

# INTRODUCTION TO BASIC TERMS OF BAND STRUCTURES<sup>©</sup>

## INSTRUCTIONS FOR TEACHERS

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### Goals

Why is graphite black and an electric conductor, while diamond is colorless and an insulator?  
Why is the silver sulphide molecule  $\text{Ag}_2\text{S}$  colorless, while silver sulphide as a bulk material is a black semiconductor?

These and similar questions relate to extended structures and cannot be answered using methods of elementary quantum chemistry. Instead, new terms and methods are needed. The explanation of extended structures starting from molecules as building blocks has been well educated in earlier publications. [1 - 4] However, all these approaches lack the visualization and interactivity needed to concretize this abstract topic, a simple consequence of the limited possibilities of printed material. Mathematical program packages such as Mathcad enable a variety of new possibilities to open this important topic to a broader audience.

Our goal in this publication is to introduce the terms and methods needed to describe extended structures and their properties in an interactive way and by extensive use of the visualization features of Mathcad. We will not answer applied questions as the ones asked above but enable the user to answer them himself using appropriate tools. He should eventually understand the concepts needed to perform quantum chemical calculations on extended systems, be able to analyze and to grasp the results of such calculations and be in the position to understand corresponding research literature.

The theory needed to describe extended systems and their properties includes the following terms which will be introduced within this publication: Translational symmetry, reciprocal space, Brillouin zones, Bloch functions, wave vectors, crystal orbitals (COs), energy bands, the Peierls distortion, band structures, density of states (DOS) and crystal orbital overlap populations (COOP).

For users who do not only want to acquire the theoretical knowledge but want to perform calculations themselves, we provide a complete freeware software package allowing to compute and visualize band structures and DOS diagrams, including many worked examples. [5]

The user can achieve the goals of this course

- by poring over the short textual explanations of the new terms, when they are introduced,
- by studying the extensive visualizations, the idea of which is to concretize the abstract theoretical approach and to provide a visual road to comprehension,
- by deepening their comprehension by modifying the values of variables and parameters and by precisely analyzing the changes resulting in the graphical representations, as suggested in the problems,
- by relentlessly solving ALL problems provided. This is indispensable since a major part of the theory is not explained in textual form but will become comprehensible within the problem-solving process,
- by spending the many hours needed to work through this densely written course.

### **Performance Objectives**

At the end of this course the user should be able to:

- explain how the energy eigenvalues and the coefficients of  $\pi$  molecular orbitals (MOs) of finite linear chains and rings are calculated.
- sketch the  $\pi$  MOs of finite linear chains and rings for different energy levels.
- explain why an extension of the basis to three functions is useful, explain the difference between the eigenvalue formulae for the different basis orbitals, and reason why the same MO coefficients are used for all three basis functions.
- explain the transition from finite to infinite rings, starting with the Bloch theorem and ending up with crystal orbitals. He should be able to emphasize the differences of MOs and COs, energy states index and wave vectors.
- precisely explain the meaning of the terms Bloch function, wave vector, crystal orbital, energy band and band structure.
- explain the characteristics of reciprocal space and know what the first Brillouin zone is and what its significance is within the theory of band structures.
- explain when and why back-folding of energy bands occurs and in what situation the bands split at the  $X$  point.
- sketch all sorts of energy band diagrams met in this course, be it split or not split back-folded or not back-folded bands, and interpret the symmetry and shape of these bands.
- explain the meaning of the DOS and argue why this measure is a valuable tool in the discussion of extended systems. He should know the definition of the DOS and should be able to sketch a typical DOS figure and correlate it with the corresponding energy band.
- describe the meaning of COOPs, compare them with Mulliken overlap populations in molecules, explain their definition, and sketch typical population curves on the basis of a given set of COs at different  $k$  points.

- explain the expansion of the band structure theory to two dimensions. He should also be able to make the logical step to three dimensions and be aware of the resulting changes and consequences.
- sketch band structure diagrams for the two-dimensional carbon lattice for all basis orbitals and explain the run of these curves.
- start working with the tight binding program package BICON-CEDiT. [5]

## Prerequisites

This Mathcad course cannot replace a textbook or a lecture on the abstract topic of band structures. Rather, it is our idea that this course should be used as an independent study project for students at the undergraduate level that is accompanied by reading a textbook such as *Solids and Surfaces* by R. Hoffmann [1] and by assistance, e.g. by a graduate student.

The following prerequisites are indispensable in order to succeed in this course:

- Knowledge and mastery of the fundamentals of quantum chemistry. An introductory lecture on quantum chemistry should have been attended.
- Moderate skills with Mathcad.
- Comprehension of the following introductory texts that can be opened via links in the main QBAND worksheet:
  - *Information about Bravais lattices*
  - *Information about reciprocal lattices*

## Overview of the Mathcad document

### 1. Preliminary Information

The goal of the course, prerequisites, performance objectives and a short introduction are given.

