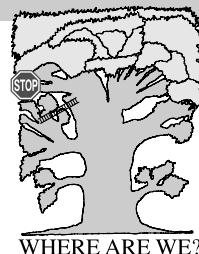


Chapter 9

ELECTRONIC MOTION IN THE MEAN FIELD: PERIODIC SYSTEMS



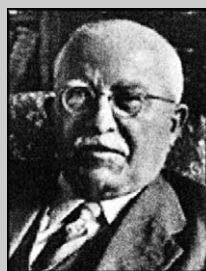
Where are we?

We are on the upper left branch of the TREE.

An example

Polyacetylene is an example of new technologically interesting materials¹ and represents a *practically* infinite polymeric chain:² $\dots\text{--CH=CH--CH=CH--CH=CH--CH=CH--}\dots$. There is no such a thing in Nature as an infinite system. Yet, if we examine larger and larger portions of a homogeneous material, we come to the idea that such quantities as energy per stoichiometric unit, electron excitation energy, vibrational frequencies, etc. depend less and less on system size. This means that a boundary-region (polymer ends, crystal surface) contribution to these quantities becomes negligible. Therefore, these (known as *intensive*) quantities attain limit values identical to those for an infinite system. *It pays to investigate the infinite system, because we can use its translational symmetry.*

Herman Staudinger (1881–1965), German polymer chemist, professor at the University of Freiburg, received the Nobel Prize in 1953 “for his discoveries in the field of macromolecular chemistry”. However strange it may sound now, as late as 1926 the concept of polymers was unthinkable in chemistry. It will be encouraging for PhD students to read that a professor advised Staudinger in the late 1920s: “Dear colleague, leave the concept of large molecules well alone: organic molecules with a molecular weight above 5000 do not exist. Purify your products, such as rubber, then they



will crystallise and prove to be lower molecular substances.”

¹The discovery of conducting polymers was highlighted by the Nobel Prize 2000 for Hideki Shirakawa (who synthesized a crystalline form of polyacetylene) as well as Allan G. MacDiarmid and Allan J. Heeger, who increased its electric conductivity by 18 orders of magnitude by doping the crystal with some electron acceptors and donors. This incredible increase is probably the largest known to humanity in any domain of experimental sciences (H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang, A.J. Heeger, *Chem. Soc. Chem. Commun.* 578 (1977)).

²That is, a macromolecule. The concept of polymer was introduced to chemistry by Herman Staudinger.

We would like to know whether polyacetylene represents a metal, a semiconductor or an insulator, and how its properties change upon doping. For the time being we have at our disposal the Hartree–Fock method, but it seems to be useless here, because the number of electrons and nuclei is infinite. We may cut out a finite section from the infinite polyacetylene chain and to saturate the resulting dangling bonds by hydrogen atoms, e.g., $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$. Calculations for such a molecule of manageable size will not give us the expected answers, because we will first meet bankruptcy. We take pains to compute integrals involving atomic orbitals, but the vast majority of the most essential of them are already in our pocket. It would certainly pay to take into account the translational symmetry of the infinite system.

What is it all about

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Choice of unit cell (✕)**p. 488**

- Field compensation method
- The symmetry of subsystem choice

If a motif (e.g., a cluster of atoms) associated with a unit cell is *regularly translated along three different directions in space*, we obtain an infinite periodic structure (with translational symmetry).

When applying the Hartree–Fock method to such periodic infinite objects one is forced to exploit the translational symmetry of the system, e.g., in calculating integrals. It would indeed be prodigal to compute the integrals many times, the equality of which is *guaranteed* by translational symmetry. When translational symmetry is taken into account, the problem reduces to the calculation of interaction of a single unit cell (reference labelled by 0) with all other unit cells, the nearest neighbour cells being most important. The infinite size of the system is hidden in the plethora of points (to be taken into account) in what is known as the First Brillouin Zone (FBZ). The FBZ represents a unit cell in what is called inverse lattice (associated with a given lattice reflecting the translation symmetry).

The electronic orbital energy becomes a function of the FBZ points and we obtain what is known as band structure of the energy levels. This band structure decides the electronic properties of the system (insulator, semiconductor, metal). We will also show how to carry out the mean field (Hartree–Fock) computations on infinite periodic systems. The calculations require infinite summations (interaction of the reference unit cell with the infinite crystal) to be made. This creates some mathematical problems, which will be also described in the present chapter.

Why is this important?

The present chapter is particularly important for those readers who are interested in solid state physics and chemistry. Others may treat it as exotic and, if they decide they do not like exotic stuff, may go directly to other chapters.

The properties of a polymer or a crystal sometimes differ very widely from those of the atoms or molecules of which they are built. *The same* substance may form *different* periodic structures, which have *different* properties (e.g., graphite and diamond). The properties of periodic structures³ could be computed by extrapolation of the results obtained for larger and larger clusters of the atoms from which the substance is composed. This avenue is however non-economic. It is easier to carry out quantum mechanical calculations for an infinite system,⁴ than for a large cluster.⁵

What is needed?

- Operator algebra (Appendix B, p. 895, necessary).
- Translation operator (Appendix C, p. 903, necessary).
- Hartree–Fock method (Chapter 8, necessary).

³Also aperiodic but homogeneous.

⁴The surface effects can be neglected and the units the system is composed of, turn out to be equivalent.

⁵Sometimes we may be interested in a particular cluster, not in an infinite system. Then it may turn out that it is more economic to perform the calculations for the infinite system, and use the results in computations for the clusters (e.g., R.A. Wheeler, L. Piela, R. Hoffmann, *J. Am. Chem. Soc.* 110 (1988) 7302).

- Multipole expansion (Appendix X, p. 1038, advised).
- Matrix diagonalization (Appendix K, p. 982, advised).

Classical works

At the age of 23, Felix Bloch published an article “*Über die Quantenmechanik der Elektronen in Kristallgittern*” in *Zeitschrift für Physik*, 52 (1928) 555 (only two years after Schrödinger’s historic publication) on the translation symmetry of the wave function. This result is known as the Bloch theorem. This was the first application of LCAO expansion. ★ A book appeared in 1931 by Leon Brillouin entitled *Quantenstatistik* (Springer Verlag, Berlin, 1931), in which the author introduced some of the fundamental notions of band theory. ★ The first *ab initio* calculations for a polymer were carried out by Jean-Marie André in a paper “*Self-Consistent Field Theory for the Electronic Structure of Polymers*” published in the *Journal of the Chemical Physics*, 50 (1969) 1536.

9.1 PRIMITIVE LATTICE

Let us imagine an *infinite crystal*, e.g., a system that exhibits the *translational symmetry* of charge distribution (nuclei and electrons). The translational symmetry will be fully determined by three (linearly independent) basis vectors:⁶ \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 having the property that \mathbf{a}_i beginning at any atom, extends to identically located atom of the crystal. The lengths of the basis vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 are called the *lattice constants* along the three periodicity axes.⁷

basis

lattice constant

There are many such basis sets possible. Any basis vectors choice is acceptable from the point of view of mathematics. For economic reasons we choose one of the possible vector sets that give the *least volume parallelepiped*⁸ with sides \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 . This parallelepiped (arbitrarily shifted in space,⁹ Fig. 9.1) represents *our* choice of the *unit cell*,¹⁰ which together with its content (motif) is to be translationally repeated.¹¹

unit cell

⁶Not necessarily perpendicular though; they determine the periodicity axes.

⁷As shown on p. 372, a symmetry of the nuclear framework does not guarantee the same symmetry of the electronic charge distribution computed using a mean field method. We may have cope with the period doubling as compared to the period of the nuclear framework (cf. BOAS, p. 8.5.2). If this happens, then we should choose such lattice constants that ensure the periodicity of both nuclear and electron distributions.

⁸Yes, because multiplicity of \mathbf{a}_i would also lead to unit cells that, when repeated, would reproduce the whole crystal. We are, however, interested in the smallest unit cell.

⁹The choice of the origin of the coordinate system is arbitrary, the basis vectors are determined within the accuracy of an arbitrary translation.

¹⁰An example of a jigsaw puzzle shows that other choices are possible as well. A particular choice may result from its convenience. This freedom will be used on p. 438.

¹¹The motif can be ascribed to the unit cell (i.e. chosen) in many different ways provided that after putting the cells together, we get the same original infinite crystal. Let me propose disregarding this problem for the time being (as well as the problem of the choice of the unit cell) and to think of the unit cell as a space-fixed *parallelepiped with the motif that has been enclosed in it*. We will come back to this complex problem at the end of the present chapter.

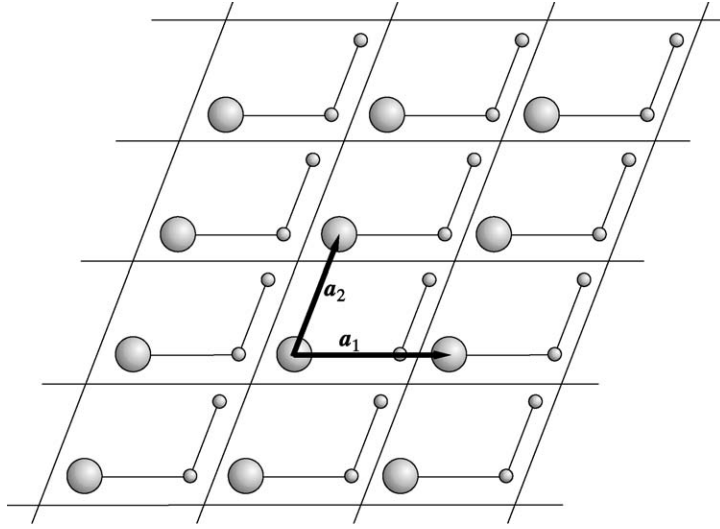


Fig. 9.1. Periodicity in 2D. We choose the unit cell (the parallelogram with vectors \mathbf{a}_1 and \mathbf{a}_2) and its content (motif) in such a way as to reproduce the whole infinite crystal by repeating the unit cells through its translation vectors $\mathbf{R}_i = n_1\mathbf{a}_1 + n_2\mathbf{a}_2$ with integers n_1, n_2 . In 3D instead of the parallelogram, we would have a parallelepiped, which would be repeated by translation vectors $\mathbf{R}_i = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ with integers n_1, n_2, n_3 .

motif

Let us now introduce the *space of translation vectors* $\mathbf{R}_i = \sum_{j=1}^3 n_{ij}\mathbf{a}_j$, where n_{ij} are *arbitrary integer numbers* (cf. Appendix B, p. 895).

The points indicated by all the translation vectors (“lattice vectors”) are called the *crystallographic lattice* or the *primitive lattice* or simply the *lattice*.

translation
operator

Let us introduce the *translation operators* $\hat{T}(\mathbf{R}_i)$ defined as translations of a *function*, on which the operator acts, by vector \mathbf{R}_i (cf. Chapter 2 and Appendix C on p. 903):

$$\hat{T}(\mathbf{R}_i)f(\mathbf{r}) = f(\mathbf{r} - \mathbf{R}_i). \quad (9.1)$$

The function $f(\mathbf{r}) \equiv f(\mathbf{r} - \mathbf{0})$ is centred in the neighbourhood of the origin of the coordinate system, while the function $f(\mathbf{r} - \mathbf{R}_i)$ is centred on the point shown by vector \mathbf{R}_i .

The crystal periodicity is reflected by the following property of the potential energy V for an electron (V depends on its position in the crystal):

$$V(\mathbf{r}) = V(\mathbf{r} - \mathbf{R}_i), \quad (9.2)$$

for any \mathbf{R}_i . The equation simply says that the infinite crystal looks exactly the same close to the origin O , as it does at the point shown by vector \mathbf{R}_i .

It is easy to see that the operators $\hat{T}(\mathbf{R}_i)$ form a *group* (Appendix C, p. 903) with respect to their multiplication as the group operation.^{12,13} In Chapter 2 it was shown that the Hamiltonian is invariant with respect to any translation of a molecule. For infinite systems, the proof looks the same for the kinetic energy operator, the invariance of V is guaranteed by eq. (9.2). Therefore, the effective one-electron Hamiltonian commutes with any translation operator:

$$\hat{H}\hat{T}(\mathbf{R}_i) = \hat{T}(\mathbf{R}_i)\hat{H}.$$

9.2 WAVE VECTOR

If $\hat{T}(\mathbf{R}_i)$ commutes with the Hamiltonian, its eigenfunctions also represent the eigenfunctions of the translation operator¹⁴ (cf. Chapter 2, p. 69, also Appendix C on p. 903), i.e. in this case $\hat{H}\psi = E\psi$ and $\hat{T}(\mathbf{R}_j)\psi(\mathbf{r}) = \psi(\mathbf{r} - \mathbf{R}_j) = \lambda_{\mathbf{R}_j}\psi(\mathbf{r})$. The symmetry of V requires the equality of the probability densities

$$|\psi(\mathbf{r} - \mathbf{R}_j)|^2 = |\psi(\mathbf{r})|^2, \quad (9.7)$$

for any lattice vector \mathbf{R}_j , which gives $|\lambda_{\mathbf{R}_j}|^2 = 1$, and therefore we may write:

$$\lambda_{\mathbf{R}_j} = \exp(-i\theta_{\mathbf{R}_j}), \quad (9.8)$$

where $\theta_{\mathbf{R}_j}$ will be found in a moment.¹⁵

¹²Indeed, first a product of such operators represents a translational operator:

$$\begin{aligned} \hat{T}(\mathbf{R}_1)\hat{T}(\mathbf{R}_2)f(\mathbf{r}) &= \hat{T}(\mathbf{R}_1)f(\mathbf{r} - \mathbf{R}_2) = f(\mathbf{r} - \mathbf{R}_1 - \mathbf{R}_2) = f(\mathbf{r} - (\mathbf{R}_1 + \mathbf{R}_2)) \\ &= \hat{T}(\mathbf{R}_1 + \mathbf{R}_2)f(\mathbf{r}) \end{aligned}$$

therefore:

$$\hat{T}(\mathbf{R}_1)\hat{T}(\mathbf{R}_2) = \hat{T}(\mathbf{R}_1 + \mathbf{R}_2). \quad (9.3)$$

The second requirement is to have a unity operator. This role is played by $\hat{T}(\mathbf{0})$, since

$$\hat{T}(\mathbf{0})f(\mathbf{r}) = f(\mathbf{r} + \mathbf{0}) = f(\mathbf{r}). \quad (9.4)$$

The third condition is the existence [for every $\hat{T}(\mathbf{R}_i)$] of the inverse operator, which in our case is $\hat{T}(-\mathbf{R}_i)$, because:

$$\hat{T}(\mathbf{R}_i)\hat{T}(-\mathbf{R}_i) = \hat{T}(\mathbf{R}_i - \mathbf{R}_i) = \hat{T}(\mathbf{0}). \quad (9.5)$$

The group is Abelian (i.e. the operations commute), since:

$$\hat{T}(\mathbf{R}_1)\hat{T}(\mathbf{R}_2) = \hat{T}(\mathbf{R}_1 + \mathbf{R}_2) = \hat{T}(\mathbf{R}_2 + \mathbf{R}_1) = \hat{T}(\mathbf{R}_2)\hat{T}(\mathbf{R}_1). \quad (9.6)$$

¹³Besides the translational group, the crystal may also exhibit what is called the *point group*, associated with rotations, reflections in planes, inversion, etc., and the *space group* that results from the translational group and the point group. In such cases, a smaller unit cell may be chosen, because the whole crystal is reproduced not only by translations, but also by other symmetry operations. In the present textbook, we will concentrate on the translational symmetry group only.

¹⁴The irreducible representations of an Abelian group are one-dimensional. In our case (translation group) this means that there is no degeneracy, and that an eigenfunction of the Hamiltonian is also an eigenfunction of all the translation operators.

¹⁵The exponent sign is arbitrary, we use “-” following a widely used convention.

From equation $\hat{T}(\mathbf{R}_j)\psi(\mathbf{r}) = \lambda_{\mathbf{R}_j}\psi(\mathbf{r})$ it follows that

$$\lambda_{\mathbf{R}_j}\lambda_{\mathbf{R}_l} = \lambda_{\mathbf{R}_j+\mathbf{R}_l}, \quad (9.9)$$

because

$$\hat{T}(\mathbf{R}_j + \mathbf{R}_l)\psi(\mathbf{r}) = \lambda_{\mathbf{R}_j+\mathbf{R}_l}\psi(\mathbf{r} - \mathbf{R}_j - \mathbf{R}_l). \quad (9.10)$$

On the other hand

$$\begin{aligned} \hat{T}(\mathbf{R}_j + \mathbf{R}_l)\psi(\mathbf{r}) &= \hat{T}(\mathbf{R}_j)\hat{T}(\mathbf{R}_l)\psi(\mathbf{r}) = \lambda_{\mathbf{R}_l}\hat{T}(\mathbf{R}_j)\psi(\mathbf{r} - \mathbf{R}_l) \\ &= \lambda_{\mathbf{R}_j}\lambda_{\mathbf{R}_l}\psi(\mathbf{r} - \mathbf{R}_j - \mathbf{R}_l). \end{aligned}$$

Since this relation has to be satisfied for any \mathbf{R}_j and \mathbf{R}_l , it is therefore sufficient to have

$$\theta_{\mathbf{R}_j} = \mathbf{k} \cdot \mathbf{R}_j, \quad (9.11)$$

because a multiplication of λ by λ corresponds to adding the exponents, which results in adding vectors \mathbf{R} , which we need to have. The dot product $\mathbf{k} \cdot \mathbf{R}_j$ for simplicity will also be written as $\mathbf{k}\mathbf{R}_j$.

CONCLUSION:

The eigenfunctions of the one-electron Hamiltonian and the translation operators correspond to the following eigenvalues of the translation operator: $\lambda_{\mathbf{R}_j} = \exp(-i\mathbf{k}\mathbf{R}_j)$,

where the wave vector \mathbf{k} characterizes the function, not the direction of \mathbf{R}_j . In other words, any one-electron wave function (crystal orbital), which is the eigenfunction of the one-electron Hamiltonian could be labelled by its corresponding vector \mathbf{k} , i.e. $\psi(\mathbf{r}) \rightarrow \psi_{\mathbf{k}}(\mathbf{r})$.

Bloch theorem

BLOCH THEOREM

The value of such a function in the point shifted by the vector \mathbf{R}_j is equal to:

$$\psi_{\mathbf{k}}(\mathbf{r} - \mathbf{R}_j) = \exp(-i\mathbf{k}\mathbf{R}_j)\psi_{\mathbf{k}}(\mathbf{r}) \quad (9.12)$$

The above equality is called the *Bloch theorem*.

Felix Bloch (1905–1983), American physicist of Swiss origin, from 1936–1971 professor at Stanford University. Bloch contributed to the electronic structure of metals, superconductivity, ferromagnetism, quantum electrodynamics and the physics of neutrons. In 1946, independently of E.M. Purcell, he discovered the nuclear magnetic resonance effect. Both scientists received the Nobel Prize in 1952 “for the development of new methods for nuclear magnetic precision measurements and the discoveries in connection therewith”.



This relation represents a necessary condition to be fulfilled by the eigenfunctions for a perfect periodic structure (crystal, layer, polymer). This equation differs widely from eq. (9.2) for potential energy. Unlike potential energy, which does not change at all upon a lattice translation, the wave function undergoes a change of its phase acquiring the factor $\exp(-ik\mathbf{R}_j)$.

Any linear combination of functions labelled by the same \mathbf{k} represents an eigenfunction of any lattice translation operator, and corresponds to the same \mathbf{k} . Indeed, from the linearity of the translation operator

$$\begin{aligned}\hat{T}(\mathbf{R}_l)(c_1\phi_{\mathbf{k}}(\mathbf{r}) + c_2\psi_{\mathbf{k}}(\mathbf{r})) &= c_1\phi_{\mathbf{k}}(\mathbf{r} - \mathbf{R}_l) + c_2\psi_{\mathbf{k}}(\mathbf{r} - \mathbf{R}_l) \\ &= c_1\exp(-ik\mathbf{R}_l)\phi_{\mathbf{k}}(\mathbf{r}) + c_2\exp(-ik\mathbf{R}_l)\psi_{\mathbf{k}}(\mathbf{r}) \\ &= \exp(-ik\mathbf{R}_l)(c_1\phi_{\mathbf{k}}(\mathbf{r}) + c_2\psi_{\mathbf{k}}(\mathbf{r})).\end{aligned}$$

Let us construct the following function (called a *Bloch function*) from a function $\chi(\mathbf{r})$, that in future will play the role of an atomic orbital:

$$\phi(\mathbf{r}) = \sum_j \exp(ik\mathbf{R}_j)\chi(\mathbf{r} - \mathbf{R}_j),$$

where the summation extends over all possible \mathbf{R}_j , i.e. over the whole crystal lattice. The function ϕ is *automatically* an eigenfunction of any translation operator and may be labelled by the index \mathbf{k} similarly $\psi_{\mathbf{k}}$. Indeed, first

$$\begin{aligned}\hat{T}(\mathbf{R}_l)\phi(\mathbf{r}) &= \hat{T}(\mathbf{R}_l) \sum_j \exp(ik\mathbf{R}_j)\chi(\mathbf{r} - \mathbf{R}_j) = \sum_j \exp(ik\mathbf{R}_j)\hat{T}(\mathbf{R}_l)\chi(\mathbf{r} - \mathbf{R}_j) \\ &= \sum_j \exp(ik\mathbf{R}_j)\chi(\mathbf{r} - \mathbf{R}_j - \mathbf{R}_l).\end{aligned}$$

Instead of the summation over \mathbf{R}_j let us introduce a summation over $\mathbf{R}_{j'} = \mathbf{R}_j + \mathbf{R}_l$, which means an *identical* summation as before, but we begin to sum the term up from another point of the lattice. Then, we can write

$$\begin{aligned}\sum_{j'} \exp(ik(\mathbf{R}_{j'} - \mathbf{R}_l))\chi(\mathbf{r} - \mathbf{R}_{j'}) &= \exp(-ik\mathbf{R}_l) \sum_{j'} \exp(ik\mathbf{R}_{j'})\chi(\mathbf{r} - \mathbf{R}_{j'}) \\ &= \exp(-ik\mathbf{R}_l)\phi(\mathbf{r})\end{aligned}$$

which had to be proven.

Our function ϕ represents, therefore, an eigenfunction of the translation operator with the same eigenvalue as that corresponding to $\psi_{\mathbf{k}}$. In the following, very often $\psi_{\mathbf{k}}$ will be constructed as a linear combination of Bloch functions ϕ .

A Bloch function is nothing but a symmetry orbital built from the functions $\chi(\mathbf{r} - \mathbf{R}_j)$.

A symmetry orbital is a linear combination of atomic orbitals, that transforms according to an irreducible representation Γ of the symmetry group of the Hamil-

tonian (cf. Appendix C). In order to obtain such a function we may use the corresponding projection operator [see eq. (C.13)].

