

Introduction to basic terms of band structures

Marc Meyer, Stephan Glaus, and Gion Calzaferri (gion.calzaferri@iac.unibe.ch)
Department of Chemistry and Biochemistry, University of Bern,
Freiestrasse 3, CH-3012 Bern, Switzerland

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1. Preliminary Information

Goals

Why is graphite black and an electric conductor, while diamond is colorless and an insulator?
Why is the silver sulphide molecule Ag_2S 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.

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Performance Objectives

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

- explain how the energy eigenvalues and the coefficients of π molecular orbitals (MOs) of finite linear chains and rings are calculated.
- sketch the π 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. [\[5\]](#)

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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:

[Information about Bravais lattices](#)

[Information about reciprocal lattices](#)

Definition of globally used variables

One should be aware of the need to clearly define all variables. To provide an overview the most important variables are given in the following table:

Variables the values of which can be changed.

$N := 20$	Number of atoms		
$\alpha := 0$	Coulomb integral for chapter 2	$\beta := -1$	Resonance integral for chapter 2
$\alpha_s := -2$	} Coulomb integrals for chapters 3 and 4	$\beta_{s\sigma} := -0.5$	} Resonance integrals for chapters 3 and 4
$\alpha_p := -1$		$\beta_{p\sigma} := -0.5$	
		$\beta_{p\pi} := -0.5$	

Hyperlinks back to:

- [2.1 \(Linear chains\)](#)
- [2.2 \(Rings\)](#)
- [3.1 \(Linear chains - Three basis functions\)](#)
- [3.2 \(Rings - Three basis functions\)](#)
- [4. \(Infinite rings - Three basis functions\)](#)

Index variables. They should not be changed.

$J := 1..N$	$j := 0..N-1$	Index of the energy levels of the chain (J) and the ring (j), respectively
$L := 1..N$	$\lambda := 0..N-1$	} Indices of the atoms (atomic orbitals) of the chain (L, M) and of the ring (λ , μ), respectively.
$M := 1..N$	$\mu := 0..N-1$	

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

For a better understanding all examples are made with the zero differential overlap (ZDO) approximation.

Information about the ZDO approximation

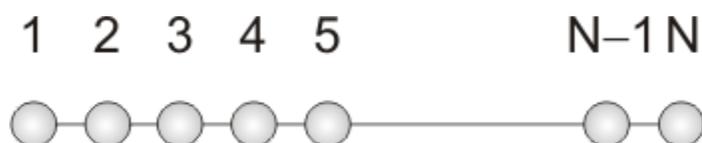
The formulae are kept simple and the numerical effort small. Furthermore, the model compounds selected have been chosen in order to keep things as simple as possible.

Since 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 - we start with molecules and will later extend them to one-dimensional crystal structures.

In the first step we consider π molecular orbitals of linear and cyclic unsaturated hydrocarbon chains, built up of N carbon atoms. Each of these carbon atoms can form π bonds with its p_z orbital. These bonds are modeled as a linear combination of the atomic orbitals to form molecular orbitals. The MOs have discrete energy values which we can calculate. Additionally, we can describe the contributions of the atomic orbitals to the MOs by coefficients.

2.1 Linear chains

The following figure represents a linear chain of N carbon atoms:



Current values of variables:

$$N = 20 \quad \alpha = 0 \quad \beta = -1$$

[Change values](#)

Considering only the p_z atomic orbitals (AOs) as a basis, we form MOs by linearly combining them (LCAO-MO method). We find:

Energy eigenvalues:
$$\varepsilon(J) := \alpha + 2 \cdot \beta \cdot \cos\left(\frac{J \cdot \pi}{N + 1}\right)$$

MO coefficients:
$$c(L, J) := \sqrt{\frac{2}{N + 1}} \cdot \sin\left(J \cdot \pi \cdot \frac{L}{N + 1}\right)$$

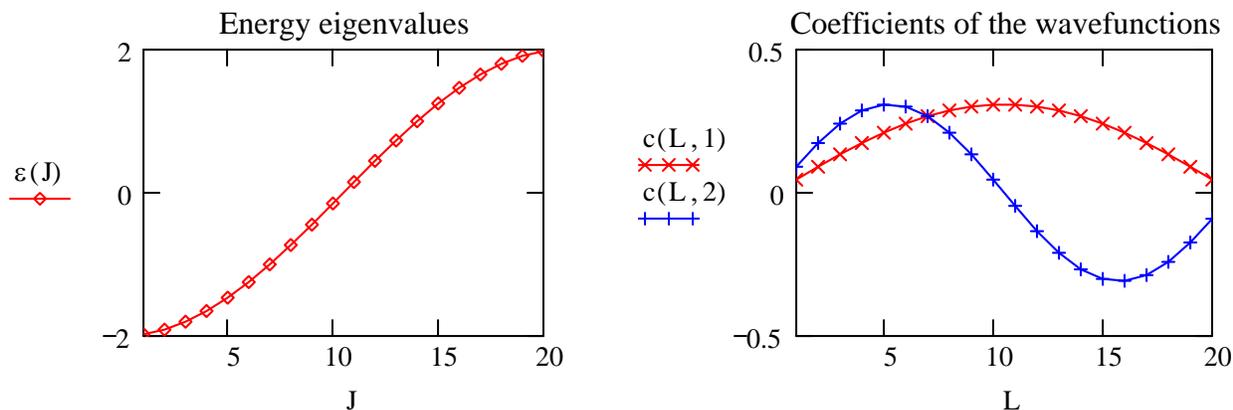
Molecular orbitals:
$$\psi(J) := \sum_L c(L, J) \cdot p_\pi(L)$$

[Explanation of the form of the molecular orbitals and derivation of the energy eigenvalues](#)

$p_\pi(L)$ is the p_z AO on carbon atom no. L .

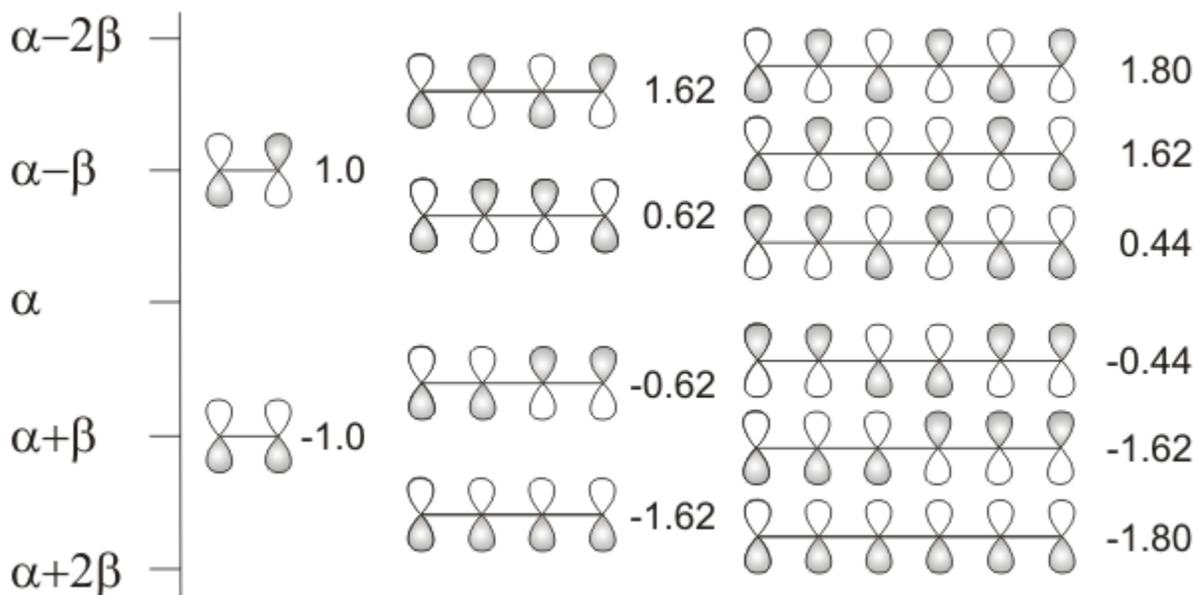
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The energy eigenvalues and the coefficients of the wavefunctions are visualized in the next two figures:



[Change variables](#)

Visualization of the energy levels and of the nodes in the various MOs for $N = 2$ (ethene), $N = 4$ (butadiene) and $N = 6$ (hexatriene). The size of the AOs is uniform; they are not scaled to represent the magnitude of the MO coefficients!



Problems

2.1 Set $N = 4$. Then compare the graph of the energy eigenvalues to the energy levels of butadiene in the figure above.

Compare the coefficients of all four MOs with the sign scheme in the energy level figure.

(The coefficients of $\psi(3)$ and $\psi(4)$ can be plotted by replacing $c(L, 1)$ and $c(L, 2)$ in the above plot with $c(L, 3)$ and $c(L, 4)$.)

Sketch the four MOs of butadiene using not only the signs of the MO coefficients but also their magnitude.

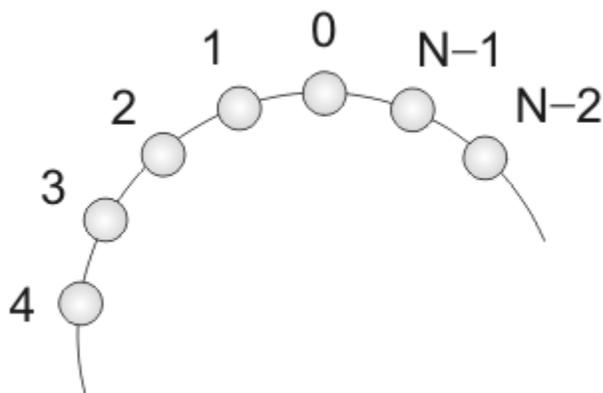
Repeat the whole procedure for $N = 6$.

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- 2.2 Verify exemplarily that for any value of N the number of nodes grows from zero in the lowest MO to $N-1$ in the highest MO.
That this must be true can also be shown mathematically. You can do this.
- 2.3 Sketch the energy eigenvalues as an energy level chart. What happens if N approaches infinity?
- 2.4 In the ground state, which energy eigenvalue corresponds to the highest occupied MO? Each carbon atom contributes one π electron. Assume that the MOs are filled with electrons from bottom to top according to the aufbau principle. Each MO can hold up to two electrons.
What is the energetic consequence of this aufbau principle for the stability of the molecule?
- 2.5 Show numerically using Mathcad that the MOs are normalized correctly.
[Hint](#)
- 2.6 Study the following tutorial showing the way to find the numerical values of the energy eigenvalues and of the MO coefficients.
[The Hückel eigenvalue problem](#)

2.2 Rings

A finite chain has a beginning and an end. Effects which derive from the border are therefore expected. Such border effects are certainly more decisive in short chains. To avoid them the so-called Born-von Karman boundary condition is implemented by introducing cyclic structures. The Born-von Karman boundary condition demands the wave function on atom N to be identical to the wave function on atom 0:



Current values of variables:
 $N = 20$ $\alpha = 0$ $\beta = -1$
[Change values](#)

Since the equivalence of all atoms in rings is advantageous for our purposes, infinitely large rings provide a more elegant approach to describe infinitely long chains. (Note that the curvature of an infinitely large circle is zero, just as it is for a straight line.) We start with the description of finite rings. This will lead us to infinite rings in section 4.

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The following energy eigenvalues and MO coefficients are found:

Energy eigenvalues: $\varepsilon(j) := \alpha + 2 \cdot \beta \cdot \cos\left(\frac{j \cdot 2 \cdot \pi}{N}\right)$

Explanation of the form of the molecular orbitals and derivation of the energy eigenvalues

MO coefficients: $c(\lambda, j) := \sqrt{\frac{1}{N}} \cdot \exp\left(i \cdot \frac{2 \cdot \pi \cdot \lambda \cdot j}{N}\right)$

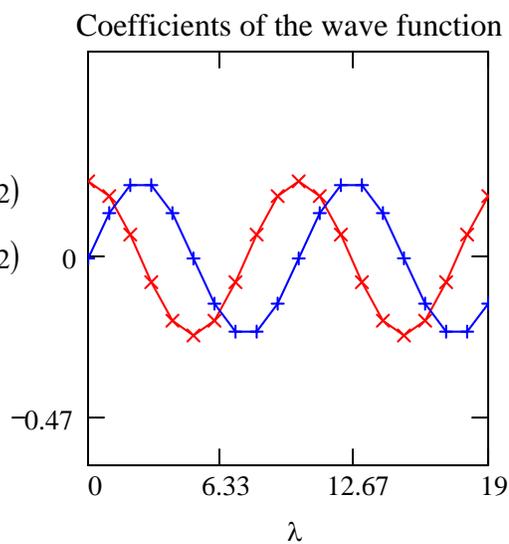
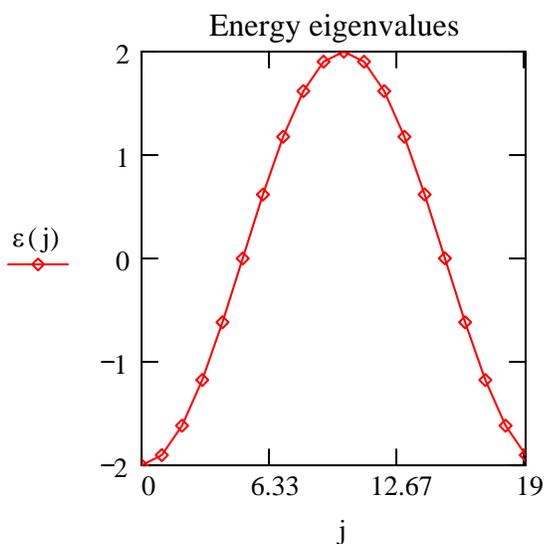
$$c_{\text{conj}}(\lambda, j) := \sqrt{\frac{1}{N}} \cdot \exp\left(-i \cdot \frac{2 \cdot \pi \cdot \lambda \cdot j}{N}\right)$$

$$c_1(\lambda, j) := \frac{1}{2} \cdot (c(\lambda, j) + c_{\text{conj}}(\lambda, j))$$

$$c_2(\lambda, j) := \frac{1}{2 \cdot i} \cdot (c(\lambda, j) - c_{\text{conj}}(\lambda, j))$$

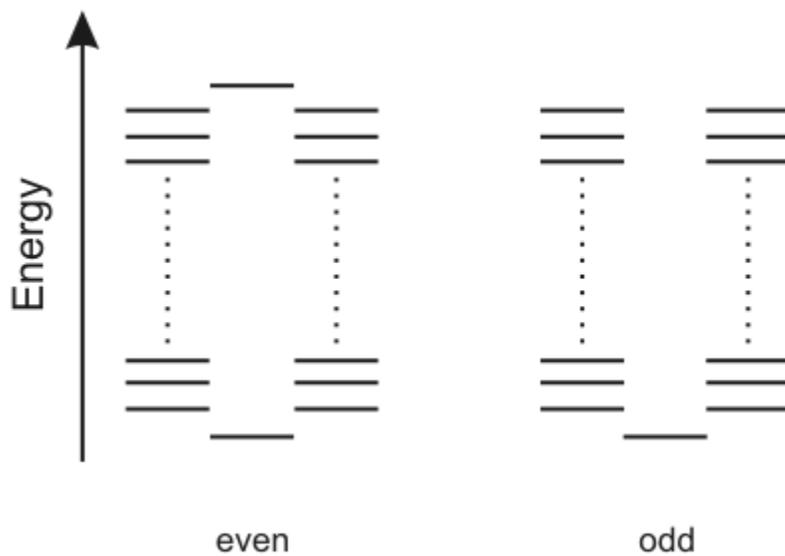
Molecular orbitals: $\psi_1(j) := \sum_{\lambda} c_1(\lambda, j) \cdot p_{\pi}(\lambda)$

$$\psi_2(j) := \sum_{\lambda} c_2(\lambda, j) \cdot p_{\pi}(\lambda)$$

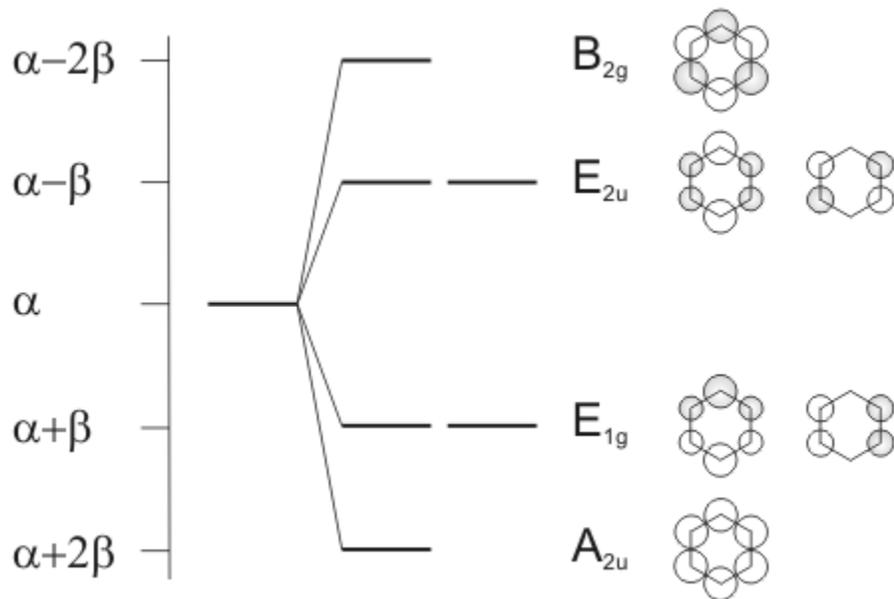


[Change variables](#) [Home](#)

Note that if N is even there will be an even number of MOs and the left situation in the following energy level chart will result, while for an odd N the right situation will result:



Visualization of the energy levels for $N = 6$ and top view of the MOs:



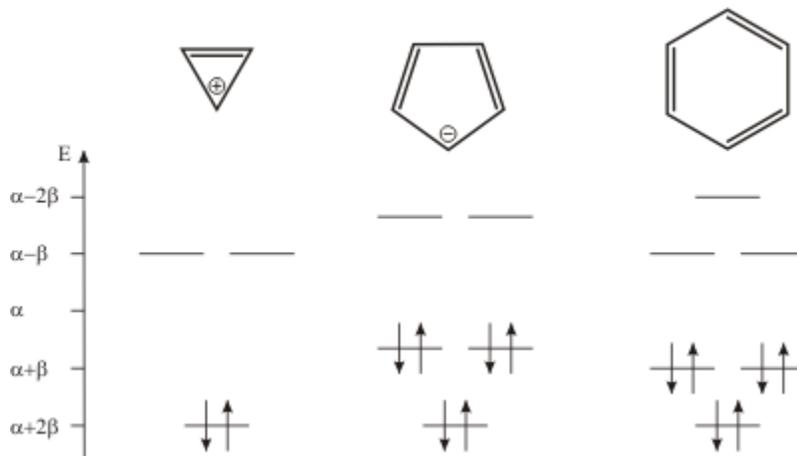
Problem

- 2.7** Set $N = 6$. Verify the distribution of energy levels and their degeneracies as predicted in the figures above. Plot the coefficients of all six wavefunctions (MOs) by modification of the plot "Coefficients of the wave function", and compare them with the MO scheme in the figure above. Repeat the whole procedure for other values of N , especially for $N = 3, 4$, and 5 .

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It turns out that some rings are stable, others are stabilized by distortion. The Hückel rule states that all rings with $4n + 2 \pi$ electrons are stable. This is a simple consequence of the degeneracy of all but the lowest (and possibly the highest) energy levels, leading to a closed shell system if $4n + 2 \pi$ electrons are present. All other rings lead to open shell configurations which are stabilized by distortion. This is known as the Jahn-Teller effect, which will be discussed in [section 5.2](#).

Since in a neutral ring the number of π electrons is equal to the number of carbon atoms, it follows that neutral $(4n + 2)$ -membered rings are stable. Rings of different size can be stable if they have an excess or a deficiency of π electrons, resulting in a total of $4n + 2 \pi$ electrons. Examples are the cyclopropenyl cation and the cyclopentadienyl anion:



Derivation of the number of stabilized MOs in rings with $4n + 2 \pi$ electrons

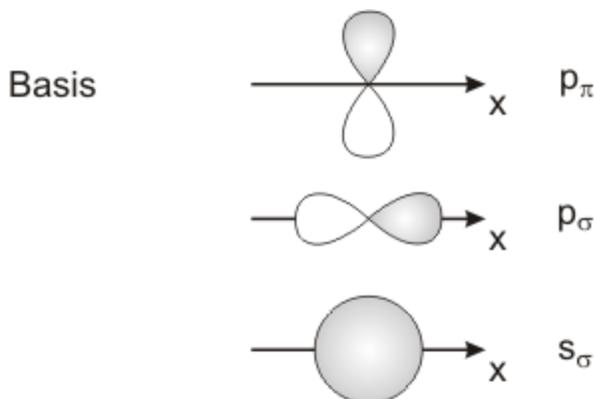
Problems

- 2.8** What are the possible values of j for even and for odd values of N ?
Show algebraically that the lowest energy level is always non-degenerate.
Show algebraically that this is also true for the highest energy level if and only if N is even.
- 2.9** Sketch the energy eigenvalues for various values of N as energy level charts, as it was done in the figure above for $N = 3, 5,$ and $6,$ and fill in the electrons for neutral molecules according to the aufbau principle. (Use at least the following values for N : 3, 4, 5, 7, 8, 10)
- 2.10** Explain why cyclobutadiene is distorted. (Use the results of problem 2.9 to argue.)
- 2.11** Observe the behavior of the HOMO and the LUMO (highest occupied and lowest unoccupied molecular orbital) levels in the charts of problem 2.9, as N approaches infinity. What happens?
- 2.12** Show numerically using Mathcad that the MOs are normalized correctly.
- Hint**
- 2.13** Compare the MOs of chains and rings. How does the number of nodes develop?
Do the edge phenomena weaken in the MOs of chains when N increases?

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

In order to make the model more general, all valence electrons of the carbon atoms in the chain or ring have to be accounted for. Hence we will include all valence orbitals in our calculations. For carbon we expect a basis set of four functions ($2s$, $2p_x$, $2p_y$, $2p_z$). However, in the linear chain case, as treated here, the p_y and p_z orbitals are indistinguishable. They both form π bonds. As a consequence, they are summarized as p_π AOs. In contrast to these p_π orbitals the $2p_x$ AOs form σ bonds. They are denoted as p_σ AOs. Finally, the s orbitals are called s_σ AOs, since they of course lead to σ bonds:



We again examine the energy levels and MOs of linear and cyclic finite chains of equidistant carbon atoms in the ZDO approximation. This means that we assume that

- an AO overlaps only with itself,
- only next neighbors do interact,
- the Coulomb and resonance integrals have constant values for each type of basis function.

Furthermore, $2p_x$ AOs will interact with $2p_x$ AOs only, $2p_y$ AOs with $2p_y$ AOs only etc.. This is a consequence of the symmetry and the orthogonality of all AO types.

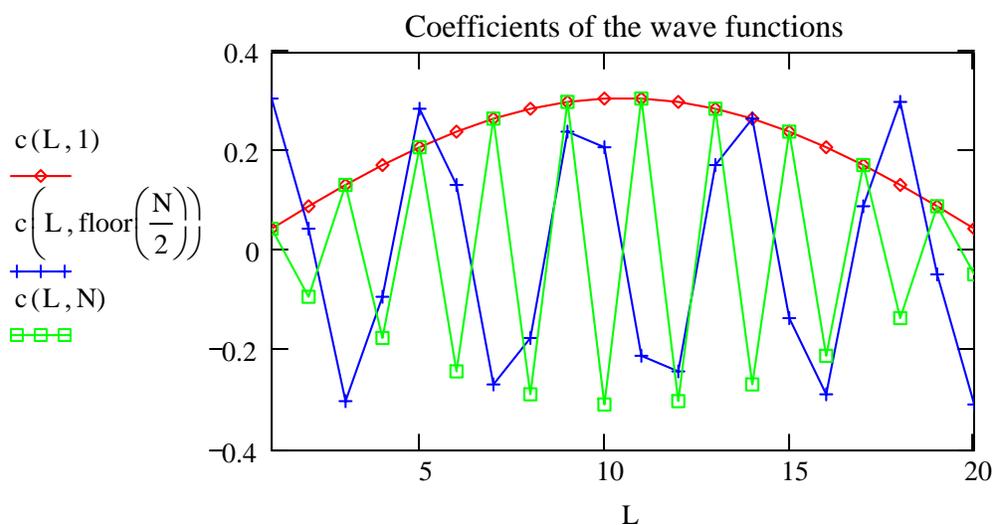
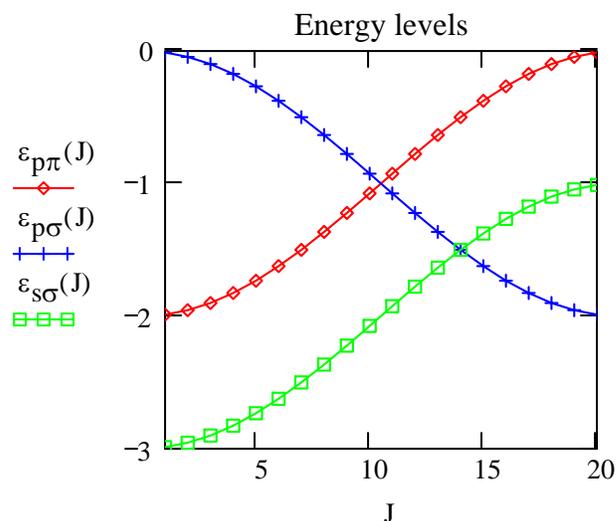
Hence we can independently describe the interactions between AOs of the same type. The only difference we make between the different basis functions (p_π , p_σ , s_σ) is the choice of the values of their Coulomb and resonance integrals.

Hence nothing will change in the derivations of the energy eigenvalues and of the MO coefficients. Apart from a sign change in the energy eigenvalues of the MOs formed from p_σ AOs (see comment below) the results remain the same.

Keep in mind that what we describe here are not molecules. There are only carbon atoms and, for example, no hydrogen atoms. Our goal is to develop a theory allowing to describe extended systems, e.g. a three-dimensional crystal of carbon atoms. In this first part we develop the theory for the one-dimensional case by investigating a linear chain and a ring of carbon atoms, respectively. The generalization to two dimensions will follow in section 10, showing the steps needed to describe systems in higher dimensions.

Since in a crystal all valence orbitals of all atoms will interact with neighboring AOs, all kinds of interactions occurring have to be considered in order to yield a comprehensive description of the system. Therefore we have subdivided the AOs into classes, according to the type of their interaction, and will now describe the resulting energy levels and MOs.

