

# Predicting band gaps of semiconductors with quantum chemistry

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**Summary.** — The following article gives a brief introduction to quantum chemistry and its application to the prediction of band gaps of inorganic and organic semiconductors. Two important quantum chemistry concepts —Density Functional Theory (DFT) and Coupled Cluster Theory (CC)— are shortly explained. These two concepts are used to calculate the optical and the transport band gap of a set of semiconductors modelled with an electrostatic embedding approach.

## 1. – Introduction

Band gaps are the most defining properties of semiconductors. They determine their application—for example in solar cells. The tools of quantum chemistry give the opportunity to predict band gap energies theoretically. This is of significant relevance for the future development of new semiconductors as well as for the understanding of the ones already existing. This paper gives a short introduction to quantum chemistry and an overview about the methodology to compute band gaps.

## 2. – What is quantum chemistry? A brief overview of common methods

Quantum chemistry transfers the rules of quantum mechanics to many-electron systems to predict and understand chemical and physical properties of chemical relevant

systems like molecules or solids. This is mainly achieved by applying the following time-independent Schrödinger equation [1]:

$$(1) \quad \hat{H}|\Psi\rangle = E|\Psi\rangle.$$

The wavefunction  $\Psi$  contains all information about the quantum mechanical system. It is an eigenfunction of the Hamiltonian operator  $\hat{H}$  with the energies  $E$  being the corresponding eigenvalues. For molecular systems  $\hat{H}$  is defined by [2]

$$(2) \quad \hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{nn} + \hat{V}_{ne}.$$

$\hat{H}$  includes the operators of the kinetic energies of the electrons  $\hat{T}_e$  and nuclei  $\hat{T}_n$  as well as the electrostatic potentials between the electrons  $\hat{V}_{ee}$ , nuclei  $\hat{V}_{nn}$  and electrons and nuclei  $\hat{V}_{ne}$ .

An exact solution of the Schrödinger equation can only be calculated for one electron systems. An approach to define the wavefunction of a system with  $N$  electrons could be made by calculating the product of the one electron wavefunctions (orbitals)  $\psi$  of each electron. This would be possible if the wavefunction is symmetric as for bosons. Electrons are fermions and therefore, the wavefunction is antisymmetric regarding the exchange of two electrons. To solve this problem the wavefunction can be approximated by a Slater determinant with a scaling factor  $N$  [3, 4] as

$$(3) \quad \Psi = N|\psi_1\psi_2 \dots \psi_N|.$$

This wavefunction is used in the Hartree-Fock theory which considers each electron in the mean field of all other electrons [5-8]. By that the electrostatic interactions as well as the electron exchange are described correctly but the individual electron-electron correlation is neglected since the electrons are not interacting directly with each other but with the average over all electrons. Hence, the exact energy  $E_{exact}$  is the Hartree-Fock energy  $E_{HF}$  plus the correlation energy  $E_{corr}$ :

$$(4) \quad E_{exact} = E_{HF} + E_{corr}.$$

There are two main approaches in quantum chemistry to the description of electron correlation. On the one hand there is Density Functional Theory (DFT) and on the other hand there are wavefunction-based/ post-Hartree Fock methods as Coupled Cluster theory (CC, CCSD = Coupled Cluster Singles Doubles, CCSDT = Coupled Cluster Singles Doubles Triples, ...).

DFT does not consider the Hartree-Fock wavefunction of a system but its electron density  $\rho(r)$ . Every ground state has an electron density with a defined potential and hence, a defined ground-state wavefunction (Hohenberg-Kohn Theorem). The electrons are seen as independent particles moving in an effective external potential  $v_{ext}$  of the

nuclei. The Schrödinger equation is replaced by the Kohn-Sham equation (eq. (5)) using one-electron Kohn-Sham orbitals  $\phi_i$  of each electron  $i$  [9]:

$$(5) \quad \hat{H}_{KS}\phi_i(r) = [\hat{T}_{KS}(r) + v_{ext}(r) + v_h(r) + v_{xc}(r)]\phi_i(r) = \varepsilon_i\phi_i(r).$$

