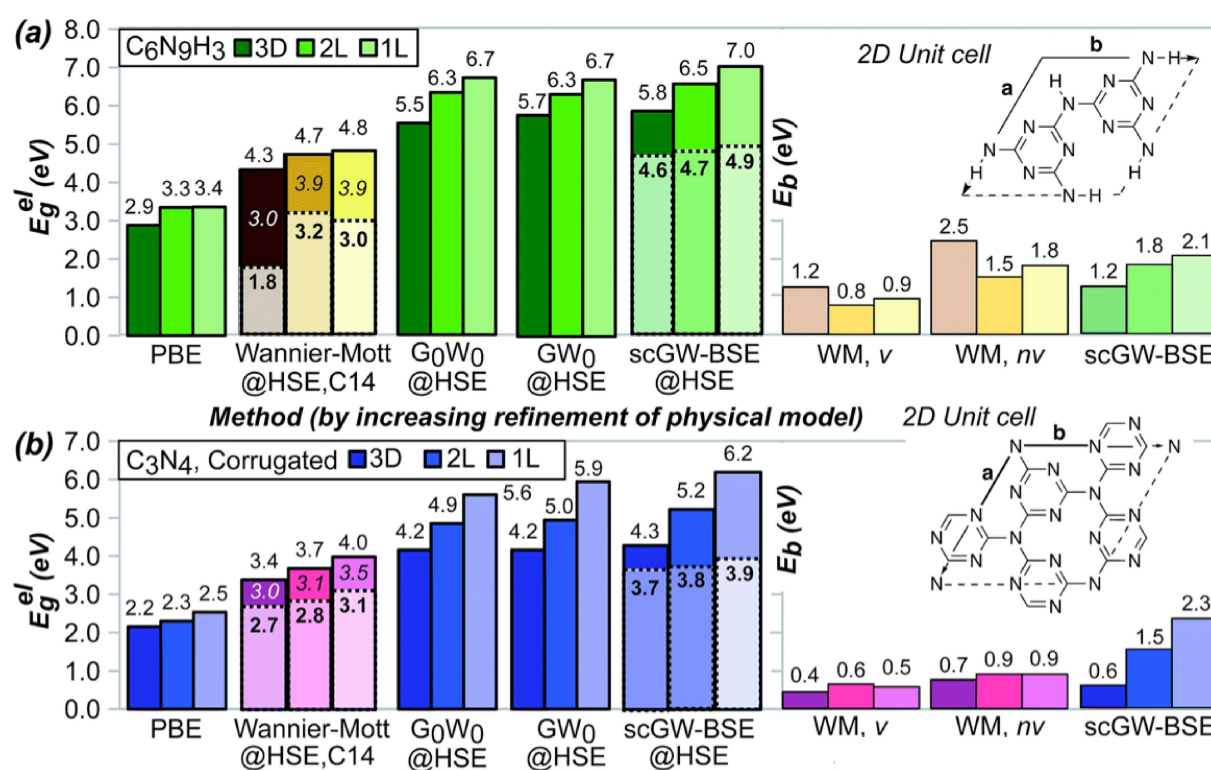


Figure 17. Electronic band gaps for (a) gt-C₆N₉H₃, (b) corrugated gt-C₃N₄ are reported. The Wannier-Mott analysis using the CRYSTAL14 code is depicted in an alternative color scheme. The optical band gaps $E_{opt,nv}$ are depicted semi-transparently. The E_{vb} -corrected band gaps are provided in italics. The WM and scGW-BSE exciton binding energies E_b are provided to the right of the bandgaps, with v and nv denoting vibrationally and not vibrationally corrected, respectively. The 2D unit cells for the studied structures are given with lattice vectors a and b. Figure reprinted with permission from [S. T. A. G. Melissen et al.