There is also another way to construct a function $\phi_{\mathbf{k}}(\mathbf{r})$ of a given \mathbf{k} from an auxiliary function $u(\mathbf{r})$ satisfying an equation similar to eq. (9.2) for the potential V

$$\hat{T}(\mathbf{R}_i)u(\mathbf{r}) = u(\mathbf{r} - \mathbf{R}_i) = u(\mathbf{r}). \quad (9.13)$$

Then, $\phi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r})u(\mathbf{r})$. Indeed, let us check

$$\begin{aligned} \hat{T}(\mathbf{R}_j)\phi_{\mathbf{k}}(\mathbf{r}) &= \hat{T}(\mathbf{R}_j)\exp(i\mathbf{k}\mathbf{r})u(\mathbf{r}) = \exp(i\mathbf{k}(\mathbf{r} - \mathbf{R}_j))u(\mathbf{r} - \mathbf{R}_j) \\ &= \exp(-i\mathbf{k}\mathbf{R}_j)\phi_{\mathbf{k}}(\mathbf{r}), \end{aligned} \quad (9.14)$$

9.3 INVERSE LATTICE

Let us now construct the so called *biorthogonal basis* $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ with respect to the basis vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ of the primitive lattice, i.e. the vectors that satisfy the *biorthogonality relations*:

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}. \quad (9.15)$$

The vectors \mathbf{b}_i can be expressed by the vectors \mathbf{a}_i in the following way

$$\mathbf{b}_i = 2\pi \sum_j \mathbf{a}_j (S^{-1})_{ji}, \quad (9.16)$$

$$S_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j. \quad (9.17)$$

The vectors $\mathbf{b}_1, \mathbf{b}_2$ and \mathbf{b}_3 form the basis of a lattice in a 3D space. This lattice will be called the *inverse lattice*.

The inverse lattice vectors are, therefore,

$$\mathbf{K}_j = \sum_{i=1}^{i=3} g_{ji} \mathbf{b}_i, \quad (9.18)$$

where g_{ij} represent arbitrary *integers*. We have

$$\mathbf{K}_j \cdot \mathbf{R}_i = 2\pi M_{ij},$$

where M_{ij} are integer numbers.

Indeed,

$$\mathbf{K}_j \cdot \mathbf{R}_i = \sum_{l=1}^3 g_{jl} \mathbf{b}_l \cdot \sum_{k=1}^3 n_{ik} \mathbf{a}_k = \sum_{l=1}^3 \sum_{k=1}^3 n_{ik} g_{jl} \mathbf{b}_l \cdot \mathbf{a}_k \quad (9.19)$$

$$= \sum_{l=1}^3 \sum_{k=1}^3 n_{ik} g_{jl} (2\pi) \delta_{lk} = 2\pi \sum_{l=1}^3 n_{il} g_{jl} = 2\pi M_{ij} \quad (9.20)$$

with n_{ik} , g_{jl} and, therefore also M_{ij} as *integers*. The inverse lattice is composed, therefore, from the isolated points indicated from the origin by the vectors \mathbf{K}_j . All the vectors that begin at the origin form the *inverse space*.

Examples

Let us see how we obtain the inverse lattice (1D, 2D, 3D) in practice.

1D

We have only a single biorthogonality relation: $\mathbf{b}_1 \mathbf{a}_1 = 2\pi$, i.e. after skipping the index $\mathbf{b} \mathbf{a} = 2\pi$. Because of the single dimension, we have to have $\mathbf{b} = \frac{2\pi}{a}(\frac{a}{a})$, where $|a| \equiv a$. Therefore,

the vector \mathbf{b} has length $\frac{2\pi}{a}$ and the same direction as \mathbf{a} .

2D

This time we have to satisfy: $\mathbf{b}_1 \mathbf{a}_1 = 2\pi$, $\mathbf{b}_2 \mathbf{a}_2 = 2\pi$, $\mathbf{b}_1 \mathbf{a}_2 = 0$, $\mathbf{b}_2 \mathbf{a}_1 = 0$. This means that the game takes place within the plane determined by the lattice vectors \mathbf{a}_1 and \mathbf{a}_2 . The vector \mathbf{b}_1 has to be perpendicular to \mathbf{a}_2 , while \mathbf{b}_2 has to be perpendicular to \mathbf{a}_1 , their directions such as shown in Fig. 9.2 (each of the \mathbf{b} vectors is a linear combination of \mathbf{a}_1 and \mathbf{a}_2 according to (9.16)).

3D

In the 3D case the biorthogonality relations are equivalent to setting

$$\mathbf{b}_1 = \mathbf{a}_2 \times \mathbf{a}_3 \frac{2\pi}{V}, \quad (9.21)$$

$$\mathbf{b}_2 = \mathbf{a}_3 \times \mathbf{a}_1 \frac{2\pi}{V}, \quad (9.22)$$

$$\mathbf{b}_3 = \mathbf{a}_1 \times \mathbf{a}_2 \frac{2\pi}{V}, \quad (9.23)$$

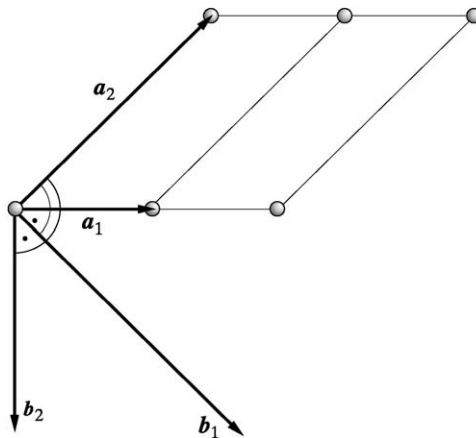


Fig. 9.2. Construction of the inverse lattice in 2D. In order to satisfy the biorthogonality relations (9.15) the vector \mathbf{b}_1 has to be orthogonal to \mathbf{a}_2 , while \mathbf{b}_2 must be perpendicular to \mathbf{a}_1 . The lengths of the vectors \mathbf{b}_1 and \mathbf{b}_2 also follow from the biorthogonality relations: $\mathbf{b}_1 \cdot \mathbf{a}_1 = \mathbf{b}_2 \cdot \mathbf{a}_2 = 2\pi$.

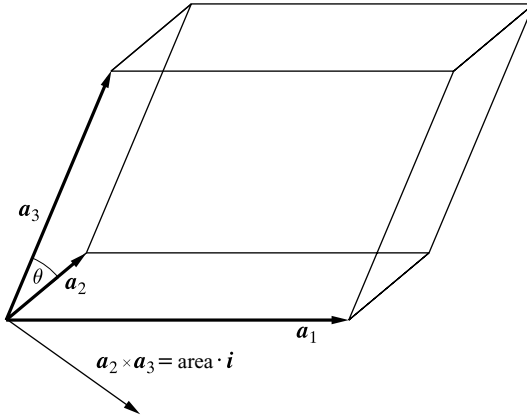


Fig. 9.3. The volume V of the unit cell is equal to $V = \mathbf{a}_1 \cdot (\text{area of the base})\mathbf{i} = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$.

where

$$V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \quad (9.24)$$

is the volume of the unit cell of the crystal (Fig. 9.3).

9.4 FIRST BRILLOUIN ZONE (FBZ)

Wigner–Seitz
cell

As was remarked at the beginning of this chapter, the example of a jigsaw puzzle shows us that a parallelepiped unit cell does not represent the only choice. Now,

we will profit from this extra freedom and will define the so called *Wigner–Seitz* unit cell. Here is the prescription of how to construct it (Fig. 9.4):

We focus on a node W , saw the crystal along the plane that dissects (symmetrically) the distance to a nearest neighbour node, throw the part that *does not* contain W into the fire-place, then repeat the procedure until we are left with a solid containing W . This solid represents the First Brillouin Zone (FBZ).

Léon Nicolas Brillouin (1889–1969), French physicist, professor at the Sorbonne and College de France in Paris, after 1941 in the USA: at the University of Madison, Columbia University, Harvard University. His contributions included quantum mechanics and solid state theory (he is one of the founders of electronic band theory).

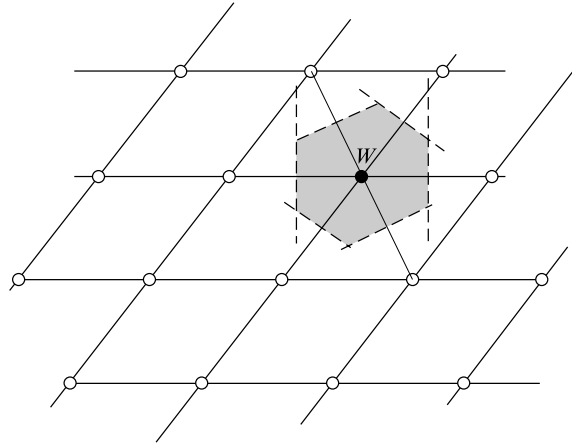


9.5 PROPERTIES OF THE FBZ

The vectors \mathbf{k} , which begin at the origin and end in the FBZ, label *all different* irreducible representations of the translational symmetry group.

Let us imagine two inverse space vectors \mathbf{k}' and \mathbf{k}'' related by the equality $\mathbf{k}'' = \mathbf{k}' + \mathbf{K}_s$, where \mathbf{K}_s stands for an inverse lattice vector. Taking into account the way the FBZ has been constructed, if one of them, say, \mathbf{k}' indicates a point in the

Fig. 9.4. Construction of the First Brillouin Zone (FBZ) as a Wigner–Seitz unit cell of the inverse lattice in 2D. The circles represent the nodes of the inverse lattice. We cut the lattice in the middle between the origin node W and all the other nodes (here it turns out to be sufficient to take only the nearest and the next nearest neighbours) and remove all the sawn-off parts that do not contain W . Finally we obtain the FBZ in the form of a hexagon. The Wigner–Seitz unit cells (after performing all allowed translations in the inverse lattice) reproduce the complete inverse space.



interior of the FBZ, then the second, k'' , “protrudes” outside the FBZ. Let us try to construct a Bloch function that corresponds to k'' :

$$\phi_{k''} = \sum_j \exp(ik''R_j) \chi(r - R_j) = \sum_j \exp(i(k' + K_s)R_j) \chi(r - R_j) \quad (9.25)$$

$$= \exp(iK_s R_j) \sum_j \exp(ik'R_j) \chi(r - R_j) \quad (9.26)$$

$$= \exp(i2\pi M_{sj}) \sum_j \exp(ik'R_j) \chi(r - R_j) \quad (9.27)$$

$$= \sum_j \exp(ik'R_j) \chi(r - R_j) = \phi_{k'}. \quad (9.28)$$

It turns out that our function ϕ does behave in a way identical to k' . We say that the two vectors are *equivalent*.

equivalent
vectors

Vector k outside the FBZ is always equivalent to a vector from inside the FBZ, while two vectors from inside of the FBZ are never equivalent.

Therefore, if we are interested in electronic states (the irreducible representation of the translation group are labelled by k vectors) it is sufficient to limit ourselves to those k vectors that are enclosed in the FBZ.

9.6 A FEW WORDS ON BLOCH FUNCTIONS

9.6.1 WAVES IN 1D

Let us take a closer look of a Bloch function corresponding to the vector k :

$$\phi_k(r) = \sum_j \exp(ikR_j) \chi(r - R_j) \quad (9.29)$$

and limit ourselves to 1D. In such a case, the wave vector \mathbf{k} reduces to a *wave number* k , and the vectors \mathbf{R}_j can all be written as $\mathbf{R}_j = aj\mathbf{z}$, where \mathbf{z} stands for the unit vector along the periodicity axis, a means the lattice constant (i.e. the nearest-neighbour distance), while $j = 0, \pm 1, \pm 2, \dots$. Let us assume that in the lattice nodes we have hydrogen atoms with orbitals $\chi = 1s$. Therefore, in 1D we have:

$$\phi_k(\mathbf{r}) = \sum_j \exp(ikja) \chi(\mathbf{r} - aj\mathbf{z}). \quad (9.30)$$

Let me stress that ϕ_k represents a function of position \mathbf{r} in the 3D space and only the periodicity has a 1D character. The function is a linear combination of the hydrogen atom $1s$ orbitals. The linear combination depends exclusively on the value of k . Eq. (9.28) tells us that the allowed $k \in (0, \frac{2\pi}{a})$, or alternatively $k \in (-\frac{\pi}{a}, \frac{\pi}{a})$. If we exceed the FBZ length $\frac{2\pi}{a}$, then we would simply repeat the Bloch functions. For $k = 0$ we get

$$\phi_0 = \sum_j \exp(0) \chi(\mathbf{r} - aj\mathbf{z}) = \sum_j \chi(\mathbf{r} - aj\mathbf{z}), \quad (9.31)$$

i.e. simply a sum of the $1s$ orbitals. Such a sum has a large value on the nuclei, and close to a nucleus ϕ_0 will be delusively similar to its $1s$ orbital, Fig. 9.5.a.

The function looks like a chain of buoys floating on a perfect water surface. If we ask whether ϕ_0 represents a wave, the answer could be, that if it does then its wave length is ∞ . What about $k = \frac{\pi}{a}$? In such a case:

$$\begin{aligned} \phi_{\frac{\pi}{a}}(\mathbf{r}) &= \sum_j \exp(ij\pi) \chi(\mathbf{r} - aj\mathbf{z}) = \sum_j (\cos \pi j + i \sin \pi j) \chi(\mathbf{r} - aj\mathbf{z}) \\ &= \sum_j (-1)^j \chi(\mathbf{r} - aj\mathbf{z}). \end{aligned}$$

If we decide to draw the function in space, we would obtain Fig. 9.5.b. When asked this time, we would answer that the wave length is equal to $\lambda = 2a$, which by the way is equal to ¹⁶ $\frac{2\pi}{|k|}$. There is a problem. Does the wave correspond to $k = \frac{\pi}{a}$ or $k = -\frac{\pi}{a}$? It corresponds to *both* of them. Well, does it contradict the theorem that the FBZ contains all *different* states? No, everything is OK. Both functions are from the border of the FBZ, their k values differ by $\frac{2\pi}{a}$ (one of the inverse lattice vectors) and therefore both functions represent *the same state*.

Now, let us take $k = \frac{\pi}{2a}$. We obtain

$$\begin{aligned} \phi_k(\mathbf{r}) &= \sum_j \exp\left(\frac{i\pi j}{2}\right) \chi(\mathbf{r} - aj\mathbf{z}) \\ &= \sum_j \left(\cos\left(\frac{\pi j}{2}\right) + i \sin\left(\frac{\pi j}{2}\right) \right) \chi(\mathbf{r} - aj\mathbf{z}) \end{aligned} \quad (9.32)$$

with some coefficients being complex numbers. For $j = 0$ the coefficient is equal to 1, for $j = 1$ equals i , for $j = 2$ it takes the value -1 , for $j = 3$ it attains $-i$, for $j = 4$ it is again 1, and the values repeat periodically. This is depicted in Fig. 9.5.c.

¹⁶In the preceding case the formula $\lambda = \frac{2\pi}{k}$ also worked, because it gave $\lambda = \infty$.

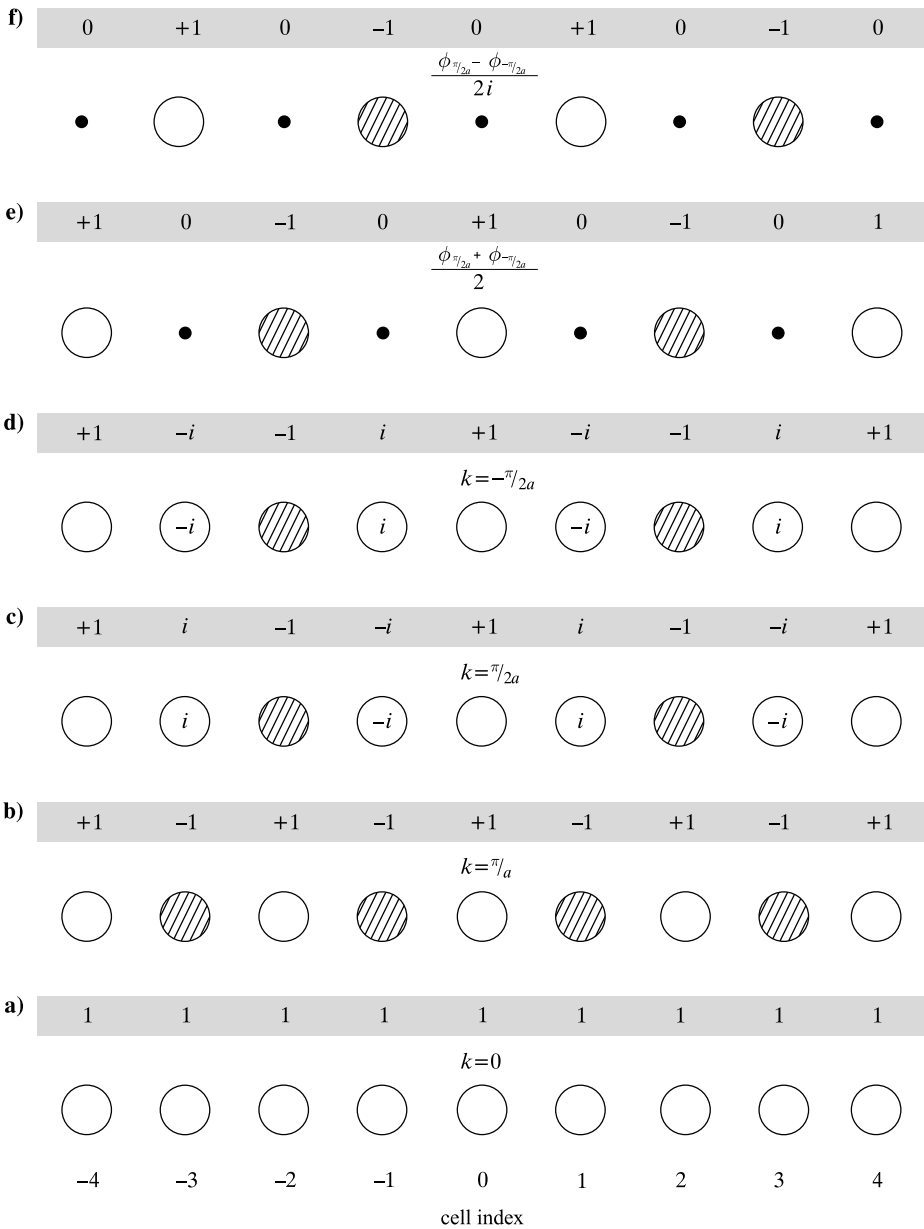


Fig. 9.5. Waves in 1D. Shaded (white) circles mean negative (positive) value of the function. Despite the fact that some waves are complex, in each of the cases (a)–(f) we are able to determine their wave length.

If this time we ask whether we see any wave there, we have to answer that yes we do, because after the length $4a$ everything begins to repeat. Therefore, $\lambda = 4a$ and again it equals to $\frac{2\pi}{k} = \frac{2\pi}{\frac{\pi}{2a}}$. Everything is OK except that humans like pictures

more than schemes. Can we help it somehow? Let us take a look of $\phi_k(\mathbf{r})$ which corresponds to $k = -\frac{\pi}{2a}$. We may easily convince ourselves that this situation corresponds to what we have in Fig. 9.5.d.

Let us stress that $\phi_{-k} = \phi_k^*$ represents *another* complex wave. By adding and subtracting $\phi_k(\mathbf{r})$ and $\phi_{-k}(\mathbf{r})$ we receive the real functions, which can be plotted and that is all we need. By adding $\frac{1}{2}(\phi_k + \phi_{-k})$, we obtain

$$\frac{1}{2}(\phi_k + \phi_{-k}) = \sum_j \cos\left(\frac{\pi j}{2}\right) \chi(\mathbf{r} - aj\mathbf{z}), \quad (9.33)$$

while $\frac{1}{2i}(\phi_k - \phi_{-k})$ results in

$$\frac{1}{2i}(\phi_k - \phi_{-k}) = \sum_j \sin\left(\frac{\pi j}{2}\right) \chi(\mathbf{r} - aj\mathbf{z}). \quad (9.34)$$

Now, there is no problem with plotting the new functions (Fig. 9.5.e,f).¹⁷

A similar technique may be applied to any k . Each time we will find that the wave we see exhibits the wave length $\lambda = \frac{2\pi}{k}$.

9.6.2 WAVES IN 2D

Readers confident in their understanding of the wave vector concept may skip this subsection.

This time we will consider the crystal as two-dimensional rectangular lattice, therefore, the corresponding inverse lattice is also two-dimensional as well as the wave vectors $\mathbf{k} = (k_x, k_y)$.

Let us take first $\mathbf{k} = (0, 0)$. We immediately obtain ϕ_k shown in Fig. 9.6.a, which corresponds to infinite wave length (again $\lambda = \frac{2\pi}{k}$) or “no wave” at all.

Let us try $\mathbf{k} = (\frac{\pi}{a}, 0)$. The summation over j may be replaced by a double summation (indices m and n along the x and y axes, respectively), therefore, $\mathbf{R}_j = m\mathbf{a} + n\mathbf{b}$, where m and n correspond to the unit cell j , a and b denote the lattice constants along the axes shown by the unit vectors \mathbf{x} and \mathbf{y} . We have

$$\begin{aligned} \phi_k &= \sum_{mn} \exp(i(k_x m a + k_y n b)) \chi(\mathbf{r} - m\mathbf{a} - n\mathbf{b}) \\ &= \sum_{mn} \exp(i\pi m) \chi(\mathbf{r} - m\mathbf{a} - n\mathbf{b}) = \sum_{mn} (-1)^m \chi(\mathbf{r} - m\mathbf{a} - n\mathbf{b}). \end{aligned}$$

If we go through all m and n , it easily seen that moving along x we will meet the signs $+1, -1, +1, -1, \dots$, while moving along y we have the same sign all the time. This will correspond to Fig. 9.6.b.

This is a wave.

¹⁷And what would happen if we took $k = \frac{\pi}{a} \frac{m}{n}$, with the integer $m < n$? We would again obtain a wave with the wave length $\lambda = \frac{2\pi}{k}$, i.e. in this case $\lambda = \frac{n}{m} 2a$. It would be quite difficult to recognize such a wave computed at the lattice nodes, because the closest wave maxima would be separated by $n2a$ and this length would have been covered by m wavelengths.