### 2. Finite, one-dimensional systems - One basis function

Most chemists are more familiar with the discrete energies of molecular orbitals than with band structures of crystal orbitals although the two approaches are essentially similar. Our didactical approach is therefore to start with the description of the  $\pi$  molecular orbitals of finite linear and cyclic unsaturated hydrocarbon chains.

### 3. Finite, one-dimensional systems - Three basis functions

The chains and rings of chapter 2 are no longer described using only  $p_\pi$  AOs but also using  $p_\sigma$ , and  $s_\sigma$  orbitals. This enhances the understanding of the effects resulting from different shape and orientation of the AOs.

4. Infinite rings - Three basis functions  
For the treatment of infinite rings or chains, the Bloch theorem is introduced as well as Bloch orbitals, the wave vector and the first Brillouin zone. Infinite rings are then described using Bloch crystal orbitals and energy bands.
5. Infinite rings - One basis function - Alternating / Non-alternating bond lengths  
The effect of bond length alternation on the shape of the energy bands is investigated. The concepts of back-folding and the Peierls distortion are introduced.
6. Infinite rings - Three basis functions - Alternating bond lengths  
The bond length alternation is applied to the expanded basis set, resulting in  $p_\pi$ ,  $p_\sigma$ , and  $s_\sigma$  bands.
7. Density of states (DOS)  
The DOS is introduced and calculated for the bands discussed in chapter 6.
8. Crystal Orbital Overlap Population (COOP)  
After introduction of the term, different COOP contributions and the total COOP are calculated for the  $p_\pi$  basis.
9. Overview: Energy band, DOS and COOP
10. Band structure of a two-dimensional carbon lattice  
The idea of this last part is to expand the learned band structure concept to two-dimensional square structures. In the course of this, the understanding of reciprocal space is deepened.
11. Summary of formulae

### **How To Work Through This Course**

- Seriously working through the course, including the solving of all problems, will take between three days and two weeks, depending on the user's previous knowledge. Users with significant lacks of previous knowledge and mathematically untrained users may have to spend more time to get the full benefit from the course.
- The crucial point deciding how valuable this course is for the user is whether ALL problems provided are solved or not. Significant parts of the theory will only be clarified as part of the problems. We therefore strongly encourage the users not just to "read" the main worksheet, "play" with some variables and solve the one or the other problem. This will undoubtedly lead to a woolly comprehension and to the feeling of not having understood what the point of all this is.  
The problems range from simple visualization exercises to quite challenging problems that relentlessly test the thorough understanding of theory.
- The theory behind this course is rather abstract. Since we can and do not want to replace a textbook the user should read a textbook before or while working through QBAND. We

especially recommend Nobel Prize winner Roald Hoffmann's excellently written book *Solids and Surfaces*. [1]

- In order not to blow up the worksheet too much and to avoid a transfer of the contents to slips the main document contains the indispensable parts of theory, while supplementary material such as further reading, more detailed explanations, mathematical derivations, hints or solutions to some problems have been put into separate worksheets. These can be opened as popup windows via hyperlinks that can be found throughout the main document. The reading of these appendices is not compulsory, and the degree to which the user goes into them is up to his or her claims. However, pretty much extra information can be found within these documents, and this may significantly deepen the insight into theory.
- People lacking fundamentals of quantum chemistry are recommended to postpone QBAND and to first fill their knowledge gaps in quantum chemistry, e.g. with John P. Lowe's book *Quantum Chemistry*. [2] This book includes – in its last chapter – a treatment of extended systems and can therefore partly replace Hoffmann's book.
- We have worked hard to draw an easily comprehensible flow from elementary quantum mechanics to research level topics such as the quantum-chemical description of three-dimensional crystalline systems. The user can find answers to most of his or her potential questions by carefully working through the worksheet, by solving the problems and by studying the linked appendices. Nevertheless, questions may arise that cannot be answered without further knowledge. Hence faculty should delegate e.g. a Ph.D. student to help the users who are stuck with their questions.
- At the end of the course, the student should be capable and encouraged to use our research-level tight binding program package BICON-CEDiT, which includes oscillator strength calculations and many more options. It is available with examples free of charge. [5] The students should also be able to understand and to benefit from the research publications [6 - 10] that will still deepen and broaden their understanding. In [8], for example, the terms related to band structures are transferred to large cluster structures. The publications are cited in the course, where suitable.
- In our department the QBAND course is organized in the following way:  
Groups of two 6<sup>th</sup> semester chemistry students work through the course. They are given half a week of time. A PhD student is at their disposal to answer questions and to help with the problems. The degree to which the students can complete the course depends on their skill. Eventually, the best students have time to calculate the two-dimensional carbon lattice with the tight binding program package BICON-CEDiT. [5]

## Technical Details

- The course was written for Mathcad 2001i.
- Interested faculty should download the zip files and extract them to an appropriate directory.
- The external links are files which must be placed in the same directory as Qband.mcd. These are supplements that enrich the material and increase the depth to which students can use the documents to learn band structure.
- All files are optimized for a display resolution of 96 dpi. 120 dpi also work, but the layout is significantly better using 96 dpi.
- A pdf file of the main program is provided for potential user examination.

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