$\hat{T}$  is the kinetic energy of non-interacting particles,  $v_h$  the classical Coulomb potential and  $v_{xc}$  the exchange-correlation energy.  $\varepsilon_i$  are the Kohn-Sham eigenenergies. The electron density is defined by

$$(6) \quad \rho(r) = \sum |\phi_i(r)|^2.$$

While this approach describes the kinetics and electrostatics of the system correctly, the exchange-correlation term is not known. The simplest approach to this problem is the Local Density Approximation (LDA) [9]. It considers that the rather local phenomenon of electron exchange-correlation at any point  $r$  of the system can be computed by using a homogeneous electron gas with the electron density computed in  $r$ . The Generalised Gradient Approximation (GGA) [10-12] corrects this model with a gradient regarding inhomogeneity. Both approaches have the problem that the electron density at point  $r$  interacts with the entire electron density and hence, also with itself (self-interaction). This results in an overestimation of the ground state. Density functionals including some Hartree-Fock exchange (hybrid functionals [13]) reduce the problem.

Opposing to DFT, CC theory considers not the electron density but uses the Hartree-Fock wavefunction and hence, has no self-interaction problem. The correlation energy in eq. (4) can be described due to the Coulomb repulsion between the electrons of the system. This force between two electrons in orbitals  $I$  and  $J$  leads to the excitation of the electrons into virtual orbitals  $A$  and  $B$ . The pairing between the occupied and virtual orbitals  $a$  and  $a^\dagger$  is named a paired cluster and can be described by the cluster operator  $\hat{T}$  in eq. (7a) for two or in eq. (7b) for more electrons:

$$(7a) \quad \hat{T}_{IJ}^{AB} = a_A^\dagger a_I a_B^\dagger a_J,$$

$$(7b) \quad \hat{T}_\mu = \hat{T}_{IJK\dots}^{ABC\dots} = a_A^\dagger a_I a_B^\dagger a_J a_C^\dagger a_K \dots$$

By applying this operator to the Hartree Fock wavefunction, the Coupled Cluster wavefunction results as in eq. (8a) either as a product or in the more efficient exponential form.  $t$  determines the probability of the excitation. Consequently the resulting Schrödinger equation is eq. (8b):

$$(8a) \quad |\Psi_{CC}\rangle = \left[ \prod_\mu (1 + t_\mu \hat{T}_\mu) \right] |\Psi_{HF}\rangle = e^{\hat{T}} |\Psi_{HF}\rangle,$$

$$(8b) \quad \hat{H}|\Psi_{CC}\rangle = \hat{H}e^{\hat{T}}|\psi_i\rangle = Ee^{\hat{T}}|\psi_i\rangle.$$

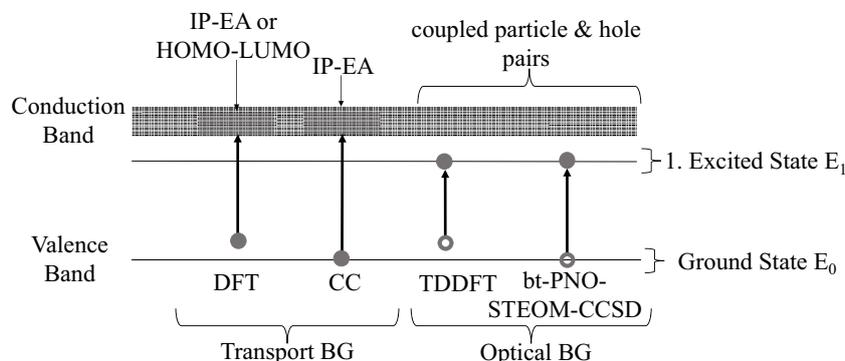


Fig. 1. – Schema of the optical and transport BG and their computation methods.

When all excitations (singles, doubles, triples, ...) are included CC theory provides the exact solution to the Schrödinger equation. CCSD (Coupled Cluster Singles Doubles) includes the excitation of one or two electrons at a time. This is already significantly more accurate than DFT [14].

The CC approach is significantly more expensive than DFT and became affordable only recently due to hardware development. To diminish the computational cost of the localised orbitals, they can be replaced with DLPNOs (domain local pair natural orbital). Roughly speaking, they reduce the virtual calculation space by treating the correlation locally without any significant loss in accuracy (recovery of correlation energy: 99.9%) [15].

### 3. – What are band gaps and how to calculate them?

Band gaps (BGs) are energy gaps in materials. For solids, it has to be differentiated between two main types of BGs: the transport and the optical BG (see fig. 1).