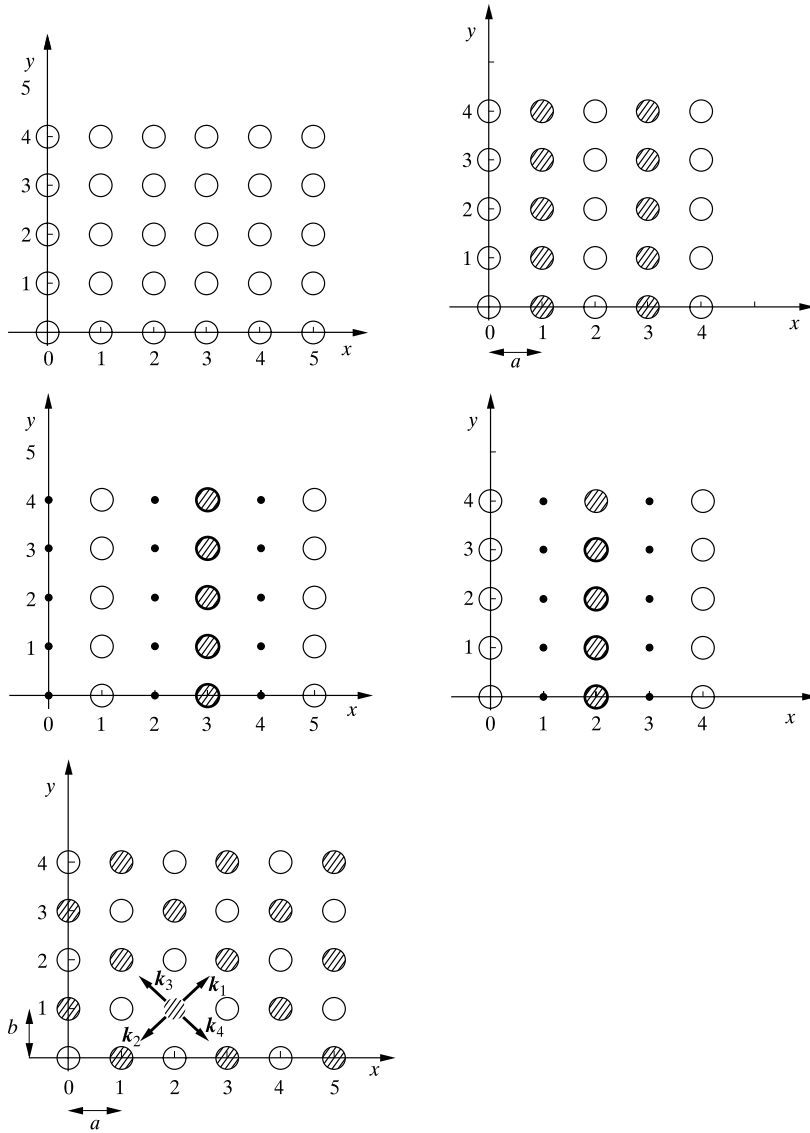


Fig. 9.6. Waves in 2D. Shaded (white) circles mean negative (positive) value of the function. In any case $\lambda = \frac{2\pi}{k}$, while the wave vector \mathbf{k} points to the direction of the wave propagation. a) $\mathbf{k} = (0, 0)$; b) $\mathbf{k} = (\frac{\pi}{a}, 0)$; c) $\mathbf{k} = (\frac{\pi}{2a}, 0)$, $\frac{1}{2i}(\phi_{\mathbf{k}} - \phi_{-\mathbf{k}})$; d) $\mathbf{k} = (\frac{\pi}{2a}, 0)$, $\frac{1}{2}(\phi_{\mathbf{k}} + \phi_{-\mathbf{k}})$; e) $\mathbf{k} = (\frac{\pi}{a}, \frac{\pi}{b})$.

The wave fronts are oriented along y , i.e. the wave runs along the x axis, therefore, in the direction of the wave vector \mathbf{k} . The same happened in the 1D cases, but we did not express that explicitly: the wave moved along the (1D) vector \mathbf{k} .

Exactly as before the wave length is equal to 2π divided by the length of \mathbf{k} . Since we are at the FBZ border, a wave with $-\mathbf{k}$ simply means the same wave as for \mathbf{k} .

If we take $\mathbf{k} = [\frac{\pi}{2a}, 0]$, then

$$\begin{aligned}\phi_{\mathbf{k}} &= \sum_{mn} \exp(i(\mathbf{k}_x m a + \mathbf{k}_y n b)) \chi(\mathbf{r} - m\mathbf{a} - n\mathbf{b}) \\ &= \sum_{mn} \exp\left(\frac{i\pi m}{2}\right) \chi(\mathbf{r} - m\mathbf{a} - n\mathbf{b}).\end{aligned}$$

This case is very similar to that in 1D for $k = \frac{\pi}{2a}$, when we look at the index m and $k = 0$, and when we take into account the index n . We may carry out the same trick with addition and subtraction, and immediately get Figs. 9.6.c and d.

Is there any wave over there? Yes, there is. The wave length equals $4a$, i.e. exactly $\lambda = \frac{2\pi}{k}$, and the wave is directed along vector \mathbf{k} . When making the figure, we also used the wave corresponding to $-\mathbf{k}$, therefore, neither the sum nor the difference correspond to \mathbf{k} or $-\mathbf{k}$, but rather to both of them (we have two standing waves). The reader may guess the wave length and direction of propagation for $\phi_{\mathbf{k}}$ corresponding to $\mathbf{k} = [0, \frac{\pi}{2b}]$.

Let us see what happens for $\mathbf{k} = [\frac{\pi}{a}, \frac{\pi}{b}]$. We obtain

$$\begin{aligned}\phi_{\mathbf{k}} &= \sum_{mn} \exp(i(k_x m a + k_y n b)) \chi(\mathbf{r} - m\mathbf{a} - n\mathbf{b}) \\ &= \sum_{mn} \exp(i(m\pi + n\pi)) \chi(\mathbf{r} - m\mathbf{a} - n\mathbf{b}) \\ &= \sum_{mn} (-1)^{m+n} \chi(\mathbf{r} - m\mathbf{a} - n\mathbf{b}),\end{aligned}$$

which produces waves propagating along \mathbf{k} . And what about the wave length? We obtain¹⁸

$$\lambda = \frac{2\pi}{\sqrt{(\frac{\pi}{a})^2 + (\frac{\pi}{b})^2}} = \frac{2ab}{\sqrt{a^2 + b^2}}. \quad (9.35)$$

In the last example there is something that may worry us. As we can see, our figure corresponds not only to $\mathbf{k}_1 = (\frac{\pi}{a}, \frac{\pi}{b})$ and $\mathbf{k}_2 = (-\frac{\pi}{a}, -\frac{\pi}{b})$, which is understandable (as discussed above), but also to the wave with $\mathbf{k}_3 = (-\frac{\pi}{a}, \frac{\pi}{b})$ and to the wave evidently coupled to it, namely, with $\mathbf{k}_4 = (\frac{\pi}{a}, -\frac{\pi}{b})$! What is going on? Again, let us recall that we are on the FBZ border and this identity is natural, because the vectors \mathbf{k}_2 and \mathbf{k}_3 as well as \mathbf{k}_1 and \mathbf{k}_4 differ by the inverse lattice vector $(0, \frac{2\pi}{b})$, which makes the two vectors equivalent.

¹⁸The formula can be easily verified in two limiting cases. The first corresponds to $a = b$. Then, $\lambda = a\sqrt{2}$, and this agrees with Fig. 9.6.e. The second case is, when $b = \infty$, which gives $\lambda = 2a$, exactly as in the 1D case with $k = \frac{\pi}{a}$. This is what we expected.

9.7 THE INFINITE CRYSTAL AS A LIMIT OF A CYCLIC SYSTEM

Band structure

Let us consider the hydrogen atom in its ground state (cf. p. 178). The atom is described by the atomic orbital $1s$ and corresponds to energy -0.5 a.u. Let us now take two such atoms. We have two molecular orbitals: bonding and antibonding (cf. p. 371), which correspond, respectively, to energies a bit lower than -0.5 and a bit higher than -0.5 (this bit is larger if the overlap of the atomic orbitals gets larger). We therefore have two energy levels, which stem directly from the $1s$ levels of the two hydrogen atoms. For three atoms we would have three levels, for 10^{23} atoms we would get 10^{23} energy levels, that would be densely distributed along the energy scale, but would not cover the whole scale. There will be a bunch of energy levels stemming from $1s$, i.e. an *energy band* of allowed electronic states. If we had an infinite chain of hydrogen atoms, there would be a band resulting from $1s$ levels, a band stemming from $2s$, $2p$, etc., the bands might be separated by *energy gaps*.

bands

energy gap

How dense would the distribution of the electronic levels be? Will the distribution be uniform? Answers to such questions are of prime importance for the electronic theory of crystals. It is always advisable to come to a conclusion by steps, starting from something as simple as possible, which we understand very well.

Fig. 9.7 shows how the energy level distribution looks for longer and longer rings (regular polygon) of hydrogen atoms. One of important features of the distribution is that

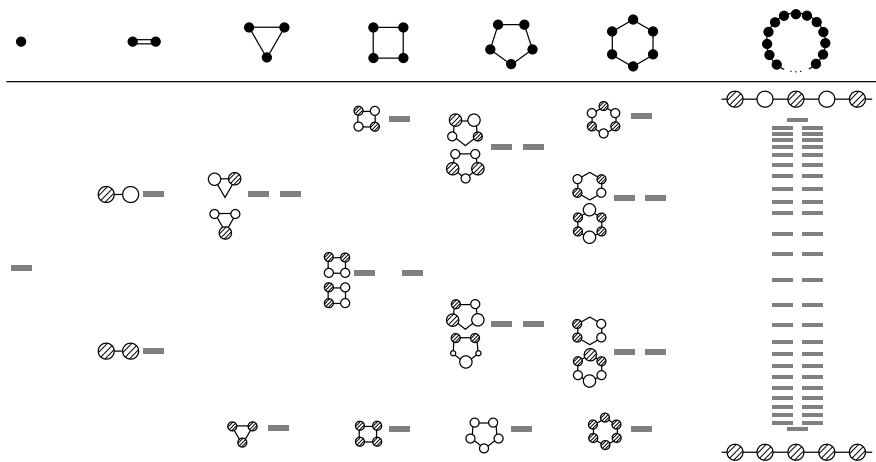


Fig. 9.7. Energy level distribution for a regular polygon built from hydrogen atoms. It is seen that the energy levels are located within an energy band, and are closer to one another at the band edges. The centre of the band is close to energy 0, taken as the binding energy in the isolated hydrogen atom (equal to -0.5 a.u.). Next to energy levels the molecular orbitals are shown schematically (the shadowed circles mean negative values). R. Hoffmann, “*Solids and Surfaces. A Chemist’s View of Bonding in Extended Structures*”, VCH Publishers, New York, © 1988 VCH Publishers. Reprinted with permission of John Wiley & Sons, Inc.

the levels extend over an energy interval and are more numerous at energy extremes.

How do the wave functions that correspond to higher and higher-energy levels in a band look? Let us see the situation in the ring H_n molecules. Fig. 9.7 indicates that the rule is very simple. The number of nodes of the wave function increases by one, when we go to the next level (higher in the energy scale).¹⁹

Born–von Kármán condition in 1D

How is it in the case of a crystal? Here we are confronted with the first difficulty. Which crystal, of what shape? Should it be an ideal crystal, i.e. with perfectly ordered atoms? There is nothing like the perfect crystal in Nature. For the sake of simplicity (as well as generality) let us assume, however, that our crystal *is* perfect indeed. Well, and now what about its surface (shape)? Even if we aimed at studying the surface of a crystal, the first step would be the infinite crystal (i.e. with no surface). This is the way theoreticians always operate.²⁰

One of the ingenious ideas in this direction is known as the *Born–von Kármán boundary conditions*. The idea is that instead of considering a crystal treated as a stick (let us consider 1D case) we treat it as a circle, i.e. *the value of the wavefunction at one end of the stick has to be equal to the wavefunction value at the other end*. In this way we remove the problem of the crystal ends, and on top of that, all the unit cells become equivalent.

Theodore von Kármán (1881–1963), American physicist of Hungarian origin, director of the Guggenheim Aeronautical Laboratory at the California Institute of Technology in Pasadena. von Kármán was also a founder of the NASA Jet Propulsion Laboratory and father of the concept of the first supersonic aeroplane. On the Hungarian stamp one can see the famous “Kármán vortex street” behind an aeroplane. He was asked by the father of the young mathematical genius John von Neumann to persuade him that the job of a mathematician is far less exciting than that of a banker. Theodore



von Kármán (to the benefit of science) did not accomplish this mission well.

The same may be done in 2D and 3D cases. We introduce usually the Born–von Kármán boundary conditions for a finite N and then go with N to ∞ . After such a procedure is carried out, we are pretty sure that the solution we are going to

¹⁹They are bound to differ by the number of nodes, because this assures their mutual orthogonality (required for the eigenfunctions of a Hermitian operator).

²⁰People say that when theoreticians attack the problem of stability of a table as a function of the number n of its legs, they do it in the following way. First, they start with $n = 0$, then they proceed with $n = 1$, then they go to $n = \infty$, and after that they have no time to consider other values of n .

obtain will not only be true for an infinite cycle but also for the mass (bulk) of the infinite crystal. This stands to reason, provided that the crystal surface does not influence the (deep) bulk properties at all.²¹ In the ideal periodic case, we have to do with the cyclic translational symmetry group (Appendix C on p. 903). The group is Abelian and, therefore, all the irreducible representations have dimension 1.

Let us assume we have to do with N equidistant atoms located on a circle, the nearest-neighbour distance being a . From the Bloch theorem for the wave function ψ we have

$$\psi(aN) = \exp(-ikaN)\psi(0), \quad (9.36)$$

where we have assumed that the wave function ψ corresponds to the wave vector k (here, in 1D, wave number k).

The Born–von Kármán condition means:

$$\psi(aN) = \psi(0), \quad (9.37)$$

or

$$\exp(-ikaN) = 1. \quad (9.38)$$

From this follows that:

$$kaN = 2\pi J, \quad (9.39)$$

where $J = 0, \pm 1, \pm 2, \dots$. This means that only *some* k are allowed, namely $k = \frac{2\pi}{a} \frac{J}{N}$.

The Bloch functions take the form [cf. eq. (9.29)]:

$$\sum_j \exp(ikja) \chi_j, \quad (9.40)$$

where χ_j denotes a given atomic orbital (e.g., $1s$) centred on atom j . The summation over j in our case is finite, because we only have N atoms, $j = 0, 1, 2, \dots, N-1$. Let us consider $J = 0, 1, 2, \dots, N-1$ and the corresponding values of $k = \frac{2\pi}{a} \frac{J}{N}$. For each k we have a Bloch function, altogether we have, therefore, N Bloch functions. Now, we may try to increase J and take $J = N$. The corresponding Bloch function may be written as

$$\sum_j \exp(i2\pi j) \chi_j = \sum_j \chi_j, \quad (9.41)$$

which turns out to be identical to the Bloch function with $k = 0$, i.e. with $J = 0$. We are reproducing what we already have. It is clear, therefore, that we have a set of those k , that form a *complete set of non-equivalent states*, they correspond to $J = 0, 1, 2, \dots, N-1$. It is also seen that if the limits of this set are shifted by the same integer, then we still have the same complete set of non-equivalent states. Staying for the time being with our primary choice of the set, we will get

²¹We circumvent the difficult problem of the crystal surface. The boundary (surface) problem is extremely important for obvious reasons: we usually *have to do with this, not with the bulk*. The existence of the surface leads to some specific surface-related electronic states.

N values of $k \in [0, \frac{2\pi}{a} \frac{N-1}{N}]$, i.e. $k \in \{0, \frac{2\pi}{a} \frac{1}{N}, \frac{2\pi}{a} \frac{2}{N}, \dots, \frac{2\pi}{a} \frac{N-1}{N}\}$. Those k values are equidistant. When $N \rightarrow \infty$ then the section to be divided attains the length $\frac{2\pi}{a}$. Hence

the non-equivalent states (going with N to infinity) correspond to those k 's that are from section $[0, \frac{2\pi}{a}]$ or shifted section $[-\frac{\pi}{a}, +\frac{\pi}{a}]$, called the FBZ. We are allowed to make any shift, because, as we have shown, we keep the same non-equivalent values of k . The allowed k values are distributed *uniformly* within the FBZ. The number of the allowed k 's is equal to ∞ , because $N = \infty$ (and the number of the allowed k 's is always equal to N).

k -dependence of orbital energy

Let us take the example of benzene ($N = 6$, Fig. 9.7) and consider only those molecular orbitals that can be written as linear combinations of the carbon $2p_z$, where z is the axis orthogonal to the plane of the molecule. The wave vectors²² ($k = \frac{2\pi}{a} \frac{J}{N}$) may be chosen as corresponding to $J = 0, 1, 2, \dots, 5$, or equivalently to $J = -3, -2, -1, 0, +1, +2$. It is seen that $J = 0$ gives a nodeless function,²³ $J = \pm 1$ lead to a pair of the Bloch functions with a single node, $J = \pm 2$ give a pair of the two-node functions, and finally $J = -3$ corresponds to a three-node function.

It has occasionally been remarked in this book (cf., e.g., Chapter 4), that increasing the number of nodes²⁴ results in higher energy. This rule becomes most transparent in the present case. A nodeless Bloch function means that all the contacts between the $2p$ orbitals are *bonding*, which results in *low energy*. A single node means introducing two nearest-neighbour *antibonding* interactions, and this is bound to cause an energy increase. Two nodes result in four antibonding interactions, and the energy goes up even more. Three nodes already give all the nearest-neighbour contacts of antibonding character and the energy is the highest possible.

bonding and
antibonding
interaction

9.8 A TRIPLE ROLE OF THE WAVE VECTOR

As has already been said, the wave vector (in 1D, 2D and 3D) plays several roles. Here they are:

1. The wave vector \mathbf{k} tells us which type of plane wave arranged from certain objects (like atomic orbitals) we are concerned with. The direction of \mathbf{k} is the propagation direction, the wave length is $\lambda = \frac{2\pi}{|\mathbf{k}|}$.

²²In this case this is a wave number.

²³We neglect here the node that follows from the reflection in the molecular plane as being shared by all the molecular orbitals considered.

²⁴That is, considering another wavefunction that has a larger number of nodes.

2. The wave vector may also be treated as a label for the irreducible representation of the translation group.

In other words, \mathbf{k} determines which irreducible representation we are dealing with (Appendix C on p. 903). This means that \mathbf{k} tells us *which permitted rhythm* is exhibited by the coefficients at atomic orbitals in a particular Bloch function (permitted, i.e. assuring that the square has the symmetry of the crystal). There are a lot of such rhythms, e.g., all the coefficients equal each other ($k = 0$), or one node introduced, two nodes, etc. The FBZ represents a set of such \mathbf{k} , which corresponds to *all possible rhythms*, i.e. non-equivalent Bloch functions.²⁵ In other words the FBZ gives us all the possible symmetry orbitals that can be formed from an atomic orbital.

3. The longer the \mathbf{k} , the more nodes the Bloch function $\phi_{\mathbf{k}}$ has: $|\mathbf{k}| = 0$ means no nodes, at the boundary of the FBZ there is the maximum number of nodes.

9.9 BAND STRUCTURE

9.9.1 BORN–VON KÁRMÁN BOUNDARY CONDITION IN 3D

The Hamiltonian \hat{H} we were talking about represents an effective one-electron Hamiltonian. From Chapter 8, we know that it may be taken as the Fock operator. A crystal represents nothing but a huge (quasi-infinite) molecule, and assuming the Born–von Kármán condition, a huge cyclic molecule. This is how we will get the Hartree–Fock solution for the crystal – by preparing the Hartree–Fock solution for a cyclic molecule and then letting the number of unit cells N go to infinity.

Hence, let us take a large piece of crystal – a parallelepiped with the number of unit cells *in each of the periodicity directions* (i.e. along the three basis vectors) equal to $2N + 1$ (the reference cell 0, N cells on the right, N cells on the left). The particular number, $2N + 1$, is not very important, we have only to be sure that such a number is large. We assume that the Born–von Kármán condition is fulfilled. This means that we treat the crystal like a snake eating its tail, and this will happen on every of the three periodicity axes. This enables us to treat the translation group as a cyclic group, which gives an enormous simplification to our task. The cyclic group of the lattice constants a, b, c implies that [cf. eq. (9.38)]

$$\exp(-ik_x a(2N + 1)) = 1, \quad (9.42)$$

$$\exp(-ik_y b(2N + 1)) = 1, \quad (9.43)$$

$$\exp(-ik_z c(2N + 1)) = 1, \quad (9.44)$$

which can be satisfied only for some special vectors $\mathbf{k} = (k_x, k_y, k_z)$ satisfying:

²⁵That is, linearly independent.

$$k_x = \frac{2\pi}{a} \frac{J_x}{2N+1}, \quad (9.45)$$

$$k_y = \frac{2\pi}{b} \frac{J_y}{2N+1}, \quad (9.46)$$

$$k_z = \frac{2\pi}{c} \frac{J_z}{2N+1}, \quad (9.47)$$

with any of J_x, J_y, J_z taking $2N+1$ consecutive integer numbers. We may, for example, assume that $J_x, J_y, J_z \in \{-N, -N+1, \dots, 0, 1, 2, \dots, N\}$. Whatever N is, \mathbf{k} will always satisfy

$$-\frac{\pi}{a} < k_x < \frac{\pi}{a}, \quad (9.48)$$

$$-\frac{\pi}{b} < k_y < \frac{\pi}{b}, \quad (9.49)$$

$$-\frac{\pi}{c} < k_z < \frac{\pi}{c}, \quad (9.50)$$

which is what we call the FBZ. We may therefore say that before letting $N \rightarrow \infty$

the FBZ is filled with the allowed vectors \mathbf{k} in a *grain-like way*; the number being equal to the number of unit cells, i.e. $(2N+1)^3$. Note that the distribution of the vectors allowed in the FBZ is *uniform*. This is assured by the numbers J , which divide the axes k_x, k_y, k_z in the FBZ into equal pieces.

9.9.2 CRYSTAL ORBITALS FROM BLOCH FUNCTIONS (LCAO CO METHOD)

crystal orbitals

What we expect to obtain finally in the Hartree–Fock method for an infinite crystal are the molecular orbitals, which in this context will be called the *crystal orbitals* (CO). As usual we will plan to expand the CO as linear combinations of atomic orbitals (cf. p. 360). Which atomic orbitals? Well, those which we consider appropriate²⁶ for a satisfactory description of the crystal, e.g., the atomic orbitals of all the atoms of the crystal. We feel, however, that we have to be defeated in trying to perform this task.

There will be a lot of atomic orbitals, and therefore also an astronomic number of integrals to compute (infinite for the infinite crystal) and that is it, we cannot help this. On the other hand, if we begin such a hopeless task, the value of any integral would repeat an infinite number of times. This indicates a chance to simplify the problem. Indeed, we have not yet used the translational symmetry of the system.

If we are going to use the symmetry, then we *may create the Bloch functions representing the building blocks that guarantee the proper symmetry in advance*. Each

²⁶As for molecules.

Bloch function is built from an atomic orbital χ :

$$\phi_{\mathbf{k}} = (2N + 1)^{-\frac{3}{2}} \sum_j \exp(i\mathbf{k}\mathbf{R}_j) \chi(\mathbf{r} - \mathbf{R}_j). \quad (9.51)$$

The function is identical to that of eq. (9.29), except it has a factor $(2N + 1)^{-\frac{3}{2}}$, which makes the function approximately normalized.²⁷

Any CO will be a linear combination of such Bloch functions, each corresponding to a given χ . This is equivalent to the LCAO expansion for molecular orbitals, the only difference is that we have cleverly preorganized the atomic orbitals (of one type) into symmetry orbitals (Bloch functions). Hence, it is indeed appropriate to call this approach as the LCAO CO method (*Linear Combination of Atomic Orbitals – Crystal Orbitals*), analogous to the LCAO MO (cf. p. 362). There is, however, a problem. Each CO should be a linear combination of the $\phi_{\mathbf{k}}$ for various types of χ and for various \mathbf{k} . Only then would we have the full analogy: a molecular orbital is a linear combination of all the atomic orbitals belonging to the atomic basis set.²⁸

It will be shown below that the situation is far better:

each CO corresponds to a single vector \mathbf{k} from the FBZ and is a linear combination of the Bloch functions, each characterized by this \mathbf{k} .

There are, however, only a few Bloch functions – their number is equal to the number of the atomic orbitals per unit cell (denoted by ω). Our optimism pertains, of course, to taking a modest atomic basis set (small ω).