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[Change variables](#)

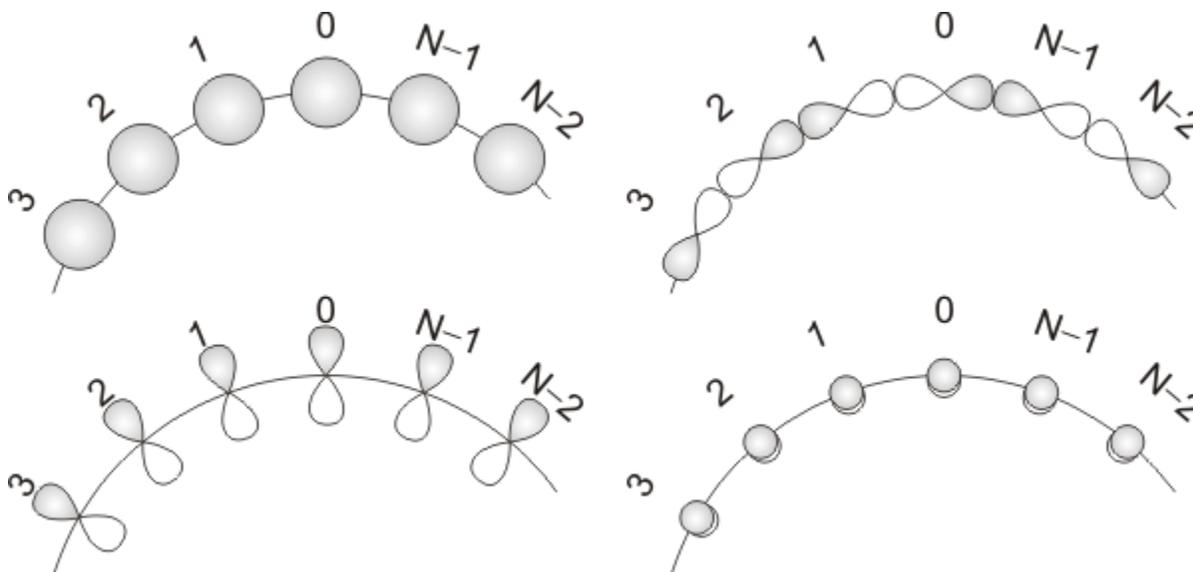
Problems

- 3.1 Change the chain length, and discuss the resulting changes in the plots above.
- 3.2 Change the values of the Coulomb and resonance integrals α_s , α_p and $\beta_{s\sigma}$, $\beta_{p\sigma}$, $\beta_{p\pi}$, respectively, and discuss the resulting changes in the above plots. Keep in mind that all these energies are negative and that the β values are smaller than the corresponding α values according to amount. ([Information about the ZDO approximation](#)) Do not choose unrealistically large values for α and β , and do not forget to reset the variables to their original values after this exercise ($\alpha_s = -2$, $\alpha_p = -1$, all $\beta = -0.5$).
- 3.3 Sketch the MOs for the three basis functions and for $J = 1$, $J = \text{floor}(N/2)$ and $J = N$ each.

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3.2 Rings - Three basis functions

The following figure shows a ring of N carbon atoms, seen perpendicular to the xy-plane. The sketched orbitals represent the 2s (top left), the 2p_x (top right), the 2p_y (bottom left), and the 2p_z (bottom right) AOs, all in the most bonding configuration. (A separate coordinate system is placed on each carbon atom with the x-axis lying tangentially to the ring.)



The derivation of energy eigenvalues and MO coefficients for rings was not dependent on the type of atomic orbitals used. Hence the results can be used as they have been derived. However, just as with linear chains, three separate formulae are needed in order to correctly describe the energy eigenvalues, since the energy eigenvalues depend on α and β and on the symmetry properties of the atomic orbitals. This can easily be understood from consideration of the above figure.

$$N = 20 \quad \alpha_s = -2 \quad \alpha_p = -1 \quad \beta_{s\sigma} = -0.5 \quad \beta_{p\sigma} = -0.5 \quad \beta_{p\pi} = -0.5 \quad \text{Change values}$$

$$\text{Energy eigenvalues: } \varepsilon_{p\pi}(j) := \alpha_p + 2 \cdot \beta_{p\pi} \cdot \cos\left(\frac{j \cdot 2\pi}{N}\right)$$

$$\varepsilon_{p\sigma}(j) := \alpha_p - 2 \cdot \beta_{p\sigma} \cdot \cos\left(\frac{j \cdot 2\pi}{N}\right)$$

$$\varepsilon_{s\sigma}(j) := \alpha_s + 2 \cdot \beta_{s\sigma} \cdot \cos\left(\frac{j \cdot 2\pi}{N}\right)$$

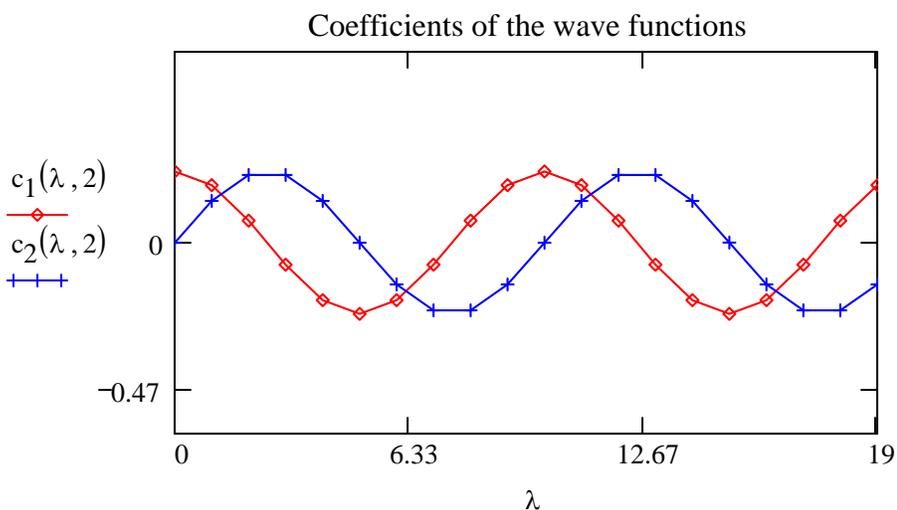
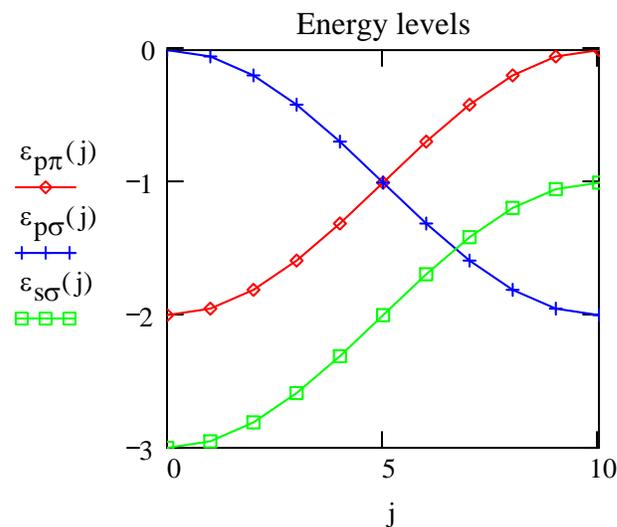
$$\text{MO coefficients: } c(\lambda, j) := \sqrt{\frac{1}{N}} \cdot \exp\left(i \cdot \frac{2\pi \cdot \lambda \cdot j}{N}\right) \quad c_{\text{conj}}(\lambda, j) := \sqrt{\frac{1}{N}} \cdot \exp\left(-i \cdot \frac{2\pi \cdot \lambda \cdot j}{N}\right)$$

$$c_1(\lambda, j) := \frac{1}{2} \cdot (c(\lambda, j) + c_{\text{conj}}(\lambda, j)) \quad c_2(\lambda, j) := \frac{1}{2 \cdot i} \cdot (c(\lambda, j) - c_{\text{conj}}(\lambda, j))$$

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Wave functions: $\psi_1(j) := \sum_{\lambda} c_1(\lambda, j) \cdot \phi(\lambda)$ $\psi_2(j) := \sum_{\lambda} c_2(\lambda, j) \cdot \phi(\lambda)$

(MOs belonging to the eigenvalue j)



[Change variables](#)

Problems

- 3.4 Change the ring size and discuss the resulting changes in the above plots.
- 3.5 Change the values of the Coulomb and resonance integrals α_s , α_p and $\beta_{s\sigma}$, $\beta_{p\sigma}$, $\beta_{p\pi}$, respectively, and discuss the resulting changes in the above plots. (See problem 3.2 for further instructions.)
- 3.6 Sketch the MOs for the three basis functions and for $j = 0$, $j = \text{floor}(N/4)$ and $j = \text{floor}(N/2)$ each.
- 3.7 Compare the energy level curves of chains and of rings.
What does this comparison show with respect to the goals of this course?

Summary of sections 1 to 3

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4. Infinite rings - Three basis functions

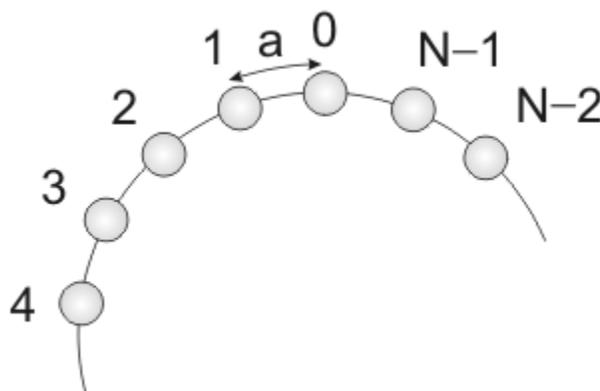
We have learned that elongated chains can be approximated by rings with a very large radius. When the number of atoms N of the ring approaches infinity, the curvature of the ring approaches zero, i.e. the ring becomes physically indistinguishable from an infinite linear chain. Approximating a chain with a ring has the advantage of removing any edge phenomena since edge phenomena do not exist in an infinite linear chain. However, they will not vanish as long as a chain approach is used to describe the infinite chain. Since it is the goal of this course to describe extended systems, i.e. systems consisting of an infinite number of atoms which are, in the one-dimensional case, aligned on a straight line, it is favorable to use the ring approach and let the ring size approach infinity.

Although with the derivation of the theory on rings in sections 2 and 3 we have already beared the brunt of work, we cannot just replace N in the above energy functions and MO coefficient formulae with infinity now in order to describe extended systems.

The problem we should overcome first is that the formulae cannot be evaluated if N is infinity! However, the use of **TRANSLATIONAL SYMMETRY** can avoid this trouble. This is the starting point for the **BLOCH** or **SYMMETRY ORBITALS**.

The Bloch theorem says that if x is an arbitrary ring position in an infinitely large ring and a is the spacing between two nearest ring positions or, more general, the length of a Wigner-Seitz cell, then the wave function at position $x + a$ is the wave function at position x times $e^{i2\pi j/N}$, where j is an integer in the range $0, 1, 2, \dots, N-1$:

$$\psi(x + a) = e^{i \cdot \frac{2\pi \cdot j}{N}} \cdot \psi(x)$$



$$a := 1$$

The following wave functions, the **BLOCH FUNCTIONS**, solve this equation:

$$\psi(x, j) = e^{i \cdot \frac{2\pi \cdot j \cdot x}{N \cdot a}} \cdot \phi(x)$$

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Mathematically $\phi(x)$ is a periodic function that is identical at each ring position, i.e. $\phi(x) = \phi(x + \lambda a)$ for any integer λ . Physically $\phi(x)$ describes the atomic orbitals. Bloch functions can be expressed more adequately if we use the integer variable λ as an atom index to describe the position on the ring, with λ running from 0 to $N-1$ corresponding to the ring positions $0, a, 2a, \dots, \lambda \cdot a, \dots, (N-1) \cdot a$:

$$\psi(\lambda, j) = e^{i \cdot \frac{2\pi \cdot j \cdot \lambda}{N}} \cdot \phi(\lambda)$$

Summing over all λ results in the wave function of the MO:

$$\psi(j) = \sum_{\lambda} e^{i \cdot \frac{2\pi \cdot j \cdot \lambda}{N}} \cdot \phi(\lambda)$$

Apart from the normalization factor, this wave function is identical to the MOs for rings that have been introduced in sections [2.2](#) and [3.2](#). This shows that we have already introduced Bloch functions when we have introduced complex MO coefficients in the mentioned sections.

We will now eliminate N and j in the exponent of the Bloch functions. Otherwise there is still no way to evaluate the coefficients for infinite systems.

The elimination of N and j is done by introducing the so-called **WAVE VECTOR** or **k-VECTOR**:

We define: $k(j) := \frac{2\pi}{N \cdot a} \cdot j$ k is called a wave vector. It has an inverse length as dimension. This step therefore marks the transition from direct space to reciprocal space! [Information about reciprocal lattices](#)
 k can be interpreted as a symmetry label. This view will be crucial in the following discussions.

Because j can have $\text{floor}(N/2) + 1$ values ([Explanation](#)), there are also $\text{floor}(N/2) + 1$ k -vectors, ranging from 0 ($j = 0$) to approximately π/a ($j = \text{floor}(N/2)$).

If N approaches infinity, the set of k -vectors becomes the continuous interval $[0, \pi/a]$.

j represents the energy levels. Obviously, this role is overtaken by k now. Therefore each k -vector represents one MO, which we now call a crystal orbital (CO) because by using Bloch functions our focus is on the whole system (i.e. on the whole crystal for N approaching infinity).

The crystal orbitals, using Bloch functions and normalization, now have the following final form:

$$\psi_B(k) = \sqrt{\frac{1}{N}} \cdot \sum_{\lambda=0}^{N-1} \exp(i \cdot k \cdot a \cdot \lambda) \cdot \phi_{\lambda} \quad \psi_{B\text{conj}}(k) := \sqrt{\frac{1}{N}} \cdot \sum_{\lambda=0}^{N-1} \exp(-i \cdot k \cdot a \cdot \lambda) \cdot \phi_{\lambda}$$

These COs are suitable to describe infinite systems.

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In the one-dimensional case the **FIRST BRILLOUIN ZONE** is defined as the set of points in reciprocal space with k-values in the interval $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$. It is therefore obvious that the

above set of k-vectors with values lying in the interval $0 \leq k \leq \frac{\pi}{a}$ corresponds to half the first Brillouin zone.

Using k-vectors outside the first Brillouin zone results in redundancy. The period is $\frac{2\pi}{a}$.

This is easily proven. For an integer m we find:

$$\begin{aligned}\psi_B\left(k + m \cdot \frac{2\pi}{a}\right) &= \sqrt{\frac{1}{N}} \cdot \sum_{\lambda} e^{i \cdot \left(k + m \cdot \frac{2\pi}{a}\right) \cdot a \cdot \lambda} \cdot \phi(\lambda) \\ \psi_B\left(k + m \cdot \frac{2\pi}{a}\right) &= \sqrt{\frac{1}{N}} \cdot \sum_{\lambda} e^{i \cdot k \cdot a \cdot \lambda} \cdot e^{i \cdot m \cdot 2\pi \cdot \lambda} \cdot \phi(\lambda) \\ \psi_B\left(k + m \cdot \frac{2\pi}{a}\right) &= \sqrt{\frac{1}{N}} \cdot \sum_{\lambda} e^{i \cdot k \cdot a \cdot \lambda} \cdot \phi(\lambda) \\ \psi_B\left(k + m \cdot \frac{2\pi}{a}\right) &= \psi_B(k)\end{aligned}$$

To conclude, the smallest complete set of k-vectors representing all COs corresponds to half the first Brillouin zone.

Note that the theory developed here for the 1D case can be generalized in order to describe two- and three-dimensional crystals. In the n-dimensional case the k-vectors have n components what makes them 'real' vectors.

In [section 10](#) a two-dimensional carbon lattice will be investigated using Bloch functions and COs.

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$$N = 20 \quad \alpha_s = -2 \quad \alpha_p = -1 \quad \beta_{s\sigma} = -0.5 \quad \beta_{p\sigma} = -0.5 \quad \beta_{p\pi} = -0.5 \quad \text{Change values}$$

Energy eigenvalues: $\varepsilon_{Bp\pi}(k) := \alpha_p + 2 \cdot \beta_{p\pi} \cdot \cos(k \cdot a)$

$$\varepsilon_{Bp\sigma}(k) := \alpha_p - 2 \cdot \beta_{p\sigma} \cdot \cos(k \cdot a)$$

$$\varepsilon_{Bs\sigma}(k) := \alpha_s + 2 \cdot \beta_{s\sigma} \cdot \cos(k \cdot a)$$

CO coefficients: $c_B(\lambda, k) := \sqrt{\frac{1}{N}} \cdot \exp(i \cdot k \cdot a \cdot \lambda) \quad c_{B\text{conj}}(\lambda, k) := \sqrt{\frac{1}{N}} \cdot \exp(-i \cdot k \cdot a \cdot \lambda)$

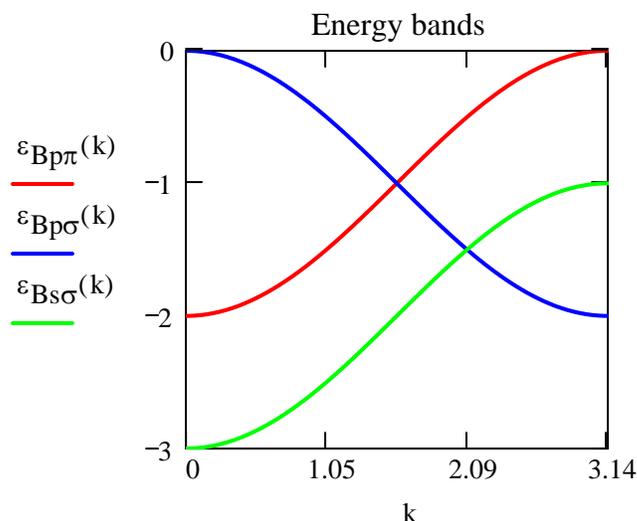
(CO coefficients on atom λ belonging to the wave-vector k)

$$c_{B1}(\lambda, k) := \frac{1}{2} \cdot (c_B(\lambda, k) + c_{B\text{conj}}(\lambda, k)) \quad \text{(Real CO coefficients belonging to the wave-vector } k)$$

$$c_{B2}(\lambda, k) := \frac{1}{2 \cdot i} \cdot (c_B(\lambda, k) - c_{B\text{conj}}(\lambda, k))$$

Wave functions: $\psi_{B1}(k) := \sum_{\lambda} c_{B1}(\lambda, k) \cdot \phi_{\lambda} \quad \psi_{B2}(k) := \sum_{\lambda} c_{B2}(\lambda, k) \cdot \phi_{\lambda}$

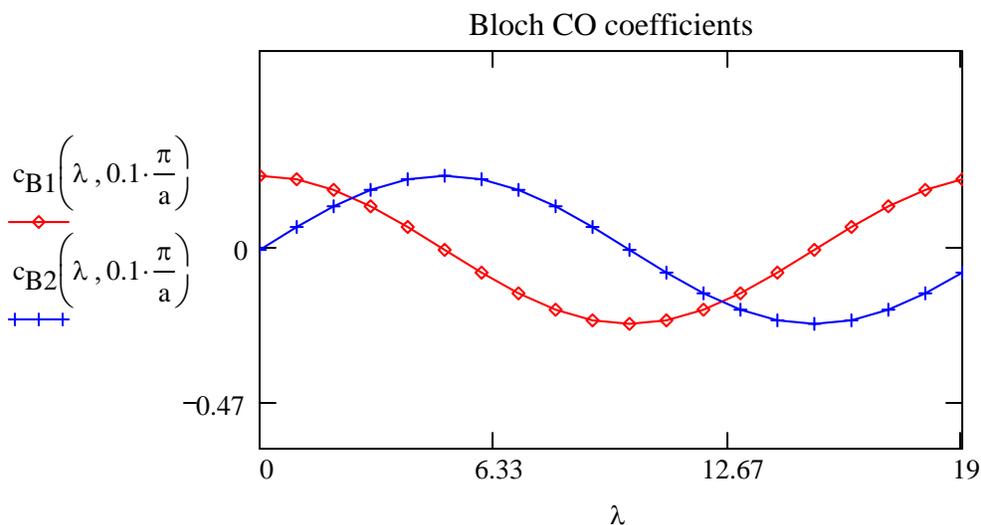
(COs belonging to the wave vector k)



The plot of the energy eigenvalues vs. k is called an **ENERGY BAND**.

Note that in principle we should only talk about energy bands when the number of atoms and hence the number of energy levels is infinite, i.e. when we describe extended systems. Nevertheless, we will go on talking about energy bands although our values of N are perfectly finite since finite systems are just our mnemonics for extended systems.

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[Change variables](#)

Problems

- 4.1 What is the difference between the energy bands displayed above and the energy vs. MO index curves displayed in chapters 2 and 3?
- 4.2 Compare the Bloch CO coefficients for wave vectors corresponding to energy levels which exist for the current value of N with the corresponding MO coefficients.
- 4.3 Prove that the Bloch functions indeed have the energy eigenvalues $\varepsilon_B(\mathbf{k}) = \alpha + 2\beta \cdot \cos(\mathbf{k} \cdot \mathbf{a})$.

Hint

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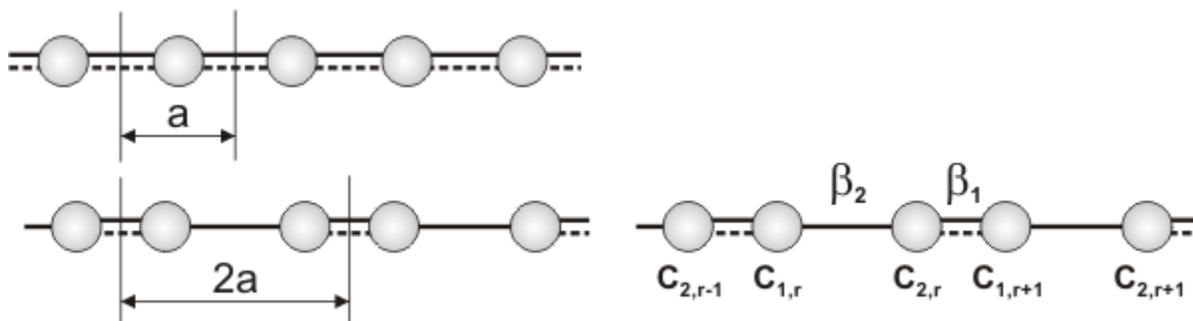
5. Infinite rings - One basis function - Alternating / Non-alternating bond lengths

It is well-known that polyacetylene has alternating bond lengths. [6] Although it is an extended and nearly linear system, this behavior cannot be described with the theory developed so far, since the latter assumes all carbon atoms to be equivalent. However, the photochemical and photophysical properties of organic dyes having a relatively elongated system of alternating double bonds, such as the carotenoids, are greatly influenced by the localization or delocalization of the double bonds. It is therefore desirable to expand our theory such that alternating bond lengths can be described.

In this section we will realize this expansion which will provide the means to deal with structures like polyacetylene in a simplified manner, and, at the same time, allow to introduce new terms and to deepen the understanding of the theory derived in chapters 1 to 4.

Up to now, we've worked with one carbon atom per unit cell. This situation is shown top left in the following figure. It implies that all carbon atoms are equivalent and, consequently, that all C-C bond lengths are equal, i.e. that we have non-alternating bond lengths. The part down left in the figure visualizes the situation present in polyacetylene: The bond lengths alternate.

How can the second evolve from the first situation, thereby showing a way how to expand our theory? The second situation is generated if neighbouring atoms alternately get slightly closer and further apart, thereby forming a chain of buckled dimers. We can mimic this behavior by doubling the unit cell from one to two carbon atoms and by assigning different resonance integrals β_1 and β_2 for the two carbon-carbon bonds in the new unit cell; see the part down right of the following figure:



In the non-alternating case, one unit cell consists of one center, thus contributing one p_π atomic orbital. In the alternating case one unit cell consists of two centers, thus contributing two p_π atomic orbitals. (In section 6 one enlarged unit cell will additionally contribute two p_σ and two s_σ atomic orbitals.)

Note that the model we use here does not directly describe polyacetylene, since it does not include hydrogen atoms and bond angles. The only aspect it takes into consideration is bond alternancy!

A possibility to manage two centers per unit cell in the ZDO approximation is by separately writing down the crystal orbitals Ψ_{1B} and Ψ_{2B} for the two center types, followed by forming linear combinations of these two CO types:

$$\Psi_B = C_1 \Psi_{1B} + C_2 \Psi_{2B}$$

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5.1 First case: $\beta_1 = \beta_2$

We redefine the values of the Coulomb and of the resonance integrals. These assignments will only be effective in chapter 5.1.

$$\alpha := -1 \quad \beta_1 := -0.5 \quad \beta_2 := \beta_1$$

We already know the solution for one center per unit cell and for the $p\pi$ orbitals from [section 4](#):

$$\varepsilon_{Bp\pi}(k) := \alpha + 2 \cdot \beta_1 \cdot \cos(k \cdot a)$$

We now introduce two centers per unit cell: ... -[-(1)-(2)-][-(-1)-(2)-][-(-1)-(2)-][- ...

In this section each center has one AO ($p\pi$).

Because the size of the unit cell has increased, the Brillouin zone gets smaller. As a result, the range of k -vectors is reduced:

$$k(j) := j \cdot \frac{2 \cdot \pi}{N \cdot (2a)} \quad 0 \leq k \leq \frac{\pi}{2a}$$

CO coefficients:

Centers of type 1:
$$c_{1B}(\lambda, k) := \sqrt{\frac{1}{N}} \cdot \exp(i \cdot k \cdot 2a \cdot \lambda)$$

Centers of type 2:
$$c_{2B}(\mu, k) := \sqrt{\frac{1}{N}} \cdot \exp(i \cdot k \cdot 2a \cdot \mu)$$

Crystal orbitals:

Centers of type 1:
$$\psi_{1B}(k) := \sum_{\lambda=0}^{N-1} c_{1B}(\lambda, k) \cdot \phi_{1,\lambda}$$

Centers of type 2:
$$\psi_{2B}(k) := \sum_{\mu=0}^{N-1} c_{2B}(\mu, k) \cdot \phi_{2,\mu}$$

Linear combinations of the two crystal orbitals:

$$\psi_B(k) := C_1 \cdot \psi_{1B}(k) + C_2 \cdot \psi_{2B}(k)$$

To find the linear combinations with minimal energy the following eigenvalue problem has to be solved:

$$\begin{pmatrix} H_{11} - \varepsilon & H_{12} \\ H_{21} & H_{22} - \varepsilon \end{pmatrix} \cdot \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

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Problems

5.1 Derive this equation. Start from the Schrödinger equation.

The Hückel eigenvalue problem

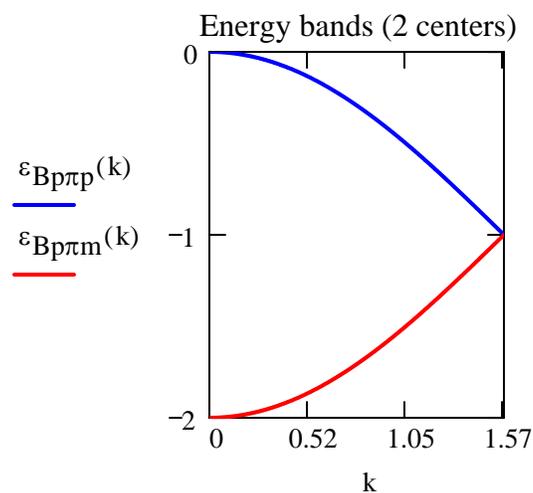
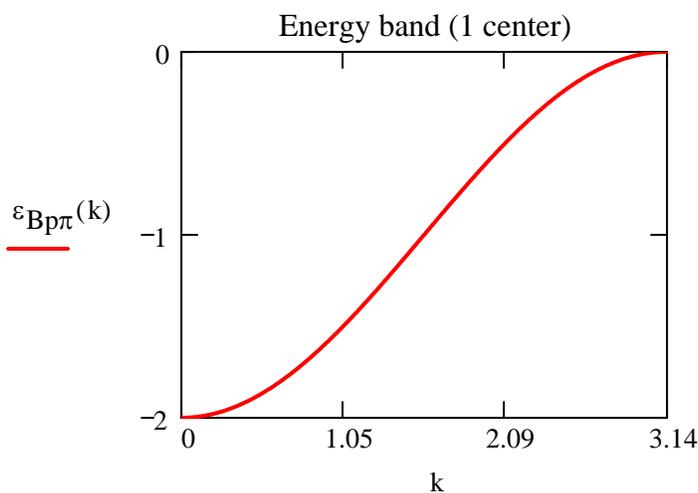
5.2 Show that the following equations hold: $H_{11} = \alpha$; $H_{12} = e^{-ik2a}\beta_1 + \beta_2$

Analogously one finds: $H_{21} = e^{ik2a}\beta_1 + \beta_2$; $H_{22} = \alpha$

5.3 Show that the formulae below hold for the energy eigenvalues.
(p and m means plus and minus, respectively.)

$$\varepsilon_{Bp\pi p}(k) := \alpha + \sqrt{\beta_1^2 + \beta_2^2 + 2 \cdot \beta_1 \cdot \beta_2 \cdot \cos(k \cdot 2a)}$$

$$\varepsilon_{Bp\pi m}(k) := \alpha - \sqrt{\beta_1^2 + \beta_2^2 + 2 \cdot \beta_1 \cdot \beta_2 \cdot \cos(k \cdot 2a)}$$



Problem

5.4 The situation on the right-hand side shows the so-called **BACK-FOLDING**: The blue band results when the upper half of the red band in the left graph is folded back.