J. Mater. Chem. A 2017, 5, 5115-5122.] and The Royal Society of Chemistry.[95]

809

810 **V. Band positions.**

811 The ability of the semiconductor to perform the two half reactions of water splitting is related
812 to the positions of the quasi-Fermi levels of the holes and electrons ($E_{F,h}$ and $E_{F,e}$ respectively)
813 representing the chemical potentials of these two charge carriers. The quasi-Fermi levels are
814 linked to the maximum of valence band (VBM) energy and minimum of conduction band
815 (CBM) energy through the following equations where k_B is the Boltzmann constant, T the
816 temperature, $N_{\text{eff},c/v}$ the effective density of states of the conduction/valence band and $n_{e/h}$ the
817 electron/hole concentration.

$$818 \quad E_{F,e} = E_C - k_B T \ln \left(\frac{N_{\text{eff},C}}{n_e} \right) \quad (35)$$

$$819 \quad E_{F,h} = E_V + k_B T \ln \left(\frac{N_{\text{eff},V}}{n_h} \right) \quad (36)$$

820 Osterloh proposes a thermodynamic interpretation of the previous formula where E_C and E_V
821 are an enthalpy contribution to the chemical potentials and the logarithm term represents the
822 entropic contribution.[53] The entropic contribution can be assimilated to the different ways
823 to distribute particles in the effective states of the CBM and VBM. Those who are interested
824 in the relationship between the different quantities (quasi-Fermi energies, chemical potentials,
825 band positions, etc.) and the origin of this entropy contribution are invited to read the very
826 clear publication of F. Osterloh.[53]

827 In general, N_{eff} is in the order of 10^{19} cm^{-3} . [228] The typical charge carrier density ranges
828 from 10^{17} - 10^{20} cm^{-3} . [253] As a consequence, the quasi-Fermi levels are very close to the
829 position of the CBM and VBM and generally researchers in the field of photoelectrocatalysis
830 assimilate the CBM and VBM to the redox potentials of the semiconductor. A better
831 estimation of the redox potential involves the knowledge of N_{eff} and $n_{e/h}$ during the working of

the device. This is possible computationally to calculate N_{eff} from the band structure obtained by DFT [159] and to obtain $n_{\text{e/h}}$ by simulating the electron and flux inside the semiconductor [253] or by using semiconductors semiclassical equations [254]. Experimentally, quasi-Fermi energies can be obtained by impedance spectroscopy as explained by Bisquert et al.[65]

It is important to mention that quasi-Fermi energies, thus redox potentials, can change from the bulk to the surface due to the change in charge carrier concentrations because of their consumption for the HER and OER and because of charge transfer with the electrolyte.[255]

This change is quantifiable only under a good simulation of $n_{\text{e/h}}$ or experimentally by an accurate fitting of the impedance spectra. For water splitting reaction, the potentials must be adapted to perform the two half-reactions, the HER and OER (equations 1 and 2).[256,257]

As we can see in Figure 18,[55] some semiconductors, like WO_3 , have suitable bandgap (~ 2.8 eV)[258], but their band positions (the conduction band in the case of WO_3) are not adapted to water splitting; this is why these properties are necessary to fully characterize a semiconductor.