It is easy to show that, indeed, we can limit ourselves to a single vector \mathbf{k} . Imagine this is false, and our CO is a linear combination of all the Bloch functions

²⁷The function without this factor is of class Q , i.e. normalizable for any finite N , but non-normalizable for $N = \infty$. The approximate normalization makes the function square integrable, even for $N = \infty$. Let us see:

$$\begin{aligned} \langle \phi_{\mathbf{k}} | \phi_{\mathbf{k}} \rangle &= (2N + 1)^{-3} \sum_j \sum_{j'} \exp(i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_{j'})) \int \chi(\mathbf{r} - \mathbf{R}_j) \chi(\mathbf{r} - \mathbf{R}_{j'}) d\tau \\ &= (2N + 1)^{-3} \sum_j \sum_{j'} \exp(i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_{j'})) \int \chi(\mathbf{r}) \chi(\mathbf{r} - (\mathbf{R}_j - \mathbf{R}_{j'})) d\tau, \end{aligned}$$

because the integral does depend on a *relative* separation in space of the atomic orbitals. Further,

$$\langle \phi_{\mathbf{k}} | \phi_{\mathbf{k}} \rangle = \sum_j \exp(i\mathbf{k}\mathbf{R}_j) \int \chi(\mathbf{r}) \chi(\mathbf{r} - \mathbf{R}_j) d\tau, \quad (9.52)$$

because we can replace a double summation over j and j' by a double summation over j and $j'' = j - j'$ (both double summations exhaust all the lattice nodes), and the later summation always gives the same independent of j ; the number of such terms is equal to $(2N + 1)^3$. Finally, we may write $\langle \phi_{\mathbf{k}} | \phi_{\mathbf{k}} \rangle = 1 +$ various integrals. The largest of these integrals is the nearest neighbour overlap integral of the functions χ . For normalized χ each of these integrals represents a fraction of 1 and additionally the contributions for further neighbours decay exponentially (cf. p. 1009). As a result, $\langle \phi_{\mathbf{k}} | \phi_{\mathbf{k}} \rangle$ is a number of the order of 1 or 2. This is what we have referred to as an approximate normalization.

²⁸Indeed, for any \mathbf{k} the number of distinct Bloch functions is equal to the number of atomic orbitals per unit cell. The number of allowed vectors, \mathbf{k} , is equal to the number of unit cells in the crystal. Hence, using the Bloch functions for all allowed \mathbf{k} would be justified, any CO would represent a linear combination of all the atomic orbitals of the crystal.

corresponding to a given \mathbf{k} , then, of all the Bloch functions corresponding to the next \mathbf{k} , etc., up to the exhaustion of all the allowed \mathbf{k} . When, in the next step, we solve the orbital equation with the effective (i.e. Fock) Hamiltonian using the Ritz method, then we will end up computing the integrals $\langle \phi_{\mathbf{k}} | \hat{F} \phi_{\mathbf{k}'} \rangle$ and $\langle \phi_{\mathbf{k}} | \phi_{\mathbf{k}'} \rangle$. For $\mathbf{k} \neq \mathbf{k}'$ such integrals *are equal zero* according to group theory (Appendix C on p. 903), because \hat{F} transforms according to the fully symmetric irreducible representation of the translation group,²⁹ while $\phi_{\mathbf{k}}$ and $\phi_{\mathbf{k}'}$ transform according to *different* irreducible representations.³⁰ Therefore the secular determinant in the Ritz method will have a *block form* (cf. Appendix C). The first block will correspond to the first \mathbf{k} , the second to the next \mathbf{k} , etc., where every block³¹ would look as if in the Ritz method we used the Bloch functions corresponding uniquely to that particular \mathbf{k} . Conclusion: since a CO has to be a wave with a *given* \mathbf{k} , let us construct it with Bloch functions, which already have just this type of behaviour with respect to translation operators, i.e. have just this \mathbf{k} . This is fully analogous with the situation in molecules, if we used atomic symmetry orbitals.

Thus each vector, \mathbf{k} , from the FBZ is associated with a crystal orbital, and therefore with a set of LCAO CO coefficients.

The number of such CO sets (each \mathbf{k} – one set) *in principle* has to be equal to the number of unit cells, i.e. infinite.³² The only profit we may expect could be associated with the hope that the computed quantities do not depend on \mathbf{k} too much, but will rather change smoothly when \mathbf{k} changes. This is indeed what will happen, *then a small number of vectors \mathbf{k} will be used, and the quantities requiring other \mathbf{k} will be computed by interpolation.*

Only a part of the computed COs will be occupied, and this depends on the orbital energy of a given CO, the number of electrons, and the corresponding \mathbf{k} , similar to which we had for molecules.

The set of SCF LCAO CO equations will be very similar to the set for the molecular orbital method (SCF LCAO MO). In principle, the only difference will be that, in the crystal case, we will consequently use symmetry orbitals (Bloch functions) instead of atomic orbitals.

That's it. The rest of this section is associated with some technical details accompanying the operation $N \rightarrow \infty$.

9.9.3 SCF LCAO CO EQUATIONS

Let us write down the SCF LCAO CO equations as if they corresponded to a large molecule (Bloch functions will be used instead of atomic orbitals). Then the n -th

²⁹Unit cells (by definition) are identical.

³⁰Recall that \mathbf{k} also has the meaning of the irreducible representation index (of the translation group).

³¹The whole problem can be split into the independent problems for individual blocks.

³²Well, we cannot fool Mother Nature! Was there an infinite molecule (crystal) to be computed or not? Then the number of such sets of computations has to be infinite. Full stop.

CO may be written as (cf. eq. (8.49))

$$\psi_n(\mathbf{r}, \mathbf{k}) = \sum_q c_{qn}(\mathbf{k}) \phi_q(\mathbf{r}, \mathbf{k}), \quad (9.53)$$

where ϕ_q is the Bloch function corresponding to the atomic orbital χ_q :

$$\phi_q(\mathbf{r}, \mathbf{k}) = (2N + 1)^{-\frac{3}{2}} \sum_j \exp(i\mathbf{k}\mathbf{R}_j) \chi_q^j, \quad (9.54)$$

with $\chi_q^j \equiv \chi_q(\mathbf{r} - \mathbf{R}_j)$ ($q = 1, 2, \dots, \omega$).

The symbol χ_q^j means the q -th atomic orbital (from the set we prepared for the unit cell motif) located in the cell indicated by vector \mathbf{R}_j (j -th cell).

In the expression for ψ_n , we have taken into account that there is no reason whatsoever that the coefficients c were \mathbf{k} -independent, since the expansion functions ϕ depend on \mathbf{k} . This situation does not differ from that, which we encountered in the Hartree–Fock–Roothaan method (cf. p. 365), with one technical exception: instead of the atomic orbitals we have symmetry orbitals, in our case Bloch functions.

The secular equations for the Fock operator will have, of course, the form of the Hartree–Fock–Roothaan equations (cf. Chapter 8, p. 365):

$$\sum_{q=1}^{\omega} c_{qn} [F_{pq} - \varepsilon_n S_{pq}] = 0 \quad \text{for } p = 1, 2, \dots, \omega,$$

where the usual notation has been applied. For the sake of simplicity, we have not highlighted the \mathbf{k} -dependence of c , F and S . Whenever we decide to do this in future, we will put it in the form $F_{pq}(\mathbf{k})$, $S_{pq}(\mathbf{k})$, etc. Of course, ε_n will become a function of \mathbf{k} , as will be stressed by the symbol $\varepsilon_n(\mathbf{k})$. Theoretically, the secular equation has to be solved for every \mathbf{k} of the FBZ.

Therefore, despite the fact that the secular determinant is of rather low rank (ω), the infinity of the crystal, forces us to solve this equation an infinite number of times. For the time being, though, do not worry too much.

9.9.4 BAND STRUCTURE AND BAND WIDTH

The number of secular equation solutions is equal to ω , and let us label them using index n . If we focus on one such solution, and check how $\varepsilon_n(\mathbf{k})$ and $\psi_n(\mathbf{r}, \mathbf{k})$ are sensitive to a tiny change of \mathbf{k} within the FBZ, it turns out that $\varepsilon_n(\mathbf{k})$ and $\psi_n(\mathbf{r}, \mathbf{k})$ change smoothly. This may not be true when \mathbf{k} passes through the border of the FBZ.

The function $\varepsilon_n(\mathbf{k})$ is called the n -th electronic band.

band width

If we travelled in the FBZ, starting from the origin and continuing along a straight line, then $\varepsilon_1, \varepsilon_2, \dots$ etc. would change as functions of \mathbf{k} and we would be concerned with several energy bands. If $\varepsilon_n(\mathbf{k})$ changes very much during our travel over the FBZ, we would say that the n -th band has a large width or *dispersion*.

As it was shown on p. 445 for the hydrogen atoms an energy band forms due to the bonding and antibonding effects. If instead of hydrogen atoms, we put a unit cell with a few atoms inside (motif), then the story is similar: the motif has some one-electron energy levels (orbital energies), putting together the unit cells makes changing these energy levels into energy bands, the number of levels in any band is equal to the number of unit cells, or the number of allowed \mathbf{k} vectors in FBZ.

The band width is related to interactions among the unit cell contents, and is roughly proportional to the overlap integral between the orbitals of the interacting unit cells.

How do we plot the band structure? For the 1D crystal, e.g., a periodic polymer, there is no problem: the wave vector \mathbf{k} means the number k and changes from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$, we plot the function $\varepsilon_n(k)$. For each n we have a single plot, e.g., for the hydrogen atom the band ε_1 collects energies resulting from the 1s atomic orbital interacting with other atoms, the band ε_2 , which resulted from 2s, etc. In the 3D case we usually choose a path in FBZ. We start from the point Γ defined as $\mathbf{k} = \mathbf{0}$. Then, we continue to some points located on the faces and edges of the FBZ surface. It is impossible to go through the whole FBZ. The band structure in the 3D case is usually shown by putting the described itinerary through the FBZ on the abscissa (Fig. 9.8), and $\varepsilon_n(\mathbf{k})$ on the ordinate. Fig. 9.8 shows an example of what we might obtain from such calculations.

9.9.5 FERMİ LEVEL AND ENERGY GAP: INSULATORS, SEMICONDUCTORS AND METALS

First of all we have to know how many electrons we have in the crystal. The answer is simple: the infinite crystal contains an infinite number of electrons. But infinities are often different. The decider is the number of electrons per unit cell. Let us denote this number by n_0 .

If this means a double occupation of the molecular orbitals of the unit cell, then the corresponding band in the crystal will also be fully occupied, because the number of energy levels in a band is equal to the number of unit cells, and each unit cell contributes two electrons from the above mentioned molecular orbital. Therefore,

conduction band

doubly occupied orbitals lead to fully occupied bands. Accordingly, singly occupied orbitals lead to bands that are *half-occupied*, while empty (virtual) orbitals lead to empty bands (unoccupied, or conduction bands).

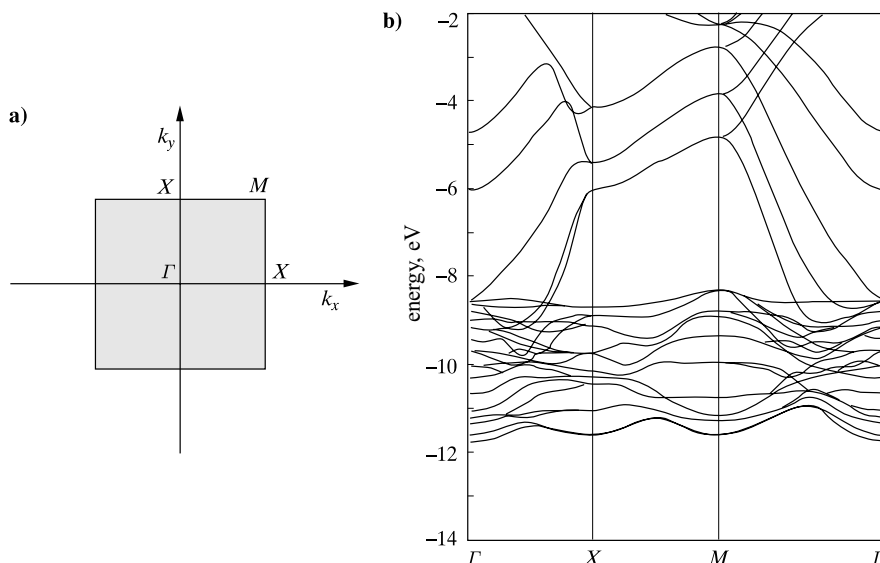


Fig. 9.8. (a) FBZ for four regular layers of nickel atoms (a crystal surface model) (b) the band structure for this system. We see that we cannot understand much: just a horrible irregular mess of lines. All the band structures look equally clumsy. Despite this, from such a plot we may determine the electrical and optical properties of the nickel slab. We will see later on why the bands have such a mysterious form. R. Hoffmann, “*Solids and Surfaces. A Chemist’s View of Bonding in Extended Structures*”, VCH Publishers, New York, © 1988 VCH Publishers. Reprinted with permission of John Wiley & Sons, Inc.

The Fermi level in the band structure of a crystal is equivalent to the HOMO of the crystal.³³ The two levels HOMO and LUMO, as always, decide the chemistry of the system, in our case the crystal. This concept leads to the possibilities depicted in Fig. 9.9, which we may find in ideal crystals

A metal is characterized by empty levels (conduction band) immediately (zero distance) above doubly occupied valence ones (highest occupied by electrons).

metal

Metals are conductors of electric current, and the reason for this is the zero gap.³⁴

A semiconductor exhibits a conduction band separated by a small energy gap (band gap) from the valence band.

valence bands

³³We sometimes find a thermodynamic definition of the Fermi level, but in this book it will always be the energy of the highest occupied crystal orbital.

³⁴When an electric field is applied to a crystal, its energy levels change. If the field is weak then the changes may be computed by perturbation theory (treating the zero-field situation as the unperturbed one). This means that the perturbed states acquire some admixtures of the excited states (cf. Chapter 5). The lower the energy gap, the more mixing is taking place. For metallic systems (gap zero), such perturbation theory certainly would not be applicable, but real excitation to the conduction band may take place.

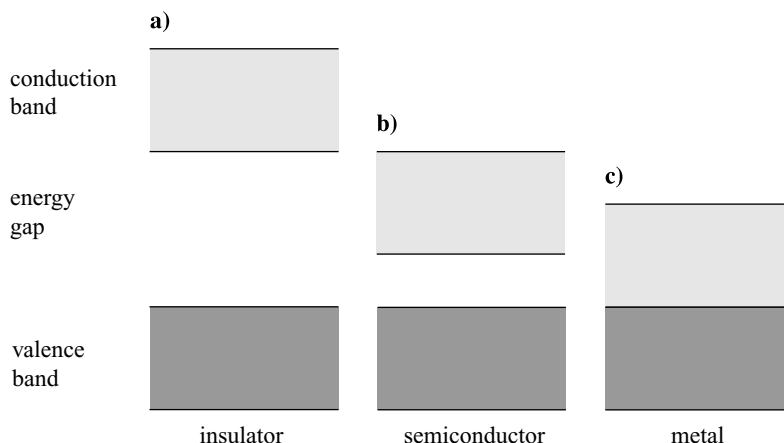


Fig. 9.9. Valence bands (highest occupied by electrons) and conduction bands (empty). The electric properties of a crystal depend on the energy gap between them (i.e. HOMO–LUMO separation). A large gap (a) is typical for an insulator, a medium gap (b) means a semiconductor, and a zero gap (c) is typical of metals.

Finally,

insulator

an insulator has a large band gap separating the valence band from the conduction band.

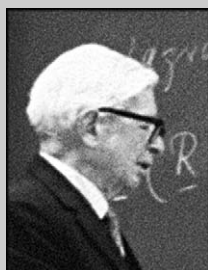
band gap

molecular wires

Peierls
transition

We know metallic systems typically represent microscopically 3D objects. Recently, 2D and 1D metals have become more and more fashionable, the latter called *molecular wires*. They may have unusual properties, but are difficult to prepare for they often undergo spontaneous dimerization of the lattice (known as the *Peierls transition*).

Rudolph Peierls (1907–1995), British physicist, professor at the universities of Birmingham and Oxford. Peierls participated in the Manhattan Project (atomic bomb) as leader of the British group.



As Fig. 9.10.a shows, dimerization makes the bonding (and antibonding) effects stronger a little below (and above) the middle of the band, whereas at $k = 0$ the effect is almost zero (since dimerization makes the bonding or antibonding effects cancel within a pair of consecutive bonds). As a result, the degeneracy is removed in the middle of the band (Fig. 9.10.b), i.e. the band gap appears

and the system undergoes metal–insulator or metal–semiconductor transition (Fig. 9.10.c). This is why polyacetylene, instead of having all the CC bonds equivalent (Fig. 9.10.d), which would make it a metal, exhibits alternation of bond lengths (Fig. 9.10.e) and it becomes an insulator or semiconductor.

To a chemist, the Peierls transition is natural. The hydrogen atoms will not stay equidistant in a chain, but will simply react and form hydrogen molecules, i.e. will

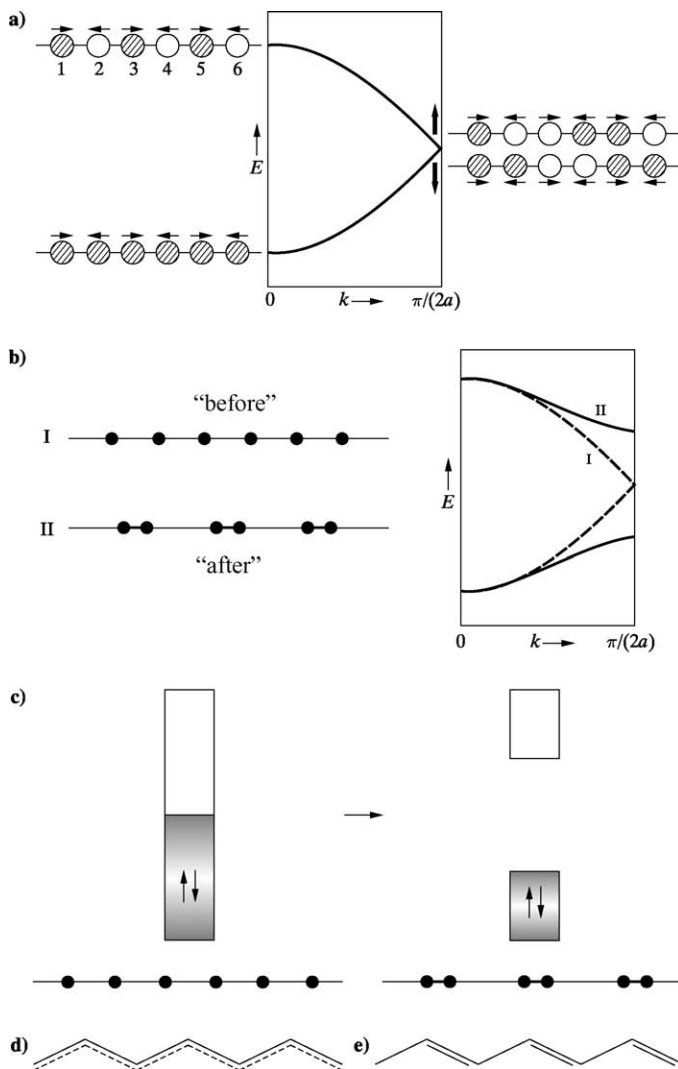


Fig. 9.10. The Peierls effect has the same origin as the Jahn–Teller effect in removing the electronic level degeneracy by distorting the system (H.A. Jahn, E. Teller, *Proc. Roy. Soc. A* 161 (1937) 220). (a) The electrons occupy half the FBZ, i.e. $-\frac{\pi}{2a} \leq k \leq \frac{\pi}{2a}$, a standing for the nearest-neighbour distance. The band has been plotted assuming that the period is equal to $2a$, hence a characteristic back folding of the band (similarly as we would fold a sheet of paper with band structure drawn, the period equal a). A lattice dimerization amplifies the bonding and antibonding effects close to the middle of the FBZ, i.e. in the neighbourhood of $k = \pm \frac{\pi}{2a}$. (b) As a result, the degeneracy at $k = \frac{\pi}{2a}$ is removed and the band gap appears, which corresponds to lattice dimerization. (c) The system lowers its energy when undergoing metal–insulator or metal–semiconductor transition. (d) The polyacetylene chain, forcing equivalence of all CC bonds, represents a metal. However, due to the Peierls effect, the system undergoes dimerization (e) and becomes an insulator. R. Hoffmann, “*Solids and Surfaces. A Chemist’s View of Bonding in Extended Structures*”, VCH Publishers, New York, © 1988 VCH Publishers. Reprinted with permission of John Wiley & Sons, Inc.

dimerize like lightning. Also the polyacetylene will try to form π bonds by binding the carbon atoms in *pairs*. There is simply a shortage of electrons to keep *all* the CC bonds strong, *there are only enough for only every second*, which means simply dimerization through creating π bonds. On the other hand, the Peierls transition may be seen as the Jahn–Teller effect: there is a degeneracy of the occupied and empty levels at the Fermi level, and it is therefore possible to lower the energy by removing the degeneracy through a distortion of geometry (i.e. dimerization). Both pictures are correct and represent the thing.

When a semiconductor is heated, this may cause a non-zero electron population in the conduction band (according to Boltzmann’s law), and these electrons may contribute to electric conductance, as for metals. The higher the temperature, the larger the conductance of such a semiconductor (called an *intrinsic semiconductor*).

intrinsic
semiconductor

The electric field will not do great things there (apart from some polarization).

Small energy gaps may appear when we dope an insulator with some dopants offering their own energy levels within the energy gap (Fig. 9.11).

If the empty energy levels of the dopant are located just over the occupied band, the dopant may serve as an electron acceptor for the electrons from the occupied band (thus introducing its own conduction band), we have a *p-type semiconductor*. If the dopant energy levels are occupied and located just under the conduction band, the dopant may serve as a *n-type semiconductor*.

p- and n-type
semiconductors

Polyacetylene (mentioned at the beginning of this chapter), after doping becomes ionized if the dopants are electron acceptors, or receives extra electrons if the dopant represents an electron donor (symbolized by D^+ in Fig. 9.12). The perfect polyacetylene exhibits the bond alternation discussed above, but it may

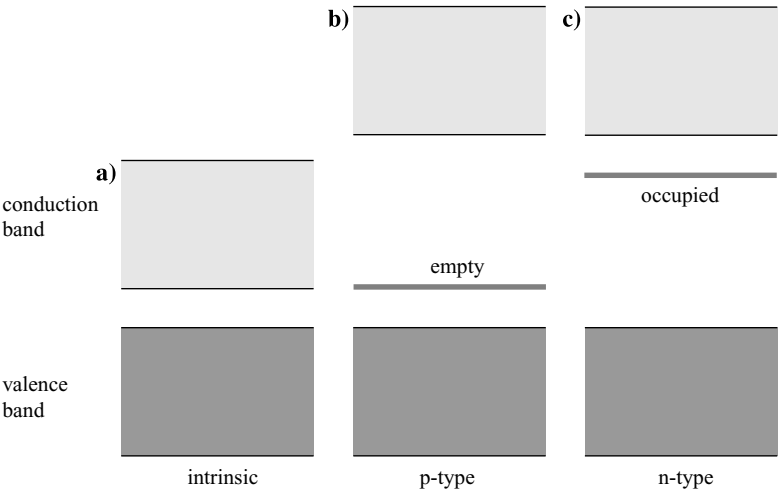


Fig. 9.11. Energy bands for semiconductors. (a) intrinsic semiconductor (small gap), (b) p type semiconductor (electron acceptor levels close to the occupied band) (c) n type semiconductor (electron donor levels close to the conduction band).