This effect can be explained by means of symmetry arguments: Every k-vector represents a specific symmetry in the pattern of the atomic orbital contributions forming a CO. If a unit cell is formed of 2 centers, pairs of AOs form symmetry units. Therefore patterns belonging to different energy levels become equivalent with regard to symmetry, i.e. they belong to the same k-vector.

- Sketch the two AO patterns for $k = 0$ and the two AO patterns for $k = \pi/(2a)$.
State a reason why the latter two AO patterns are energetically degenerate.

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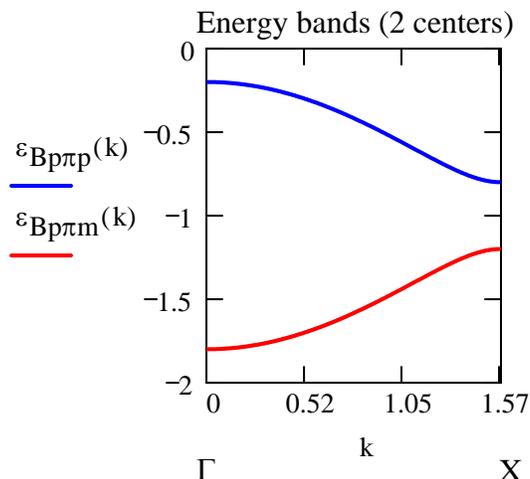
5.2 Second case: $\beta_1 \neq \beta_2$

The assignment of different values for β_1 and β_2 will now lead to bond alternation:

$$\alpha := -1 \quad \beta_1 := -0.5 \quad \beta_2 := -0.3$$

$$\varepsilon_{\text{Bp}\pi\text{p}}(k) := \alpha_{\text{p}} + \sqrt{\beta_1^2 + \beta_2^2 + 2 \cdot \beta_1 \cdot \beta_2 \cdot \cos(k \cdot 2a)}$$

$$\varepsilon_{\text{Bp}\pi\text{m}}(k) := \alpha_{\text{p}} - \sqrt{\beta_1^2 + \beta_2^2 + 2 \cdot \beta_1 \cdot \beta_2 \cdot \cos(k \cdot 2a)}$$



Problem

5.5 Explain the splitting of the energy bands at the so-called X point for $\beta_1 \neq \beta_2$ by means of an orbital scheme.

Solution

The splitting of the bands is called **PEIERLS DISTORTION**.

Note:

- The Peierls distortion is a special case of the Jahn-Teller distortion observed in molecules.
- It results from choosing different values for β_1 and β_2 .
- The Γ point lies at $k = 0$. It is the point of highest symmetry of the COs.
The X point lies at $k = \pi/a'$ (here $a' = 2a$).

Problems

5.6 Explain the Jahn-Teller distortion for cyclobutadiene.

Solution

5.7 Explain why one is entitled to use linear combinations of MOs belonging to degenerate energy levels instead of the original MOs, as it is done in the solution of problem 5.6. Assign all π MOs of cyclobutadiene to the Γ and X point. Explain why alternating bond lengths are energetically more favourable in cyclobutadiene but not in benzene.

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6. Infinite rings - Three basis functions - Alternating bond lengths

The concept of section 5 is now expanded to 3 basis functions (p_π , p_σ and s_σ). As in section 3 the model is thereby made more general since interactions between all valence orbitals are made possible. However, in contrast to sections 3 and 4 we now have two sets of non-equivalent carbon atoms, a situation that is frequently encountered in crystals and takes us a step closer to the description of real systems.

Different Peierls distortions can be seen for different bands in this section, and we will finally see, for the first time, a band structure and understand what it is.

Values of the Coulomb and resonance integrals:

$$\alpha_{s\sigma} := -5 \quad \beta_{s\sigma 1} := -1 \quad \beta_{s\sigma 2} := -1$$

$$\alpha_{p\sigma} := -1 \quad \beta_{p\sigma 1} := -0.9 \quad \beta_{p\sigma 2} := -0.6$$

$$\alpha_{p\pi} := -1 \quad \beta_{p\pi 1} := -0.5 \quad \beta_{p\pi 2} := -0.4$$

Resulting energy eigenvalues:

$$\varepsilon_{s\sigma}(k) := \sqrt{\beta_{s\sigma 1}^2 + \beta_{s\sigma 2}^2 + 2 \cdot \beta_{s\sigma 1} \cdot \beta_{s\sigma 2} \cdot \cos(k \cdot 2a)}$$

$$\varepsilon_{p\sigma}(k) := \sqrt{\beta_{p\sigma 1}^2 + \beta_{p\sigma 2}^2 + 2 \cdot \beta_{p\sigma 1} \cdot \beta_{p\sigma 2} \cdot \cos(k \cdot 2a)}$$

$$\varepsilon_{p\pi}(k) := \sqrt{\beta_{p\pi 1}^2 + \beta_{p\pi 2}^2 + 2 \cdot \beta_{p\pi 1} \cdot \beta_{p\pi 2} \cdot \cos(k \cdot 2a)}$$

$$\varepsilon_{Bs\sigma p}(k) := \alpha_{s\sigma} + \varepsilon_{s\sigma}(k)$$

$$\varepsilon_{Bs\sigma m}(k) := \alpha_{s\sigma} - \varepsilon_{s\sigma}(k)$$

$$\varepsilon_{Bp\sigma p}(k) := \alpha_{p\sigma} + \varepsilon_{p\sigma}(k)$$

$$\varepsilon_{Bp\sigma m}(k) := \alpha_{p\sigma} - \varepsilon_{p\sigma}(k)$$

$$\varepsilon_{Bp\pi p}(k) := \alpha_{p\pi} + \varepsilon_{p\pi}(k)$$

$$\varepsilon_{Bp\pi m}(k) := \alpha_{p\pi} - \varepsilon_{p\pi}(k)$$

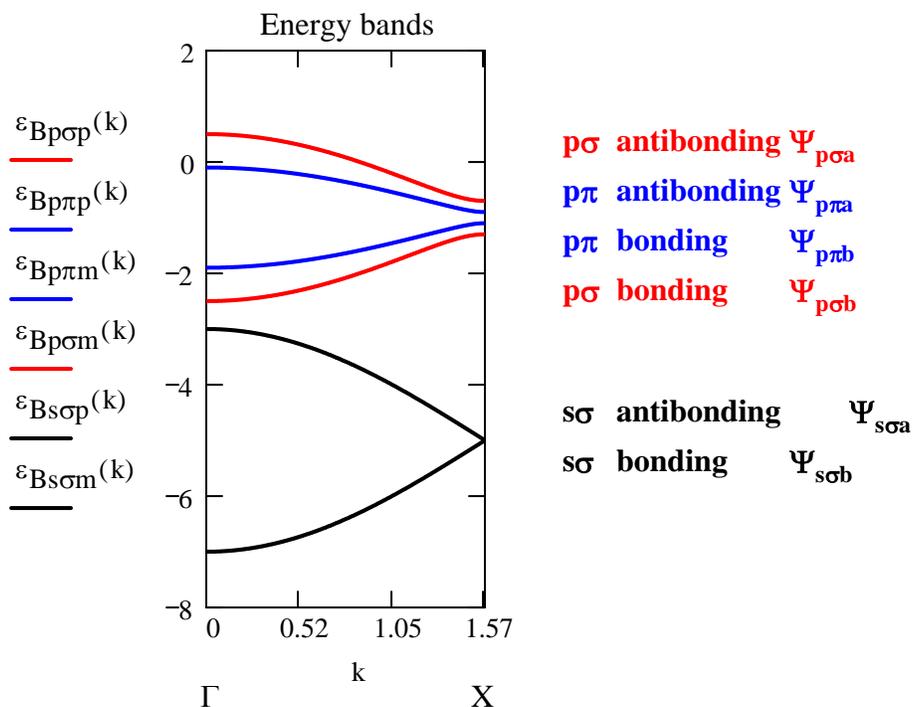
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The following figure shows the resulting energy bands for all basis functions. The Peierls distortion is more pronounced for the p_σ bands than for the p_π bands. There is no such distortion for the s_σ bands. This is a direct consequence of the choice of different β values. Hence it would be wrong to draw the conclusion that s_σ bands show no Peierls distortion!

Bonding and antibonding bands appear because back-folding occurs.

The figure is an example of a **BAND STRUCTURE** diagram, since it displays all interactions present in a crystal. Given a k -vector, every band reveals the energy resulting from the interactions of the corresponding basis function on all atoms in this symmetry state.

Additionally, the relative sequence of the bands at every k -vector allows to decide which COs are occupied and which are not occupied at this k -point.



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Problems

- 6.1** Change the values of the Coulomb and resonance integrals. Consider what will happen before changing parameters. Keep in mind that all these energies are negative and that the β values are smaller than the corresponding α values according to amount. ([Information about the ZDO approximation](#)) Do not choose unrealistically large values for α and β , and do not forget to reset the variables to their original values after this exercise. ([Original values](#))
- 6.2** In section 3 we have taken the different orientation of the p_σ orbitals into consideration by 'manually' changing the sign of the interaction term in the energy eigenvalues of the MOs formed by this basis function. ([Comment](#)) This resulted in a horizontal reflection of the p_σ band. Explain why here the p_σ bands qualitatively have the same shape as the bands of the other COs. Find geometric as well as algebraic reasons.
- 6.3** Sketch the p_π COs for cyclohexatriene at the Γ and X point. Write a Mathcad worksheet in order to find the coefficients of the COs at all centers. Why are the COs at the X point not the same as any of the MOs of benzene? Why do the two COs at the X point have a different number of bonding and antibonding interactions, although this is impossible because of the common energy eigenvalue?
[Solution](#)

Note that the above band structure only results if one neglects the fact that all Ψ_σ COs actually interact. The $\Psi_{p\pi b}$ and $\Psi_{p\pi a}$ COs do not interact with the Ψ_σ COs because of their symmetry. To take the interaction of the Ψ_σ COs with each other into account, one would have to use the following linear combination:

$$\Psi_\sigma := C_{s\sigma b} \cdot \Psi_{s\sigma b} + C_{s\sigma a} \cdot \Psi_{s\sigma a} + C_{p\sigma b} \cdot \Psi_{p\sigma b} + C_{p\sigma a} \cdot \Psi_{p\sigma a}$$

Although it would be possible, we will not solve this problem within Mathcad. More suitable software for this purpose is available, for example the band structure program package [BICON-CEDiT](#) which contains many more features.

Problems

- 6.4** Up to now we have worked with the three basis functions p_π , p_σ and s_σ . Which extension of the basis makes it possible to describe the band structure of polyacetylene?
- 6.5** Explain figure 2 in [\[6\]](#). You may find help in [\[7\]](#).

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7. Density of states (DOS)

How are energy bands actually interpreted? Since k can be interpreted as a CO index (such as j can be interpreted as an MO index) an energy band provides the information how many COs exist on a certain level of energy. This is valuable information since in an extended structure the number of energy levels approaches infinity. In contrast to a molecule where we can talk about frontier orbitals or single MOs which control the molecule's geometry or reactivity, such effects do not result from one out of a nearly infinite number of energy levels in a crystal. Instead, a collective of energy levels may play such a role. Hence it is useful to group energy levels with respect to their affiliation to certain energy intervals. Crystal properties such as reactivity may then be derived from such groups of energy levels.

The **DENSITY OF STATES (DOS)** is a measure to perform such a grouping of energy levels. $\text{DOS}(E)$ is the density of states at energy E ; $\text{DOS}(E) \cdot dE$ is thus the number of energy levels between E and $E + dE$. If N_E is the number of energy levels up to energy E , then the DOS can formally be defined as follows:

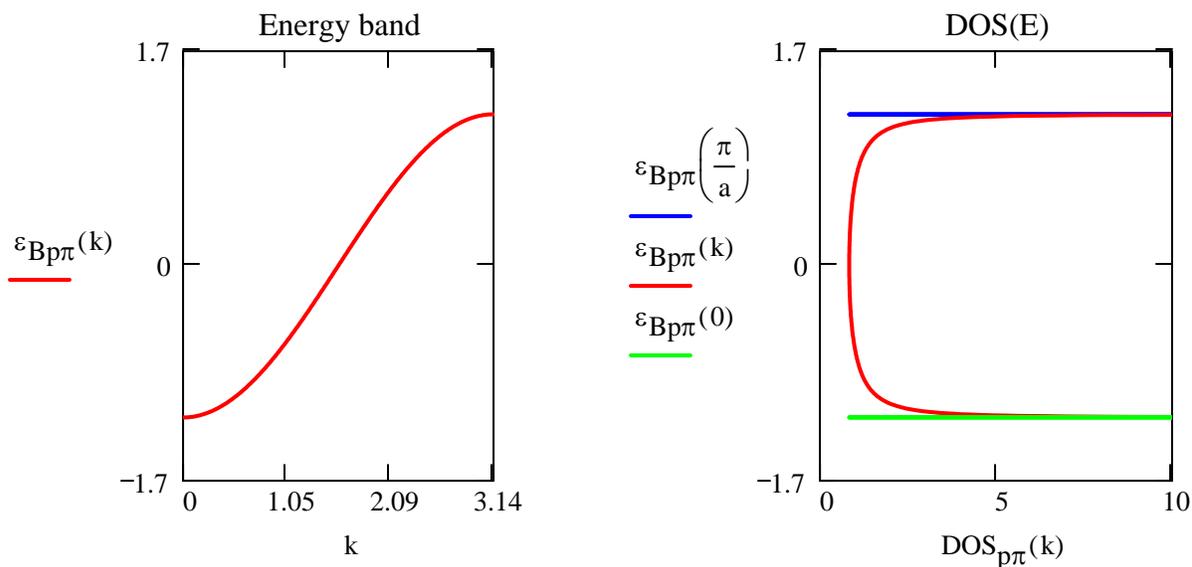
$$\text{DOS}(E) := \left| \frac{dN_E}{dE} \right| \quad \text{and consequently:} \quad \text{DOS}(N_E) := \left| \left(\frac{dE}{dN_E} \right)^{-1} \right|$$

We examine the bands considered in [section 4](#):

$$\text{Parameter values: } \alpha_{s\sigma} := -5 \quad \alpha_{p\sigma} := -1 \quad \alpha_{p\pi} := 0 \quad \beta_{s\sigma} := -1 \quad \beta_{p\sigma} := -0.6 \quad \beta_{p\pi} := -0.6$$

7.1 DOS of the p_π band

$$\varepsilon_{Bp\pi}(k) := \alpha_{p\pi} + 2 \cdot \beta_{p\pi} \cdot \cos(k \cdot a) \quad \text{DOS}_{p\pi}(k) := \left| \left(\frac{d}{dk} \varepsilon_{Bp\pi}(k) \right)^{-1} \right| \quad k := 0, 0.01 \dots \frac{\pi}{a}$$



Problem

7.1 Explain the shape of the DOS plot.

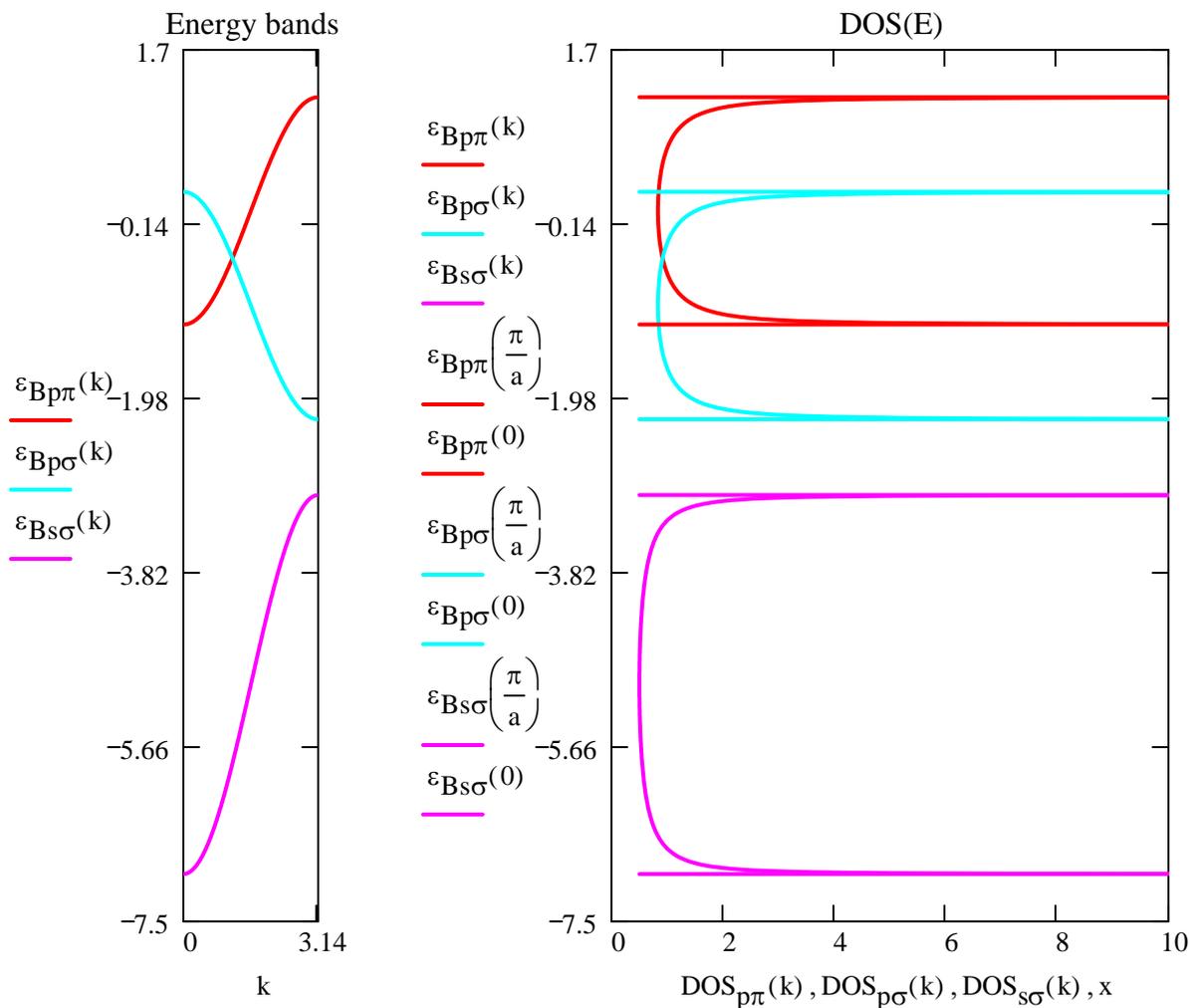
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An important aspect is that a band structure diagram is, as a plot of energy vs. k , a representation in indirect space, while a DOS diagram is, as a plot of the density of energy levels against energy (rotated by 90° clockwise), a representation in direct space. Since representations in direct space are mentally more accessible, the conversion into direct space, made possible through the introduction of the DOS, is quite helpful. Furthermore, since a DOS diagram is a kind of histogram of the number of energy levels as a function of the energy with horizontal "peaks" at energies where high densities of energy levels exist, such diagrams have a close relation to the MO energy level diagrams familiar to chemists.

7.2 DOS of the p_σ and the s_σ bands

$$\varepsilon_{Bp\sigma}(k) := \alpha_{p\sigma} - 2 \cdot \beta_{p\sigma} \cdot \cos(k \cdot a) \quad \text{DOS}_{p\sigma}(k) := \left| \left(\frac{d}{dk} \varepsilon_{Bp\sigma}(k) \right)^{-1} \right|$$

$$\varepsilon_{Bs\sigma}(k) := \alpha_{s\sigma} + 2 \cdot \beta_{s\sigma} \cdot \cos(k \cdot a) \quad \text{DOS}_{s\sigma}(k) := \left| \left(\frac{d}{dk} \varepsilon_{Bs\sigma}(k) \right)^{-1} \right|$$



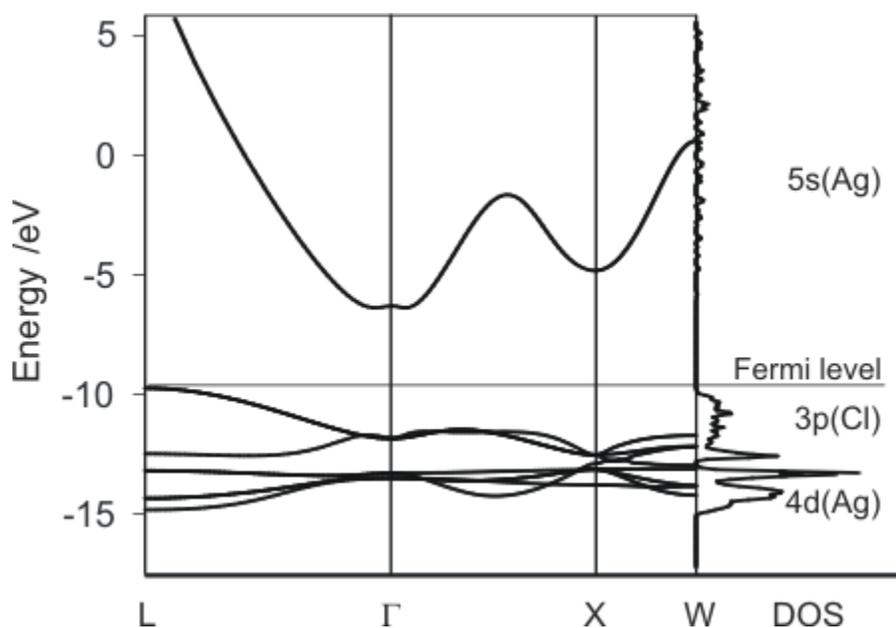
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Note in the above DOS plots that $\text{DOS}(k)$ is the inverse of the slope of $\epsilon(k)$, i.e. the steeper the energy band is, the lower is the DOS at that energy or vice versa: The flatter the energy band is, the higher is the DOS at that energy.

Another aspect of the DOS is also important: From its definition it follows that the integral of the DOS with respect to energy results in a number of energy levels. Hence the integral of DOS up to the Fermi level (the Fermi level is the energy level of the highest occupied crystal orbital, i.e. it is the analog of the HOMO for extended structures) equals the total number of occupied COs. If the value of this integral is doubled, the result is the total number of electrons.

To conclude, the DOS curves include the information about the distribution of electrons in energy.

The following figure shows a band structure (left) and a DOS diagram (right) of an AgCl crystal along different symmetry lines. [8, 10] AgCl forms face-centered cubic crystals with an AgCl distance of 2.77 Å. The DOS below the Fermi level is mainly composed of 3p(Cl) levels, followed by levels of 4d(Ag) character. The DOS above the Fermi level shows 5s(Ag) character.



Advanced use of DOS can be found in [8].

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8. Crystal Orbital Overlap Population (COOP)

In a molecule the overlap population between two atomic orbitals ϕ_λ and ϕ_μ due to one electron in MO $\psi(j)$ is defined as $2 \cdot c(\lambda, j) \cdot c(\mu, j) \cdot S_{\lambda\mu}$. Summed over all electrons present, this is the Mulliken overlap population for the AO pair ϕ_λ and ϕ_μ , providing information about the bonding or antibonding nature of the interactions between these two AOs.

How can the bonding or antibonding character of the interactions between basis functions be described in an extended structure?

When we look at the energy bands and the corresponding DOS plots in section 7, we see that e.g. at the high energy end of a band, corresponding to highly antibonding interactions, we have a high density of states. Hence we there have a high density of antibonding states. On the other hand, at the low energy end of an energy band we have a high density of bonding states.

Since the bonding or antibonding nature of the interactions between two AOs can nicely be described by overlap populations, the combination of overlap populations and DOS results in a useful measure to describe **the density of bonding or antibonding interactions between basis functions of a specific type at a given energy**. The interactions can include all possible interactions or only one specific interaction, e.g. the interaction between nearest neighbors.

(Note that in a crystal orbital we actually do not describe the interactions between two specific AOs but the average of the interactions between all pairs of AOs.)

The measure we introduce is an overlap population-weighted density of states. Hoffmann called it **CRYSTAL ORBITAL OVERLAP POPULATION (COOP)**. [1]

We formally define COOP as follows:

$$\text{COOP}_n(E) = (1 / N) \cdot \text{DOS}(E) \cdot \sum_\lambda (C^*(\lambda, E) \cdot C(\mu, E) + C(\lambda, E) \cdot C^*(\mu, E)) \cdot S_{\lambda\mu}$$

where $\mu = \lambda + n$ ($n \in \mathbb{N}$, constant)

- n represents the kind of interaction we wish to describe. If $n = 1$, then the interaction between nearest neighboring AOs is considered. If $n = 2$, the interaction between AOs separated by one AO is considered.
- N is the number of AOs, and λ is the AO index, as usual.
- $\text{DOS}(E)$ is the density of states of the chosen basis function at energy E .
- The C 's are the CO coefficients.
- For the overlap integrals $S_{\lambda\mu}$ the ZDO approximation cannot be used ($S_{\lambda\mu} = \delta_{\lambda\mu}$), since this would make it impossible to calculate overlap populations and hence COOPs.

Here we allow overlap between AOs separated by maximal 2 AOs:

$S_{\lambda, \lambda \pm 1} := S_2$ (nearest neighbors), $S_{\lambda, \lambda \pm 2} := S_3$, $S_{\lambda, \lambda \pm 3} := S_4$ (two separating AOs).

$S_{\lambda\mu}$ rapidly decreases for increasing n .