The transport BG of a solid is the gap between the valence and the conduction band. The equivalent for molecules is the fundamental BG. The electron is “transported” through the material as a free charge carrier. It is the difference of the energy needed to remove an electron of the valence band out of the material (ionization potential (IP)) and the one to add one electron from outside to the conduction band (electron affinity (EA)). This results in the following equation with  $N$  being the number of electrons of the system [16]:

$$(9) \quad BG_{trans} = IP - EA = [E_{N-1} - E_N] - [E_N - E_{N+1}].$$

IP and EA can be calculated with both, DFT and CC theories (see fig. 1). A common approximation to compute the transport BG is by calculating the HOMO-LUMO gap (Highest Occupied and Lowest Unoccupied Molecular Orbital). The main problem of

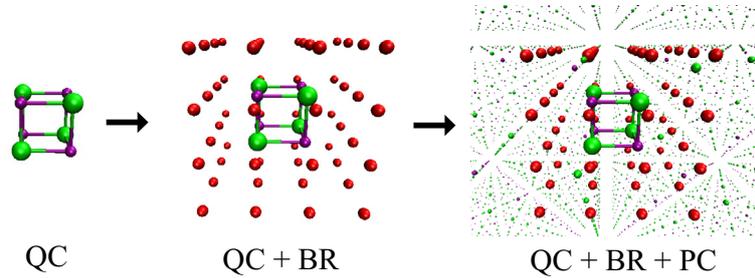


Fig. 2. – Representation of the electrostatic embedding approach for NaCl - QC: Quantum Cluster, BR: Boundary Region, PC: Point Charges.

this approximation is that molecular orbitals and bands are conceptually different. A band is made out of multiple molecular orbitals.

The optical BG is the energy difference between the ground state and the first optical excited state (see fig. 1). Contrary to the transport BG, the excited electron is not a free charge carrier but still bound to its origin (electron-hole pair = exciton) [16]. It can be calculated via linear response theory as in time-dependent DFT (TDDFT). Here, the excited states are computed applying a time-dependent external perturbation  $\delta V_{ext}(t)$  added to the Hamiltonian in the Kohn-Sham equation [17]

$$(10) \quad [\hat{H}_{KS} + \delta V_{ext}(t)]\phi_i(r) = \varepsilon_i \phi_i(r).$$

Due to the discussed self-interaction and the resulting overestimation of the ground state in DFT, the BG will be most likely underestimated (see fig. 1). This is not the case for CC due to the “correct” treatment of energy correlation. To compute excited states with CC the linear response theory based equation of motion (EOM) can be used. A linear excitation operator  $\hat{R}_k$  is applied to eq. (8b) of the ground state  $\Psi_0$  [18, 19] as follows:

$$(11) \quad \hat{H} \hat{R}_k |\Psi_0\rangle = E_0 \hat{R}_k |\Psi_0\rangle.$$

To make the calculation less demanding EOM can be similarity transformed (STEOM) and DLPNOs —as mentionend in sect. 2— can be used. The resulting method is bt-PNO-STEOM-CCSD (back transformed-pair natural orbital-STEOM-CCSD). Here, the excited states are calculated with canonical orbitals —back transformed from the DLPNO— CCSD ground-state calculation [20].

#### 4. – How to model a semiconductor?

So far only the different methods to calculate energies of quantum chemical systems have been discussed. In this section it will be explained how the models of the systems can be constructed, to which the methods are then applied. The positions of the atoms in

TABLE I. – *Test set of organic and inorganic semiconductors.*

Organic semiconductors		Inorganic semiconductors		
Oligoacenes	$\alpha$ -oligothiophenes	Rock salt	Zinc blende	Orthorhombic
Napthalene (2A)	$\alpha$ -2T	LiF	MgS	GeS
Anthracene (3A)	$\alpha$ -3T	LiCl	MgSe	
Tetracene (4A)	$\alpha$ -4T	NaCl	ZnO	
Pentacene (5A)	$\alpha$ -5T	LiBr	ZnS	
	$\alpha$ -6T	NaBr	ZnSe	
		MgO		
		MgSe		

the system are set with Cartesian or internal coordinates. The model can be constructed from scratch or based on experimental data as for example X-ray structures which is the case for the example of NaCl shown in fig. 2.

If NaCl would be a molecule in gas phase and not a solid state material, the beforehand discussed methods could be applied to the cluster (QC) on the left-hand side of fig. 2. But this is not the case. It has to be taken into account that a typical NaCl crystal will be much larger than only these eight ions. With each electron included into the calculation the computation time will increase. Hence, it makes sense to keep the systems as small as possible. Taking a typical NaCl crystal of billions of ions would be very unhandy.