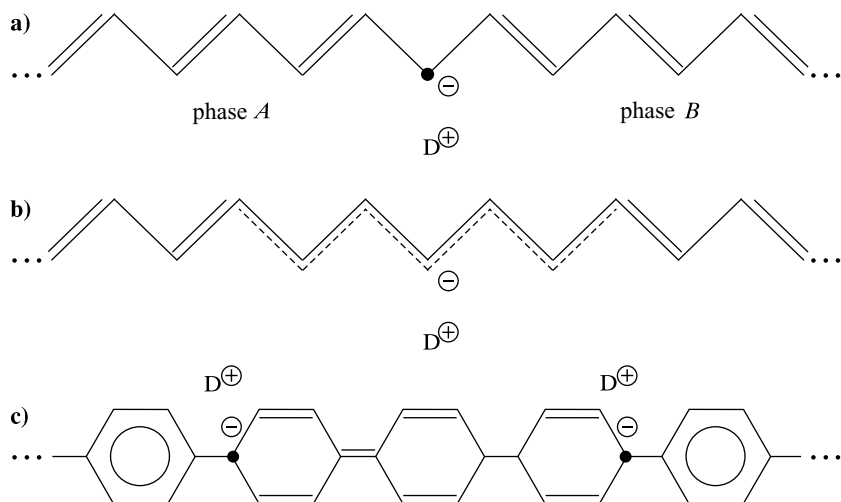


Fig. 9.12. Solitons and bipolarons as models of electric conductivity in polymers. (a) two phases of polyacetylene separated by a defect. Originally the defect was associated with an unpaired electron, but when a donor, D, gave its electron to the chain, the defect became negatively charged. The energy of such a defect is independent of its position in the chain (important for charge transportation) (b) in reality the change of phase takes place in sections of about 15 CC bonds, not two bonds as Fig. a suggests. Such a situation is sometimes modelled by a non-linear differential equation, which describes a soliton motion (“solitary wave”) that represents the travelling phase boundary. (c) in the polyparaphenylene chain two phases (low-energy aromatic and high-energy quinoid) are possible as well, but in this case they are of different energies. Therefore, the energy of a single defect (aromatic structures-kink-quinoid structures) depends on its position in the chain (therefore, no charge transportation). However, a *double* defect with a (higher-energy) section of a quinoid structure has a position-independent energy, and when charged by dopants (*bipolaron*) can conduct electricity. The above mentioned polymers can be doped either by electron donors (e.g., arsenium, potassium) or electron acceptors (iodine), which results in a spectacular increase in their electric conductivity.

be that we have a defect that is associated with a region of “changing rhythm” (or “phase”): from³⁵ (= – – – =) to (– – – –). Such a kink is sometimes described as a *soliton* wave (Fig. 9.12.a,b), i.e. a “solitary” wave first observed in the XIX century in England on a water channel, where it preserved its shape while moving over a distance of several kilometres. The soliton defects cause some new energy levels (“solitonic levels”) to appear within the gap. These levels too form their own solitonic band.

soliton

Charged solitons may travel when subject to an electric field, and therefore the doped polyacetylene turns out to be a good conductor (organic metal).

In polyparaphenylene, soliton waves are impossible, because the two phases (aromatic and quinoid, Fig. 9.12.c) differ in energy (low-energy aromatic phase and high-energy quinoid phase). However, when the polymer is doped, a charged double defect (*bipolaron*, Fig. 9.12.c) may form, and the defect may travel when

bipolaron

³⁵This possibility was first recognized by J.A. Pople, S.H. Walmsley, *Mol. Phys.* 5 (1962) 15, fifteen years before the experimental discovery of this effect.

an electric field is applied. Hence, the doped polyparaphenylene, similarly to the doped polyacetylene, is an “organic metal”.

9.10 SOLID STATE QUANTUM CHEMISTRY

A calculated band structure, with information about the position of the Fermi level, tell us a lot about the electric properties of the material under study (insulator, semiconductor, metal). They tell us also about basic optical properties, e.g., the band gap indicates what kind of absorption spectrum we may expect. We can calculate any measurable quantity, because we have at our disposal the computed wave function.

However, despite this very precious information, which is present in the band structure, there is a little worry. When we stare at any band structure, such as that shown in Fig. 9.8, the overwhelming feeling is a kind of despair. All band structures look similar, well, just a tangle of plots. Some go up, some down, some stay unchanged, some, it seems without any reason, change their direction. Can we understand this? What is the theory behind this band behaviour?

9.10.1 WHY DO SOME BANDS GO UP?

Let us take our beloved chain of hydrogen atoms in the $1s$ state, to which we already owe so much (Fig. 9.13).

When will the state of the chain have the lowest energy possible? Of course, when all the atoms interact in a bonding, and not antibonding, way. This corresponds to Fig. 9.13.a (no nodes of the wave function). When, in this situation,

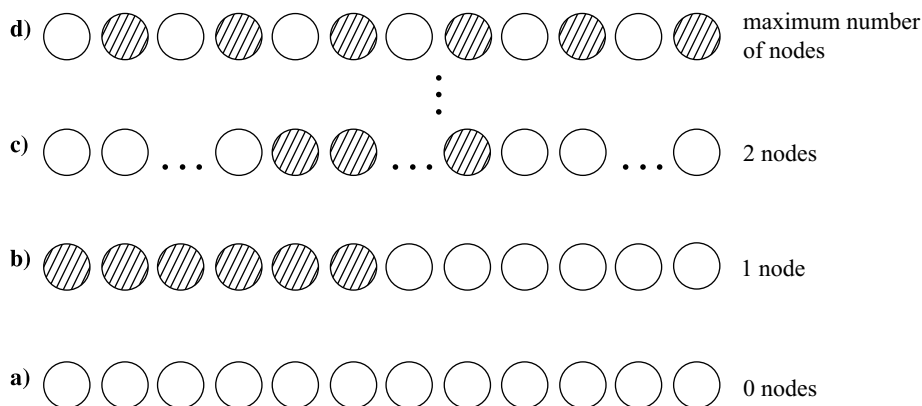


Fig. 9.13. The infinite chain of ground-state hydrogen atoms and the influence of bonding and antibonding effects, p. 371. a) all interactions are bonding; b) introduction of a single node results in an energy increase; c) two nodes increase the energy even more; d) maximum number of nodes – the energy is the highest possible.

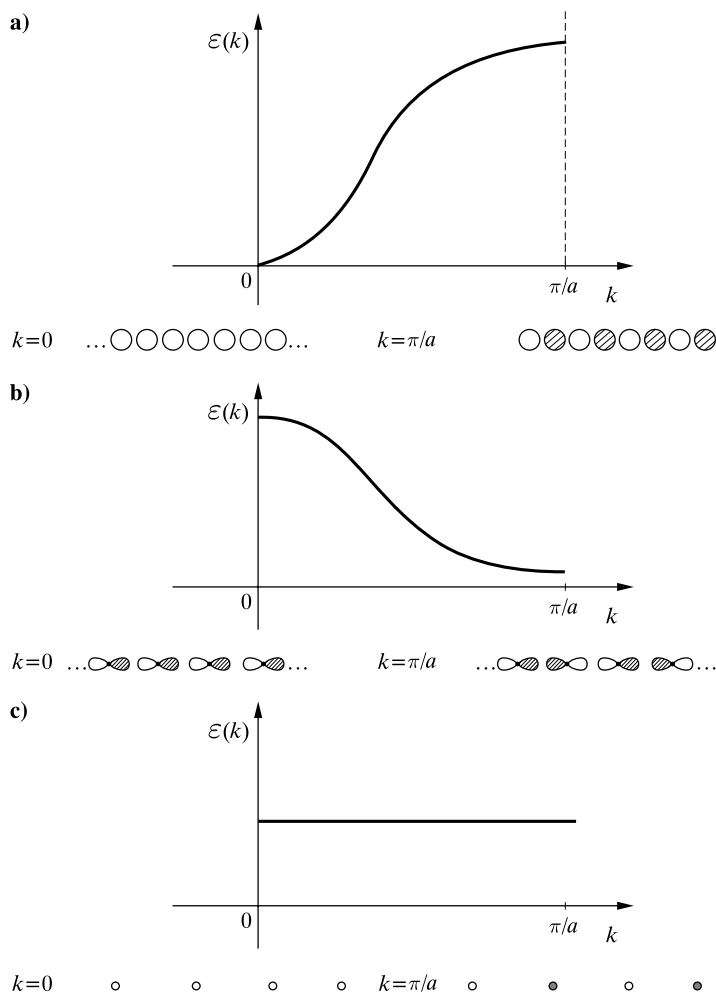


Fig. 9.14. Three typical band plots in the FBZ; a) 1s orbitals. Increasing k is accompanied by an *increase* of the antibonding interactions and this is why the energy goes up; b) $2p_z$ orbitals (z denotes the periodicity axis). Increasing k results in *decreasing* the number of antibonding interactions and the energy goes down; c) inner shell orbitals. The overlap is small as it is, therefore, the band width is practically zero.

we introduce a single nearest-neighbour antibonding interaction, the energy will for sure increase a bit (Fig. 9.13.b). When two such interactions are introduced (Fig. 9.13.c), the energy goes up even more, and the plot corresponds to two nodes. Finally, the highest-energy situation: all nearest-neighbour interactions are antibonding (maximum number of nodes), Fig. 9.13.d. Let us recall that the wave vector was associated with the number of nodes. Hence, if k increases from zero to $\frac{\pi}{a}$, the energy increases from the energy corresponding to the nodeless wave function to the energy characteristic for the maximum-node wave function. We understand, therefore, that some band plots are such as in Fig. 9.14.a.

9.10.2 WHY DO SOME BANDS GO DOWN?

Sometimes the bands go in the opposite direction: the lowest energy corresponds to $k = \frac{\pi}{a}$, the highest energy to $k = 0$. What happens over there? Let us once more take the hydrogen atom chain, this time, however, in the $2p_z$ state (z is the periodicity axis). This time the Bloch function corresponding to $k = 0$, i.e. a function that follows just from locating the orbitals $2p_z$ side by side, describes the highest-energy interaction – the *nearest-neighbour interactions are all antibonding*. Introduction of a node (increasing k) means a relief for the system – instead of one painful antibonding interaction we get a soothing bonding one. The energy goes down. No wonder, therefore, some bands look like those shown in Fig. 9.14.b.

9.10.3 WHY DO SOME BANDS STAY CONSTANT?

According to numerical rules (p. 362) inner shell atomic orbitals do not form effective linear combinations (crystal orbitals). Such orbitals have very large exponential coefficients and the resulting overlap integral, and therefore the band width (bonding vs antibonding effect), is negligible. This is why the nickel $1s$ orbitals (deep-energy level) result in a low-energy band of almost zero width (Fig. 9.14.c), i.e. staying flat as a pancake all the time. Since they are always of very low energy, they are doubly occupied and their plot is so boring, they are not even displayed (as in Fig. 9.8).

9.10.4 HOW CAN MORE COMPLEX BEHAVIOUR BE EXPLAINED?

We understand, therefore, at least why some bands are monotonically going down, some up, some stay constant. In explaining these cases, we have assumed that a given CO is dominated by a single Bloch function. Other behaviours can be explained as well by detecting what kind of Bloch function *combination* we have in a given crystal orbital.

2D regular lattice of the hydrogen atoms

Let us take a planar regular lattice of hydrogen atoms in their ground state.³⁶ Fig. 9.8 shows the FBZ of similar lattice, we (arbitrarily) choose as the itinerary through the FBZ: $\Gamma - X - M - \Gamma$. From Fig. 9.6.a we easily deduce, that the band energy for the point Γ has to be the lowest, because it corresponds to all the interaction bonding. What will happen at the point X ? This situation is related to Fig. 9.6.b. If we focus on any of the hydrogen atoms, it has four nearest neighbour interactions: two bonding and two antibonding. This corresponds, to good approximation, to the non-bonding situation (hydrogen atom ground-state energy), because the two effects nearly cancel. Halfway between Γ and X , we go through the point that corresponds to Fig. 9.6.c,d. For such a point, any hydrogen atom has two bonding and two non-bonding interactions, i.e. the energy is the average of the Γ

³⁶A chemist's first thought would be that this could never stay like this, when the system is isolated. We are bound to observe the formation of hydrogen molecules.

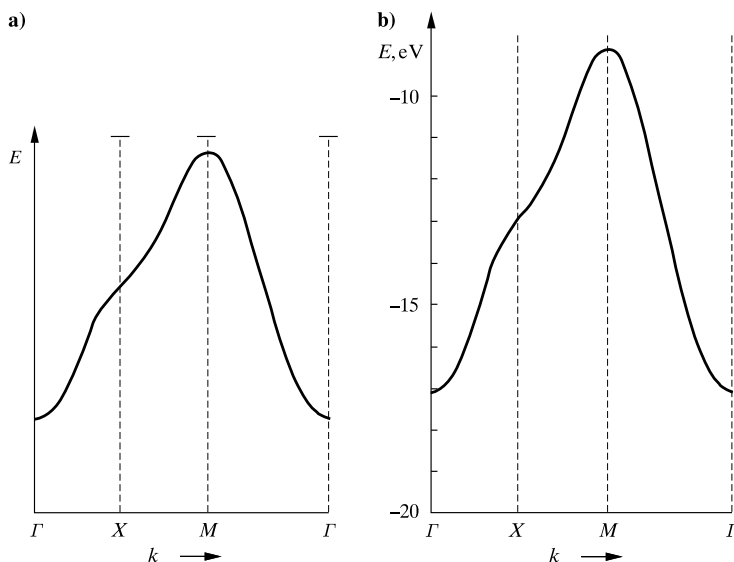


Fig. 9.15. a) A sketch of the valence band for a regular planar lattice of ground-state hydrogen atoms and b) the valence band, as computed in the laboratory of Roald Hoffmann, for nearest neighbour distance equal to 2 \AA . The similarity of the two plots confirms that we are able, at least in some cases, to predict band structure. R. Hoffmann, “*Solids and Surfaces. A Chemist’s View of Bonding in Extended Structures*”, VCH Publishers, New York, © 1988 VCH Publishers. Reprinted with permission of John Wiley & Sons, Inc.

and X energies. The point M is located in the corner of the FBZ, and corresponds to Fig. 9.6.e. All the nearest-neighbour interactions are antibonding there, and the energy will be very high. We may, therefore, anticipate a band structure of the kind sketched in Fig. 9.15.a. The figure has been plotted to reflect the fact that the density of states for the band edges is the largest, and therefore the slope of the curves has to reflect this. Fig. 9.15 shows the results of the computations.³⁷ It is seen that, even very simple reasoning may rationalize the main features of band structure plots.

Trans-polyacetylene (regular 1D polymer)

Polyacetylene already has quite a complex band structure, but as usual the bands close to the Fermi level (valence bands) are the most important in chemistry and physics. All these bands are of the π type, i.e. their COs are antisymmetric with respect to the plane of the polymer. Fig. 9.16 shows how the valence bands are formed. We can see, the principle is identical to that for the chain of the hydrogen atoms: the more nodes the higher the energy. The highest energy corresponds to the band edge.

The resulting band is only *half-filled* (metallic regime), because each of the carbon atoms offers one electron, and the number of COs is equal to the number

³⁷R. Hoffmann, “*Solids and Surfaces. A Chemist’s View of Bonding in Extended Structures*”, VCH Publishers, New York, 1988.

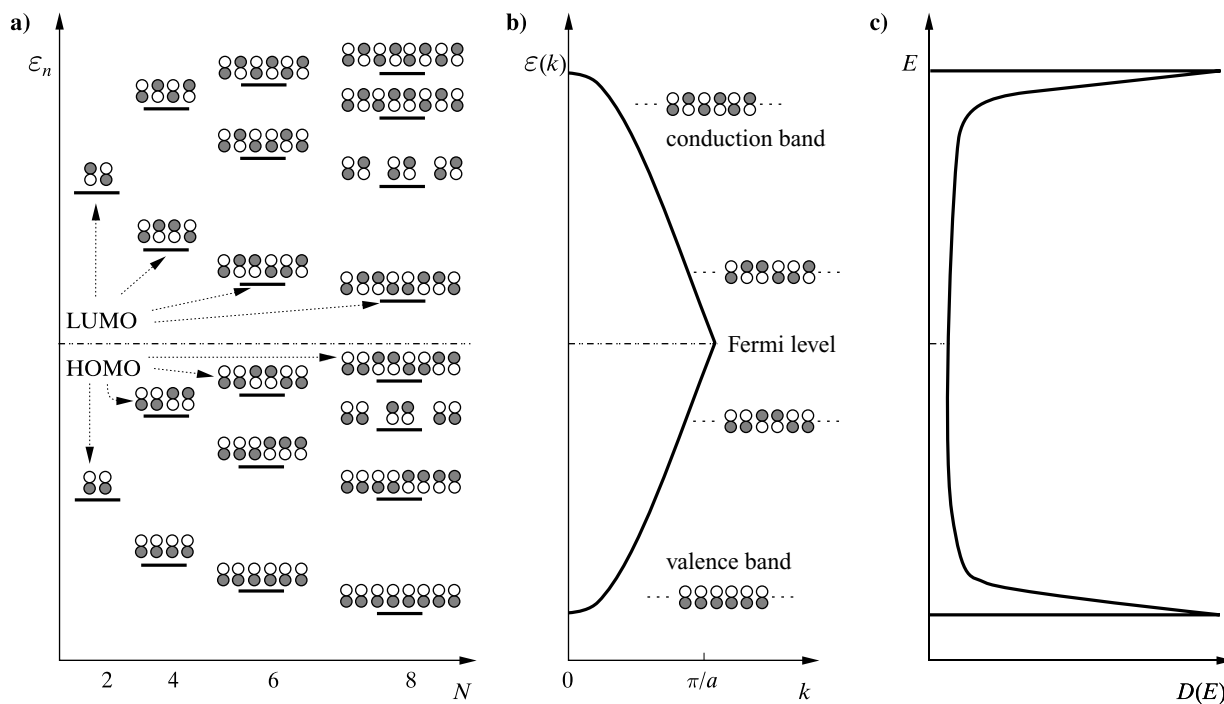


Fig. 9.16. a) π -band formation in polyenes (N stands for the number of carbon atoms) with the assumption of CC bond equivalence (each has length $a/2$). For $N = \infty$ this gives the metallic solution (no Peierls effect). As we can see, the band formation principle is identical to that, which we have seen for hydrogen atoms. b) band structure; c) density of states $D(E)$, i.e. the number of states per energy unit at a given energy E . The density has maxima at the extremal points of the band. If we allowed the Peierls transition, at $k = \pm\pi/a$ we would have a gap. J.-M. André, J. Delhalle, J.-L. Brédas, “*Quantum Chemistry Aided Design of Organic Polymers*”, World Scientific, Singapore, 1991. Reprinted with permission from the World Scientific Publishing Co. Courtesy of the authors.

of carbon atoms (each CO can accommodate two electrons). Therefore, Peierls mechanism (Fig. 9.10) is bound to enter into play, and in the middle of the band a gap will open. The system is, therefore, predicted to be an insulator (or semiconductor) and indeed it is. It may change to a metal when doped. Fig. 9.16 shows a situation analogous to the case of a chain of the ground state hydrogen atoms.

Polyparaphenylene

The extent to which the COs conform to the rule of increasing number of nodes with energy (or k) will be seen in the example of a planar conformation of polyparaphenylene.³⁸ On the left-hand side of Fig. 9.17 we have the valence π -orbitals of benzene:

- the lowest-energy has a nodeless³⁹ doubly occupied molecular orbital φ_1 ,
- then, we have a doubly degenerate and fully occupied level with the corresponding orbitals, φ_2 and φ_3 , each having a single node,
- next, a similar double degenerate empty level with orbitals φ_4 and φ_5 (each with two nodes),
- and finally, the highest-energy empty three-node orbital φ_6 .

Thus, even in the single monomer we have fulfilled the rule.

Binding phenyl rings by using CC σ bonds results in polyparaphenylene. Let us see what happens when the wave number k increases (the middle and the right-hand side of Fig. 9.17). What counts now is how two *complete monomer orbitals* combine: in-phase or out-of-phase. The lowest-energy π -orbitals of benzene (φ_1) arranged in-phase ($k = 0$) give point Γ – the lowest-energy in the polymer, while out-of-phase, point $k = \frac{\pi}{a}$ – the highest-energy. At $k = \frac{\pi}{a}$ there is a degeneracy of this orbital and of φ_3 arranged out-of-phase. The degeneracy is quite interesting because, despite a superposition of the orbitals with the different number of nodes, the result, for obvious reasons, corresponds to the same number of nodes. Note the extremely small dispersion of the band which results from the arrangement of φ_2 . The figure shows that it is bound to be small, because it is caused by the arrangement of two molecular orbitals that are further away in space than those so far considered (the overlap results from the overlap of the atomic orbitals separated by three bonds, and not by a single bond as it has been). We see a similar regularity in the conduction bands that correspond to the molecular orbitals φ_4 , φ_5 and φ_6 . The rule works here without any exception and results from the simple statement that a bonding superposition has a lower energy than the corresponding antibonding one.

Thus, when looking at the band structure for polyparaphenylene we stay cool: we understand every detail of this tangle of bands.

³⁸J.-M. André, J. Delhalle, J.-L. Brédas, “*Quantum Chemistry Aided Design of Organic Polymers*”, World Scientific, Singapore, 1991.

³⁹Besides the nodal plane of the nuclear framework.