As an example we define and visualize the COOPs for the p_π basis function. Values of the variables:

$$S_2 := 1 \quad S_3 := 0.6 \quad S_4 := 0.1 \quad N := 100 \quad \lambda := 0..N-1$$

$$\text{CO coefficients:} \quad c(\lambda, k) := \sqrt{\frac{1}{N}} \cdot \exp(i \cdot k \cdot a \cdot \lambda) \quad c_{\text{conj}}(\lambda, k) := \sqrt{\frac{1}{N}} \cdot \exp(-i \cdot k \cdot a \cdot \lambda)$$

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$$\mu_1(\lambda) := \text{mod}(\lambda + 1, N)$$

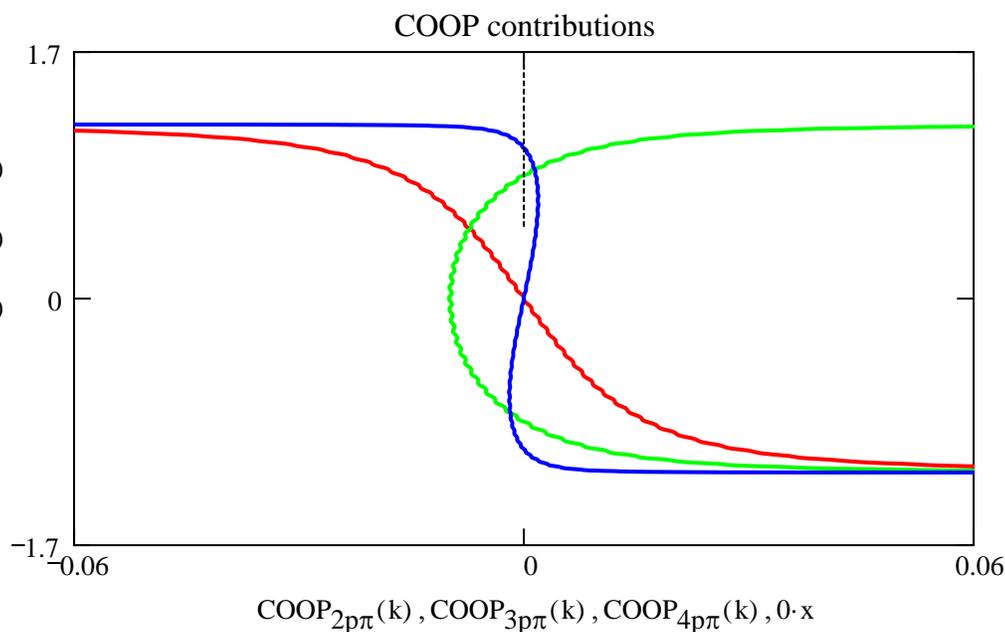
$$\text{COOP}_{2p\pi}(k) := \frac{1}{N} \cdot \text{DOS}_{p\pi}(k) \cdot \left[\sum_{\lambda} \left(c_{\text{conj}}(\lambda, k) \cdot c(\mu_1(\lambda), k) + c(\lambda, k) \cdot c_{\text{conj}}(\mu_1(\lambda), k) \right) \cdot S_2 \right]$$

$$\mu_2(\lambda) := \text{mod}(\lambda + 2, N) \quad (N \geq 4)$$

$$\text{COOP}_{3p\pi}(k) := \frac{1}{N} \cdot \text{DOS}_{p\pi}(k) \cdot \left[\sum_{\lambda} \left(c_{\text{conj}}(\lambda, k) \cdot c(\mu_2(\lambda), k) + c(\lambda, k) \cdot c_{\text{conj}}(\mu_2(\lambda), k) \right) \cdot S_3 \right]$$

$$\mu_3(\lambda) := \text{mod}(\lambda + 3, N) \quad (N \geq 6)$$

$$\text{COOP}_{4p\pi}(k) := \frac{1}{N} \cdot \text{DOS}_{p\pi}(k) \cdot \left[\sum_{\lambda} \left(c_{\text{conj}}(\lambda, k) \cdot c(\mu_3(\lambda), k) + c(\lambda, k) \cdot c_{\text{conj}}(\mu_3(\lambda), k) \right) \cdot S_4 \right]$$



General remarks:

- Regions with positive COOP contributions are bonding, regions with negative COOP contributions are antibonding.
- The amplitude of COOP(E) depends on
 - the density of states at energy E
 - the value of the overlap integral,
 - and the CO coefficients.

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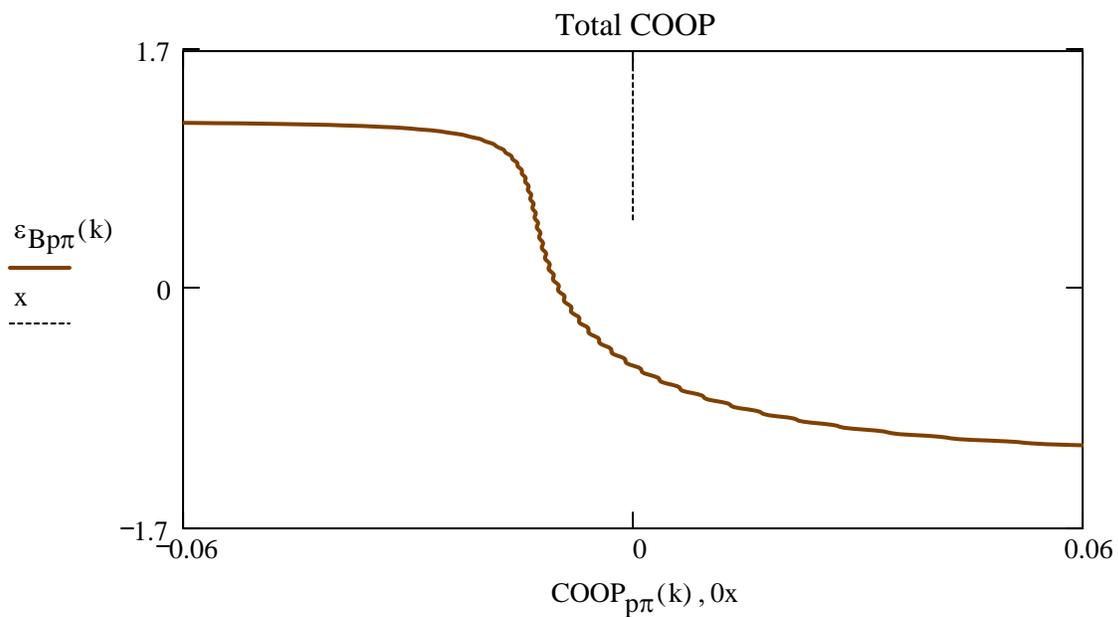
Problem

8.1 Interpret the $\text{COOP}_{2p\pi}$, $\text{COOP}_{3p\pi}$ and $\text{COOP}_{4p\pi}$ curves at the k-points 0 , $\pi/2a$ and π/a .

Solution

The total COOP is the sum of all contributing COOPs:

$$\text{COOP}_{p\pi}(k) := \text{COOP}_{2p\pi}(k) + \text{COOP}_{3p\pi}(k) + \text{COOP}_{4p\pi}(k)$$

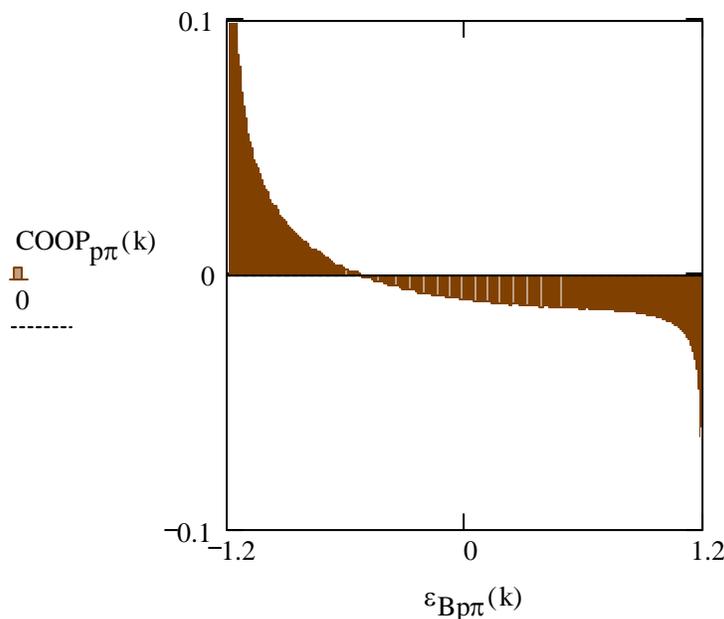


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COOP(E)·ΔE takes all states in a certain energy interval and measures their bonding tendency by means of overlap population. I.e. COOP(E)·ΔE is the contribution to the total overlap population of those crystal orbitals (states) whose energy levels lie in the interval [E, E+ΔE]. Hence the integral of COOP(E) with respect to energy up to the Fermi level is the total overlap population of all occupied energy levels and thus the total overlap population of the specified interaction. If the total COOP is integrated up to the Fermi level, the result is the total overlap population of a specific basis function. If this integral is positive, this basis function provides a bonding contribution, otherwise an antibonding contribution.

In the following plot the total COOP curve as a function of the energy is rotated by 90 degrees counterclockwise and reflected horizontally. The shaded area visualizes the integral of the COOP(E) function.

The integral is calculated below the figure for an assumed Fermi level. Since the result is positive for this Fermi level, the interactions contributed by the p_π basis function are overall bonding.



Current value of N: N = 100
 Current values of S_2 , S_3 and S_4 :
 $S_2 = 1$ $S_3 = 0.6$ $S_4 = 0.1$

[Change values](#)

Assumption: Fermi_Level := 0.4

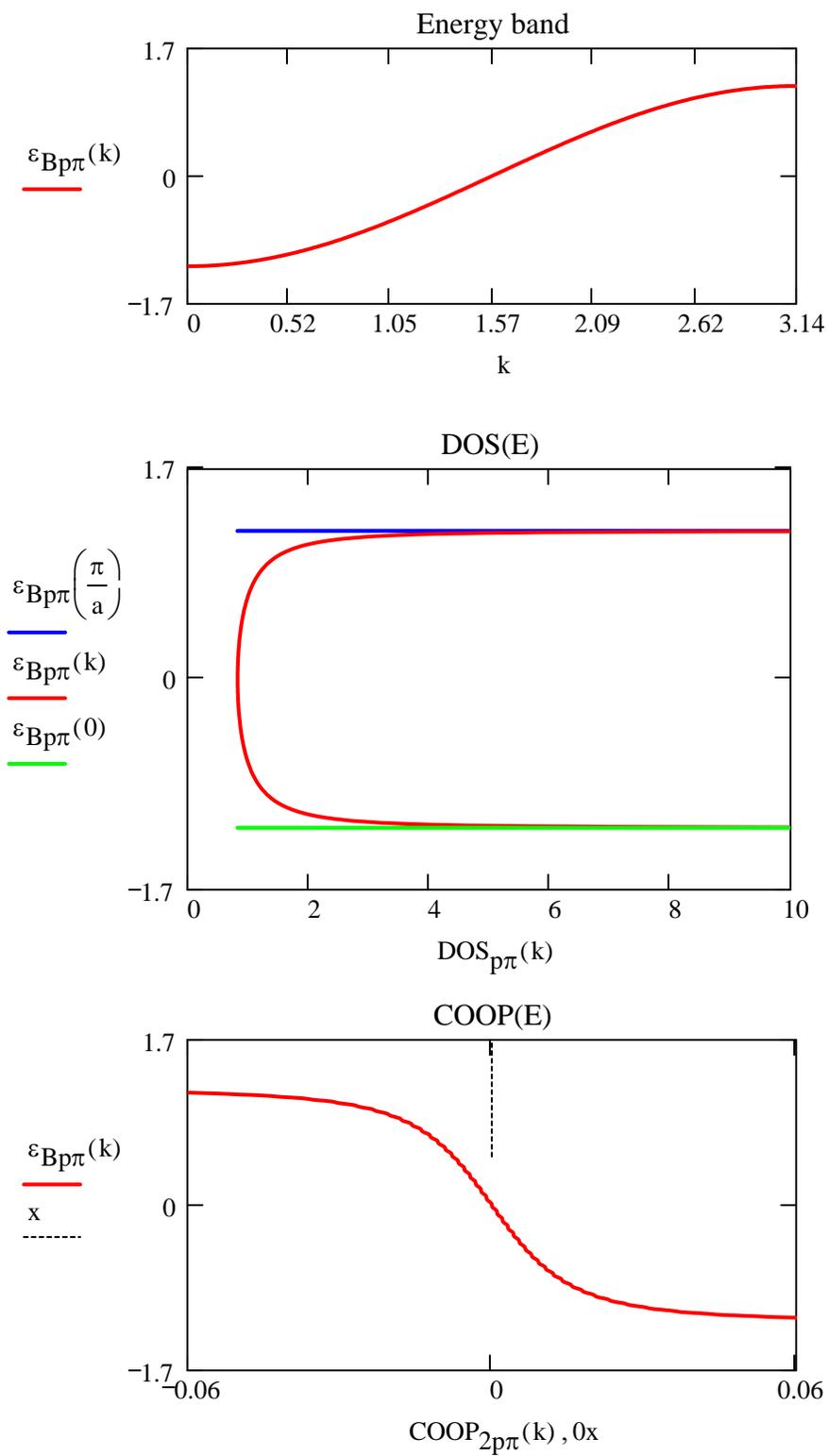
$$\int_{\varepsilon_{Bp\pi}(0)}^{\text{Fermi_Level}} \text{COOP}_{p\pi} \left(\frac{1}{a} \cdot \arccos \left(\frac{E - \alpha_{p\pi}}{2 \cdot \beta_{p\pi}} \right) \right) dE = 0.015$$

Problem

8.2 Interpret the values of $\text{COOP}_{2p\pi}$, $\text{COOP}_{3p\pi}$ and $\text{COOP}_{4p\pi}$ at the Γ and X point for cyclohexatriene (N = 6). Use the COs sketched in problem 6.3.

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9. Overview: Energy band, DOS and COOP



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The above figures allow linking the information provided by energy bands, the DOS and COOPs. The figures show the corresponding curves for the p_π basis function.

All three visualizations plot the dependency of energy and another variable.

In the case of energy bands the second variable is the k-vector. An energy band shows the energy of all crystal orbitals of a specified basis function (here: the p_π AOs) as a function of the CO index k. This corresponds to an energy level chart for the discrete MO energy levels in a molecule, formed by all p_π AOs. Since in a crystal, there is an infinite number of AOs, an energy band consists of an infinite number of points, thereby forming a continuous line and not a finite set of points.

In the second case the density of states is plotted as a function of energy. Conventionally this plot is reflected with respect to the bisecting line of the first and the third quadrant, resulting in a plot with the DOS-axis pointing to the right and the energy axis pointing upwards. The DOS is large at energies E where a large number of crystal orbitals exists within a small energy interval $[E, E + \Delta E]$ and vice versa. In the above example DOS is large in the region of k-points 0 and π/a and smallest in the region of k-point $\pi/2a$. Hence the above DOS figure visualizes that most of the p_π COs stay at the high and at the low energy end of the energy interval in which all p_π COs lie.

The third figure shows the dependency of the CO energy and the overlap population for the 1,2-interaction of the p_π basis functions in the p_π COs. There is a high density of bonding 1,2-interactions for p_π COs of low energy, while a high density of antibonding 1,2-interactions appears for energetically high p_π COs. COs at average energies have 1,2-interactions which are neither bonding nor antibonding. Such interactions are called non-bonding.

You should now be able to understand the paper [\[7\]](#). Advanced use of DOS and COOP can be found in [\[8\]](#).

[Summary of sections 4 to 8](#)

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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.

Definition of the unit cell vector lengths in the direct lattice:

$$a_x := 1 \quad a_y := 1$$

Definition of the k-point set in the reciprocal lattice:

$$k_x := -\frac{\pi}{a_x}, -\frac{9}{10} \cdot \frac{\pi}{a_x} \dots \frac{\pi}{a_x} \quad k_y := -\frac{\pi}{a_y}, -\frac{9}{10} \cdot \frac{\pi}{a_y} \dots \frac{\pi}{a_y}$$

Coulomb integral: $\alpha := 0$

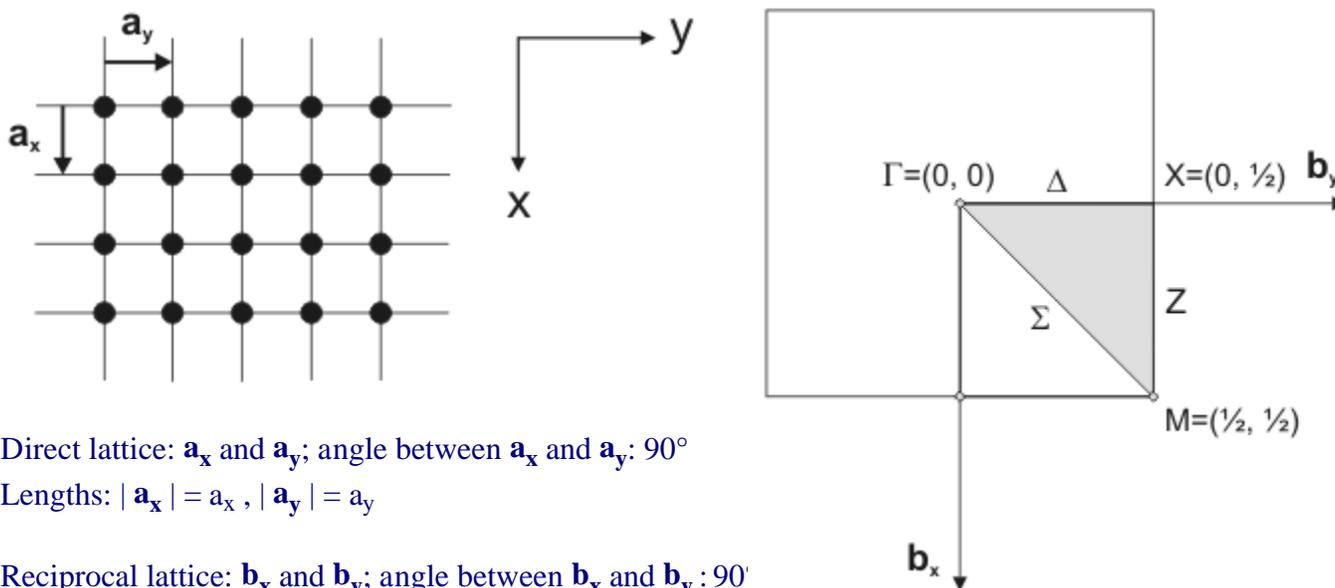
Resonance integral: $\beta := -1$

We want to study a planar square carbon lattice with one atom per unit cell.

For the analysis of this band structure the knowledge of the direct and the reciprocal space (i.e. the first Brillouin zone) is necessary. The two-dimensional lattice is shown on the left side of the figure below, the first Brillouin zone is shown on the right side.

The reciprocal vectors \mathbf{b}_x and \mathbf{b}_y (bold = vectors) are constructed as follows ([Comment](#)):

$\mathbf{b}_x \perp \mathbf{a}_y \Rightarrow \mathbf{b}_x \cdot \mathbf{a}_y = 0$ and $\mathbf{b}_y \perp \mathbf{a}_x \Rightarrow \mathbf{b}_y \cdot \mathbf{a}_x = 0$ and $\mathbf{a}_x \cdot \mathbf{b}_x = 2\pi$ and $\mathbf{a}_y \cdot \mathbf{b}_y = 2\pi$.



Direct lattice: \mathbf{a}_x and \mathbf{a}_y ; angle between \mathbf{a}_x and \mathbf{a}_y : 90°

Lengths: $|\mathbf{a}_x| = a_x$, $|\mathbf{a}_y| = a_y$

Reciprocal lattice: \mathbf{b}_x and \mathbf{b}_y ; angle between \mathbf{b}_x and \mathbf{b}_y : 90°

Lengths: $\mathbf{a}_x \cdot \mathbf{b}_x = |\mathbf{a}_x| \cdot |\mathbf{b}_x| \cdot \cos(\alpha)$

$$2\pi = a_x \cdot |\mathbf{b}_x| \cdot 1$$

$$|\mathbf{b}_x| = 2\pi/a_x$$

$$|\mathbf{b}_y| = 2\pi/a_y$$

The coordinates in reciprocal space

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In a two-dimensional square lattice the transformation from the direct to the reciprocal lattice is easy. The gray-shaded area is the **IRREDUCIBLE WEDGE** of the first Brillouin zone of the quadratic lattice. The irreducible wedge of a Brillouin zone is the region that will give all information for the calculation of average quantities (e.g. energy, COOP) over all occupied states.

It is impossible to analyze all k-points. We therefore restrict the analysis to points and lines of high symmetry. The point with the highest symmetry is always called Γ . Its coordinates are (0, 0) and it lies at $k = (0, 0)$. Further points of interest here are X and M. In a cubic (square) lattice X has the coordinates (0, $\frac{1}{2}$) and lies at k-point (0, π/a_y) whereas M has the coordinates ($\frac{1}{2}$, $\frac{1}{2}$) and lies at $k = (\pi/a_x, \pi/a_y)$ (see figure above).

The lines of interest are those connecting the points of interest, here: Δ , Σ and Z (see figure).

Problem

10.1 Draw the first Brillouin zone for a two-dimensional hexagonal lattice and mark the irreducible part. The two direct lattice base vectors \mathbf{a}_x and \mathbf{a}_y are equal in length and separated by a 120° angle.

In a first step **only the 2s(C)** orbitals are considered. With this restriction we can define the crystal orbitals as follows:

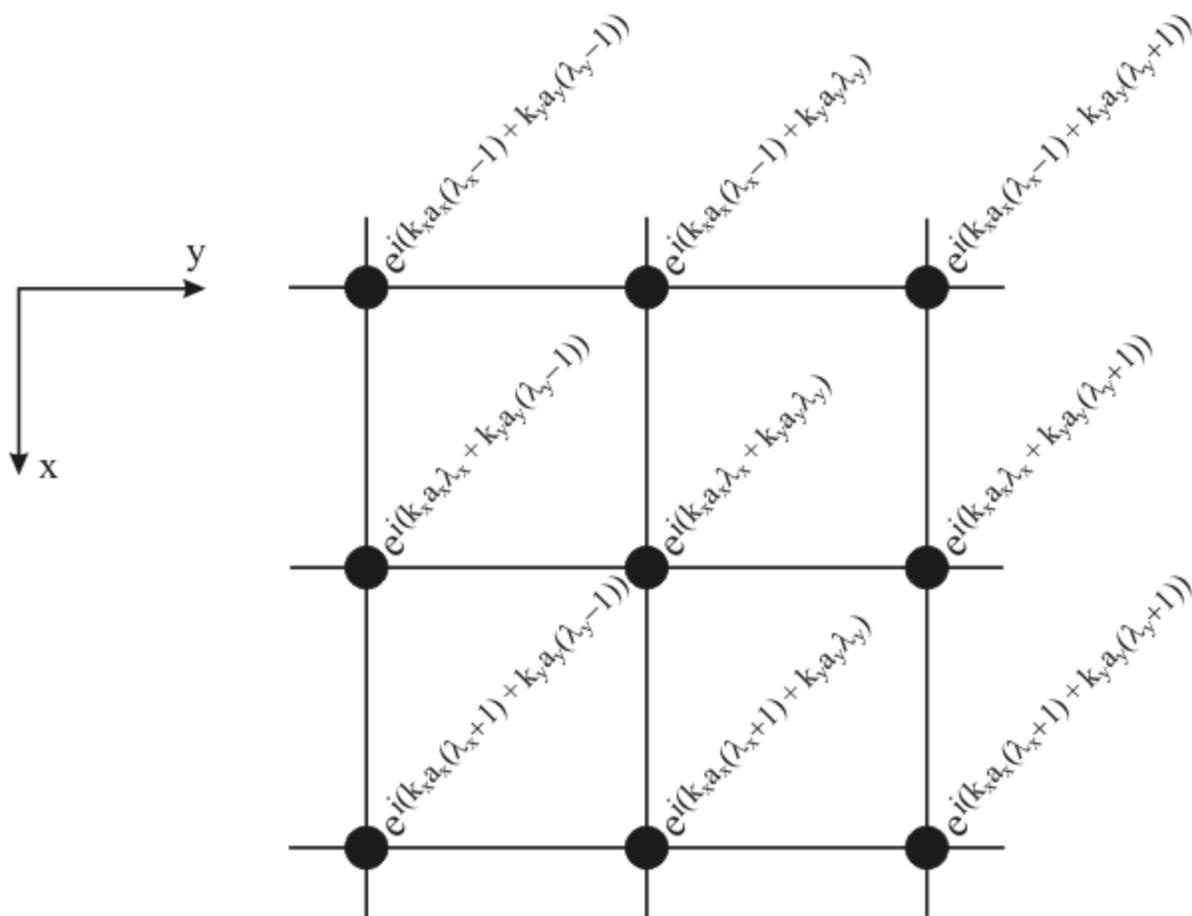
$$\psi(\mathbf{k}) := \frac{1}{\sqrt{N}} \cdot \sum_{\lambda_x=0}^{\sqrt{N}-1} \sum_{\lambda_y=0}^{\sqrt{N}-1} e^{i \cdot \mathbf{k} \cdot \mathbf{a} \cdot \lambda} \cdot \phi_\lambda \quad \mathbf{k} := \begin{pmatrix} k_x & k_y \end{pmatrix} \quad \mathbf{a} := \begin{pmatrix} a_x & 0 \\ 0 & a_y \end{pmatrix} \quad \lambda := \begin{pmatrix} \lambda_x \\ \lambda_y \end{pmatrix}$$

The coordinates in reciprocal space

The sum runs over every unit cell in the plane, and ϕ_λ symbolizes the 2s(C) orbital in the unit cell at lattice site λ .

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The following figure shows a clipping of the direct lattice with the exponential factors of the Bloch basis orbitals relative to the exponential factor of the Bloch orbital belonging to the lattice point in the center:



We now calculate the energy of the crystal orbital depending on the k-vector.