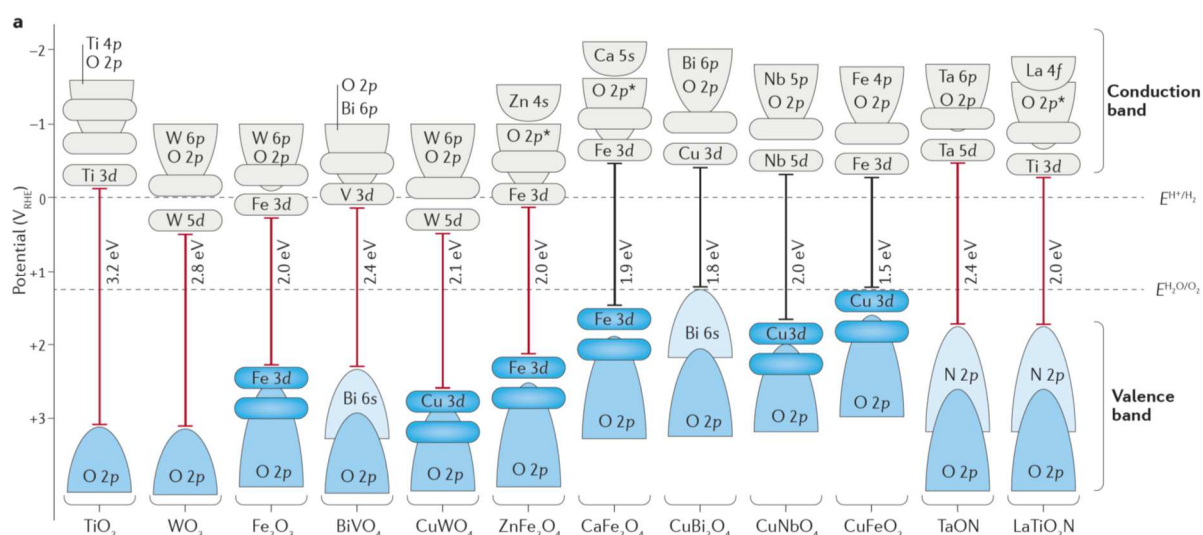


Figure 18. Band positions with respect to SHE reference of several semiconductors used for photoelectrocatalysis. Figure adapted with permission from [K. Sivula and R. van de Krol, *Nat. Rev.* 2016, 1, 15010]. Copyright (2018) Springer.

The measurement of binding energies of occupied valence electrons is possible by conducting photoemission spectroscopies. This can then be translated to estimate the valence band maxima. One of the useful techniques is the photoelectron spectroscopy in the air (PESA)[259]; the measurement is easily conducted in the open air with relatively simple sample preparation. Accordingly, extra attention is necessary to check whether the surface is at an oxidized state, which might change the observed Fermi level. A similar method that requires ultrahigh vacuum (UHV) is ultraviolet photoelectron spectroscopy (UPS)[259,260]. The reference point can be the vacuum level, which is rationalized to obtain absolute potential, e.g., standard hydrogen electrode (SHE) potential is at -4.44 eV.[261]

In the form of photoelectrode, the flatband potential can be estimated from impedance spectroscopy using Mott-Schottky analysis.[262–266] The practical methodology can be found in the references.[164,267–269] In short, the space-charge capacity of the semiconductor, C , is given by the following equation;

$$\frac{1}{C^2} = \frac{1}{e\epsilon_0\epsilon_r A^2 N_D} \left(E_{\text{app}} - E_{\text{FB}} - \frac{kT}{e} \right) \quad (37)$$

where A is the surface area of the electrode, and E_{app} is the applied potential. By varying the applied potential, the Mott-Schottky plot, $1/C^2$ vs. the applied potential, is obtained and then the line is extrapolated when $1/C^2$ becomes zero to derive the flatband potential. The important aspect of the Mott-Schottky analysis is the fact that the measurement can be conducted with the sample immersed in liquid, and thus the conditions should reflect the actual situation of the relevant photoelectrocatalysis. The importance of the surface state, potentially determining ions and pH, was emphasized to significantly contribute to the determination of flatband potential.[270–274] Therefore, it is challenging to accurately interpret the Mott-Schottky analysis of the high surface area electrodes, typical for powder-semiconductor based electrodes. Similarly, there are some interesting discussions about the correlation of flatband potential with atomic electronegativities of oxide.[274]

In computational chemistry, one difficulty for defining the energy levels of semiconductors is to obtain the ionization potential and electron affinity with respect to a reference electrode. A first assumption frequently made is the Koopman's theorem assuming that the crystalline orbitals energy can be considered as the ionization potential and the electron affinity, as we have discussed in the bandgap section. The natural reference system used in quantum chemistry is the vacuum level, being at +4.44 V vs. SHE.[95,275,276] In a quantum chemical calculation, a part of the system must be a vacuum to have orbital energies obtained with respect to this reference. In other words, the band positions are not obtained for a bulk material but for a surface. Each computed band position depends on the surface chosen to be exposed to the vacuum, and the results are surface dependent, as illustrated by the work of Stevanovic et al.[277] (Figure 19). In general, quantum chemists choose non-polar surfaces because polar surfaces are prone to reconstruction and defects, and from a technical point of view, this leads to a non-stoichiometry or strong dipole moment, ultimately affecting the electronic structure, as can be seen in the case of SrTiO₃ in Figure 19.[277–285] As for the bandgap calculation, the only very accurate computational protocol can lead to reliable band positions, such as range-separated hybrid calculation or GW calculations.[148,159,277,278,286,287]

Even with the most accurate computational chemistry approach, to obtain a band position close to the experiment is not guaranteed. Indeed, the slab directly cut in the bulk material is frequently far to be a good model of the real surface. Surfaces can experience important reconstruction, especially for the polar ones, such as in the case of SrTiO₃, or change of composition compared to the bulk like for Ta₃N₅. [281,282,288] Furthermore, put into the electrolyte of water splitting device, the nature of the surface can change. Thus, determining the band edge positions can be a difficult task.