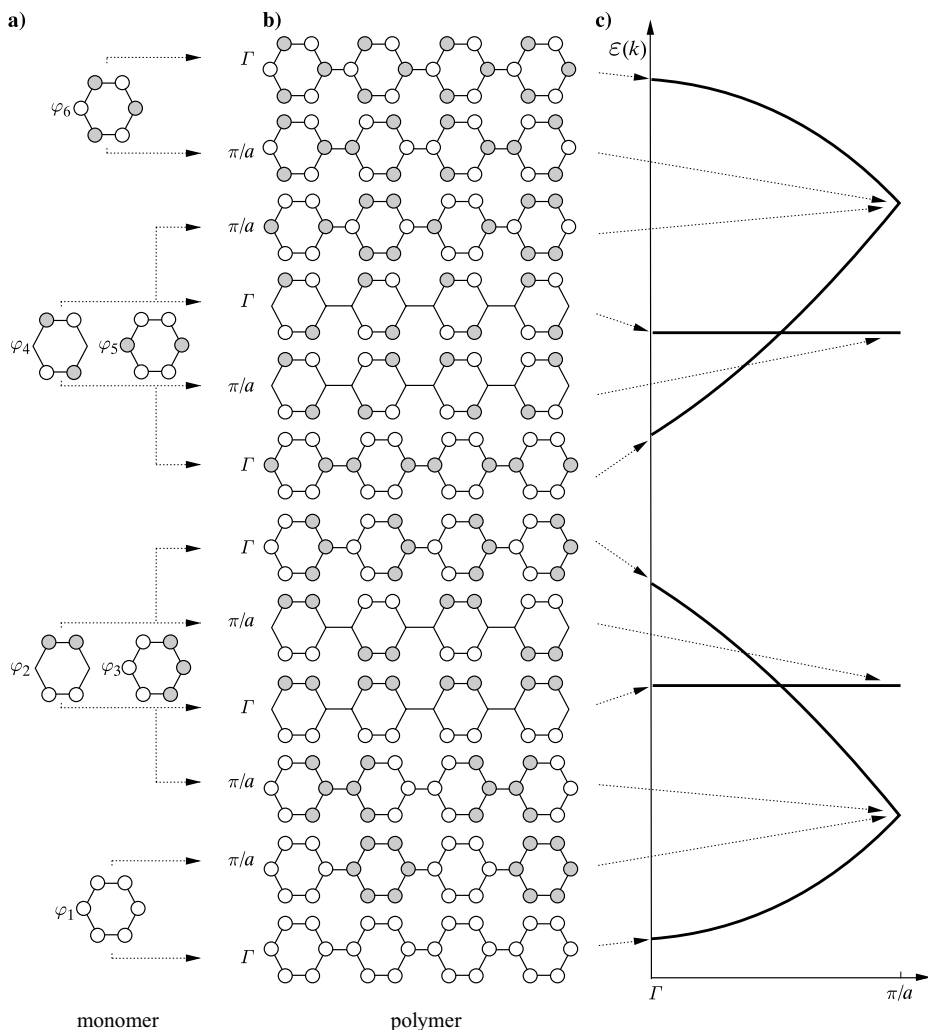


Fig. 9.17. Rationalizing the band structure of polyparaphenylene (π -bands). The COs (in centre) built as in-phase or out-of-phase combinations of the benzene π molecular orbitals (left-hand side). It is seen that energy of the COs for $k = 0$ and $k = \frac{\pi}{a}$ agree with the rule of increasing number of nodes. A small band width corresponds to small overlap integrals of the monomer orbitals. J.-M. André, J. Delhalle, J.-L. Brédas, “*Quantum Chemistry Aided Design of Organic Polymers*”, World Scientific, Singapore, 1991. Reprinted with permission from the World Scientific Publishing Co. Courtesy of the authors.

A stack of Pt(II) square planar complexes

Let us try to predict⁴⁰ qualitatively (without making calculations) the band structure of a stack of platinum square planar complexes, typically $[\text{Pt}(\text{CN}^-)_4]_{\infty}^{2-}$. Con-

⁴⁰R. Hoffmann, “*Solids and Surfaces. A Chemist’s View of Bonding in Extended Structures*”, VCH Publishers, New York, 1988.

sider the eclipsed configuration of all the monomeric units. Let us first simplify our task. Who likes cyanides? Let us throw them away and take something theoreticians really love: H^- . This is a little less than just laziness. If needed, we are able to make calculations for cyanides too, but to demonstrate that we really understand the machinery we are always recommended to make the system as simple as possible (but not simpler). We suspect that the main role of CN^- is just to interact electrostatically, and H^- does this too (being much smaller).

The electronic dominant configuration of the platinum atom in its ground state is⁴¹ $(\text{Xe})(4f^{14})5d^96s^1$ (see the Mendelev Table in the Web Annex). As we can see, we have the xenon-like closed shell and also the full closed subshell $4f$. The orbital energies corresponding to these closed shells are much lower than the orbital energy of the hydrogen anion (they are to be combined to). This is why they will not participate in the Pt–H bonds. They will of course contribute to the band structure, but this contribution will be trivial: flat bands (because of small overlap integrals) with energies very close to the energies characterizing the corresponding atomic orbitals. The Pt valence shell is therefore $5d^96s^16p^0$ for Pt^0 , and $5d^86s^06p^0$ for Pt^{2+} , which we have in our stack. The corresponding orbital energies are shown on the left-hand side of Fig. 9.18.a.

Let us choose a Cartesian coordinate system with the origin on the platinum atom and the four ligands at equal distances on the x and y axes. In the Koopmans

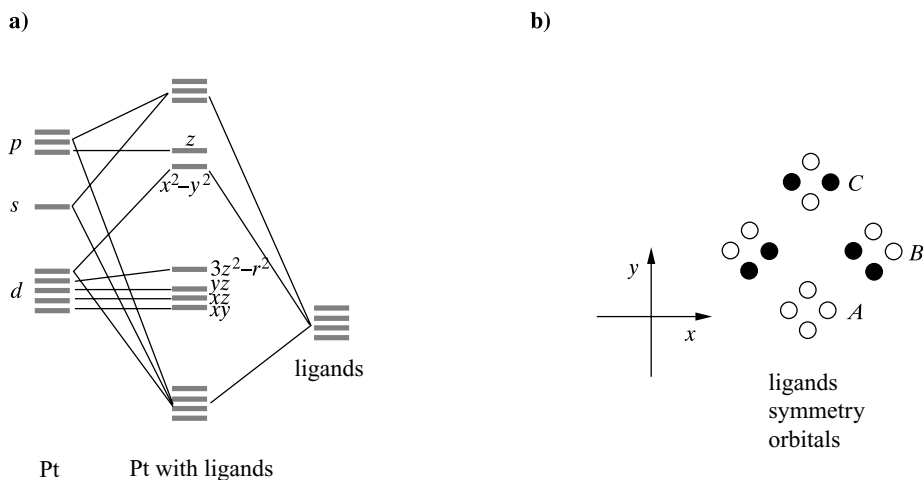


Fig. 9.18. Predicting the band structure of $(\text{PtH}_4^{2-})_\infty$. (a) monomer (PtH_4^{2-}) molecular orbitals built from the atomic orbitals of Pt^{2+} (the three p and five d Pt atomic orbitals correspond to two degenerate energy p and d levels) and four ligand (H^-) orbitals. One of the platinum orbitals ($5d_{x^2-y^2}$) corresponds to high energy, because it protrudes right across to the negatively charged ligands. The four ligand AOs, due to the long distance practically do not overlap, and are shown as a quadruply degenerate level. (b) The ligand orbitals form linear combinations with those of the metal. See the text.

⁴¹Xe denotes the xenon-like configuration of electrons.

approximation (cf. Chapter 8, p. 393) an orbital energy represents the electron energy on a given orbital. We see, that because the ligands are negatively charged, all the platinum atom orbital energies will go up (destabilization; in Fig. 9.18.a this shift is not shown, only a relative shift is given). The largest shift up will be undergone by the $5d_{x^2-y^2}$ orbital energy, because the orbital lobes protrude right across to the negative ligands. Eight electrons of Pt^{2+} will therefore occupy four other orbitals⁴² ($5d_{xy}$, $5d_{xz}$, $5d_{yz}$, $5d_{3z^2-r^2}$), while $5d_{x^2-y^2}$ will become LUMO. The four ligand atomic orbitals practically do not overlap (long distance) and this is why in Fig. 9.18.a they are depicted as a quadruply degenerate level. The ligand symmetry orbitals are shown in Fig. 9.18.b: the nodeless orbital (A), and two single-node orbitals (B) corresponding to the same energy, and the two-node orbital (C). The effective linear combinations (cf. p. 362, what counts most is symmetry) are formed by the following pairs of orbitals: $6s$ with A, $6p_x$ and $6p_y$ with B, and the orbital $5d_{x^2-y^2}$ with C (in each case we obtain the bonding and the antibonding orbital); the other platinum orbitals, $5d$ and $6p_z$ do not have partners of the appropriate symmetry (and therefore their energy does not change). Thus we obtain the energy level diagram of the monomer in Fig. 9.18.a.

Now, we form a stack of PtH_4^{2-} along the periodicity axis z . Let us form the Bloch functions (Fig. 9.19.a) for each of the valence orbitals at two points of the FBZ: $k = 0$ and $k = \frac{\pi}{a}$. The results are given in Fig. 9.19.b. Because of the large overlap of the $6p_z$ orbitals with themselves, and $3d_{3z^2-r^2}$ also with themselves, these σ bands will have very large dispersions. The smallest dispersion will correspond to the $5d_{xy}$ band (as well as to the empty band $5d_{x^2-y^2}$), because the orbital lobes of $5d_{xy}$ (also of $5d_{x^2-y^2}$) are oriented perpendicularly to the periodicity axis. Two bands $5d_{xz}$ and $5d_{yz}$ have a common fate (i.e. the same plot) due to the symmetry, and a medium band width (Fig. 9.19.b). We predict therefore,⁴⁰ the band structure shown in Fig. 9.20. The prediction turns out to be correct.

9.11 THE HARTREE-FOCK METHOD FOR CRYSTALS

9.11.1 SECULAR EQUATION

What has been said previously about the Hartree-Fock method is only a sort of general theory. The time has now arrived to show how the method works in practice. We have to solve the Hartree-Fock-Roothaan equation (cf. Chapter 8, pp. 365 and 453).

⁴²Of these four the lowest-energy will correspond to the orbitals $5d_{xz}$, $5d_{yz}$, because their lobes just avoid the ligands. The last two orbitals $5d_{xy}$ and $5d_{3z^2-r^2} = 5d_{z^2-x^2} + 5d_{z^2-y^2}$ will go up somewhat in the energy scale (each to different extent), because they aim in part at the ligands. However, these splits will be smaller when compared to the fate of the orbital $5d_{x^2-y^2}$ and therefore, these levels have been shown in the figure as a single degenerate level.

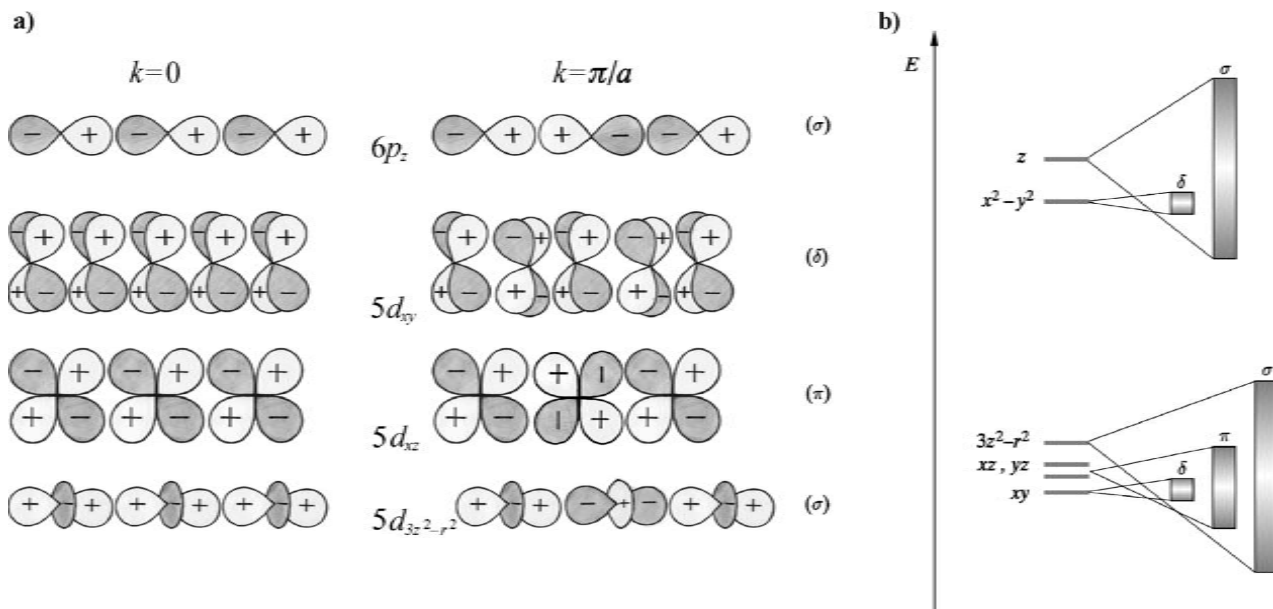


Fig. 9.19. Predicting the band structure of $(\text{PtH}_4^{2-})_\infty$. (a) the Bloch functions for $k=0$ and $k=\frac{\pi}{a}$ corresponding to the atomic orbitals $6p_z$ (σ type orbitals), $5d_{xy}$ (δ type orbitals), $5d_{xz}$ (π type orbitals, similarly for $5d_{yz}$), $5d_{3z^2-r^2}$ (σ type orbitals); (b) the band width is very sensitive to the overlap of the atomic orbitals. The band widths in $(\text{PtH}_4^{2-})_\infty$ resulting from the overlap of the (PtH_4^{2-}) orbitals.

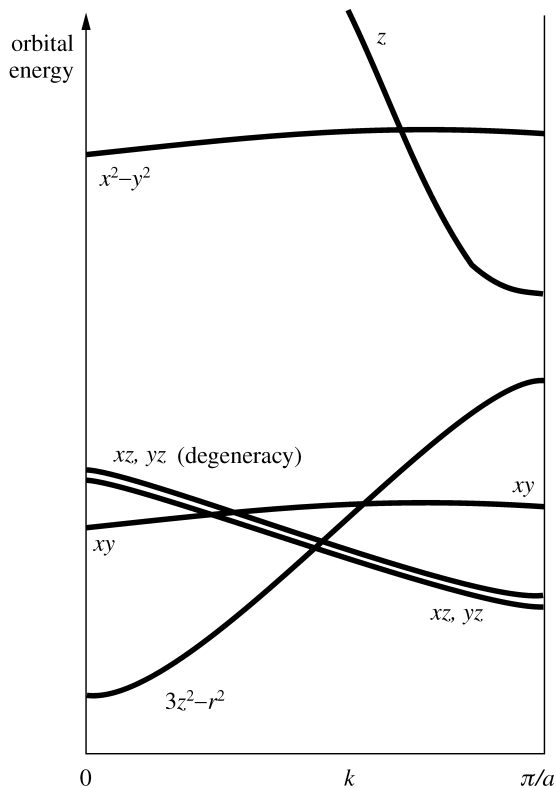


Fig. 9.20. The predicted band structure of $(\text{PtH}_4^{2-})_\infty$.

The Fock matrix element is equal to (noting that $(\chi_p^j | \hat{F} \chi_q^{j'}) \equiv F_{pq}^{jj'}$ depends on the difference⁴³ between the vectors \mathbf{R}_j and $\mathbf{R}_{j'}$):

$$F_{pq} = (2N + 1)^{-3} \sum_{jj'} \exp(i\mathbf{k}(\mathbf{R}_j' - \mathbf{R}_j)) (\chi_p^j | \hat{F} \chi_q^{j'}) = \sum_j \exp(i\mathbf{k}\mathbf{R}_j) F_{pq}^{0j}.$$

The same can be done with S_{pq} and therefore the Hartree–Fock–Roothaan secular equation (see p. 453) has the form:

$$\sum_{q=1}^{\omega} c_{qn}(\mathbf{k}) \left(\sum_j \exp(i\mathbf{k}\mathbf{R}_j) (F_{pq}^{0j}(\mathbf{k}) - \varepsilon_n(\mathbf{k}) S_{pq}^{0j}(\mathbf{k})) \right) = 0, \quad (9.55)$$

for $p = 1, 2, \dots, \omega$. The integral S_{pq} equals

$$S_{pq} = \sum_j \exp(i\mathbf{k}\mathbf{R}_j) S_{pq}^{0j}, \quad (9.56)$$

⁴³As a matter of fact, all depends on how distant the unit cells j and j' are. We have used the fact that \hat{F} exhibits the crystal symmetry and the sums over j all give the same result, independent of j' .

the summation \sum_j goes over the lattice nodes. In order to be explicit, let us see what is inside the Fock matrix elements $F_{pq}^{0j}(\mathbf{k})$. We have to find a dependence there on the Hartree–Fock–Roothaan solutions (determined by the coefficients c_{pn}), and more precisely on the bond order matrix.⁴⁴ Any CO, according to (9.53), has the form

$$\psi_n(\mathbf{r}, \mathbf{k}) = (2N + 1)^{-\frac{3}{2}} \sum_q \sum_j c_{qn}(\mathbf{k}) \exp(i\mathbf{k}\mathbf{R}_j) \chi_q^j(\mathbf{r}), \quad (9.57)$$

where we promise to use such c_{qn} that ψ_n are normalized. For molecules the bond order matrix element (for the atomic orbitals χ_p and χ_q) has been defined (p. 365) as $P_{pq} = 2 \sum c_{pi} c_{qi}^*$ (the summation is over the doubly occupied orbitals), where the factor 2 results from the double occupation of the closed shell. We have exactly the same for the crystal, where we define the bond order matrix element corresponding to atomic orbitals χ_q^j and χ_p^l as:

$$P_{pq}^{lj} = 2(2N + 1)^{-3} \sum c_{pn}(\mathbf{k}) \exp(i\mathbf{k}\mathbf{R}_l) c_{qn}(\mathbf{k})^* \exp(-i\mathbf{k}\mathbf{R}_j), \quad (9.58)$$

where the summation goes over all the occupied COs (we assume double occupation, hence factor 2). This means that, in the summation we have to go over all the occupied bands (index n), and in each band over all allowed COs, i.e. all the allowed \mathbf{k} vectors in the FBZ. Thus,

$$P_{pq}^{lj} = 2(2N + 1)^{-3} \sum_n \sum_{\mathbf{k}}^{\text{FBZ}} c_{pn}(\mathbf{k}) c_{qn}(\mathbf{k})^* \exp(i\mathbf{k}(\mathbf{R}_l - \mathbf{R}_j)). \quad (9.59)$$

The matrix element has to have four indices (instead of the two indices in the molecular case), because we have to describe the atomic orbitals indicating that atomic orbital p is from unit cell l , and atomic orbital q from unit cell j . It is easily seen that P_{pq}^{lj} depends on the *difference* $\mathbf{R}_l - \mathbf{R}_j$, not on the \mathbf{R}_l , \mathbf{R}_j themselves. The reason for this is that in a crystal everything is repeated and the important thing are the *relative* distances.

9.11.2 INTEGRATION IN THE FBZ

There is a problem with P , because it requires a summation over \mathbf{k} . We do not like this, because the number of the permitted \mathbf{k} is huge for large N (and N has to be large, because we are dealing with a crystal). We have to do something with it.

Let us try a small exercise. Imagine, we have to perform a summation $\sum_{\mathbf{k}} f(\mathbf{k})$, where f represents a smooth function in the FBZ. Let us denote the sum to be found by X . Let us multiply X by a small number $\Delta = \frac{V_{\text{FBZ}}}{(2N+1)^3}$, where V_{FBZ} stands

⁴⁴We have met the same in the Hartree–Fock method for molecules, where the Coulomb and exchange operators depended on the solutions to the Fock equation, cf. p. 346.

for the FBZ volume:

$$X\Delta = \sum_{\mathbf{k}}^{\text{FBZ}} f(\mathbf{k})\Delta. \quad (9.60)$$

In other words we just cut the FBZ into tiny segments of volume Δ , their number equal to the number of the permitted \mathbf{k} 's. It is clear that if N is large (as it is in our case), then a very good approximation of $X\Delta$ would be

$$X\Delta = \int_{\text{FBZ}} f(\mathbf{k}) d^3\mathbf{k}. \quad (9.61)$$

Hence,

$$X = \frac{(2N+1)^3}{V_{\text{FBZ}}} \int_{\text{FBZ}} f(\mathbf{k}) d^3\mathbf{k}. \quad (9.62)$$

After applying this result to the bond order matrix we obtain

$$P_{pq}^{lj} = \frac{2}{V_{\text{FBZ}}} \int \sum_n^{\text{FBZ}} c_{pn}(\mathbf{k}) c_{qn}(\mathbf{k})^* \exp(i\mathbf{k}(\mathbf{R}_l - \mathbf{R}_j)) d^3\mathbf{k}. \quad (9.63)$$

For a periodic *polymer* (in 1D: $V_{\text{FBZ}} = \frac{2\pi}{a}$, $\Delta = \frac{V}{2N+1}$) we would have:

$$P_{pq}^{lj} = \frac{a}{\pi} \int \sum_n c_{pn}(k) c_{qn}(k)^* \exp(ika(l-j)) dk. \quad (9.64)$$

9.11.3 FOCK MATRIX ELEMENTS

In full analogy with the formula (8.53), we can express the Fock matrix elements by using the bond order matrix \mathbf{P} for the crystal:

$$F_{pq}^{0j} = T_{pq}^{0j} - \sum_h \sum_u Z_u V_{pq}^{0j}(A_u^h) + \sum_{hl} \sum_{rs} P_{sr}^{lh} \left[\begin{pmatrix} 0h & jl \\ pr & qs \end{pmatrix} - \frac{1}{2} \begin{pmatrix} 0h & lj \\ pr & sq \end{pmatrix} \right], \quad (9.65)$$

this satisfies the normalization condition⁴⁵

⁴⁵The \mathbf{P} matrix satisfies the normalization condition, which we obtain in the following way. As in the molecular case the normalization of CO's means:

$$\begin{aligned} 1 &= \langle \psi_n(\mathbf{r}, \mathbf{k}) | \psi_n(\mathbf{r}, \mathbf{k}) \rangle \\ &= (2N+1)^{-3} \sum_{pq} \sum_{jl} c_{pn}(\mathbf{k})^* c_{qn}(\mathbf{k}) \exp[i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_l)] S_{pq}^{lj} \\ &= (2N+1)^{-3} \sum_{pq} \sum_{jl} c_{pn}(\mathbf{k})^* c_{qn}(\mathbf{k}) \exp[i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_l)] S_{pq}^{0(j-l)} \\ &= \sum_{pq} \sum_j c_{pn}(\mathbf{k})^* c_{qn}(\mathbf{k}) \exp(i\mathbf{k}\mathbf{R}_j) S_{pq}^{0j}. \end{aligned}$$

Now let us do the same for all the occupied COs and sum the results. On the left-hand side we sum just 1, therefore we obtain the number of doubly occupied COs, i.e. $n_0(2N+1)^3$, because n_0 denotes

$$\sum_j \sum_{pq} P_{qp}^{j0} S_{pq}^{0j} = 2n_0, \quad (9.68)$$

where $2n_0$ means the number of electrons in the unit cell.

The first term on the right-hand side of (9.65) represents the kinetic energy matrix element

$$T_{pq}^{0j} = \left(\chi_p^0 \left| -\frac{1}{2} \Delta \right| \chi_q^j \right), \quad (9.69)$$

the second term is a sum of matrix elements, each corresponding to the nuclear attraction of an electron and the nucleus of index u and charge Z_u in the unit cell h :

$$V_{pq}^{0j}(A_u^h) = \left(\chi_p^0 \left| \frac{1}{|\mathbf{r} - \mathbf{A}_u^h|} \right| \chi_q^j \right), \quad (9.70)$$

where the upper index of χ denotes the cell number, the lower index – the number of the atomic orbital in a cell, the vector \mathbf{A}_u^h indicates nucleus u (numbering within the unit cell) in unit cell h (from the coordinate system origin). The third term is connected to the Coulombic operator (the first of two terms) and the exchange operator (the second of two terms). The summations over h and l go over the unit cells of the whole crystal, and therefore are very difficult and time consuming.