As usual, we start with the following equation, directly derived from the Schrödinger equation:

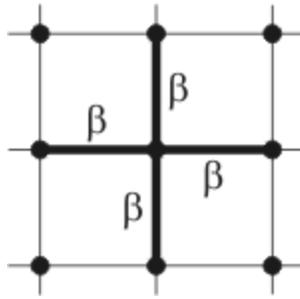
$$\langle \Psi(k) | H | \Psi(k) \rangle = E \langle \Psi(k) | \Psi(k) \rangle$$

Instead of summing over all 2s(C) orbitals in both wave functions, we take only one of them in the second wave function as a reference and multiply by N assuming that for each and every 2s(C) orbital the interactions with all other 2s(C) orbitals are the same. This assumption naturally implies that in our two-dimensional lattice all atoms have the same environment, i.e. that there are no edge phenomena. We have been working with this assumption ever since we started to use Bloch functions!

$$\begin{aligned} \langle \Psi(k) | H | N \cdot (1/N)^{1/2} e^{i(k_x a_x \lambda_x + k_y a_y \lambda_y)} \phi_{\lambda_x, \lambda_y} \rangle &= E \langle \Psi(k) | N \cdot (1/N)^{1/2} e^{i(k_x a_x \lambda_x + k_y a_y \lambda_y)} \phi_{\lambda_x, \lambda_y} \rangle \\ \sum \sum e^{-i k a \lambda} \cdot e^{i(k_x a_x \lambda_x + k_y a_y \lambda_y)} \langle \phi_{\lambda} | H | \phi_{\lambda_x, \lambda_y} \rangle &= E \cdot \sum \sum e^{-i k a \lambda} \cdot e^{i(k_x a_x \lambda_x + k_y a_y \lambda_y)} \langle \phi_{\lambda} | \phi_{\lambda_x, \lambda_y} \rangle \end{aligned}$$

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We consider only nearest neighbor interactions, as shown in the next figure, and use the symbols of the ZDO approximation ([Information about the ZDO approximation](#)):



We find:

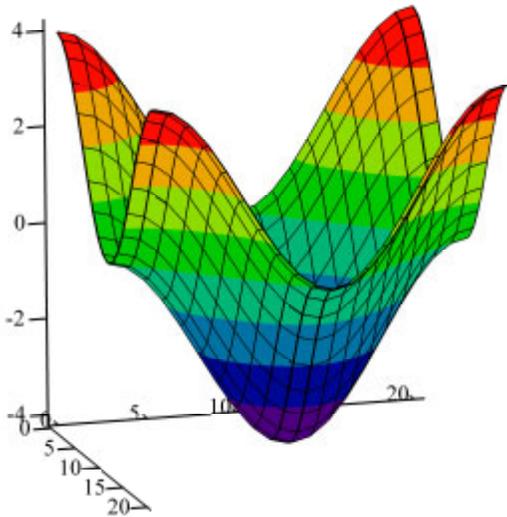
$$E(k_x, k_y) = \alpha + \beta(e^{ik_x a_x} + e^{iky a_y} + e^{-ik_x a_x} + e^{-iky a_y})$$

Evaluation finally results in:

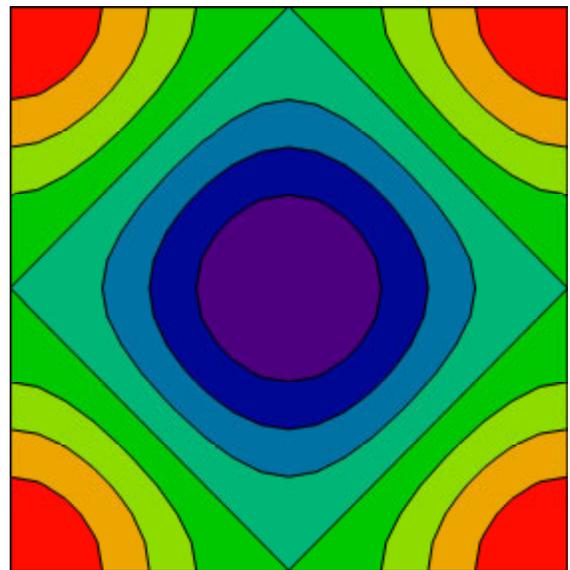
$$E(k_x, k_y) := \alpha + 2 \cdot \beta \cdot (\cos(k_x \cdot a_x) + \cos(k_y \cdot a_y))$$

Note that this result is consistent with the [result for the 1D case](#) ($\epsilon_{B_{S\sigma}}(k) := \alpha_s + 2 \cdot \beta_{s\sigma} \cdot \cos(k \cdot a)$)

$$\text{Energy}_{\text{round}\left[\frac{10}{\pi} \cdot (k_x \cdot a_x + \pi)\right], \text{round}\left[\frac{10}{\pi} \cdot (k_y \cdot a_y + \pi)\right]} := E(k_x, k_y)$$



Energy



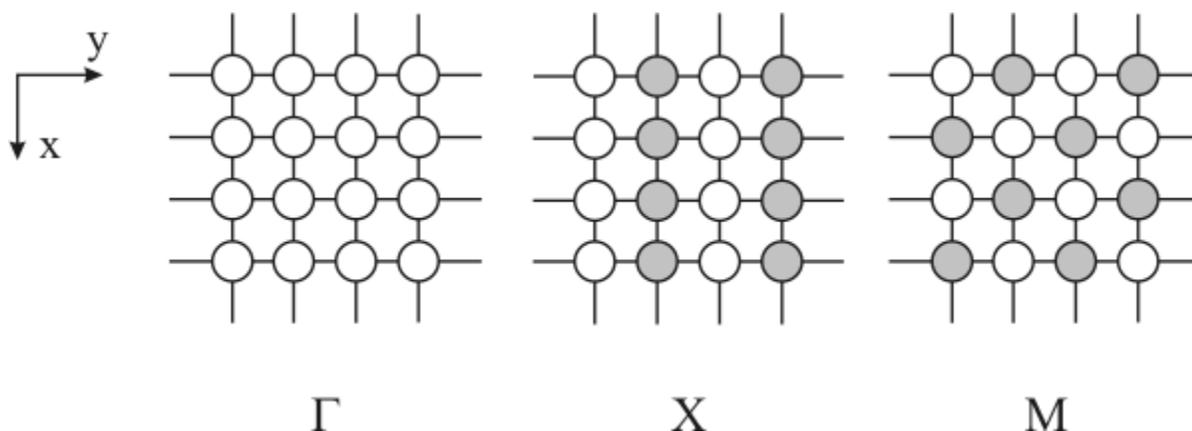
Energy

This energy surface describes the k-dependence of the crystal orbital energy.

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The k-coordinates and the symmetries of the COs at the points and on the lines of high symmetry mentioned above are given in the following table. The symmetries can be understood by examining the wave functions at the k-points Γ , X and M shown in the graph below:

Γ point	$k_x=0, k_y=0$:	Full symmetry of the unit cell	(D_{4h})
X point	$k_x=0, k_y=\pi/a_y$:	E, $3\times C_2$, i, $3\times\sigma$	(D_{2h})
M point	$k_x=\pi/a_x, k_y=\pi/a_y$:	Full symmetry of the unit cell	(D_{4h})
Δ line (line ΓX)	$k_x=0, k_y=0..\pi/a_y$:	E, $3\times C_2$, i, $3\times\sigma$	(D_{2h})
Z line (line XM)	$k_x=0..\pi/a_x, k_y=\pi/a_y$:	E, $3\times C_2$, i, $3\times\sigma$	(D_{2h})
Σ line (line ΓM)	$k_x=0..\pi/a_x, k_y=0..\pi/a_y$:	Full symmetry of the unit cell	(D_{4h})



Problems

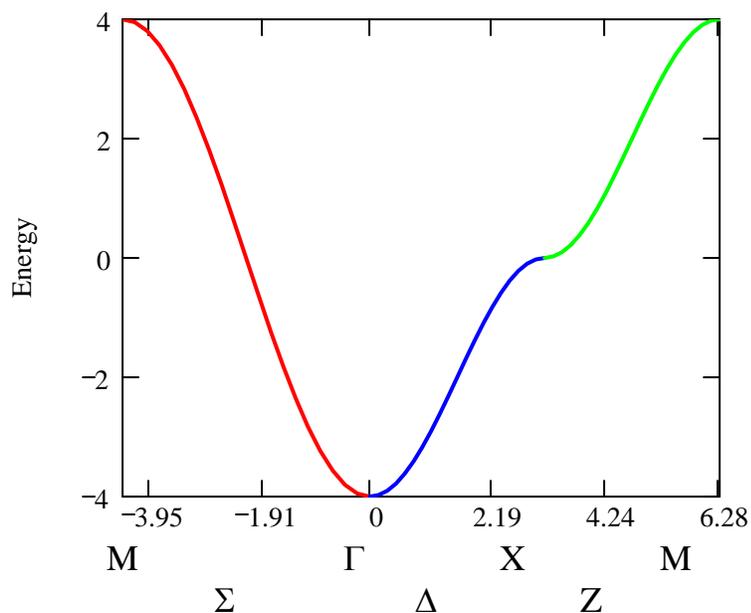
10.2 Verify the symmetries of the described points and lines using the above orbital scheme.

10.3 Compare the situation, which is shown in the energy surface plot, to a one-dimensional structure.

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The energies of the COs at the k-points Γ , X, and M and on the lines of high symmetry Σ , Δ , and Z are shown in the following figure:



[View Brillouin zone](#)

To describe the valence electron structure of a planar square carbon lattice, the basis must be expanded to all four atomic valence orbitals: $2s$, $2p_x$, $2p_y$, $2p_z$. Hence there will be four bands.

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Problems

10.4 In the following figure a scheme of the $2p_x$ -COs at the k-points M, Γ , and X is shown.

Sketch schemes of the $2p_y$ - and $2p_z$ -COs at the same k-points.

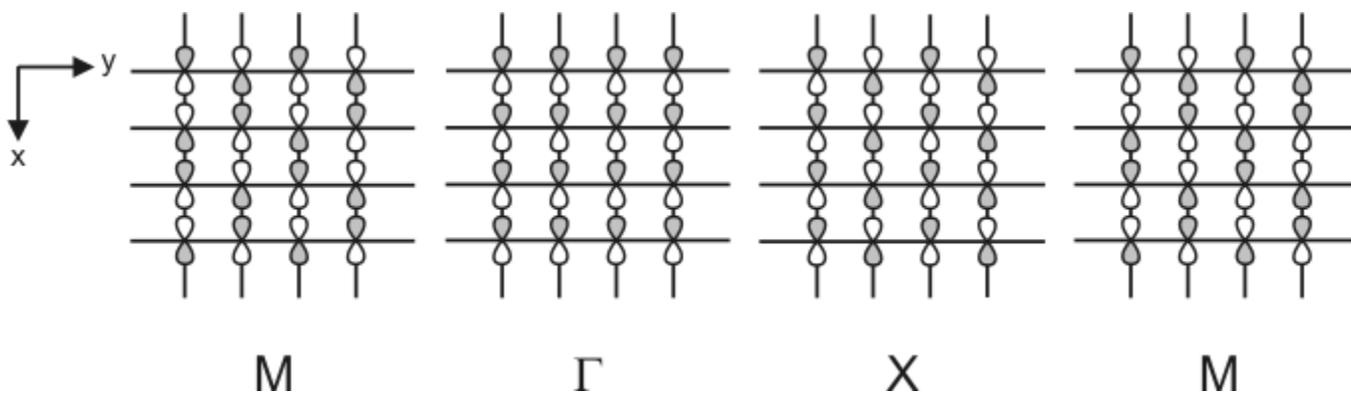
Compare the schemes of the $2p_z$ -COs with the schemes of the $2s$ -COs on p. 41.

Note that, for example, Γ is the k-point of highest symmetry although this seems not to be true regarding the following figure since there are antibonding interactions. However, keep in mind that the Γ point is characterized through the equal orientation (and the equal scaling) of all basis functions in the CO and not through the kind of the resulting interactions.

10.5 Draw the band structure diagram of a planar, square carbon lattice by expanding the figure above by the other three energy bands. Use the assumption that there is no interaction between each orbital type.

The energies of the bands relative to each other can be estimated from the σ - and π -interactions in the COs at different k-points.

Because of the difference between α_s and α_p the energy band of the $2s$ -COs lies at lower energy than the bands of the $2p$ -COs. Furthermore, the $2s$ -band is stretched vertically relative to the $2p$ -bands because $|\beta_s| > |\beta_p|$.



The examination of more complex chemical problems lies beyond the abilities of Mathcad. We refer to the tight binding program package, including oscillator strength calculations, which is available with examples at <http://www.dcb.unibe.ch/groups/calzaferri>.

THREE DIMENSIONS

The band study of diamond is an instructive example. It was shown that $3s$ orbitals must be included in order to get it right; see [9].

Cubic lattices are especially simple. See as example the comparative study of the band structures of the face centered cubic silver halides AgF, AgCl, and AgBr, published in [10].

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11. Summary of formulae

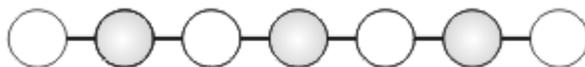
Energy eigenvalues

Wave functions

Linear chains:

$$\varepsilon(J) := \alpha + 2 \cdot \beta \cdot \cos\left(\frac{J \cdot \pi}{N+1}\right)$$

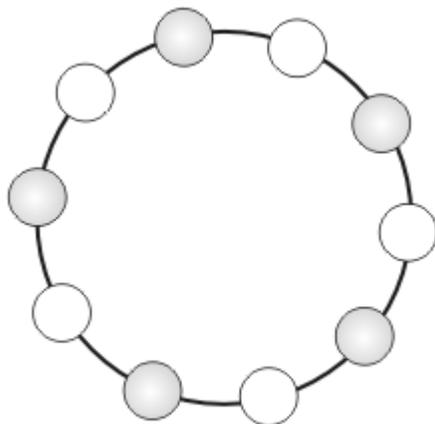
$$\psi(J) := \sqrt{\frac{2}{N+1}} \cdot \sum_L \sin\left(\frac{\pi \cdot L \cdot J}{N+1}\right) \cdot \phi_L$$



Cyclic chains:

$$\varepsilon(j) := \alpha + 2 \cdot \beta \cdot \cos\left(\frac{j \cdot 2 \cdot \pi}{N}\right)$$

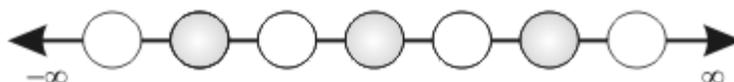
$$\psi(j) := \sqrt{\frac{1}{N}} \cdot \sum_{\lambda} \exp\left(i \cdot \frac{2\pi \cdot \lambda \cdot j}{N}\right) \cdot \phi_{\lambda}$$



Infinite systems:

$$\varepsilon(k) := \alpha + 2 \cdot \beta \cdot \cos(k \cdot a)$$

$$\psi(k) := \sqrt{\frac{1}{N}} \cdot \sum_{\lambda} \exp(i \cdot k \cdot a \cdot \lambda) \cdot \phi_{\lambda}$$



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BRAVAIS LATTICES

A **BRAVAIS LATTICE** describes the periodic structure of a crystal, not the crystal structure itself. It is an infinite set of discrete equivalent points that are ordered in such a way that the point pattern looks the same no matter from where you are looking.

Any point of the lattice can be described in the following way, relative to another point:

$T = \lambda_1 a_1 + \lambda_2 a_2 + \lambda_3 a_3$ where a_1, a_2, a_3 are the primitive basis vectors and λ_1, λ_2 and λ_3 are integers.

The basis vectors a_i , also called primitive vectors, span the lattice.

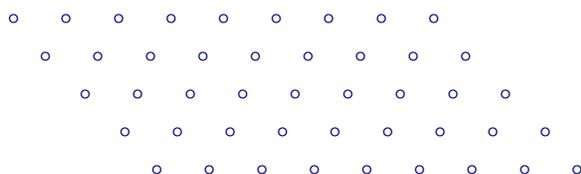
Examples:

(1D = one-dimensional, 2D = two-dimensional, 3D = three-dimensional lattices or elementary cells)

1D example ($T = \lambda a$)



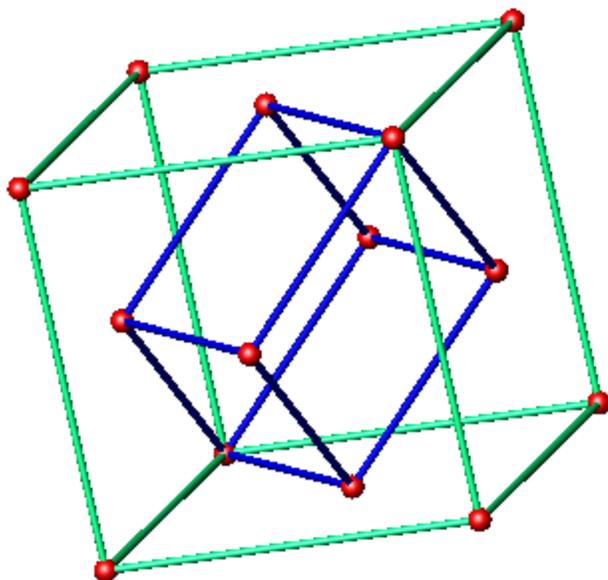
2D example: ($T = \lambda_1 a_1 + \lambda_2 a_2$)



A **PRIMITIVE ELEMENTARY / UNIT CELL** of the lattice is a parallelepiped fulfilling the condition that the whole crystal is generated if the complete set of primitive translations is applied to it. A primitive unit cell can simply be spanned by the three basis vectors a_i . However, the primitive unit cell is not uniquely defined, and it does not necessarily display the full symmetry of the lattice.

Each primitive elementary cell contains **one LATTICE POINT**.

Note that the conventional unit cell can be larger than the primitive unit cell by the requirement to show the full symmetry of the Bravais lattice. The following figure visualizes this by showing the primitive (blue) as well as the conventional (green) unit cell of a face-centered cubic Bravais lattice:



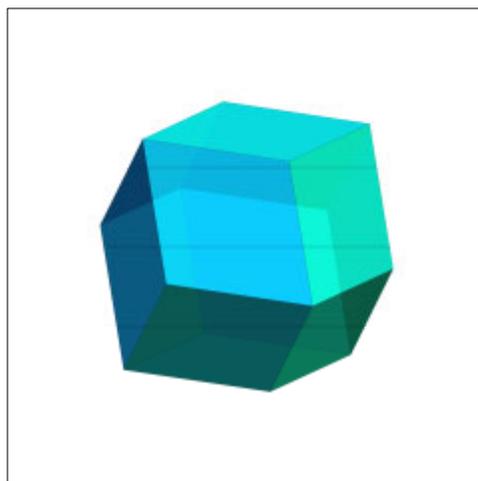
Primitive elementary cells having the full symmetry of the Bravais lattice are called **WIGNER-SEITZ (PRIMITIVE) CELLS**.

Recipe for the construction of a Wigner-Seitz cell:

- From a given lattice point straight lines to all neighbouring lattice points are drawn.
- In 2D (3D) the perpendicular bisectors (bisecting planes) of the sides are constructed for all these connecting lines.
- The smallest volume which is thereby formed is the Wigner-Seitz cell.

Thus, given a lattice point, a Wigner-Seitz cell is the set of points in space which are closer to this lattice point than to any other lattice point.

The following rotatable 3D figure shows the Wigner-Seitz cell for a face-centered cubic Bravais lattice.



Polyhedron("rhombic dodecahedron")

Overview of all existing Bravais lattices

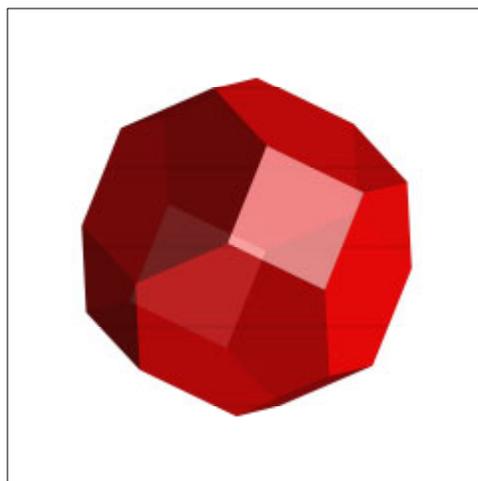
Dim.	Number of Bravais lattices	Possible symmetry operations*	Space groups generated
1	1	5: t, g; C_2 , σ_v , σ_h	7 (1-dimensional)
2	5	8: t, g, C_n (n=2,3,4,6), 2 m	17 (2-dimensional)
3	14	32	230 (3-dimensional)

* t = translation, g = glide plane

RECIPROCAL SPACE AND LATTICE, FIRST BRILLOUIN ZONE

Two lattices belong to each crystal structure: The Bravais lattice and the **RECIPROCAL LATTICE**. Crystallographers make extensive use of reciprocal lattices in X-Ray diffraction because the diffraction image of a crystal is the representation of the reciprocal lattice of the crystal. In contrast, a microscopy image is the representation of the crystal structure in real space.

One therefore calls a reciprocal lattice a Bravais lattice in **RECIPROCAL SPACE**. The reciprocal lattice of the reciprocal lattice is the original direct lattice. In reciprocal space the elementary cell analogous to the Wigner-Seitz primitive cell in real space is called the first **BRILLOUIN ZONE**. The following rotatable 3D figure shows the first Brillouin zone of a face-centered cubic lattice:



Polyhedron("truncated octahedron")

Why do we need reciprocal lattices?

One of the most important tools in theoretical treatments of crystalline materials is Bloch's theorem for periodic systems. By the use of this theorem, it is possible to express the wavefunction of an infinite crystal in terms of wavefunctions at reciprocal space vectors.

The reciprocal space vectors of a Bravais lattice are called **WAVE VECTORS**, Bloch wave vectors or **K-VECTORS**.

Not only the Bravais lattice is periodic but also the reciprocal lattice. Both lattices are invariant under application of a translation vector which is a linear combination of the basis vectors of the corresponding lattice.

How can the basis vectors of the reciprocal space be derived from the basis vectors of real space? Let a_1 , a_2 and a_3 be basis vectors of real space, defining a Bravais lattice, and b_1 , b_2 and b_3 be the unknown basis vectors of reciprocal space, defining the corresponding reciprocal lattice.

Translation vectors in the two lattices can then be written in the following form:

Direct lattice vectors:

$$\mathbf{T} = \lambda_1 \mathbf{a}_1 + \lambda_2 \mathbf{a}_2 + \lambda_3 \mathbf{a}_3 \quad \text{where } \lambda_1, \lambda_2 \text{ and } \lambda_3 \text{ are integers.}$$

Reciprocal lattice vectors:

$$\mathbf{K} = \mu_1 \mathbf{b}_1 + \mu_2 \mathbf{b}_2 + \mu_3 \mathbf{b}_3 \quad \text{where } \mu_1, \mu_2 \text{ and } \mu_3 \text{ are integers.}$$

Because of the periodicity of the reciprocal lattice the following equation must hold:

$$\Psi(\mathbf{k} + \mathbf{K}, \mathbf{r}) = \Psi(\mathbf{k}, \mathbf{r}) \quad (1)$$

where Ψ is a wave function, \mathbf{k} is a wave vector, specifying the particular solution of the Schrödinger equation under discussion, and \mathbf{r} is an arbitrary vector in direct space.

Bloch's theorem says that wave functions can only differ from one point of the direct lattice to another by a linear phase factor:

$$\Psi(\mathbf{k}, \mathbf{r} + \mathbf{T}) = \Psi(\mathbf{k}, \mathbf{r}) \cdot e^{i\mathbf{k} \cdot \mathbf{T}} \quad (2)$$

Hence the following equations must hold:

$$\text{Using (1) we find:} \quad \Psi(\mathbf{k} + \mathbf{K}, \mathbf{r} + \mathbf{T}) = \Psi(\mathbf{k}, \mathbf{r} + \mathbf{T}) \quad (3)$$

$$\text{Using (2) we find:} \quad \Psi(\mathbf{k} + \mathbf{K}, \mathbf{r} + \mathbf{T}) = \Psi(\mathbf{k} + \mathbf{K}, \mathbf{r}) \cdot e^{i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{T}}$$

$$\text{Using (1) we find:} \quad = \Psi(\mathbf{k}, \mathbf{r}) \cdot e^{i\mathbf{k} \cdot \mathbf{T}} \cdot e^{i\mathbf{K} \cdot \mathbf{T}}$$

$$\text{Using (2) we find:} \quad = \Psi(\mathbf{k}, \mathbf{r} + \mathbf{T}) \cdot e^{i\mathbf{K} \cdot \mathbf{T}} \quad (4)$$

Comparison of (3) and (4) shows that $e^{i\mathbf{K} \cdot \mathbf{T}} = 1$ must hold. This is true if $\mathbf{K} \cdot \mathbf{T} = m \cdot 2\pi$ for an integer m . This condition is fulfilled with the following definition of the basis vectors of reciprocal space:

$$\mathbf{b}_j := 2 \cdot \pi \cdot \frac{\mathbf{a}_i \times \mathbf{a}_k}{\mathbf{a}_j \cdot (\mathbf{a}_i \times \mathbf{a}_k)} \quad \text{or} \quad \mathbf{B} := 2 \cdot \pi \cdot (\mathbf{A}^T)^{-1} \quad \text{with} \quad \mathbf{A} := \begin{pmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{pmatrix}$$

$$\text{where} \quad \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} := \begin{pmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{e}_x \\ \mathbf{e}_y \\ \mathbf{e}_z \end{pmatrix} \quad \begin{pmatrix} \mathbf{b}_1 \\ \mathbf{b}_2 \\ \mathbf{b}_3 \end{pmatrix} := \begin{pmatrix} b_{1x} & b_{1y} & b_{1z} \\ b_{2x} & b_{2y} & b_{2z} \\ b_{3x} & b_{3y} & b_{3z} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{e}_x \\ \mathbf{e}_y \\ \mathbf{e}_z \end{pmatrix}$$

Proof:

$$\mathbf{b}_j \cdot \mathbf{a}_m = 2\pi \frac{\mathbf{a}_i \times \mathbf{a}_k}{\mathbf{a}_j \cdot (\mathbf{a}_i \times \mathbf{a}_k)} \cdot \mathbf{a}_m = \begin{cases} 2\pi & m = j \\ 0 & m \neq j \Leftrightarrow m \in \{i, k\} \end{cases}$$

$$\begin{aligned} \text{Hence: } \mathbf{K} \cdot \mathbf{T} &= (\mu_1 \mathbf{b}_1 + \mu_2 \mathbf{b}_2 + \mu_3 \mathbf{b}_3) \cdot (\lambda_1 \mathbf{a}_1 + \lambda_2 \mathbf{a}_2 + \lambda_3 \mathbf{a}_3) \\ &= \mu_1 \lambda_1 \mathbf{b}_1 \cdot \mathbf{a}_1 + \mu_1 \lambda_2 \mathbf{b}_1 \cdot \mathbf{a}_2 + \dots + \mu_3 \lambda_3 \mathbf{b}_3 \cdot \mathbf{a}_3 \\ &= \mu_1 \lambda_1 \cdot 2\pi + \mu_1 \lambda_2 \cdot 0 + \dots + \mu_3 \lambda_3 \cdot 2\pi \\ &= 2\pi (\mu_1 \lambda_1 + \mu_2 \lambda_2 + \mu_3 \lambda_3) \end{aligned}$$

SOME EXAMPLES

Hexagonal 2D lattice:

$$\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} := \begin{pmatrix} 1 & 0 \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} \end{pmatrix} \cdot \begin{pmatrix} e_x \\ e_y \end{pmatrix}$$

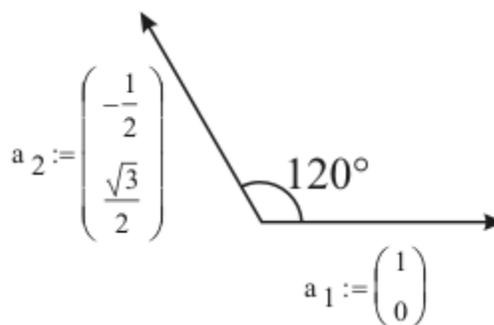
$$\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} := 2 \cdot \pi \cdot \left(\begin{pmatrix} 1 & 0 \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} \end{pmatrix}^T \right)^{-1} \cdot \begin{pmatrix} e_x \\ e_y \end{pmatrix}$$

$$\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} := 2 \cdot \pi \cdot \begin{pmatrix} 1 & \frac{1}{3} \cdot \sqrt{3} \\ 0 & \frac{2}{3} \cdot \sqrt{3} \end{pmatrix} \cdot \begin{pmatrix} e_x \\ e_y \end{pmatrix}$$

Remarks:

$$\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} := \begin{pmatrix} 1 & 0 \\ \cos\left(\frac{2\pi}{3}\right) & \sin\left(\frac{2\pi}{3}\right) \end{pmatrix} \cdot \begin{pmatrix} e_x \\ e_y \end{pmatrix}$$

$$\left(\begin{pmatrix} 1 & 0 \\ \cos\left(\frac{2\pi}{3}\right) & \sin\left(\frac{2\pi}{3}\right) \end{pmatrix}^T \right)^{-1} = \begin{pmatrix} 1 & -\cot\left(\frac{2\pi}{3}\right) \\ 0 & \frac{1}{\sin\left(\frac{2\pi}{3}\right)} \end{pmatrix}$$