Figure 19. Calculated band edge energies (vs. vacuum) from GW single point calculations on top of PBE optimized surfaces. Experimental energies (obtained by photoemission) are given as bold lines. Figure reprinted with permission from [V. Stevanović et al. *Phys. Chem. Chem. Phys.* 2014, 16, 3706–3714]. Copyright (2018) The Royal Society of Chemistry.

The description of a realistic interface by computational chemistry has been the subject of several developments, summarized by the review of Phan *et al.*[91] Modeling highlighted the influence of water adsorbed on the semiconductor surface on the electronic properties of the surface, including band positions.[289] The most important achievements in that field are clearly the description of the semiconductor/water interface by quantum chemical molecular dynamics.[290] This type of calculation has been applied to several types of semiconductors/electrolyte interfaces, such as the TiO₂/water interface simulation[291–293], Fe₂O₃/water interface simulation[294], ZnO/water interface simulation[295], and Al₂O₃/water interface simulation[296]. While *ab initio* molecular dynamics is probably the best tool to model the surface of the semiconductor placed in water, the very demanding computational resources and time prevent the use of this approach for high-throughput simulation of semiconductors. Another difficulty to manage during the simulation of the semiconductor/electrolyte interface is the electrolyte composition, frequently containing a large concentration of ions. Several approaches can be used to model such systems, including explicit simulation of the ions[297–299] or implicit simulation generally based on the Poisson-Boltzmann equations[300–304] of the electrolyte. The simulation of band positions will probably gain in reliability in the future due to the large work devoted to the simulation of surface/electrolyte interfaces.[255]

The band positions of semiconductors are also affected by the interaction of the surface with the co-catalyst deposited on the surface. This influence can be modeled by directly simulating the interface between the two materials, for example, the WO₃/IrO₂ interface by Ping et al.[305] and TiO₂/IrO₂ interface by Pastore et al.[306] In photocatalytic

water splitting, the decoration with active electrocatalysts is essential to achieve high efficiency, so this catalyst decoration must be taken into consideration. Since this local electronic structure generated at the catalyst-semiconductor interface is effectively utilized to separate charges, this should be a critical investigation for the future direction of the research in photoelectrocatalysis. Also, it is important to determine whether the interface is constructed with inclusion of an electrolyte (semiconductor-electrolyte interface) or effectively isolated with an electrolyte by a catalyst [91,307–309] or protecting layer.[310,311] Concurrent investigations on both experimental measurements and theoretical description of such complicated interface would be suggested to be the key for improved photocatalytic reactions.

Conclusions and perspectives.

New semiconductors are now frequently proposed in the literature for photocatalytic applications. A deep characterization of new semiconductors is important to assess their potentialities for the desired application. Unfortunately, these characterizations are sometimes lacking or performed using unreliable techniques. Collective efforts should be dedicated to establishing very reliable approaches to characterize semiconductors, both experimentally and theoretically. For some properties, the quantum chemical approaches have reached accuracy very close to the experiment with very reasonable computational resources. Those calculations should be performed for all newly synthesized semiconductors, such as to obtain a kind of identity card of the new material.

Computational chemistry can go beyond the characterization of a single material. Because the tools of quantum chemists have achieved a degree of precision close to the experiment, projects of high throughput prediction of materials properties are appearing.[312–317] The objective is to predict new materials with the desired properties before starting a long and costly experimental synthesis.

A complete semiconductor characterization is also necessary for multi-scale simulations. This type of modeling aims at simulating the full process of photoelectrocatalysis from light absorption to chemicals production[57,254,318–320] and involves several fields of physics and chemistry, as well as with several scales in space and time. Among the phenomena simulated by multi-scale modeling, charge carrier generation and transport in the semiconductor, leading to the flux of electrons and holes arriving at the surface of the semiconductor, are governed by semi-classical semiconductor equations involving several properties discussed in the manuscript (dielectric constants and mobilities).[253]

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