The definition of the two-electron integral

$$({}^{0h}_{pr} | {}^{jl}_{qs}) = \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \chi_p^0(\mathbf{r}_1)^* \chi_r^h(\mathbf{r}_2)^* \frac{1}{r_{12}} \chi_q^j(\mathbf{r}_1) \chi_s^l(\mathbf{r}_2) \quad (9.71)$$

is analogous to eq. (8.5) and Appendix M, p. 986.

the number of doubly occupied bands, and in each band we have in 3D $(2N + 1)^3$ allowed vectors \mathbf{k} . Therefore, we have

$$\begin{aligned} n_0(2N + 1)^3 &= \sum_{pq} \sum_j \left(\sum_n \sum_{\mathbf{k}}^{\text{FBZ}} c_{pn}(\mathbf{k})^* c_{qn}(\mathbf{k}) \exp(i\mathbf{k}\mathbf{R}_j) \right) S_{pq}^{0j} \\ &= \sum_{pq} \sum_j \frac{1}{2} (2N + 1)^3 P_{qp}^{j0} S_{pq}^{0j}, \end{aligned}$$

where from (9.59) after exchanging $p \leftrightarrow q, j \leftrightarrow l$ we had:

$$P_{qp}^{jl} = 2(2N + 1)^{-3} \sum_n \sum_{\mathbf{k}}^{\text{FBZ}} c_{qn}(\mathbf{k}) c_{pn}(\mathbf{k})^* \exp(i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_l)) \quad (9.66)$$

and then

$$P_{qp}^{j0} = 2(2N + 1)^{-3} \sum_n \sum_{\mathbf{k}}^{\text{FBZ}} c_{qn}(\mathbf{k}) c_{pn}(\mathbf{k})^* \exp(i\mathbf{k}\mathbf{R}_j). \quad (9.67)$$

Hence, $\sum_{pq} \sum_j P_{qp}^{j0} S_{pq}^{0j} = 2n_0$.

9.11.4 ITERATIVE PROCEDURE

How does the Hartree–Fock method for periodic systems work?

- First (zeroth iteration), we start from a guess⁴⁶ for \mathbf{P} .
- Then, we calculate the elements F_{pq}^{0j} for all atomic orbitals p, q for unit cells $j = 0, 1, 2, \dots, j_{\max}$. What is j_{\max} ? The answer is certainly non-satisfactory: $j_{\max} = \infty$. In practice, however, we often take j_{\max} as being of the order of a few cells, most often we take⁴⁷ $j_{\max} = 1$.
- For each \mathbf{k} from the FBZ we calculate the elements F_{pq} and S_{pq} and then solve the secular equations within the Hartree–Fock–Roothaan procedure. This step requires diagonalization⁴⁸ (see Appendix K, p. 982). As a result, for each \mathbf{k} we obtain a set of coefficients c .
- We repeat all this for the values of \mathbf{k} covering in some optimal way (some recipes exist) the FBZ. We are then all set to carry out the numerical integration in the FBZ and we calculate an approximate matrix \mathbf{P} .
- This enables us to calculate a new approximation to the matrix \mathbf{F} and so on, until the procedure converges in a self-consistent way, i.e. produces \mathbf{P} very close to that matrix \mathbf{P} which has been inserted into the Fock matrix \mathbf{F} . In this way we obtain the band structure $\varepsilon_n(\mathbf{k})$ and all the corresponding COs.

9.11.5 TOTAL ENERGY

How do we calculate the total energy for an infinite crystal? We know the answer without any calculation: $-\infty$. Indeed, since the energy represents an extensive quantity, for an infinite number of the unit cells we get $-\infty$, because a single cell usually represents a bound state (negative energy). Therefore, the question has to be posed in another way.

How to calculate the total energy *per unit cell*? Aha, this is a different story. Let us denote this quantity by E_T . Since a crystal only represents a *very* large molecule, we may use the expression (8.41) for the total energy of a molecule [noting that $\varepsilon_i = (i|\hat{F}|i)$]. In the 3D case we have:

$$(2N + 1)^3 E_T = \frac{1}{2} \sum_{pq} \sum_{lj} P_{qp}^{jl} (h_{pq}^{lj} + F_{pq}^{lj}) + \frac{1}{2} \sum_{lj} \sum_{uv}' \frac{Z_u Z_v}{R_{uv}^{lj}}, \quad (9.72)$$

where the summation over p and q extends over the ω atomic orbitals that any unit cell offers, and l and j tell us in which cells these orbitals are located. The last term on the right-hand side refers to the nuclear repulsion of all the nuclei in the crystal, u, v number the nuclei in a unit cell, while l, j indicate the cells (a prime

⁴⁶The result is presumed to be independent of this choice.

⁴⁷“Nearest-neighbour approximation”. We encounter a similar problem *inside* the F_{pq}^{0j} , because we have somehow to truncate the summations over h and l . These problems will be discussed later in this chapter.

⁴⁸Unlike the molecular case, this time the matrix to diagonalize is Hermitian, and not necessarily symmetric. Methods of diagonalization exist for such matrices, and there is a guarantee that their eigenvalues are real.

means that there is no contribution from the charge interaction with itself). Since the summations over l and j extend over the whole crystal, therefore

$$(2N+1)^3 E_T = \frac{1}{2}(2N+1)^3 \sum_{pq} \sum_j P_{qp}^{j0} [h_{pq}^{0j} + F_{pq}^{0j}] + (2N+1)^3 \frac{1}{2} \sum_j \sum_{uv} \frac{Z_u Z_v}{R_{uv}^{0j}}, \quad (9.73)$$

because each term has an equal contribution, and the number of such terms is equal to $(2N+1)^3$.

Therefore, the total energy per unit cell amounts to

$$E_T = \frac{1}{2} \sum_j \sum_{pq} P_{qp}^{j0} (h_{pq}^{0j} + F_{pq}^{0j}) + \frac{1}{2} \sum_j \sum_u \sum_v \frac{Z_u Z_v}{R_{uv}^{0j}}. \quad (9.74)$$

The formula is correct, but we can easily see that we are to be confronted with some serious problems. For example, the summation over nuclei represents a divergent series and we will get $+\infty$. *This problem appears only because we are dealing with an infinite system and we confront the long-range interactions.* We have to manage the problem somehow.

9.12 LONG-RANGE INTERACTION PROBLEM

What is left to be clarified are some problems about how to go with N to infinity.⁴⁹ It will be soon shown how dangerous this problem is.

We see from eqs. (9.65) and (9.74) that, despite using the translational symmetry to simplify the problem, we may treat each \mathbf{k} separately. There are an infinite

⁴⁹I will tell you about my adventure with this problem, because I remember very well how as a student I wanted to hear about struggles with understanding matter and ideas, instead of dry summaries.

The story began quite accidentally. In 1977, at the University of Namur (Belgium) Professor Joseph Delhalle asked the PhD student Christian Demanet to perform a numerical test. The test consisted of taking a simple infinite polymer (the infinite chain ... LiH LiH LiH ... had been chosen), to use the simplest atomic basis set possible and to see what we should take as N , to obtain the Fock matrix with sufficient accuracy. Demanet first took $N = 1$, then $N = 2$, $N = 3$ – the Fock matrix changed all the time. He got impatient, took $N = 10$, $N = 15$ – the matrix continued to change. Only when he used $N = 200$ did the Fock matrix elements stabilize within the accuracy of six significant figures. We could take $N = 200$ for an extremely poor basis set and for a few such tests, but the quality of calculations will never be good and their cost would become astronomic. Even for the case in question the computations had to be done overnight. In a casual discussion at the beginning of my six-week stay at the University of Namur, Joseph Delhalle told me about the problem. He said also that in a recent paper the Austrian scientists Alfred Karpfen and Peter Schuster also noted that the results depend strongly on the chosen value of N . They made a correction *after* the calculations with a small N had been performed. They added the dipole–dipole electrostatic interaction of the cell 0 with a few hundred neighbouring cells, and for the dipole moment of a cell, they took the dipole moment of the isolated LiH molecule. As a result the Fock matrix elements changed much less with N . This information made me think about implementing the multipole expansion right from the beginning of the self-consistent Hartree–Fock–Roothaan procedure for a polymer. Below you will see what has been done. The presented theory pertains to a regular polymer (a generalization to 2D and 3D is possible).

number of them and this makes us a little nervous. In eq. (9.65) for F_{pq}^{0j} we have a summation (over the whole infinite crystal) of the interactions of an electron with all the nuclei, and in the next term a summation over the whole crystal of the electron–electron interactions. This is of course perfectly natural, because our system is infinite. The problem is, however, that both summations diverge: the first tends to $-\infty$, the second to $+\infty$. On top of this to compute the bond order matrix P we have to perform another summation in eq. (9.63) over the FBZ of the crystal. We have a similar, very unpleasant, situation in the total energy expression, where the first term tends to $-\infty$, while the nuclear repulsion term goes $+\infty$.

The routine approach was to replace the infinity by taking the first-neighbour interactions. This approach is quite understandable, because any attempt to take further neighbours ends up with an exorbitant bill to pay.⁵⁰

9.12.1 FOCK MATRIX CORRECTIONS

A first idea we may think of is to carefully separate the long-range part of the Fock matrix elements and of the total energy from these quantities as calculated in a traditional way, i.e. by limiting the infinite-range interactions to those for the N neighbours on the left from cell 0 and N neighbours on the right of it. For the Fock matrix element we would have:

$$F_{pq}^{0j} = F_{pq}^{0j}(N) + C_{pq}^{0j}(N), \quad (9.75)$$

where $C_{pq}^{0j}(N)$ stands for the long-range correction, while $F_{pq}^{0j}(N)$ is calculated assuming interactions with the N right and N left neighbours of cell 0:

$$F_{pq}^{0j}(N) = T_{pq}^{0j} + \sum_{h=-N}^{h=+N} \left(- \sum_u Z_u V_{pq}^{0j}(A_u^h) + \sum_{l=h-N}^{l=h+N} \sum_{rs} P_{sr}^{lh} \left(\langle 0h | jl \rangle_{pr} \langle qs \rangle - \frac{1}{2} \langle 0h | lj \rangle_{pr} \langle qs \rangle \right) \right), \quad (9.76)$$

$$C_{pq}^{0j}(N) = \sum_h^{\#} \left(- \sum_u Z_u V_{pq}^{0j}(A_u^h) + \sum_{l=h-N}^{l=h+N} \sum_{rs} P_{sr}^{lh} \langle 0h | jl \rangle_{pr} \langle qs \rangle \right), \quad (9.77)$$

where the symbol $\sum_h^{\#}$ will mean a summation over all the unit cells *except* the section of unit cells with numbers $-N, -N+1, \dots, 0, 1, \dots, N$, i.e. the neighbourhood of cell 0 (“short-range”). The nuclear attraction integral:⁵¹

$$V_{pq}^{0j}(A_u^h) = \left(\chi_p^0 \left| \frac{1}{|\mathbf{r} - (A_u + h\mathbf{a}z)|} \right| \chi_q^j \right), \quad (9.78)$$

where the vector A_u shows the position of the nucleus u in cell 0, while $A_u^h \equiv A_u + h\mathbf{a}z$ points to the position of the equivalent nucleus in cell h (z denotes the unit vector along the periodicity axis).

⁵⁰The number of two-electron integrals, which quantum chemistry positively dislikes, increases with the number of neighbours taken (N) and the atomic basis set size per unit cell (ω) as $N^3 \omega^4$. Besides, the nearest-neighbours *are* indeed the most important.

⁵¹Without the minus sign in the definition the name is not quite adequate.

The expression for $C_{pq}^{0j}(N)$ has a clear physical interpretation. The first term represents the interaction of the charge distribution $-\chi_p^0(1)^* \chi_q^j(1)$ (of electron 1, hence the sign $-$) with *all the nuclei*,⁵² except those enclosed in the short-range region (i.e. extending from $-N$ to $+N$). The second term describes the interaction of the same electronic charge distribution with the *total electronic distribution* outside the short-range region. How do we see this? The integral $(0h|_{pr}^j|_{qs})$ means the Coulombic interaction of the distribution under consideration $-\chi_p^0(1)^* \chi_q^j(1)$ with its partner-distribution $-\chi_r^h(2)^* \chi_s^l(2)$, doesn't it? This distribution is multiplied by P_{sr}^{lh} and then summed over all possible atomic orbitals r and s in cell h and its neighbourhood (the sum over cells l from the neighbourhood of cell h), which gives the total partner electronic distribution $-\sum_{l=h-N}^{l=h+N} \sum_{rs} P_{sr}^{lh} \chi_r^h(2)^* \chi_s^l(2)$. This, however, simply represents the electronic charge distribution of cell h . Indeed, the distribution, when integrated gives [(just look at eq. (9.68)] $-\sum_{l=h-N}^{l=h+N} \sum_{rs} P_{sr}^{lh} S_{rs}^{hl} = 2n_0$. Therefore, our electron distribution, $-\chi_p^0(1)^* \chi_q^j(1)$, interacts electrostatically with the charge distribution of all cells except those enclosed in the short-range region, because eq. (9.77) contains the summation over all cells h except the short-range region. Finally,

the long-range correction to the Fock matrix elements $C_{pq}^{0j}(N)$ represents the Coulombic interaction of the charge distribution $-\chi_p^0(1)^* \chi_q^j(1)$ with all the unit cells (nuclei and electrons) from outside the short-range region.

In the $C_{pq}^{0j}(N)$ correction, in the summation over l , we have neglected the exchange term $-\frac{1}{2} \sum_{l=h-N}^{l=h+N} \sum_{rs} P_{sr}^{lh} (0h|_{pr}^{lj}|_{sq})$. The reason for this was that we have been convinced, that P_{sr}^{lh} vanishes very fast, when cell l separates from cell h . Subsequent reasoning would then be easy: the most important term ($l = h$) would be $-\frac{1}{2} \sum_{rs} P_{sr}^{hh} (0h|_{pr}^{hj}|_{sq})$. It contains the differential overlap $\chi_p^0(1)^* \chi_s^h(1)$, which decays exponentially when the cells 0 and h separate, and we have a *guarantee* [eq. (9.77)], that this separation is large.⁵³ We will come back to this problem.

9.12.2 TOTAL ENERGY CORRECTIONS

The total energy per unit cell could similarly be written as

$$E_T = E_T(N) + C_T(N), \quad (9.79)$$

⁵²Cf. interpretation of the integral $-V_{pq}^{0j}(A_u^h) = -(\chi_p^0(r)|\frac{1}{|r-A_u^h|}|\chi_q^j(r))$.

⁵³The exchange interactions are notorious for an exponential decay with distance when the two object separate. The matrix elements of \mathbf{P} corresponding to distant atomic orbitals "should be" small. For the time being let us postpone the problem. We will come back to it and will see how delusive such feelings may be. We have to stress, however, that trouble will come only in some "pathological" situations. In most common cases everything will be all right.

where $E_T(N)$ means the total energy per unit cell as calculated by the traditional approach, i.e. with truncation of the infinite series on the N left and N right neighbours of the cell 0. The quantity $C_T(N)$ therefore represents the error, i.e. the long-range correction. The detailed formulae for $E_T(N)$ and $C_T(N)$ are the following

$$E_T(N) = \frac{1}{2} \sum_{j=-N}^{j=+N} \sum_{pq} P_{qp}^{j0} (h_{pq}^{0j} + F_{pq}^{0j}(N)) + \frac{1}{2} \sum_{j=-N}^{j=+N} \sum_u \sum_v' \frac{Z_u Z_v}{R_{uv}^{0j}}, \quad (9.80)$$

$$C_T(N) = \frac{1}{2} \sum_j \sum_{pq} P_{qp}^{j0} C_{pq}^{0j}(N) + \frac{1}{2} \sum_h^{\#} \left(\sum_j \sum_{pq} P_{qp}^{j0} \sum_u [-Z_u V_{pq}^{0j}(A_u^h)] + \sum_u \sum_v' \frac{Z_u Z_v}{R_{uv}^{0h}} \right), \quad (9.81)$$

where we have already separated from F_{pq}^{0j} its long-range contribution $C_{pq}^{0j}(N)$, so that $C_T(N)$ contains *all* the long-range corrections.

Eq. (9.81) for $C_T(N)$ may be obtained by *just looking* at eq. (9.80). The first term with $C_{pq}^{0j}(N)$ is evident,⁵⁴ it represents the Coulombic interaction of the *electronic distribution* (let us recall condition (9.68)) associated with cell 0 with *the whole polymer chain* except the short-range region. What, therefore, is yet to be added to $E_T(N)$? What it lacks is the Coulombic interaction of the *nuclei* of cell 0 with *the whole polymer chain*, except the short-range region. Let us see whether we have it in eq. (9.81). The last term means the Coulombic interaction of the nuclei of cell 0 with *all the nuclei of the polymer* except the short-range region (and again we know, why we have the factor $\frac{1}{2}$). What, therefore, is represented by the middle term?⁵⁵ It

⁵⁴The factor $\frac{1}{2}$ may worry us a little. Why just $\frac{1}{2}$? Let us see. Imagine N identical objects $i = 0, 1, 2, \dots, N-1$ playing identical roles in a system (like our unit cells). We will be interested in the energy per object, E_T . The total energy may be written as (let us assume here pairwise interactions only) $NE_T = \sum_j E_j + \sum_{i < j} E_{ij}$, where E_j and E_{ij} are, respectively, the isolated object energy and the pairwise interaction energy. Since the objects are identical, then

$$NE_T = NE_0 + \frac{1}{2} \sum_{i,j}' E_{ij} = NE_0 + \frac{1}{2} \sum_i \left(\sum_j' E_{ij} \right) = NE_0 + \frac{1}{2} N \left(\sum_j' E_{0j} \right),$$

where the prime means excluding self-interaction and the term in parentheses means the interaction of object 0 with all others. Finally, $E_T = E_0 + \frac{1}{2} (\sum_j' E_{0j})$, where we have the factor $\frac{1}{2}$ before the interaction of one of the objects with the rest of the system.

⁵⁵As we can see, we have to sum (over j) to infinity the expressions h_{pq}^{0j} , which contain T_{pq}^{0j} [but these terms decay very fast with j and can all be taken into account in $E_T(N)$] and the long-range terms, the Coulombic interaction of the electronic charge distribution of cell 0 with the nuclei beyond the short-range region (the middle term in $C_T(N)$). The argument about fast decay with j of the kinetic energy matrix elements mentioned before follows from the double differentiation with respect to the coordinates of the electron. Indeed, this results in another atomic orbital, but with the same centre. This leads to the overlap integral of the atomic orbitals centred like those in $\chi_p^0 \chi_q^j$. Such an integral decays exponentially with j .

is clear, that it has to be (with the factor $\frac{1}{2}$) the Coulombic interaction of the *nuclei of cell 0* with the total electronic distribution outside the short-range region. We look at the middle term. We have the sign “-”. This is very good indeed, because we have to have an attraction. Further, we have the factor $\frac{1}{2}$, that is also OK, then we have $\sum_h^\#$, that is perfect, because we expect a summation over the long-range only, and finally we have $\sum_j \sum_{pq} P_{qp}^{j0} \sum_u [-Z_u V_{pq}^{0j}(A_u^h)]$ and we do not like this. This is the Coulombic interaction of the total *electronic distribution of cell 0* with the *nuclei of the long-range region*, while we expected the interaction of the *nuclei of cell 0* with the *electronic charge distribution of the long-range region*. What is going on? Everything is OK. Just count the interactions pairwise and at each of them reverse the locations of the interacting objects – the two interactions mean the same. Therefore,

the long-range correction to the total energy per cell $C_T(N)$ represents the Coulombic interaction of cell 0 with all the cells from outside the short-range region.

We are now all set to calculate the long-range corrections $C_{pq}^{0j}(N)$ and $C_T(N)$. It is important to realize that all the interactions to be calculated pertain to objects that are *far away in space*.⁵⁶ This is what we have carefully prepared. This is the condition that enables us to apply the multipole expansion to each of the interactions (Appendix X).

9.12.3 MULTIPOLE EXPANSION APPLIED TO THE FOCK MATRIX

Let us first concentrate on $C_{pq}^{0j}(N)$. As seen from eq. (9.77) there are two type of interactions to calculate: the nuclear attraction integrals $V_{pq}^{0j}(A_u^h)$ and the electron repulsion integrals $(\overset{0h}{pr} \overset{j}{l} \overset{0j}{qs})$. In the second term, we may use the multipole expansion of $\frac{1}{r_{12}}$ given in the Appendix X on p. 1039. In the first term, we will do the same,

⁵⁶Let us check this. What objects are we talking about? Let us begin from $C_{pq}^{0j}(N)$. As it is seen from the formula one of the interacting objects is the charge distribution of the first electron $\chi_p^0(1)^* \chi_q^j(1)$. The second object is the whole polymer except the nuclei and electrons of the neighbourhood of the cell 0. The charge distributions $\chi_p^0(1)^* \chi_q^j(1)$ with various j are always close to cell 0, because the orbital $\chi_p^0(1)$ is anchored at cell 0, and such a distribution decays exponentially when cell j goes away from cell 0. The fact that the nuclei with which the distribution $\chi_p^0(1)^* \chi_q^j(1)$ interacts are far apart is evident, but less evident is that the electrons with which the distribution interacts are also far away from cell 0. Let us have a closer look at the electron–electron interaction. The charge distribution of electron 2 is $\chi_r^h(2)^* \chi_s^l(2)$, and the summation over cells h excludes the neighbourhood of cell 0. Hence, because of the exponential decay there is a guarantee that the distribution $\chi_r^h(2)^* \chi_s^l(2)$ is bound to be close to cell h , if this distribution is to be of any significance. Therefore, the charge distribution $\chi_r^h(2)^* \chi_s^l(2)$ is certainly far away from cell 0.

Similar reasoning may be used for $C_T(N)$. The interacting objects are of the type $\chi_p^0(1)^* \chi_q^j(1)$, i.e. always close to cell 0, with the nuclei of cell h , and there is a guarantee that h is far away from cell 0. The long distance of the interacting nuclei (second term) is evident.

but this time one of the interacting particles will be the nucleus indicated by vector A_u^h . The corresponding multipole expansion reads as (in a.u.; the nucleus u of the charge Z_u interacts with the electron of charge -1 , $n_k = n_l = \infty$, $S = \min(k, l)$):

$$-\frac{Z_u}{r_{u1}} = \sum_{k=0}^{n_k} \sum_{l=0}^{n_l} \sum_{m=-S}^{m=+S} A_{kl|m|} R^{-(k+l+1)} \hat{M}_a^{(k,m)}(1)^* \hat{M}_b^{(l,m)}(u), \quad (9.82)$$

where R stands for the distance between the origins of the coordinate system centred in cell 0 and the coordinate system in cell h , which, of course, is equal to $R = ha$. The multipole moment operator of electron 1, $\hat{M}_a^{(k,m)}(1)$, reads as

$$\hat{M}_a^{(k,m)}(1) = -r_a^k P_k^{|m|}(\cos \theta_{a1}) \exp(im\phi_{a1}), \quad (9.83)$$

while

$$\hat{M}_b^{(l,m)}(u) = Z_u r_u^l P_l^{|m|}(\cos \theta_u) \exp(im\phi_u) = M_b^{(l,m)}(u) \quad (9.84)$$

denotes the multipole moment of nucleus u computed in the coordinate system of the cell h . When this expansion as well as the expansion for $\frac{1}{r_{12}}$, are inserted into (9.77) for $C_{pq}^{0j}(N)$, we obtain

$$\begin{aligned} C_{pq}^{0j}(N) &= \sum_h^\# \sum_{k=0}^{n_k} \sum_{l=0}^{n_l} \sum_{m=-S}^{m=+S} A_{kl|m|} R^{-(k+l+1)} \\ &\quad \times \left((\chi_p^0 | \hat{M}_a^{(k,m)}(1)^* | \chi_q^j) \left[\sum_u M_b^{(l,m)}(A_u^h) \right] \right. \\ &\quad \left. + (\chi_p^0 | \hat{M}_a^{(k,m)}(1)^* | \chi_q^j) \sum_{l'=h-N}^{l'=h+N} \sum_{rs} P_{sr}^{l'h} (\chi_r^h | \hat{M}_b^{(l,m)}(2) | \chi_s^{l'}) \right) \\ &= \sum_h^\# \sum_{k=0}^{n_k} \sum_{l=0}^{n_l} \sum_{m=-S}^{m=+S} A_{kl|m|} R^{-(k+l+1)} (\chi_p^0 | \hat{M}_a^{(k,m)}(1)^* | \chi_q^j) \\ &\quad \times \left[\sum_u M_b^{(l,m)}(A_u^h) + \sum_{l'=h-N}^{l'=h+N} \sum_{rs} P_{sr}^{l'h} (\chi_r^h | \hat{M}_b^{(l,m)}(2) | \chi_s^{l'}) \right]. \end{aligned}$$

Let us note that in the square parentheses we have nothing but a multipole moment of *unit cell* h . Indeed, the first term represents the multipole moment of all the nuclei of cell h , while the second term is the multipole moment of electrons of unit cell h . The later can best be seen if we recall the normalization condition (9.68): $\sum_{l'=h-N}^{l'=h+N} \sum_{rs} P_{sr}^{l'h} S_{rs}^{hl'} = \sum_{l'=-N}^{l'=+N} \sum_{rs} P_{sr}^{l'0} S_{rs}^{0l'} = 2n_0$, with $2n_0$ denoting

the number of electrons per cell. Hence, we can write

$$C_{pq}^{0j}(N) = \sum_h^\# \sum_{k=0} \sum_{l=0} \sum_{m=-S}^{m=+S} A_{kl|m|} R^{-(k+l+1)} (\chi_p^0 | \hat{M}_a^{(k,m)}(1)^* | \chi_q^j) M^{(l,m)}(h), \quad (9.85)$$

where the dipole moment of cell h is given by:

$$M^{(l,m)}(h) = \left[\sum_u M_b^{(l,m)}(A_u^h) + \sum_{l'=h-N}^{l'=h+N} \sum_{rs} P_{sr}^{l'h} (\chi_r^h | \hat{M}_b^{(l,m)}(2) | \chi_s^{l'}) \right], \quad (9.86)$$

because the summation over u goes over the nuclei belonging to cell h , and the coordinate system b is anchored in cell h . Now it is time to say something most important.