Test:

$$(\mu_1 \cdot b_1 + \mu_2 \cdot b_2) \cdot (\lambda_1 \cdot a_1 + \lambda_2 \cdot a_2) \text{ factor} \rightarrow 2 \cdot \pi \cdot (\lambda_1 \cdot \mu_1 + \mu_2 \cdot \lambda_2)$$



Simple cubic lattice:

$$\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} := \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix} \cdot \begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix} \quad \blacksquare$$
$$\begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix} := 2 \cdot \pi \cdot \begin{pmatrix} \frac{1}{a} & 0 & 0 \\ 0 & \frac{1}{a} & 0 \\ 0 & 0 & \frac{1}{a} \end{pmatrix} \cdot \begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix} \quad \blacksquare$$



Test:

$$(\mu_1 \cdot b_1 + \mu_2 \cdot b_2 + \mu_3 \cdot b_3) \cdot (\lambda_1 \cdot a_1 + \lambda_2 \cdot a_2 + \lambda_3 \cdot a_3) \text{ factor} \rightarrow 2 \cdot \pi \cdot (\lambda_1 \cdot \mu_1 + \mu_2 \cdot \lambda_2 + \lambda_3 \cdot \mu_3)$$

Face-centered cubic lattice:

$$\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} := \begin{pmatrix} 0 & \frac{a}{2} & \frac{a}{2} \\ \frac{a}{2} & 0 & \frac{a}{2} \\ \frac{a}{2} & \frac{a}{2} & 0 \end{pmatrix} \cdot \begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix} \quad \blacksquare$$
$$\begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix} := 2 \cdot \pi \cdot \begin{pmatrix} \frac{-1}{a} & \frac{1}{a} & \frac{1}{a} \\ \frac{1}{a} & \frac{-1}{a} & \frac{1}{a} \\ \frac{1}{a} & \frac{1}{a} & \frac{-1}{a} \end{pmatrix} \cdot \begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix} \quad \blacksquare$$



Test:

$$(\mu_1 \cdot b_1 + \mu_2 \cdot b_2 + \mu_3 \cdot b_3) \cdot (\lambda_1 \cdot a_1 + \lambda_2 \cdot a_2 + \lambda_3 \cdot a_3) \text{ factor} \rightarrow 2 \cdot \pi \cdot (\lambda_1 \cdot \mu_1 + \mu_2 \cdot \lambda_2 + \lambda_3 \cdot \mu_3)$$

Body-centered cubic lattice:

$$\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} := \begin{pmatrix} \frac{a}{2} & \frac{a}{2} & \frac{a}{2} \\ \frac{a}{2} & -\frac{a}{2} & \frac{a}{2} \\ \frac{a}{2} & \frac{a}{2} & -\frac{a}{2} \end{pmatrix} \cdot \begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix}$$

$$\begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix} := 2 \cdot \pi \cdot \begin{pmatrix} 0 & \frac{1}{a} & \frac{1}{a} \\ \frac{1}{a} & 0 & \frac{1}{a} \\ \frac{1}{a} & \frac{1}{a} & 0 \end{pmatrix} \cdot \begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix}$$



Test:

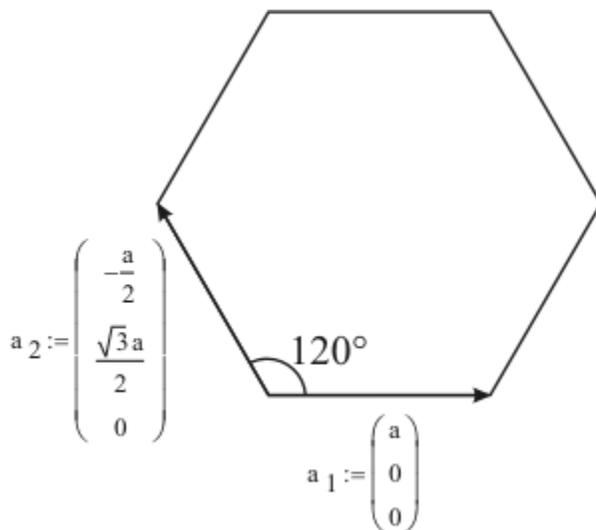
$$(\mu_1 \cdot b_1 + \mu_2 \cdot b_2 + \mu_3 \cdot b_3) \cdot (\lambda_1 \cdot a_1 + \lambda_2 \cdot a_2 + \lambda_3 \cdot a_3) \text{ factor} \rightarrow 2 \cdot \pi \cdot (\lambda_1 \cdot \mu_1 + \mu_2 \cdot \lambda_2 + \lambda_3 \cdot \mu_3)$$

Close-packed hexagonal lattice:

$$\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} := \begin{pmatrix} a & 0 & 0 \\ -\frac{a}{2} & \frac{\sqrt{3} \cdot a}{2} & 0 \\ 0 & 0 & c \end{pmatrix} \cdot \begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix}$$

$$\begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix} := 2 \cdot \pi \cdot \begin{pmatrix} \frac{1}{a} & \frac{1}{3 \cdot a} \cdot \sqrt{3} & 0 \\ 0 & \frac{2}{3 \cdot a} \cdot \sqrt{3} & 0 \\ 0 & 0 & \frac{1}{c} \end{pmatrix} \cdot \begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix}$$

Remarks:



Test:

$$(\mu_1 \cdot b_1 + \mu_2 \cdot b_2 + \mu_3 \cdot b_3) \cdot (\lambda_1 \cdot a_1 + \lambda_2 \cdot a_2 + \lambda_3 \cdot a_3) \text{ factor} \rightarrow 2 \cdot \pi \cdot (\lambda_1 \cdot \mu_1 + \mu_2 \cdot \lambda_2 + \lambda_3 \cdot \mu_3)$$

ZDO APPROXIMATION

The ZDO ("Zero Differential Overlap") approximation involves the following relations and symbols, where ϕ_λ and ϕ_μ are atomic orbitals:

$$s_{\lambda\mu} = \langle \phi_\lambda | \phi_\mu \rangle = \delta_{\lambda\mu} \quad \text{Overlap integral}$$
$$h_{\lambda\mu} = \langle \phi_\lambda | H | \phi_\mu \rangle = \begin{cases} \alpha & \lambda = \mu \\ \beta & \lambda = \mu \pm 1 \\ 0 & \text{else} \end{cases} \quad \begin{array}{l} \text{Coulomb integral} \\ \text{Resonance integral} \end{array}$$

- The meaning of the overlap integral is obvious:
An AO overlaps completely with itself, but not at all with any other AO.
- The Coulomb integral α approximately corresponds to the negative ionization energy of an electron, localized in a carbon atomic orbital ϕ . Hence α is a negative quantity.
- The resonance energy β describes the additional stabilization, which occurs when an electron delocalizes over neighboring atomic orbitals. It is also a negative quantity. However, its value is smaller than α according to amount.

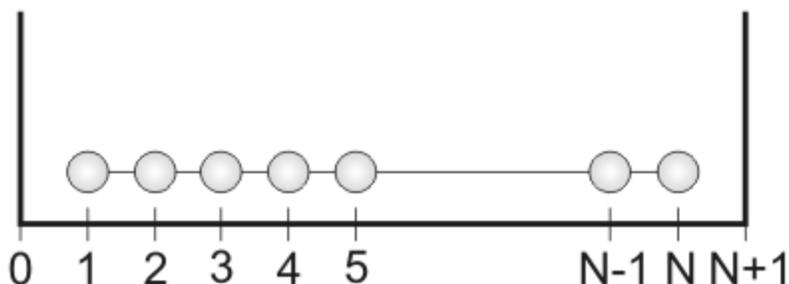
Note that in the ZDO approximation resonance is only accounted for between nearest next neighbors.

MOs AND ENERGY EIGENVALUES OF LINEAR CHAINS

MOs

The MOs are formed as linear combinations of the AOs (p_π orbitals) according to the LCAO-MO approximation.

The coefficients of the AOs are formed on the basis of a chain placed in a box of length $N+1$:



The wave function must be zero at the walls. This leads to the following ansatz for the coefficients:

$$c(L) := A \cdot \sin\left(\frac{L \cdot \pi}{N+1}\right)$$

with L running from 1 to N .

There is no node for these coefficients what corresponds to the lowest state of energy. An additional factor J in the argument of the sine provides nodes for the higher energy levels:

$$c(L, J) := A \cdot \sin\left(\frac{L \cdot J \cdot \pi}{N+1}\right)$$

with J running from 1 to N .

The prefactor A is chosen so that the MOs are normalized correctly:

$$c(L, J) := \sqrt{\frac{2}{N+1}} \cdot \sin\left(\frac{L \cdot J \cdot \pi}{N+1}\right)$$

In one of the problems the correct normalization of the MOs has to be shown numerically for some values of N using the abilities of Mathcad.

(An analytical proof is - of course - also possible, but tricky.)

ENERGY EIGENVALUES

We start with the time-independent Schrödinger equation. To simplify the notation, we substitute n for $N+1$ and ϕ for p_π :

$$H \cdot \Psi = E \cdot \Psi$$

$$\Psi^* \cdot H \cdot \Psi = E \cdot \Psi^* \cdot \Psi$$

$$\int \Psi^* \cdot H \cdot \Psi \, d\tau = E \cdot \int \Psi^* \cdot \Psi \, d\tau$$

$$2/n \left(\sum_{i=1..N} \sum_{k=1..N} \int \sin(iJ\pi/n) \phi_i^* \cdot H \cdot \sin(kJ\pi/n) \phi_k \, d\tau \right) = 2E/n \left(\sum_{i=1..N} \sum_{k=1..N} \int \sin(iJ\pi/n) \phi_i^* \cdot \sin(kJ\pi/n) \phi_k \, d\tau \right)$$

Using the approximations and symbols of the ZDO approximation simplifies this equation.

Left-hand side:

$$2/n \cdot (\alpha \cdot \sum_{k=1..N} \sin^2(kJ\pi/n) + 2\beta \cdot \sum_{k=1..N-1} \sin(kJ\pi/n) \cdot \sin((k+1)J\pi/n))$$

It can be shown that the first sum is equal to $n/2$.

The second sum is equal to the sum with the index running from 0 to N instead of running from 1 to $N-1$.

It can be shown that this sum equals $n/2 \cdot \cos(J\pi/n)$.

Therefore the left-hand side becomes very simple:

$$2/n \cdot (\alpha \cdot n/2 + 2\beta \cdot n/2 \cdot \cos(J\pi/n))$$
$$\alpha + 2\beta \cdot \cos(J\pi/n)$$

Right-hand side:

$$2E/n \cdot \sum_{k=1..N} \sin^2(kJ\pi/n)$$

Again this sum equals $n/2$. Therefore the right-hand side equals E .

Resubstituting $N+1$ for n , the equation has the following final form:

$$E = \alpha + 2\beta \cdot \cos(J\pi/(N+1))$$

Note that this derivation holds for basis functions (AOs) which are symmetric with respect to a plane extending perpendicularly to the chain axis. For orbitals which are antisymmetric with respect to this plane (e.g. the p_σ orbitals) the different symmetry must be taken into account. This leads to a negative sign in the interaction term of the energy eigenvalue.

NORMALIZATION

The MO $\psi(J) = \sum_L c(L,J) \cdot p_\pi(L)$ is said to be normalized if the following equation holds:

$$\int \overline{\psi(J)} \cdot \psi(J) d\tau = 1 \quad (\text{Integration is over all space.})$$

We expand this integral using the explicit form of ψ :

$$\int \left(\sum_L \overline{c(L,J1) \cdot p_\pi(L)} \right) \cdot \left(\sum_M c(M,J2) \cdot p_\pi(M) \right) d\tau$$

This can be simplified in the following way:

$$\sum_M \sum_L \overline{c(L,J1)} \cdot c(M,J2) \cdot \int \overline{p_\pi(L)} \cdot p_\pi(M) d\tau$$

Due to the ZDO approximation, the integrals are either equal to zero or to one:

$$\sum_M \sum_L \overline{c(L,J1)} \cdot c(M,J2) \cdot \delta(L,M)$$

We can therefore formulate the normalization condition in the following way:

For chains, where the MO coefficients are real:

$$\sum_M \sum_L c(L,J1) \cdot c(M,J2) \cdot \delta(L,M) = 1$$

For rings, using the slightly different variables introduced in QBAND:

$$\sum_\mu \sum_\lambda c_{\text{conj}}(\lambda, j1) \cdot c(\mu, j2) \cdot \delta(\lambda, \mu) = 1$$

In order to solve the problem define the left sides of the above equations as matrices, e.g.:

$$Q_{J1-1, J2-1} := \sum_M \sum_L c(L, J1) \cdot c(M, J2) \cdot \delta(L, M)$$

J1 and J2 have to be defined. They can be equated to J.

Subtraction of 1 from the matrix indices **for chains** is because matrix indexing starts at 0 in Mathcad.

The matrix can then be displayed using the command 'Q = '.

Note that Mathcad can display Q as a matrix only up to N = 17. For larger values of N change the matrix display style to 'table'. Also adjust the number format if rounding errors occur.

THE HÜCKEL EIGENVALUE PROBLEM

Eigenvalue problem for $N = 4$

We start with the Schrödinger equation: $H \cdot \psi = \varepsilon \cdot \psi$ (1)

Using the variational theorem we find:

$$\psi(j) = \sum_{\lambda} c(\lambda, j) \cdot p_{\pi}(\lambda) \quad (2)$$

Hence:
$$\sum_{\lambda} c(\lambda, j) \cdot (H - \varepsilon(j)) \cdot p_{\pi}(\lambda) = 0 \quad (3)$$

Expansion, left-multiplication with $p_{\pi}(1)^*$, and integration over all spatial coordinates yields:

$$c(1, j) \cdot \int \overline{p_{\pi}(1)} \cdot (H - \varepsilon(j)) \cdot p_{\pi}(1) \, d\tau + \dots + c(4, j) \cdot \int \overline{p_{\pi}(1)} \cdot (H - \varepsilon(j)) \cdot p_{\pi}(4) \, d\tau = 0 \quad (4)$$

We introduce the following substitutes:

$$h_{\lambda\lambda} := \int \overline{p_{\pi}(\lambda)} \cdot H \cdot p_{\pi}(\lambda) \, d\tau \quad (5) \qquad s_{\lambda\mu} := \int \overline{p_{\pi}(\lambda)} \cdot p_{\pi}(\mu) \, d\tau \quad (6)$$

$h_{\lambda\lambda}$ is the energy of orbital $p_{\pi}(\lambda)$.

$h_{\lambda\mu}$ ($\lambda \neq \mu$) is the energy of interaction between the orbitals $p_{\pi}(\lambda)$ and $p_{\pi}(\mu)$.

$s_{\lambda\mu}$ is the overlap integral of the orbitals $p_{\pi}(\lambda)$ and $p_{\pi}(\mu)$.

Equation (4) can now be rewritten in the following way (7):

$$c(1, j) \cdot h_{11} - \varepsilon(j) \cdot c(1, j) \cdot s_{11} + c(2, j) \cdot h_{12} - \varepsilon(j) \cdot c(2, j) \cdot s_{12} + \dots + c(4, j) \cdot h_{14} - \varepsilon(j) \cdot c(4, j) \cdot s_{14} = 0$$

Since the AOs are all normalized, this equation simplifies to:

$$c(1, j) \cdot (h_{11} - \varepsilon(j)) + c(2, j) \cdot (h_{12} - \varepsilon(j) \cdot s_{12}) + c(3, j) \cdot (h_{13} - \varepsilon(j) \cdot s_{13}) + c(4, j) \cdot (h_{14} - \varepsilon(j) \cdot s_{14}) = 0$$

Instead of multiplication with $p_{\pi}(1)^*$, equation (3) could also have been multiplied with any other atomic orbital, resulting in the following equations (8) - (10):

$$c(1, j) \cdot (h_{21} - \varepsilon(j) \cdot s_{21}) + c(2, j) \cdot (h_{22} - \varepsilon(j)) + c(3, j) \cdot (h_{23} - \varepsilon(j) \cdot s_{23}) + c(4, j) \cdot (h_{24} - \varepsilon(j) \cdot s_{24}) = 0$$

$$c(1, j) \cdot (h_{31} - \varepsilon(j) \cdot s_{31}) + c(2, j) \cdot (h_{32} - \varepsilon(j) \cdot s_{32}) + c(3, j) \cdot (h_{33} - \varepsilon(j)) + c(4, j) \cdot (h_{34} - \varepsilon(j) \cdot s_{34}) = 0$$

$$c(1, j) \cdot (h_{41} - \varepsilon(j) \cdot s_{41}) + c(2, j) \cdot (h_{42} - \varepsilon(j) \cdot s_{42}) + c(3, j) \cdot (h_{43} - \varepsilon(j) \cdot s_{43}) + c(4, j) \cdot (h_{44} - \varepsilon(j)) = 0$$

Matrix notation leads to a simplified representation of equations (7) to (10):

$$\begin{pmatrix} h_{11} - \varepsilon(j) & h_{12} - \varepsilon(j) \cdot s_{12} & h_{13} - \varepsilon(j) \cdot s_{13} & h_{14} - \varepsilon(j) \cdot s_{14} \\ h_{21} - \varepsilon(j) \cdot s_{21} & h_{22} - \varepsilon(j) & h_{23} - \varepsilon(j) \cdot s_{23} & h_{24} - \varepsilon(j) \cdot s_{24} \\ h_{31} - \varepsilon(j) \cdot s_{31} & h_{32} - \varepsilon(j) \cdot s_{32} & h_{33} - \varepsilon(j) & h_{34} - \varepsilon(j) \cdot s_{34} \\ h_{41} - \varepsilon(j) \cdot s_{41} & h_{42} - \varepsilon(j) \cdot s_{42} & h_{43} - \varepsilon(j) \cdot s_{43} & h_{44} - \varepsilon(j) \end{pmatrix} \begin{pmatrix} c(1,j) \\ c(2,j) \\ c(3,j) \\ c(4,j) \end{pmatrix} = 0 \quad (11)$$

This equation can only have nontrivial solutions for the c's if the matrix of the coefficients of the c's forms a determinant equal to zero. This determinant is called the **SECULAR DETERMINANT**.

If the numerical values of the $h_{\lambda\mu}$'s and $s_{\lambda\mu}$'s are known or found by estimation or computation, the **SECULAR EQUATION** (secular determinant = 0) can be solved, resulting in the possible values of ε , defining the energy levels of the system. The values of ε , together with the values of the $h_{\lambda\mu}$'s and $s_{\lambda\mu}$'s, define the c's.

We now introduce the ZDO (Hückel) approximation:

$$\alpha = h_{11} = h_{22} = h_{33} = h_{44}$$

$$\beta = h_{12} = h_{21} = h_{23} = h_{32} = h_{34} = h_{43}$$

$$h_{\lambda\mu} = 0 \text{ else}$$

$$s_{\lambda\mu} = 0 \text{ if } \lambda \neq \mu$$

Writing equation (11) using these substitutes, we find:

$$\begin{pmatrix} \alpha - \varepsilon(j) & \beta & 0 & 0 \\ \beta & \alpha - \varepsilon(j) & \beta & 0 \\ 0 & \beta & \alpha - \varepsilon(j) & \beta \\ 0 & 0 & \beta & \alpha - \varepsilon(j) \end{pmatrix} \begin{pmatrix} c(1,j) \\ c(2,j) \\ c(3,j) \\ c(4,j) \end{pmatrix} = 0 \quad (12)$$

Using the substitution $-x(j) = \frac{\alpha - \varepsilon(j)}{\beta}$ makes it possible to rewrite (12) in the following way:

$$\begin{pmatrix} -x(j) & 1 & 0 & 0 \\ 1 & -x(j) & 1 & 0 \\ 0 & 1 & -x(j) & 1 \\ 0 & 0 & 1 & -x(j) \end{pmatrix} \cdot \begin{pmatrix} c(1,j) \\ c(2,j) \\ c(3,j) \\ c(4,j) \end{pmatrix} = 0$$

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} c(1,j) \\ c(2,j) \\ c(3,j) \\ c(4,j) \end{pmatrix} = x(j) \cdot \begin{pmatrix} c(1,j) \\ c(2,j) \\ c(3,j) \\ c(4,j) \end{pmatrix}$$

This is a classical eigenvalue problem. Solution:

$$x := \text{eigenvals} \left(\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \right) \quad x = \begin{pmatrix} 0.618 \\ 1.618 \\ -0.618 \\ -1.618 \end{pmatrix} \quad \varepsilon(j) = \alpha + \beta \cdot x(j)$$

$$c := \text{eigenvecs} \left(\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \right) \quad c = \begin{pmatrix} 0.602 & 0.372 & 0.602 & -0.372 \\ 0.372 & 0.602 & -0.372 & 0.602 \\ -0.372 & 0.602 & -0.372 & -0.602 \\ -0.602 & 0.372 & 0.602 & 0.372 \end{pmatrix}$$

The j^{th} column of c is an eigenvector corresponding to the j^{th} eigenvalue returned by eigenvals.

MOs AND ENERGY EIGENVALUES OF RINGS

MOs

The MOs are formed as linear combinations of the AOs (p_π orbitals) according to the LCAO-MO approximation.

The coefficients of the AOs are constructed in a manner that they show a periodic behaviour with a period of $2\pi/j$ (j : natural number) in order to provide a continuous course around the ring and in order to let the number of nodes grow when the MO index increases.

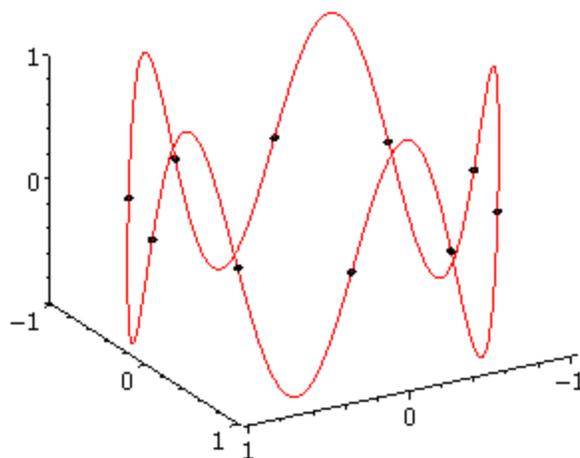
The following ansatz is a first step in the construction of the coefficients $c(\lambda, j)$. It accounts for the mentioned demands:

$$c(\lambda, j) := \sin\left(2 \cdot \pi \cdot \frac{\lambda}{N} \cdot j\right)$$

λ , the atom index, is running from 0 to $N-1$. j is the energy level index, also running from 0 to $N-1$.

As a visualization the coefficients are plotted along the ring. To do this, the formula above is interpreted as a function of the variable λ with λ running continuously from 0 to N . This segment of the λ -axis is then wound up to a circle. Chosen values: $j = 5$, $N = 10$.

Keep in mind that only the N black dots correspond to the coefficients:



However, there are two problems with this formulation of the coefficients:

- First they vanish for $j = 0$, i.e. in the energetical ground state, and for $j = 5$, as can be seen above.

This is clearly wrong:

For $j = 0$ there should be a constant non-zero value for the amplitude and no node. (As a consequence of the equivalence of all atoms in the ring, the lowest energy will result if all AOs provide the same contribution to an MO.)

For $j = 5$ the coefficients can obviously not vanish, less than ever.

- Second there are 10 nodes for $j = 5$.

This must be so because for a continuous sinusoidal curve of the kind above there will be $2j = 10$ nodes on the interval $[0, 2\pi]$.

However, if we have, for example, 10 atoms ($N = 10$), the most antibonding MO will have a node between every pair of two atoms, i.e. there will be 10 nodes. As seen above, this is true for $j = 5$.

So $j = 5$ must correspond to the highest energy level for $N = 10$. But with 10 AOs we will have 10 MOs. Hence there must be more than one MO for some energy levels, i.e. there must be degenerate energy levels!

Performing a linear variation calculation, one finds that for $N = 10$ there are non-degenerate energy levels for $j = 0$ and for $j = 5$ and doubly degenerate energy levels for $j = 1$ to 4. This results in a total of 10 MOs, as required.

In general, for an even number of AOs all energy levels but the lowest and the highest are doubly degenerate, while the two levels mentioned are not degenerate. For an odd number of AOs all energy levels but the lowest are doubly degenerate.

These considerations lead to the idea to accompany the coefficient introduced above with another coefficient, which meets the same needs, but which does not vanish for $j = 0$ and, if N is even, for $j = N/2$.

The following choice is obvious:

$$c(\lambda, j) := \cos\left(2 \cdot \pi \cdot \frac{\lambda}{N} \cdot j\right)$$

This pair of coefficients is able to correctly describe all MOs.

It seems reasonable that a non-vanishing MO constructed with the first kind of coefficient has the same energy like an MO constructed with the second kind of coefficient, the same value of j assumed.

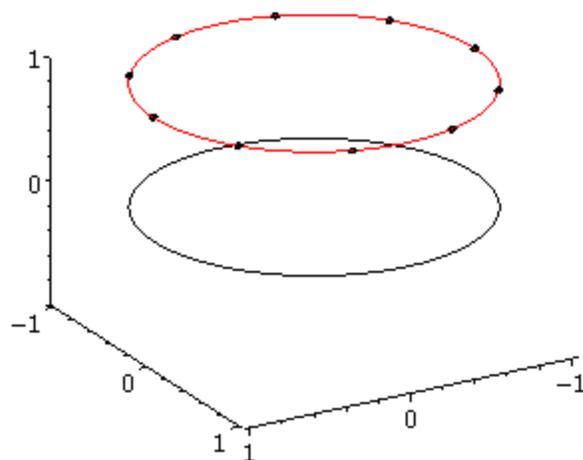
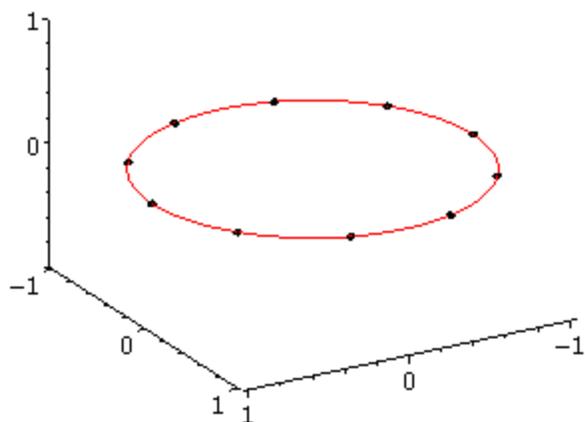
A mathematical proof of this degeneracy follows at the end of this document.