In a solid —especially in a highly ionic solid— the interactions that a certain ion in the bulk experiences with the rest of the system are of mainly classical electrostatic nature. Therefore, the ions around the cluster can be substituted by point charges representing the electrostatic character of anions and cations on the respective positions in the solid (small dots in fig. 2). This approach is called the “electrostatic embedding approach”. It is a combination of the quantum mechanical described QC and the classical described PC field. To avoid charge flow between the two areas a boundary region of core potentials (red dots in fig. 2) is introduced interjacent. The core potentials satisfy on a simplified level the quantum mechanical interactions of the QC surface with the embedding [21,22].

A more common approach to model solids creates a supercell with periodic boundary conditions in a plane-wave function framework mainly used for DFT. This is often not compatible with many of the beforehand described approaches as for example DLPNOs. Therefore, the electrostatic embedding will be used here.

## 5. – Can theory predict experiment?

After discussing different types of band gaps and how to compute them and also introducing a model which makes it possible to model solid state materials those two aspects will be combined to answer the question if theory can predict experimental BGs. A test set of semiconductors —organic and inorganic— as listed in table I will be used to answer the question. The main focus is set on the differences of DFT and CC as

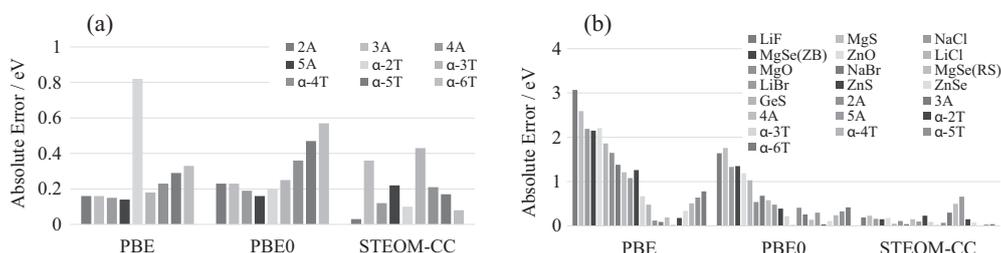


Fig. 3. – Absolute error of computed BGs with respect to experiment. STEOM-CC = bt-PNO-STEOM-CCSD. (a) Transport BG of organic semiconductors. (b) Optical BG of organic and inorganic semiconductors.

described beforehand. The inorganic semiconductors are modelled with electrostatic embedding while the organic ones are treated without embedding since their long-range electrostatic effects are neglectable. The experimental data can be found in ref. [22].

In fig. 3(a) the absolute error of the computed results of the transport BG in respect to experiment using DFT and CCSD are shown for the organic semiconductors. PBE [23] and PBE0 [24] are both DFT functionals. PBE is a meta-GGA functional and does not include any Hartree-Fock correction as discussed in sect. 2. PBE0 on the other hand, is a hybrid functional including 25% Hartree-Fock energy.

The experimental transport BGs vary between 4.23 eV and 8.16 eV. The mean absolute error of DFT for both functionals is about 0.30 eV and for CCSD it is 0.19 eV. The theory appears to be in good agreement with experiment. For DFT, all three energies needed to calculate the transport BG from IP and EA according to eq. (8) are computed separately. Hence, all energies include the self-interaction error. This leads to error cancelation.

Contrary to the transport BG a significant difference between DFT and CC can be seen for the optical BG of the organic as well as the inorganic semiconductors (see fig. 3(b)). The experimental optical BGs vary between 1.84 eV and 11.6 eV. The mean absolute error of the CC method is 0.16 eV while the one of PBE0 is 0.61 eV and PBE is 1.12 eV. The errors of DFT are significantly higher than the one of the CC method. Also the error of the functional including 25% Hartree-Fock energy (PBE0) is significantly smaller than the one which does not (PBE). This leads to the conclusion that an accurate prediction of the optical BG is possible if the self-interaction error is cancelled out and the electron correlation is described accurately.

For more details and a comparison of more functionals see ref. [22].

## 6. – Summary

This article gave a short introduction to quantum chemical methods with the focus on DFT and CC theories. Their different approaches to compute correlation energies and the resulting self-interaction problem of DFT were described. By applying those theo-

ries to compute the optical BG of semiconductors with linear response theory (TDDFT vs. EOM-CC), the self-interaction in DFT leads to less reliable results compared to experiment than CC. The difference is not as pronounced for transport BGs due to error cancellation.

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