As a visualization, the coefficients for $j = 0$ to 5 (using $N = 10$) are again plotted along the ring.
 (Please remember that only the black dots, which correspond to the coefficients, have a physical meaning.)

$$\sin\left(2 \cdot \pi \cdot \frac{\lambda}{N} \cdot j\right)$$

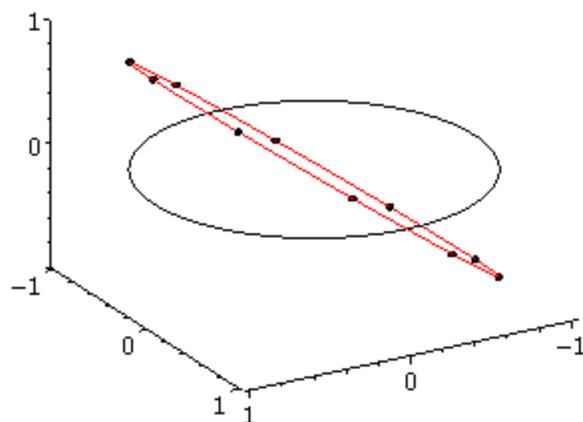
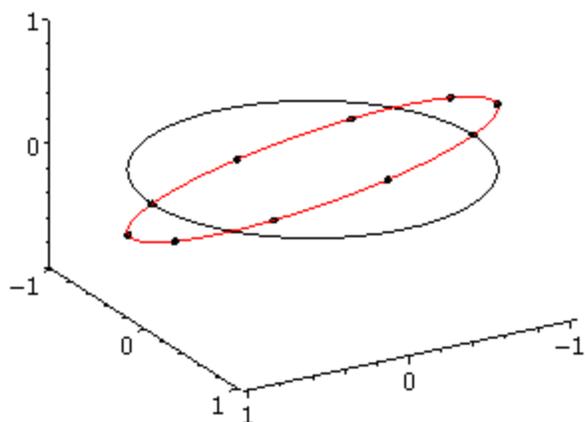
$$\cos\left(2 \cdot \pi \cdot \frac{\lambda}{N} \cdot j\right)$$

$j = 0$:

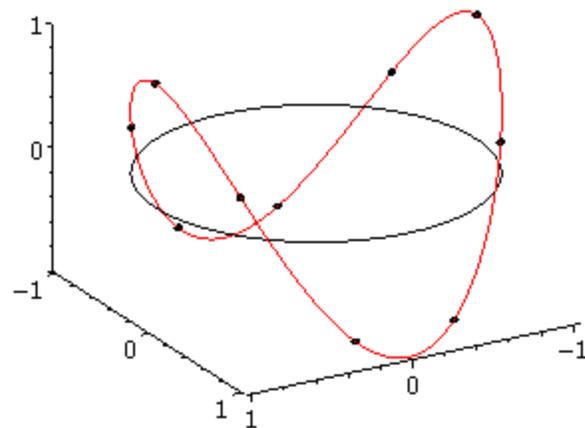
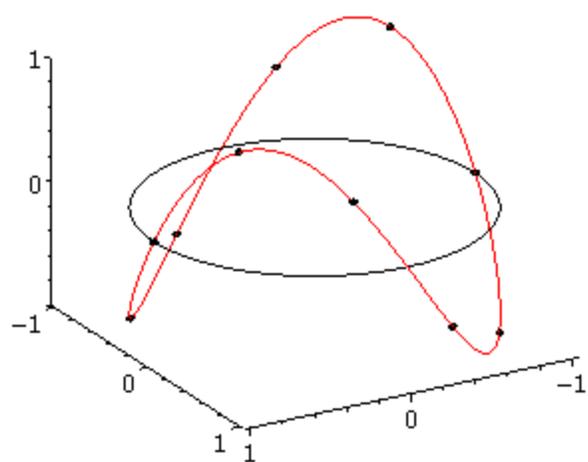


Does not create an MO.

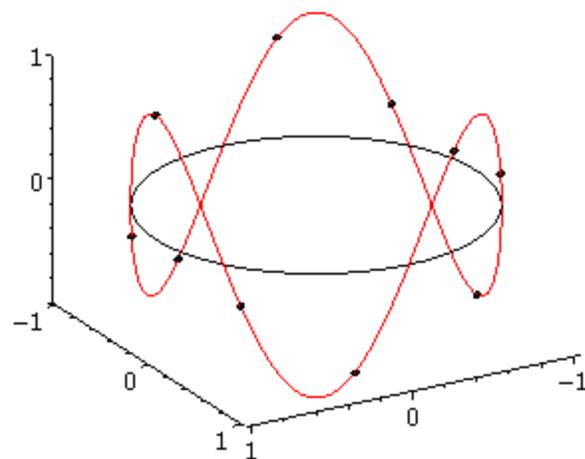
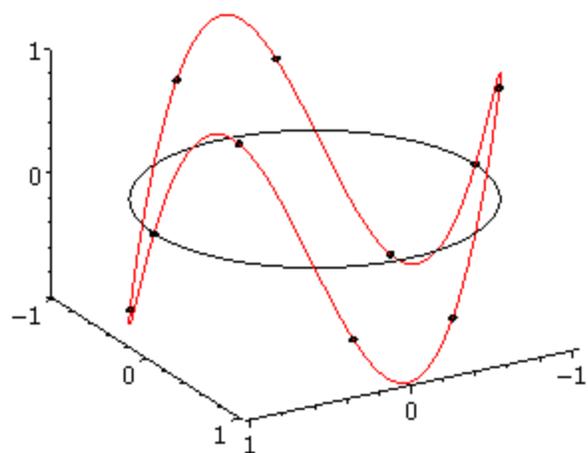
$j = 1$:



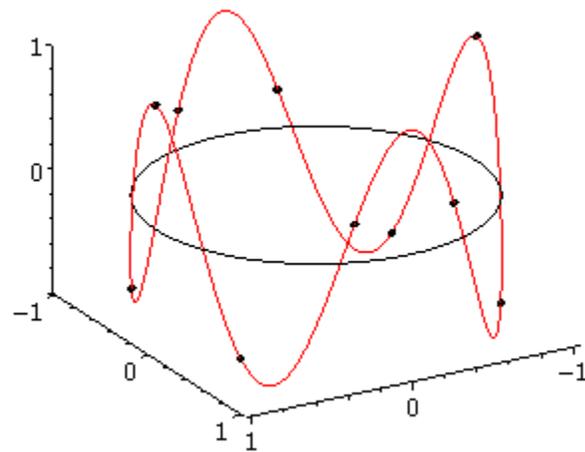
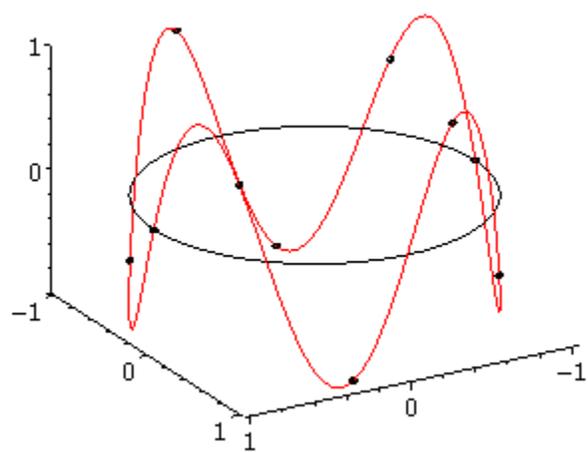
$j = 2$:



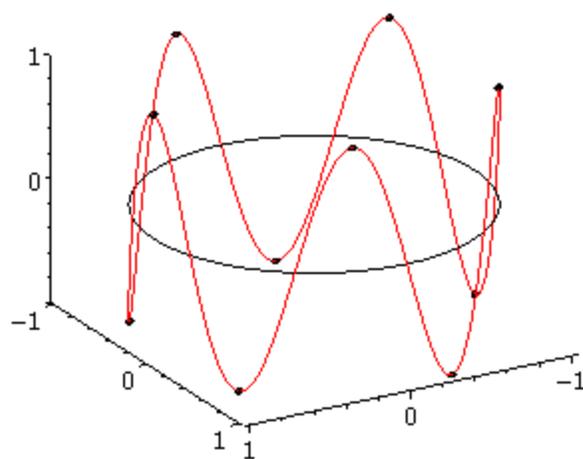
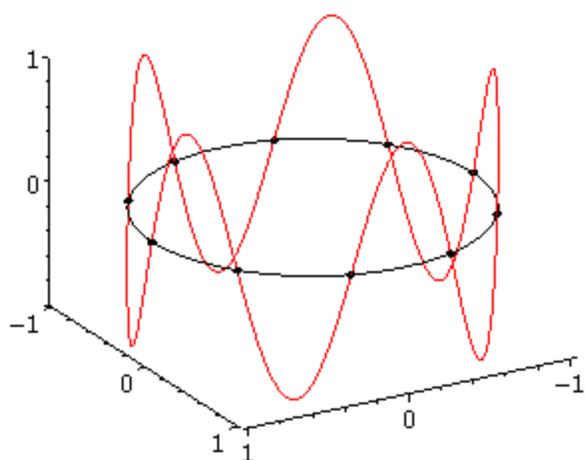
$j = 3$:



$j = 4$:



$j = 5$:



Does not create an MO.

Combining the coefficients in a complex exponential provides a convenient shortcut:

$$c(\lambda, j) := \exp\left(i \cdot 2 \cdot \pi \cdot \frac{\lambda}{N} \cdot j\right)$$

The real part of this coefficient is identical to the cosine-coefficient, the imaginary part is identical to the sine-coefficient.

The final form of the coefficient includes a normalizing constant:

$$c(\lambda, j) := \sqrt{\frac{1}{N}} \cdot \exp\left(i \cdot 2 \cdot \pi \cdot \frac{\lambda}{N} \cdot j\right)$$

It has to be shown numerically in one of the problems that these coefficients lead to normalized MOs.

ENERGY EIGENVALUES

Again we start with the Schrödinger equation. To simplify the notation, we substitute ϕ for p_π .

$$H \cdot \Psi = E \cdot \Psi$$

$$\Psi^* \cdot H \cdot \Psi = E \cdot \Psi^* \cdot \Psi$$

$$\int \Psi^* \cdot H \cdot \Psi \, d\tau = E \cdot \int \Psi^* \cdot \Psi \, d\tau$$

$$1/N \cdot \int (\sum_{\lambda=0..N-1} e^{i2\pi\lambda j/N} \phi_\lambda)^* \cdot H \cdot (\sum_{\mu=0..N-1} e^{i2\pi\mu j/N} \phi_\mu) \, d\tau = E/N \cdot \int (\sum_{\lambda=0..N-1} e^{i2\pi\lambda j/N} \phi_\lambda)^* \cdot (\sum_{\mu=0..N-1} e^{i2\pi\mu j/N} \phi_\mu) \, d\tau$$

$$1/N \cdot (\sum_{\lambda=0..N-1} \sum_{\mu=0..N-1} e^{-i2\pi\lambda j/N} \cdot e^{i2\pi\mu j/N} \cdot \int \phi_\lambda^* \cdot H \cdot \phi_\mu \, d\tau) = E/N \cdot (\sum_{\lambda=0..N-1} \sum_{\mu=0..N-1} e^{-i2\pi\lambda j/N} \cdot e^{i2\pi\mu j/N} \cdot \int \phi_\lambda^* \cdot \phi_\mu \, d\tau)$$

Using the approximations and symbols of the ZDO approximation simplifies this equation:

$$1/N \cdot (\sum_{\mu=\lambda-1} e^{-i2\pi j/N} \cdot \beta + \sum_{\mu=\lambda} 1 \cdot \alpha + \sum_{\mu=\lambda+1} e^{i2\pi j/N} \cdot \beta) = E/N \cdot (\sum_{\mu=\lambda} 1 \cdot 1)$$

$$1/N \cdot (N \cdot \beta \cdot (\cos(2\pi j/N) - i \cdot \sin(2\pi j/N)) + N \cdot \alpha + N \cdot \beta \cdot (\cos(2\pi j/N) + i \cdot \sin(2\pi j/N))) = E/N \cdot N$$
$$\alpha + 2\beta \cdot \cos(2\pi j/N) = E$$

Note that this derivation holds for basis functions (AOs) which are symmetric with respect to a plane extending perpendicularly to the ring at the AO position. For orbitals which are antisymmetric with respect to this plane (e.g. the p_σ orbitals) the different symmetry must be taken into account. This leads to a negative sign in the interaction term of the energy eigenvalue.

DEGENERACY OF THE ENERGY EIGENVALUES

We consider the complex conjugate of the coefficient:

$$c_{\text{conj}}(\lambda, j) := \sqrt{\frac{1}{N}} \cdot \exp\left(-i \cdot 2 \cdot \pi \cdot \frac{\lambda}{N} \cdot j\right)$$

The fourth equation in the above derivation shows that identical solutions result for $c(\lambda, j)$ as well as for $c_{\text{conj}}(\lambda, j)$ and that therefore the wave functions for $c(\lambda, j)$ and for $c_{\text{conj}}(\lambda, j)$ have the same energy (if the value of j does not cause the two kinds of coefficients and hence the MOs to become equal).

Most of the energy levels are therefore expected to be doubly degenerate, i.e. for one energy two linearly independent eigenfunctions exist.

Any linear combination of two eigenfunctions to the same (energy) eigenvalue is also an eigenfunction to this (energy) eigenvalue.

We can therefore create other eigenfunctions by forming linear combinations of the above MOs. It is desirable to find linear combinations which are real, because real functions can be visualized.

The following linear combinations convert the two complex wave functions ψ and ψ_{conj} to the real wave functions ψ_1 and ψ_2 :

$$\psi_1 = \frac{1}{2} \cdot (\psi + \psi_{\text{conj}})$$

$$\psi_2 = \frac{1}{2i} \cdot (\psi - \psi_{\text{conj}})$$

This can easily be seen:

$$\Psi = c(0,j) \cdot p_{\pi}(0) + c(1,j) \cdot p_{\pi}(1) + \dots + c(N-1,j) \cdot p_{\pi}(N-1)$$

$$\Psi_{\text{conj}} = c_{\text{conj}}(0,j) \cdot p_{\pi}(0) + c_{\text{conj}}(1,j) \cdot p_{\pi}(1) + \dots + c_{\text{conj}}(N-1,j) \cdot p_{\pi}(N-1)$$

$$\Psi_1 = \frac{1}{2} \cdot (c(0,j) + c_{\text{conj}}(0,j)) \cdot p_{\pi}(0) + \frac{1}{2} \cdot (c(1,j) + c_{\text{conj}}(1,j)) \cdot p_{\pi}(1) + \dots + \frac{1}{2} \cdot (c(N-1,j) + c_{\text{conj}}(N-1,j)) \cdot p_{\pi}(N-1)$$

$$\Psi_2 = (1/2i) \cdot (c(0,j) - c_{\text{conj}}(0,j)) \cdot p_{\pi}(0) + (1/2i) \cdot (c(1,j) - c_{\text{conj}}(1,j)) \cdot p_{\pi}(1) + \dots + (1/2i) \cdot (c(N-1,j) - c_{\text{conj}}(N-1,j)) \cdot p_{\pi}(N-1)$$

A short consideration shows that the following equations hold:

$$\frac{1}{2} \cdot (c(\lambda, j) + c_{\text{conj}}(\lambda, j)) \equiv \sqrt{\frac{1}{N}} \cdot \cos\left(2 \cdot \pi \cdot \frac{\lambda}{N} \cdot j\right)$$

$$\frac{1}{2 \cdot i} \cdot (c(\lambda, j) - c_{\text{conj}}(\lambda, j)) \equiv \sqrt{\frac{1}{N}} \cdot \sin\left(2 \cdot \pi \cdot \frac{\lambda}{N} \cdot j\right)$$

Simplification leads to:

$$\Psi_1(j) = \sum_{\lambda} \sqrt{\frac{1}{N}} \cdot \cos\left(2 \cdot \pi \cdot \frac{\lambda}{N} \cdot j\right) \cdot p_{\pi}(\lambda)$$

$$\Psi_2(j) = \sum_{\lambda} \sqrt{\frac{1}{N}} \cdot \sin\left(2 \cdot \pi \cdot \frac{\lambda}{N} \cdot j\right) \cdot p_{\pi}(\lambda)$$

This means that the real MO coefficients introduced first and sketched above produce linearly independent real MOs of the correct energy.

The values of these coefficients can easily be obtained by taking the real or the imaginary part of the

complex coefficient $c(\lambda, j) = \sqrt{\frac{1}{N}} \cdot \exp\left(i \cdot 2 \cdot \pi \cdot \frac{\lambda}{N} \cdot j\right)$.

DERIVATION OF THE NUMBER OF STABILIZED MOs IN RINGS WITH $4n + 2\pi$ ELECTRONS

The energy eigenvalues are given by the following formula:

$$\varepsilon(j) = \alpha + 2\beta \cdot \cos\left(\frac{j \cdot 2 \cdot \pi}{N}\right)$$

Algebraic proof of the degeneracy of the energy levels in rings

We show that $\varepsilon(j) = \varepsilon(N - j)$ for j ranging from 1 to $N - 1$:

$$\varepsilon(N - j) = \alpha + 2\beta \cdot \cos\left[\frac{(N - j)2\pi}{N}\right]$$

$$\varepsilon(N - j) = \alpha + 2\beta \cdot \cos\left(2\pi - \frac{j2\pi}{N}\right)$$

$$\varepsilon(N - j) = \alpha + 2\beta \cdot \cos\left(\frac{j2\pi}{N}\right)$$

$$\varepsilon(N - j) = \varepsilon(j)$$

The degeneracy vanishes when $N - j = j$, i.e. when $j = N/2$. Therefore the highest energy level for even values of N is not degenerate, while for odd values of N all but the lowest energy level are degenerate.

Number of stabilized MOs with respect to α

It will do to find the largest value of $j < N/2$ for which $\varepsilon(j) < \alpha$ holds. Because of the degeneracy of the energy levels the number of stabilized MOs will be known then:

$$\begin{aligned} \varepsilon(j) &< \alpha \\ \alpha + 2\beta \cdot \cos\left(\frac{j \cdot 2 \cdot \pi}{N}\right) &< \alpha \\ \cos\left(\frac{j \cdot 2 \cdot \pi}{N}\right) &> 0 && (\beta \text{ is negative.}) \\ \frac{j \cdot 2 \cdot \pi}{N} < \frac{\pi}{2} \quad \text{or} \quad \frac{j \cdot 2 \cdot \pi}{N} > \frac{3\pi}{2} && \left(0 \leq \frac{j \cdot 2\pi}{N} < 2\pi\right) \\ j < \frac{1}{4}N \quad \text{or} \quad j > \frac{3}{4}N && \end{aligned}$$

The right condition can be ignored since $3N/4 > N/2$. Hence this condition provides no information about the number of stabilized MOs not provided by the left condition.

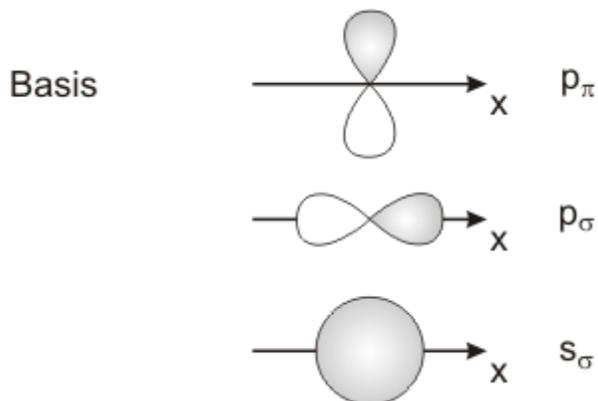
Hence if $N = 4k$ (k natural) there are $1 + 2(k-1) = 2k - 1$ stabilized MOs.
(One MO for $j = 0$, two degenerate MOs for $j = 1, 2, \dots, k-1$)

If $N = 4k + m$ with $m = 1, 2$ or 3 , there are $1 + 2k = 2k + 1$ stabilized MOs.
(One MO for $j = 0$, two degenerate MOs for $j = 1, 2, \dots, k$)

CHANGE OF SIGN IN THE FORMULA FOR THE p_σ ENERGY EIGENVALUES

In our approach the p_π , p_σ and s_σ basis functions have the shapes shown below.

The p_π and s_σ orbitals both are symmetric relative to a plane extending perpendicularly to the x axis drawn in the following orbital sketch, while the p_σ orbitals are antisymmetric relative to this plane:



The ZDO approximation does not automatically take this change in symmetry into account. Consequently, we have to keep this in mind when deriving the formula for the energy eigenvalues. This is not necessary if the symmetry of the AOs is explicitly taken into account when the overlap integral is actually calculated, as e.g. in BICON-CEDiT [5], because then the sign of the interaction term in the formula for the energy eigenvalues is always correct.

HINT TO PROBLEM 4.3

Starting with the Schrödinger equation, one finds:

$$\varepsilon_B(k) \cdot \langle \Psi_B(k) | \Psi_B(k) \rangle = \langle \Psi_B(k) | H | \Psi_B(k) \rangle$$

Where:

$$\overline{\Psi_B(k)} = \sqrt{\frac{1}{N}} \left[\overline{\phi_0} + e^{-i \cdot k \cdot a} \cdot \overline{\phi_1} + e^{-i \cdot k \cdot a \cdot 2} \cdot \overline{\phi_2} + \dots + e^{-i \cdot k \cdot a \cdot (N-1)} \cdot \overline{\phi_{(N-1)}} \right]$$

$$\Psi_B(k) = \sqrt{\frac{1}{N}} \left[\phi_0 + e^{i \cdot k \cdot a} \cdot \phi_1 + e^{i \cdot k \cdot a \cdot 2} \cdot \phi_2 + \dots + e^{i \cdot k \cdot a \cdot (N-1)} \cdot \phi_{N-1} \right]$$

(Here a complex Bloch function has been used and not one of the real linear combinations. For the calculation of the energy eigenvalues, this makes things easier and does not change the result.)

In the ZDO approximation the following is valid (consider why!):

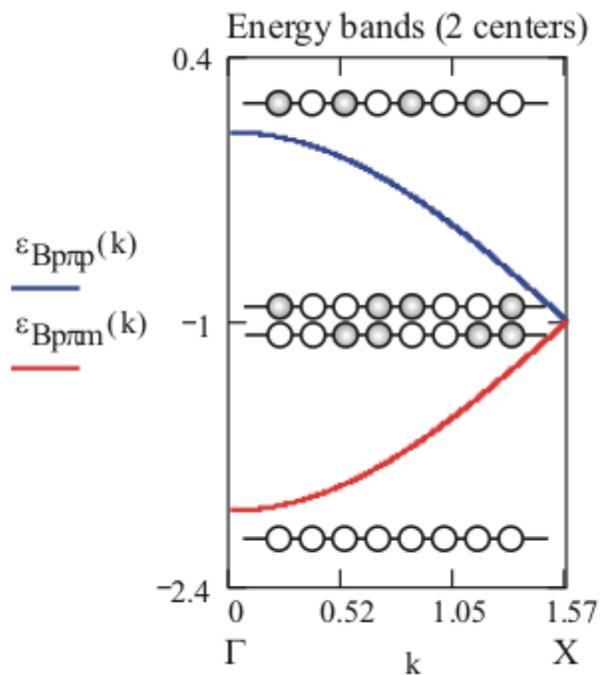
$$\langle e^{i \cdot k \cdot a \cdot \lambda} \cdot \phi_\lambda | H | e^{i \cdot k \cdot a \cdot \mu} \cdot \phi_\mu \rangle = \alpha \cdot \delta(\lambda, \mu) \cdot e^0 + \beta \cdot \delta(\lambda, \mu \mp 1) \cdot e^{i \cdot k \cdot a \cdot (\mp 1)}$$

Evaluating the equation using this relation and using the fact that in a ring every atom has two neighbors, the formula for the energy eigenvalues follows.

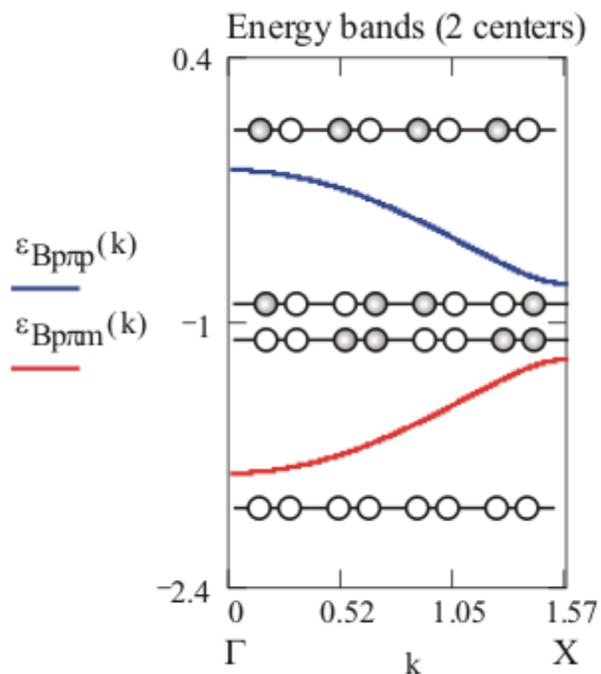
SOLUTION TO PROBLEM 5.5

We describe the orbital situation at special points of the bands. The instability of the orbitals increases from bottom to top. At lowest energy we have only bonding nearest neighbor interactions, at highest energy the nearest neighbour interactions are all antibonding.

First we visualize the situation without Peierls distortion, i.e. the situation for $\beta_1 = \beta_2$. The need for a degeneracy of the two bands at the X point is obvious, since the two orbital patterns can be transformed one into the other by translation. (Remember that we are dealing with infinitely long chains.)



The next graph shows the effect of the Peierls distortion ($\beta_1 \neq \beta_2$). The distance between two atoms is no longer constant. Again there are only bonding interactions at lowest energy and only antibonding interactions at highest energy. Of course the energies at these points differ a little bit from the corresponding energies in the situation above, but not too much. However, on the right side of the graph a much stronger effect is found: The formerly degenerate bands split up significantly. At the X point we must have a stabilized and a destabilized orbital situation. This can easily be explained by realizing that due to the alternating bond lengths in one case the bonding interactions dominate, while in the other case the antibonding interactions dominate:

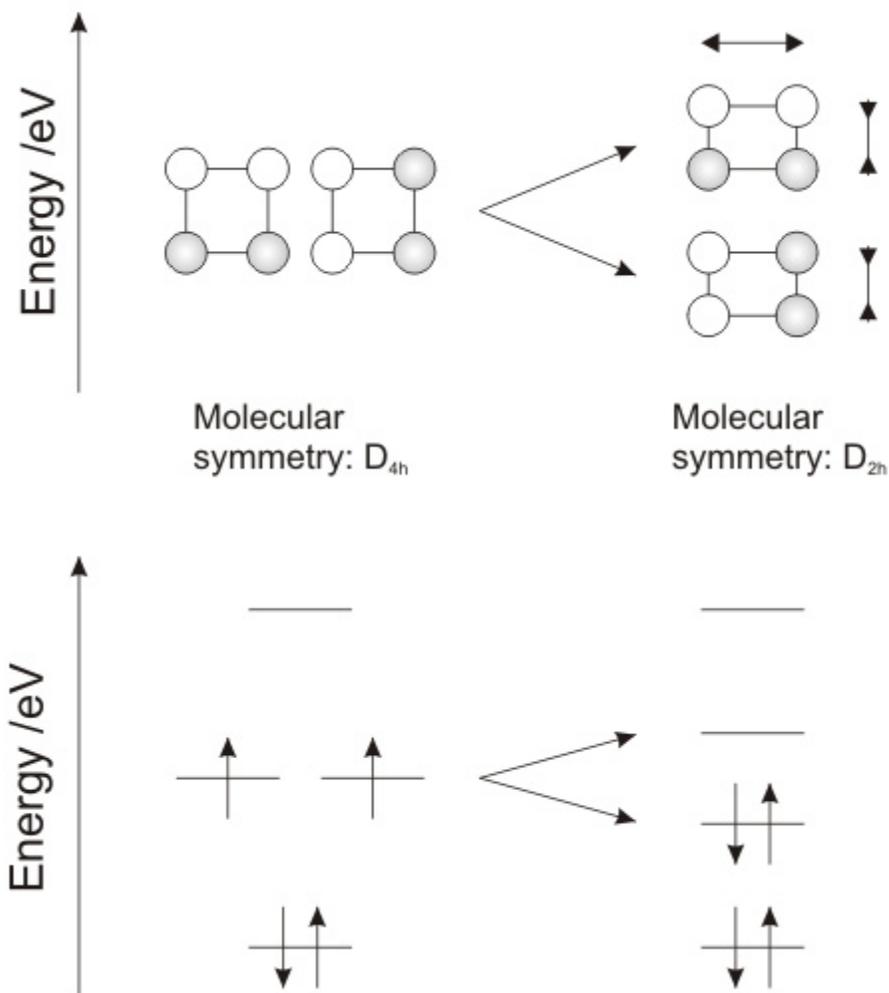


THE JAHN-TELLER EFFECT

The **JAHN-TELLER EFFECT** plays an important role in chemistry and physics. The Jahn-Teller theorem predicts an instability for degenerate states of nonlinear molecules. The framework of the molecule will be distorted in a way that the degeneracy is broken, if thereby the energy can be lowered.

Below we give cyclobutadiene as an example. In a molecule of D_{4h} symmetry doubly degenerate energy levels would occur. The first figure shows on the left side the two degenerate π MOs of cyclobutadiene, as seen from above. Note that these MOs are equivalent linear combinations of the MOs of cyclobutadiene found in section 2. According to the Jahn-Teller theorem this situation is not stable, and consequently a distortion to D_{2h} symmetry with the corresponding splitting of the energy levels is observed, as seen on the right side. The second figure visualizes the splitting of the energy levels in an energy level chart.

Note that the splitting of the energy levels occurs because here the two MOs are occupied with two electrons. Therefore the splitting yields a fully occupied MO at lower energy and an unoccupied MO at higher energy. If the two MOs were fully occupied, no stabilization would result through the splitting, and the degenerated situation would be favored. This is the situation occurring in benzene.



ORIGINAL VALUES OF THE COULOMB AND RESONANCE INTEGRALS IN SECTION 6

$$\begin{array}{lll} \alpha_{s\sigma} := -5 & \beta_{s\sigma 1} := -1 & \beta_{s\sigma 2} := -1 \\ \alpha_{p\sigma} := -1 & \beta_{p\sigma 1} := -0.9 & \beta_{p\sigma 2} := -0.6 \\ \alpha_{p\pi} := -1 & \beta_{p\pi 1} := -0.5 & \beta_{p\pi 2} := -0.4 \end{array}$$

SOLUTION TO PROBLEM 6.3

$$a := 1 \quad \alpha := -5 \quad \beta_1 := -1 \quad \beta_2 := -1 \quad \text{Values for the } p_\pi \text{ orbitals}$$

$$N := 3 \quad \lambda := 0..N-1 \quad \mu := 0..N-1$$

Note:

$$\psi_{1B}(k) := \sum_{\lambda=0}^{N-1} c_{1B}(\lambda, k) \cdot \phi_{1, \lambda} \quad \psi_{2B}(k) := \sum_{\mu=0}^{N-1} c_{2B}(\mu, k) \cdot \phi_{2, \mu}$$

$$\Psi(k) := C_1 \cdot \psi_{1B}(k) + C_2 \cdot \psi_{2B}(k)$$

COs at the Γ point:

$$k := 0$$

$$H_{12}(k) := \exp(-i \cdot k \cdot 2a) \cdot \beta_1 + \beta_2 \quad H_{21}(k) := \exp(i \cdot k \cdot 2a) \cdot \beta_1 + \beta_2$$

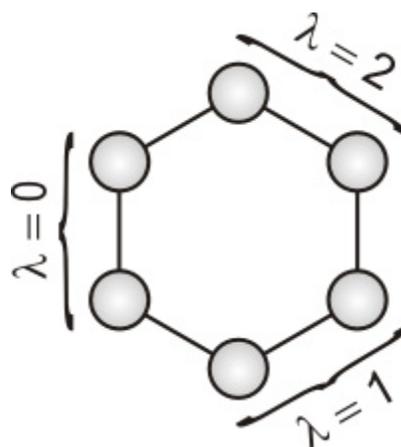
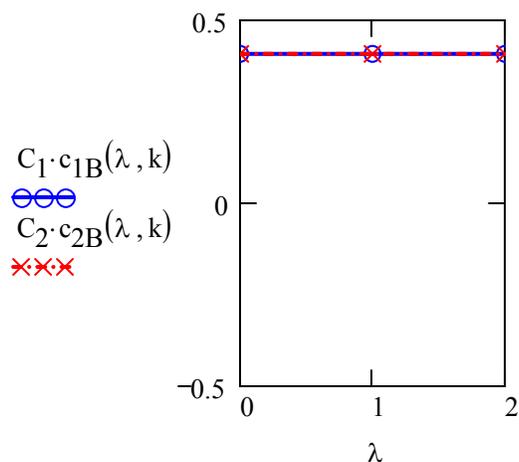
$$\text{EVal} := \text{eigenvals} \left(\begin{pmatrix} \alpha & H_{12}(k) \\ H_{21}(k) & \alpha \end{pmatrix} \right) \quad \text{EVal} = \begin{pmatrix} -3 \\ -7 \end{pmatrix}$$

$$\text{EV} := \text{eigenvecs} \left(\begin{pmatrix} \alpha & H_{12}(k) \\ H_{21}(k) & \alpha \end{pmatrix} \right) \quad \text{EV} = \begin{pmatrix} 0.707 & 0.707 \\ -0.707 & 0.707 \end{pmatrix}$$

Solution for the eigenvalue $E_{Val_1} = -7$:

$$C_1 := EV_{0,1} \quad C_1 = 0.707 \quad C_2 := EV_{1,1} \quad C_2 = 0.707$$

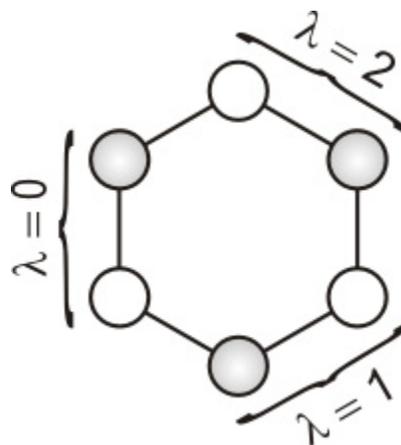
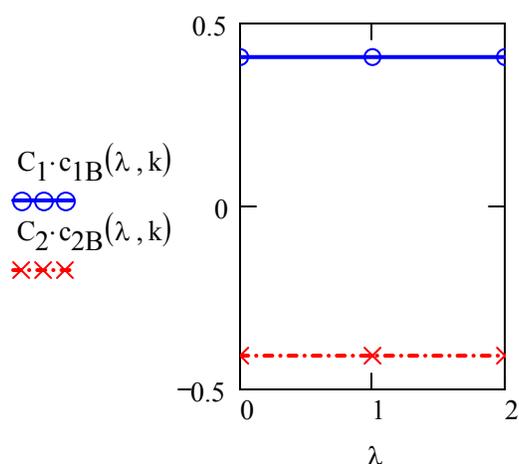
$$c_{1B}(\lambda, k) := \sqrt{\frac{1}{N}} \cdot \exp(i \cdot k \cdot 2a \cdot \lambda) \quad c_{2B}(\mu, k) := \sqrt{\frac{1}{N}} \cdot \exp(i \cdot k \cdot 2a \cdot \mu)$$



Solution for the eigenvalue $E_{Val_0} = -3$:

$$C_1 := EV_{0,0} \quad C_1 = 0.707 \quad C_2 := EV_{1,0} \quad C_2 = -0.707$$

$$c_{1B}(\lambda, k) := \sqrt{\frac{1}{N}} \cdot \exp(i \cdot k \cdot 2a \cdot \lambda) \quad c_{2B}(\mu, k) := \sqrt{\frac{1}{N}} \cdot \exp(i \cdot k \cdot 2a \cdot \mu)$$



COs at the X point:

$$k := \frac{\pi}{2a}$$

$$\beta_2 := \beta_2 + 10^{-5} \quad \text{Mathcad encounters problems for } \beta_1 = \beta_2.$$

$$H_{12}(k) := \exp(-i \cdot k \cdot 2a) \cdot \beta_1 + \beta_2 \quad H_{21}(k) := \exp(i \cdot k \cdot 2a) \cdot \beta_1 + \beta_2$$

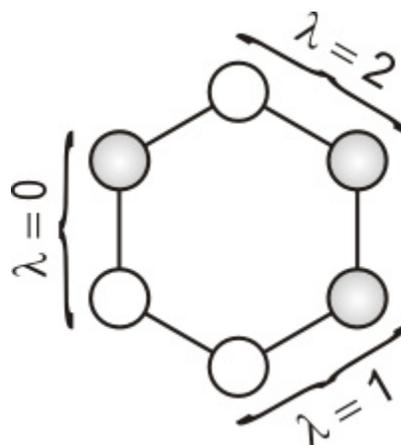
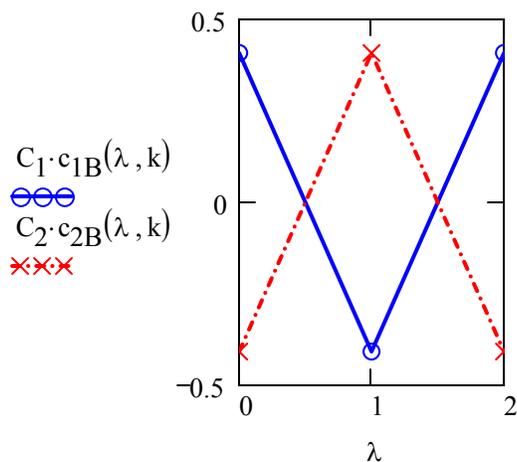
$$\text{EVal} := \text{eigenvals} \left(\begin{pmatrix} \alpha & H_{12}(k) \\ H_{21}(k) & \alpha \end{pmatrix} \right) \quad \text{EVal} = \begin{pmatrix} -5 \\ -5 \end{pmatrix}$$

$$\text{EV} := \text{eigenvecs} \left(\begin{pmatrix} \alpha & H_{12}(k) \\ H_{21}(k) & \alpha \end{pmatrix} \right) \quad \text{EV} = \begin{pmatrix} 0.707 & 0.707 \\ -0.707 & 0.707 \end{pmatrix}$$

Solution for the eigenvalue $\text{EVal}_0 = -5$:

$$C_1 := \text{EV}_{0,0} \quad C_1 = 0.707 \quad C_2 := \text{EV}_{1,0} \quad C_2 = -0.707$$

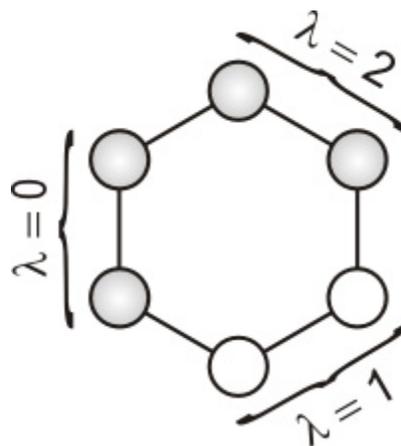
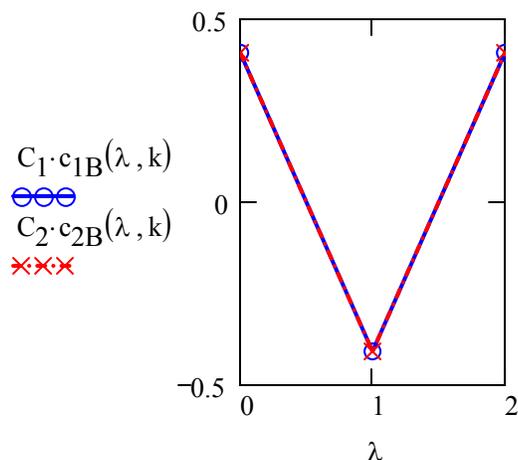
$$c_{1B}(\lambda, k) := \sqrt{\frac{1}{N}} \cdot \exp(i \cdot k \cdot 2a \cdot \lambda) \quad c_{2B}(\mu, k) := \sqrt{\frac{1}{N}} \cdot \exp(i \cdot k \cdot 2a \cdot \mu)$$



Solution for the eigenvalue $E_{\text{Val}1} = -5$:

$$C_1 := EV_{0,1} \quad C_1 = 0.707 \quad C_2 := EV_{1,1} \quad C_2 = 0.707$$

$$c_{1B}(\lambda, k) := \sqrt{\frac{1}{N}} \cdot \exp(i \cdot k \cdot 2a \cdot \lambda) \quad c_{2B}(\mu, k) := \sqrt{\frac{1}{N}} \cdot \exp(i \cdot k \cdot 2a \cdot \mu)$$



The COs of benzene at the X point do not correspond to any MOs of benzene since the X point corresponds to $k = \pi/2a$, i.e. to $j = 3/2$. However, there is no MO at a non-integer value of j ! The COs at the X point can therefore be imagined as virtual MOs, energetically lying in the middle between the MOs belonging to $j = 1$ and $j = 2$ (cf. section 2). This prediction can easily be verified by recognizing that the energy of such MOs must be equal to α (cf. section 2). This is in agreement with the energy of the COs at the X point resulting from the formula in section 6.

The COs at the X point have the same energy. Hence the number of bonding and antibonding interactions should be equal. Furthermore, the CO coefficients of the 2 centers should change their sign from unit cell to unit cell since the X point corresponds to the highest k-vector, thus representing a situation with a node between every two unit cells.

Both properties are not fulfilled. This is a consequence of the fact that the benzene ring is not an extended system. However, the theory we have developed is only suitable to describe extended structures. (The Bloch theorem, on which the theory is based, refers to infinitely large rings!)

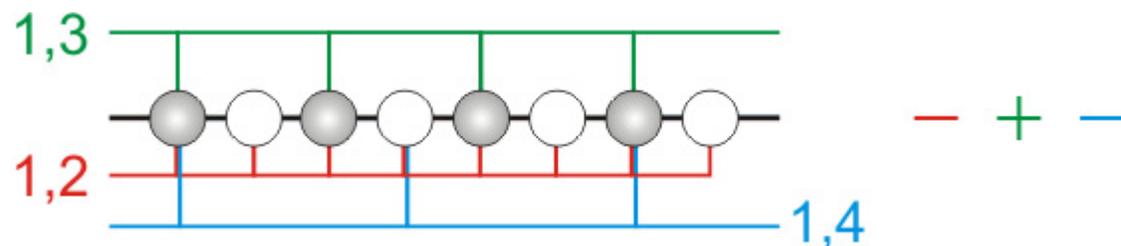
Hence, the above properties are only fulfilled if the ring is cut between unit cells 0 and 2.

To conclude, the fact that the ring ends join already after the third unit cell and not after an infinite number of unit cells results in the loss of the two properties mentioned.

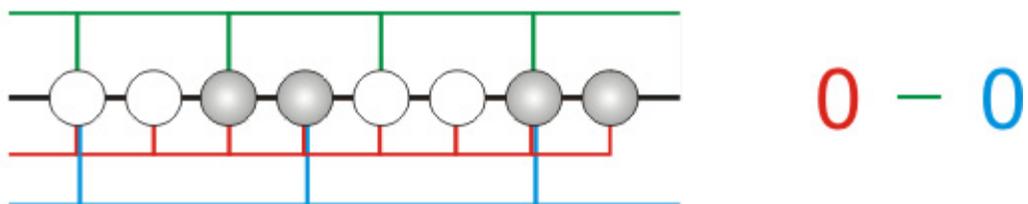
SOLUTION TO PROBLEM 8.1

We show the nearest neighbor interactions ($\text{COOP}_{2p\pi}$) in red, the 1-3 interactions ($\text{COOP}_{3p\pi}$) in green and the 1-4 interactions ($\text{COOP}_{4p\pi}$) in blue. On the right side the positive, negative or neutral total contribution of the corresponding interaction is shown.

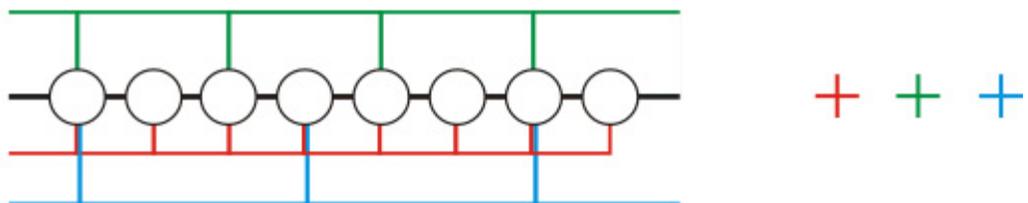
$k = \pi/a$:



$k = \pi/2a$:



$k = 0$:



THE COORDINATES IN RECIPROCAL SPACE

Note that in the figure the coordinates of point X are $(0, 1/2)$ whereas in the 1D case (sections 5 and 6) we stated that X lies at coordinate π/a .

In the first notation X is written relative to the basis of the reciprocal lattice, whereas in the second notation X is written relative to the canonical basis. The notations are consistent:

$$\mathbf{X} = (0, 1/2)_b = 0 \cdot \mathbf{b}_x + 1/2 \cdot \mathbf{b}_y = 0 \cdot (2\pi/a_x, 0)_e + 1/2 \cdot (0, 2\pi/a_y)_e = (0, \pi/a_y)_e.$$

A similar question is what we mean if we talk about the components k_x and k_y of the k-vector.

K-vectors are defined relative to the basis of reciprocal space: $\mathbf{k} = (\mu_x, \mu_y)_b$

If we express \mathbf{k} relative to this basis, then $\mu_x, \mu_y \in] -1/2, 1/2]$ for the whole first Brillouin zone in the 2D cubic lattice case.

If we express \mathbf{k} relative to the canonical basis, we get:

$$\mathbf{k} = \mu_x \cdot \mathbf{b}_x + \mu_y \cdot \mathbf{b}_y = \mu_x \cdot (2\pi/a_x, 0)_e + \mu_y \cdot (0, 2\pi/a_y)_e = (\mu_x \cdot 2\pi/a_x, \mu_y \cdot 2\pi/a_y)_e.$$

We call the first component of \mathbf{k} k_x and the second component k_y .

$$\text{Hence: } k_x = \mu_x \cdot 2\pi/a_x \in] -\pi/a_x, \pi/a_x]$$

$$k_y = \mu_y \cdot 2\pi/a_y \in] -\pi/a_y, \pi/a_y]$$

To conclude:

k_x and k_y are the x- and the y-component of the k-vector relative to the canonical basis.

(This is consistent with the way the k-vector has been defined in the 1D case: In section 4 we

have defined: $k := \frac{2 \cdot \pi}{N \cdot a} \cdot j = \frac{j}{N} \cdot \frac{2 \cdot \pi}{a} = \mu \cdot \frac{2 \cdot \pi}{a}$ or $k := \mu \cdot b$ with $\mu \in [0, 1/2]$ and $k \in [0, \pi/a]$

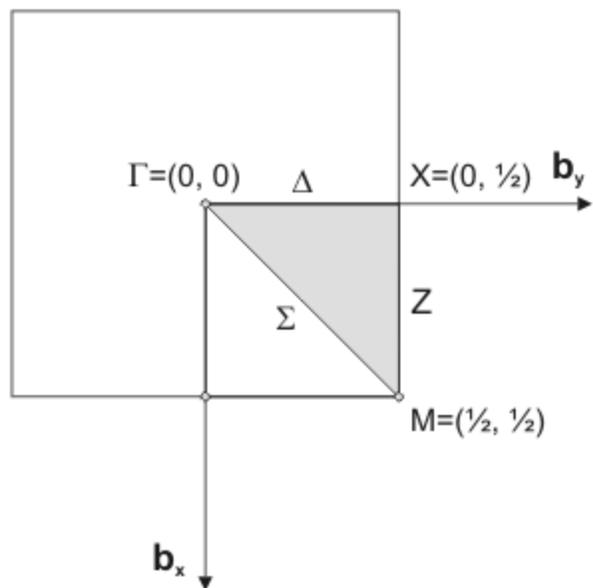
Finally, one should be aware of the fact that $e^{i \cdot \mathbf{k} \cdot \mathbf{a} \cdot \lambda}$ is the linear phase factor, resulting from

Bloch's theorem. Its general form is $e^{i \cdot \mathbf{k} \cdot \mathbf{T}}$, where $\mathbf{k} = \mu_x \cdot \mathbf{b}_x + \mu_y \cdot \mathbf{b}_y$ is the wave vector, and \mathbf{T} is a translation vector of the direct lattice which here has the form

$$\mathbf{T} = \lambda_x \cdot \mathbf{a}_x + \lambda_y \cdot \mathbf{a}_y = \lambda_x \cdot (a_x, 0) + \lambda_y \cdot (0, a_y) = (\lambda_x \cdot a_x, \lambda_y \cdot a_y)$$

The special notation for the translation vector $\mathbf{a} \cdot \lambda$ using a matrix was chosen to keep the notation of the phase factor equivalent to its notation in the 1D case.

THE FIRST BRILLOUIN ZONE FOR THE TWO DIMENSIONAL CARBON LATTICE



SUMMARY

SECTIONS 1 TO 3

Linear chains and rings, built of N carbon atoms, are considered.

In a first step the MOs resulting from only the $2p_z$ atomic orbitals are of interest. The $2p_z$ AOs are oriented perpendicularly to the plane of the worksheet, while the chain and the ring lie in this plane. Hence the MOs resulting are π MOs and, consequently, the p_z AOs are henceforth called p_π AOs.

Using the LCAO-MO method in the ZDO approximation, the energy eigenvalues and the MOs are derived that describe these two systems.

In both cases the number of nodes increases with the energy level. On the lowest level there are no nodes, on the highest level there is a node between any two carbon atoms.

In chains no energy level is degenerate. In odd-membered rings all but the lowest and in even-membered rings all but the lowest and the highest energy level are doubly degenerate.

The separation of the energy levels decreases with an increasing number of atoms forming the chain or the ring.

The Hückel rule is discussed.

In a second step the basis is augmented with $2s$, $2p_x$, and $2p_y$ orbitals, resulting in four basis functions, two of which are degenerate: The $2p_y$ orbitals are, with respect of forming molecular orbitals and their energies, indistinguishable from the $2p_z$ orbitals in non-alternating chains and rings. Hence both orbital types are summarized as p_π AOs, while the $2s$ orbitals are denoted as s_σ orbitals and the $2p_x$ orbitals as p_σ AOs.

The qualitative difference between the energy vs. MO index curves for the different basis functions is that the curve for MOs formed from p_σ AOs falls with increasing MO index, while the other curves rise. This is because of the different symmetry of the p_σ basis function with respect to the symmetry of the s_σ and the p_π basis functions.

A comparison between chains and rings shows that the energy vs. MO index curves for a particular basis function have a similar course.

Since the curvature of a ring approaches zero when its radius approaches infinity, any intercept of an infinitely large ring is undistinguishable from a segment of a linear chain.

In an infinite chain edge phenomena do not exist. However, the linear chain approach made in chapters 2 and 3 will always produce wave functions with typical edge phenomena, no matter how many atoms are included in the calculation.

Since it is the goal of this course to describe extended systems, i.e. systems consisting of an infinite number of atoms, it is therefore favorable to use rings and let the ring size approach infinity.

SECTIONS 4 TO 8

The description of extended systems is based on Bloch's theorem which states that the wave function (for a given basis function and a given energy eigenvalue) of an infinitely large ring has such a form that it only differs by a constant phase factor between neighboring ring positions.

The Bloch functions / orbitals describe the wave function at a given ring position in agreement with this requirement.

MOs for extended systems, built of Bloch functions, are called crystal orbitals. They are no longer functions of a discrete MO index, as MOs are. Instead, they are functions of the continuous wave-vector or k-vector k , which can be imagined as a symmetry label of the crystal orbitals. In the one-dimensional case the k-vectors belonging to all possible COs form the interval $[0, \pi/a]$, which corresponds to half the first Brillouin zone of reciprocal space. $k = 0$ represents the most bonding crystal orbital, $k = \pi/a$ the most antibonding CO with respect to the chosen basis.

Since in extended systems there is an infinite number of energy levels, the plot showing the CO energy as a function of the k-vector results in a continuous curve, which is called an energy band.

The superposition of the energy bands of several / all basis functions of interest is called a band structure diagram. In such a diagram one can see in what energy regions the COs of the various basis functions lie.

A difficulty of band structure diagrams is that they hide information that MO energy level diagrams immediately provide, namely, the information in which energy regions the number of energy levels is higher and where it is lower. This information is provided by density of states (DOS) diagrams.

$DOS(E)dE$ is the number of energy levels between E and $E+dE$.

As a consequence of this definition, the inverse of the slope of an energy band is equal to the DOS. A good mnemonic is to keep in mind that the flatter an energy band for a basis function is at a certain energy, the larger is its DOS at this energy.

Integration of the DOS up to the Fermi level results in the total number of occupied COs.

The great benefit of the DOS is that the superposition of all DOS curves of a band structure is a diagram analogous to the familiar energy level charts used when dealing with molecules. It visualizes how many energy levels exist in a certain energy region of an extended structure.

The crystal orbital overlap population (COOP) is an overlap population weighted density of states.

COOP curves visualize the density of bonding or antibonding interactions between basis functions of a specific type as a function of energy. Regions with positive COOP contributions are bonding, regions with negative COOP contributions are antibonding.

COOPs can describe specific interactions (e.g. 1,3-interactions) or the sum of all interactions, if all non-zero COOPs are added. In the latter case one talks about the total COOP.

The integral of $COOP(E)$ with respect to energy up to the Fermi level is the total overlap population of all occupied energy levels for the specified interaction. If the total COOP is integrated up to the Fermi level, the result is the total overlap population of a specific basis function.

Many extended systems show a behavior which indicates that there are two or more sets of non-equivalent atoms. Hence there are also two or more sets of non-equivalent basis functions. Such a system is polyacetylene, a substance with alternating C-C bond lengths, a phenomenon that can not be described with one set of equivalent atoms.

In cases like these more than one atom is contained in the unit cell. The Coulomb and resonance integrals of the basis orbitals of these atoms can be chosen independently in order to model the situation observed. The crystal orbitals for the non-equivalent basis orbitals are formulated separately, and linear combinations of these crystal orbitals are formed in such a way that energy is minimized. The resulting energy bands show the phenomenon of back-folding: Because of the increased size of the unit cell, the Brillouin zone gets smaller. Consequently, the energy bands have to fold back one or several times to fit in the smaller Brillouin zone.

The non-equivalence of the basis orbitals can also lead to a splitting of the energy bands at the folding points. This phenomenon is called Peierls distortion. It is a special case of the Jahn-Teller distortion observed in molecules.

INTRODUCTION TO BASIC TERMS OF BAND STRUCTURES[©]

INSTRUCTIONS FOR TEACHERS

Marc Meyer, Stephan Glaus, and Gion Calzaferri
University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

Goals

Why is graphite black and an electric conductor, while diamond is colorless and an insulator?

Why is the silver sulphide molecule Ag_2S 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 π molecular orbitals (MOs) of finite linear chains and rings are calculated.
- ✚ sketch the π 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 π 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_π AOs but also using p_σ , and s_σ 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_π , p_σ , and s_σ 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_π 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 6th 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.

Contact

Gion Calzaferri
Department of Chemistry and Biochemistry,
University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland
E-Mail gion.calzaferri@iac.unibe.ch
Tel. +41 31 631 42 36
Fax +41 31 631 39 94

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