Despite the fact that $M^{(l,m)}(h)$ depends formally on h , in reality it is h -independent, because all the unit cells are identical.

Therefore, we may safely write that $M^{(l,m)}(h) = M^{(l,m)}$.

Now we will try to avoid a well hidden trap, and then we will be all set to prepare ourselves to pick the fruit from our orchard. The trap is that $A_{kl|m|}$ depends on h . How is this? Well, in the $A_{kl|m|}$ there is $(-1)^l$, while the corresponding $(-1)^k$ is absent, i.e. there is a thing that is associated with the 2^l -pole in the coordinate system b , and there no an analogous expression for its partner, the 2^k -pole of coordinate system a . Remember, however (Appendix X), that the axes z of both coordinate systems have been chosen in such a way that a “shoots” towards b , and b does not shoot towards a . Therefore, the two coordinate systems are not equivalent, and hence one may have $(-1)^l$, and not $(-1)^k$. The coordinate system a is associated with cell 0, the coordinate system b is connected to cell h . If $h > 0$, then it is true that a shoots to b , but if $h < 0$ their roles are exchanged. In such a case, in $A_{kl|m|}$ we should not put $(-1)^l$, but $(-1)^k$. If we do this then in the summation over h in eq. (9.85) the only dependence on h appears in a simple term $(ha)^{-(k+l+1)}$!

It appears, therefore, to be a possibility of exactly summing the electrostatic interaction along an infinite polymer chain.

Indeed, the sum

$$\sum_{h=1}^{\infty} h^{-(k+l+1)} = \zeta(k+l+1), \quad (9.87)$$

where $\zeta(n)$ stands for the Riemann dzeta function, which is known to a high degree of accuracy and available in mathematical tables.⁵⁷

Riemann dzeta
function

⁵⁷For example, M. Abramovitz, I. Stegun (eds.), “*Handbook of Mathematical Functions*”, Dover, New York, 1968, p. 811.

Georg Friedrich Bernhard Riemann (1826–1866), German mathematician and physicist, professor at the University of Göttingen. Nearly all his papers gave rise to a new mathematical theory. His life was full of personal tragedies, he lived only 40 years, but despite this he made a giant contribution to mathematics, mainly in non-Euclidean geometries (his geometry plays an important role in the general theory of relativity), in the theory of integrals (Riemann integral), and in the theory of trigonometric series.



The interactions of cell 0 with all the other cells are enclosed in this number. When this is inserted into $C_{pq}^{0j}(N)$, then we obtain

$$C_{pq}^{0j}(N) = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} U_{pq}^{0j(k,l)} \frac{\Delta_N^{(k+l+1)}}{a^{(k+l+1)}}, \quad (9.88)$$

where

$$U_{pq}^{0j(k,l)} = \sum_{m=-S}^{m=+S} (-1)^m [(-1)^k + (-1)^l] \frac{(k+l)!}{(k+|m|)!(l+|m|)!} M_{pq}^{0j(k,m)*} M^{(l,m)}, \quad (9.89)$$

$$\Delta_N^{(n)} = \zeta(n) - \sum_{h=1}^N h^{-n}. \quad (9.90)$$

Note that the formula for $C_{pq}^{0j}(N)$ represents a sum of the multipole–multipole interactions. The formula also shows that

electrostatic interactions in a regular polymer come from a multipole–multipole interaction with the same parity of the multipoles,

which can be seen from the term⁵⁸ $[(-1)^k + (-1)^l]$.

According to the discussion in Appendix X, to preserve the invariance of the energy with respect to translation of the coordinate system, when computing $C_{pq}^{0j}(N)$

⁵⁸The term appears due to the problem discussed above of “who shoots to whom” in the multipole expansion. What happens, is that the interaction of an even (odd) multipole of cell 0 with an odd (even) multipole on the right-hand side of the polymer cancels with a similar interaction with the left-hand side. It is easy to understand. Let us imagine the multipoles as non-pointlike objects built of the appropriate point charges. We look along the periodicity axis. An even multipole has the same signs at both ends, an odd one has the opposite signs. Thus, when the even multipole is located in cell 0, and the odd one on its right-hand side, this interaction will cancel exactly with the interaction of the odd one located on the left-hand side (at the same distance).

we have to add all the terms with $k + l + 1 = \text{const}$, i.e.:

$$C_{pq}^{0j}(N) = \sum_{n=3,5,\dots}^{\infty} \frac{\Delta_N^{(n)}}{a^n} \sum_{l=1}^{n-1} U_{pq}^{0j(n-l-1,l)}. \quad (9.91)$$

The above expression is equivalent to eq. (9.88), but automatically assures the translational invariance by taking into account all the necessary multipole–multipole interactions.⁵⁹

What should we know, therefore, to compute the long-range correction $C_{pq}^{0j}(N)$ to the Fock matrix?⁶⁰ From eq. (9.91) it is seen that one has to know how to calculate three numbers: $U_{pq}^{0j(k,l)}$, a^{-n} and $\Delta_N^{(n)}$. The equation for the first one is given in Table 9.1, the other two are trivial, Δ is easy to calculate knowing the Riemann ζ function (from tables): in fact we have to calculate the multipole moments, and these are *one*-electron integrals (easy to calculate). Originally, before the multipole expansion method was designed we also had a large number of *two*-electron integrals (expensive to calculate). Instead of overnight calculations, the computer time was reduced to about 1 s and the results were more accurate.

9.12.4 MULTIPOLE EXPANSION APPLIED TO THE TOTAL ENERGY

As shown above, the long-range correction to the total energy means the interaction of cell 0 with all the cells from the long-range region multiplied by $\frac{1}{2}$. The reasoning pertaining to its computation may be repeated exactly in the way we have shown in the previous subsection. We have, however, to remember a few differences:

- what interacts is not the charge distribution $\chi_p^{0*} \chi_q^j$, but the complete cell 0,
- the result has to be multiplied by $\frac{1}{2}$ for reasons discussed earlier.

Finally we obtain:

$$C_T(N) = \frac{1}{2} \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} U_T^{(k,l)} \frac{\Delta_N^{(k+l+1)}}{a^{k+l+1}}, \quad (9.92)$$

⁵⁹Indeed, $\sum_{l=1}^{n-1} U_{pq}^{0j(n-l-1,l)} = U_{pq}^{0j(n-2,1)} + U_{pq}^{0j(n-3,2)} + \dots + U_{pq}^{0j(0,n-1)}$, i.e. a review of all terms with $k + l + 1 = n$ except $U_{pq}^{0j(n-1,0)}$. This term is absent and that is OK, because it requires calculation of $M^{(0,0)}$, i.e. of the *charge of the elementary cell*, which has to stay electrically neutral (otherwise the polymer falls apart), therefore $M^{(0,0)} = 0$. Why, however, does the summation over n not simply represent $n = 1, 2, \dots, \infty$, but contains only odd n 's except $n = 1$? What would happen if we took $n = 1$? Look at eq. (9.88). The value $n = 1$ requires $k = l = 0$. This leads to the “monopole–monopole” interaction, but this is 0, since the whole unit cell (and one of the multipoles is that of the unit cell) carries no charge. The summation in (9.91) does not contain any even n 's, because they would correspond to k and l of different parity, and such interactions (as we have shown before) are equal to 0. Therefore, indeed, (9.91) contains all the terms that are necessary.

⁶⁰L. Piela, J. Delhalle, *Intern. J. Quantum Chem.* 13 (1978) 605.

Table 9.1. The quantities $U^{(k,l)}$ for $k + l < 7$ are necessary for calculating the long-range corrections to the Fock matrix elements $U_{pq}^{0j(k,l)}$ and to the total energy per unit cell $U_T^{(k,l)}$. The parentheses [] mean the corresponding multipole moment. When computing the Fock matrix correction the first multipole moment [] stands for the multipole moment of the charge distribution $\chi_p^0 \chi_q^j$, the second, of the unit cell. For example, $U^{(0,2)}$ for the correction $C_{pq}^{0j}(N)$ is equal to $(\chi_p^0 | q) (\sum_u Z_u (3z_u^2 - r_u^2) - \sum_{l'=-N}^{l'=+N} \sum_{rs} P_{sr}^{l'0} (\chi_r^0 | 3z^2 - r^2 | \chi_s^{l'}))$, while $U^{(0,2)}$ for $C_T(N)$ is equal 0, because [1] means the *charge* of the unit cell, which is equal to zero. In the table only U 's for $k \leq l$ are given. If $l < k$, then the formula is the same, but the order of the moments is reversed

n	$U^{(k,l)}, k + l + 1 = n$
3	$U^{(0,2)} = [1][3z^2 - r^2]$ $U^{(1,1)} = 2[x][x] + 2[y][y] - 4[z][z]$
5	$U^{(0,4)} = \frac{1}{4}[1][35z^4 - 30z^2r^2 + 3r^4]$ $U^{(1,3)} = 4[x][3r^2z - 5z^3] + 3[x][5xz^2 - r^2x] + 3[y][5yz^2 - r^2y]$ $U^{(2,2)} = 3[3z^2 - r^2][3z^2 - r^2] - 24[xz][xz] - 24[yz][yz]$ $+ \frac{3}{2}[x^2 - y^2][x^2 - y^2] + 6[xy][xy]$
7	$U^{(0,6)} = \frac{1}{8}[1][231z^6 - 315z^4r^2 + 105z^2r^4 - 5r^6]$ $U^{(1,5)} = -\frac{3}{2}[z][63z^5 - 70z^3r^2 + 15zr^4] + \frac{15}{4}[x][21z^4x - 14z^2xr^2 + xr^4]$ $+ \frac{15}{4}[y][21z^4y - 14z^2yr^2 + yr^4]$ $U^{(2,4)} = \frac{15}{8}[3z^2 - r^2][35z^4 - 30z^2r^2 + 3r^4] - 30[xz][7z^3x - 3x zr^2]$ $- 30[yz][7z^3y - 3y zr^2] + \frac{15}{4}[x^2 - y^2][7z^2(x^2 - y^2) - r^2(x^2 - y^2)]$ $+ 15[xy][7z^2xy - x yr^2]$ $U^{(3,3)} = -10[5z^3 - 3zr^2][5z^3 - 3zr^2] + \frac{45}{4}[5z^2x - xr^2][5z^2x - xr^2]$ $+ \frac{45}{4}[5z^2y - yr^2][5z^2y - yr^2] - 45[zx^2 - zy^2][zx^2 - zy^2]$ $- 180[xyz][xyz] + \frac{5}{4}[x^3 - 3xy^2][x^3 - 3xy^2] + \frac{5}{4}[y^3 - 3x^2y][y^3 - 3x^2y]$

where

$$U_T^{(k,l)} = \sum_{m=-S}^{m=+S} ((-1)^k + (-1)^l) \frac{(k+l)!(-1)^m}{(k+|m|)!(l+|m|)!} M^{(k,m)*} M^{(l,m)}. \quad (9.93)$$

Let us note that (for the same reasons as before)

interaction of multipoles of different parity gives zero

and this time we have to do with the interaction of the multipoles of complete cells. The quantities $U_T^{(k,l)}$ are given in Table 9.1.

Do the Fock matrix elements and the total energy per cell represent finite values?

If the Fock matrix elements were infinite, then we could not manage to carry out the Hartree–Fock–Roothaan self-consistent procedure. If E_T were infinite, the pe-

periodic system could not exist at all. It is, therefore, important to know when we can safely *model* an infinite system.

For any finite system there is no problem: the results are always finite. The only danger, therefore, is the summation to infinity ("lattice sums"), which always ends with the interaction of a part or whole unit cell with an infinite number of distant cells. Let us take such an example in the simplest case of a single atom per cell. Let us assume that the atoms interact by the Lennard-Jones pairwise potential (p. 284):

$$E = \varepsilon \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right],$$

where r means the interatomic distance, r_0 means the equilibrium distance and ε the depth of the potential well. Let us try to compute the lattice sum $\sum_j E_{0j}$, where E_{0j} means the interaction energy of the cells 0 and j . We see that, due to the form of the potential, for long distances what counts is the uniquely attractive term $-2\varepsilon(\frac{r_0}{r})^6$. When we take such interactions which pertain to a sphere of the radius R (with the origin located on atom 0), each individual term (i.e. its absolute value) decreases with increasing R . This is very important, because when we have a 3D lattice, the number of such interactions within the sphere *increases* as R^3 . We see that the decay rate of the interactions will finally win and the lattice sum will converge. We can, however, easily see that if the decay of the pairwise interaction energy were slower, then we might have had trouble calculating the lattice sum. For example, if, instead of the neutral Lennard-Jones atoms, we took ions of the same charge, the interaction energy would explode to ∞ . It is evident, therefore, that for each periodic system there are some conditions to be fulfilled if we want to have finite lattice sums.

These conditions are more severe for the Fock matrix elements because each of the terms represent the interaction of a *charge* with complete distant unit cells. The convergence depends on the asymptotic interaction energy of the potential. In the case of the multipole–multipole interaction, we know what the asymptotic behaviour looks like, it is $R^{-(0+l+1)} = R^{-(l+1)}$, where R stands for the intercell distance. The lattice summation in a n D lattice ($n = 1, 2, 3$) gives the partial sum dependence on R as $\frac{R^n}{R^{l+1}} = R^{n-l-1}$. This means that⁶¹

in 1D the unit cell cannot have any non-zero net charge ($l = 0$), in 2D it cannot have a non-zero charge and dipole moment ($l = 1$), in 3D it cannot have a non-zero charge, dipole moment and quadrupole moment ($l = 2$).

9.13 BACK TO THE EXCHANGE TERM

The long-range effects discussed so far result from the Coulomb interaction in the Fock equation for a regular polymer. There is, however, also an exchange contri-

⁶¹L.Z. Stolarczyk, L. Piela, *Intern. J. Quantum Chem.* 22 (1982) 911.

bution, which has been postponed in the long-range region (p. 477). It is time now to consider this again. The exchange term in the Fock matrix element F_{pq}^{0j} had the form (see (9.65))

$$-\frac{1}{2} \sum_{h,l} \sum_{rs} P_{sr}^{lh} (0h|l_j|sq) \quad (9.94)$$

and gave the following contribution to the total energy per unit cell

$$E_{\text{exch}} = \sum_j E_{\text{exch}}(j), \quad (9.95)$$

where the cell 0-cell j interaction has the form (see (9.81)):

$$E_{\text{exch}}(j) = -\frac{1}{4} \sum_{h,l} \sum_{pqrs} P_{qp}^{j0} P_{sr}^{lh} (0h|l_j|sq). \quad (9.96)$$

It would be very nice to have the exchange contribution $E_{\text{exch}}(j)$ decaying fast, when j increases, because it could be enclosed in the short-range contribution. Do we have good prospects for this? The above formula shows (the integral) that the summation over l is *safe*: the contribution of those cells l that are far from cell 0 is negligible due to differential overlaps of type $\chi_p^0(1)^* \chi_s^l(1)$. The summation over cells h is safe as well (for the same reasons), because it is bound to be limited to the neighbourhood of cell j (see the integral).

In contrast, the only guarantee of a satisfactory convergence of the sum over j is that *we hope* the matrix element P_{qp}^{j0} decays fast if j increases.

So far, exchange contributions have been neglected, and there has been an indication suggesting that this was the right procedure. This was the magic word “exchange”. All the experience of myself and my colleagues in intermolecular interactions whispers “this is surely a short-range type”. In a manuscript by Sandor Suhai, I read that the exchange contribution is of a long-range type. To our astonishment this turned out to be right (just a few numerical experiments). We have a long-range exchange. After an analysis was performed it turned out that

the long-range exchange interaction appears if and only if the system is metallic.

A metallic system is notorious for its HOMO–LUMO quasidegeneracy, therefore, we began to suspect that when the HOMO–LUMO gap decreases, the P_{qp}^{j0} coefficients do not decay with j .

Such things are most clearly seen when the simplest example is taken, and the hydrogen molecule at long internuclear distance is the simplest prototype of a metal. Indeed, this is a system with half-filled orbital energy levels when the LCAO MO method is applied (in the simplest case: two atomic orbitals). Note that, after

subsequently adding two extra electrons, the resulting system (let us not worry too much that such a molecule could not exist!) would model an insulator, i.e. all the levels are doubly occupied.⁶²

Analysis of these two cases convinces us that indeed our suspicions were justified. Here are the bond order matrices we obtain in both cases (see Appendix S, p. 1015, S denotes the overlap integral of the $1s$ atomic orbitals of atoms a and b):

$$\mathbf{P} = (1 + S)^{-1} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad \text{for } \text{H}_2, \quad (9.97)$$

$$\mathbf{P} = (1 - S^2)^{-1} \begin{pmatrix} 1 & -S \\ -S & 1 \end{pmatrix} \quad \text{for } \text{H}_2^{2-}. \quad (9.98)$$

We see⁶³ how profoundly these two cases differ in the off-diagonal elements (they are analogues of P_{qp}^{j0} for $j \neq 0$).

In the second case the proportionality of P_{qp}^{j0} and S ensures an *exponential, therefore very fast, decay* if j tends to ∞ . In the first case there is no decay of P_{qp}^{j0} at all.

A detailed analysis for an infinite chain of hydrogen atoms ($\omega = 1$) leads to the following formula⁶⁴ for P_{qp}^{j0} :

$$P_{11}^{j0} = \frac{2}{\pi j} \sin\left(\frac{\pi j}{2}\right). \quad (9.99)$$

This means an extraordinarily slow decay of these elements (and therefore of the exchange contribution) with j . When the metallic regime is even slightly removed, the decay gets much, much faster.

This result shows that the long-range character of the exchange interactions does not exist in reality. It represents an indication that the Hartree–Fock method fails in such a case.

⁶²Of course, we could take two helium atoms. This would also be good. However, the first principle in research is “in a single step only change a single parameter, analyze the result, draw the conclusions, and make the second step”.

Just *en passant*, a second principle, also applies here. If we do not understand an effect, what should we do? Just divide the system in two parts and look where the effect persists. Keep dividing until the effect disappears. Take the simplest system in which the effect still exists, analyze the problem, understand it and go back slowly to the original system (this is why we have H_2 and H_2^{2-} here).

⁶³L. Piela, J.-M. André, J.G. Fripiat, J. Delhalle, *Chem. Phys. Lett.* 77 (1981) 143.

⁶⁴I.I. Ukrainski, *Theor. Chim. Acta* 38 (1975) 139, $q = p = 1$ means that we have a single $1s$ hydrogen orbital per unit cell.

9.14 CHOICE OF UNIT CELL

The concept of the unit cell has been important throughout the present chapter. The unit cell represents an object that, when repeated by translations, gives an infinite crystal. In this simple definition almost every word can be a trap.

Is it feasible? Is the choice unique? If not, then what are the differences among them? How is the motif connected to the unit cell choice? Is the motif unique? Which motifs may we think about?

As we have already noted, the choice of unit cell as well as of motif is not unique. This is easy to see. Indeed Fig. 9.21 shows that the unit cell and the motif can be chosen in many different and equivalent ways.

Moreover, there is no chance of telling, in a responsible way, which of the choices are reasonable and which are not. And it happens that in this particular case we really have a plethora of choices. Putting no limits to our fantasy, we may choose a unit cell in a particularly capricious way, Figs. 9.21.b and 9.22.

Fig. 9.22 shows six different, fully legitimate, choices of motifs associated with a unit cell in a 1D “polymer” $(\text{LiH})_\infty$. Each motif consists of the lithium nucleus, a proton and an electronic charge distribution in the form of two Gaussian 1s orbitals that accommodate four electrons altogether. By repeating any of these motifs we reconstitute the same original chain.

We may say there may be many legal choices of motif, but this is without any theoretical meaning, because all the choices lead to the same infinite system. Well, this is true with respect to theory, but in practical applications the choice of motif may be of prime importance. We can see this from Table 9.2, which corresponds to Fig. 9.22.

The results without the long-range interactions, depend very strongly on the choice of unit cell motif.

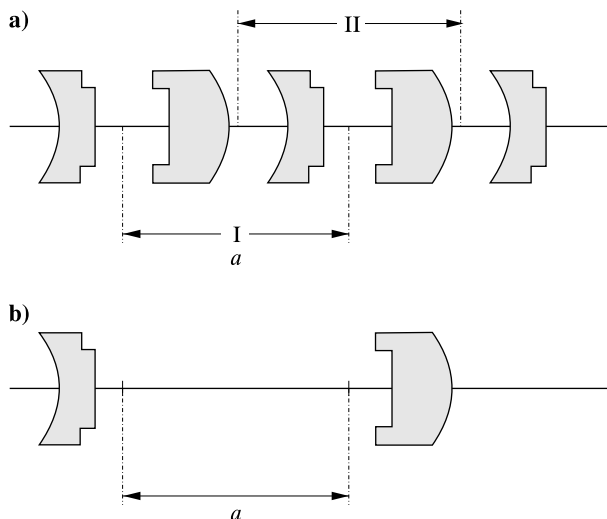


Fig. 9.21. Three of many possible choices of the unit cell motif. a) choices I and II differ, but both look “reasonable”; b) choice III might be called strange. Despite this strangeness, choice III is as legal (from the point of view of mathematics) as I or II.

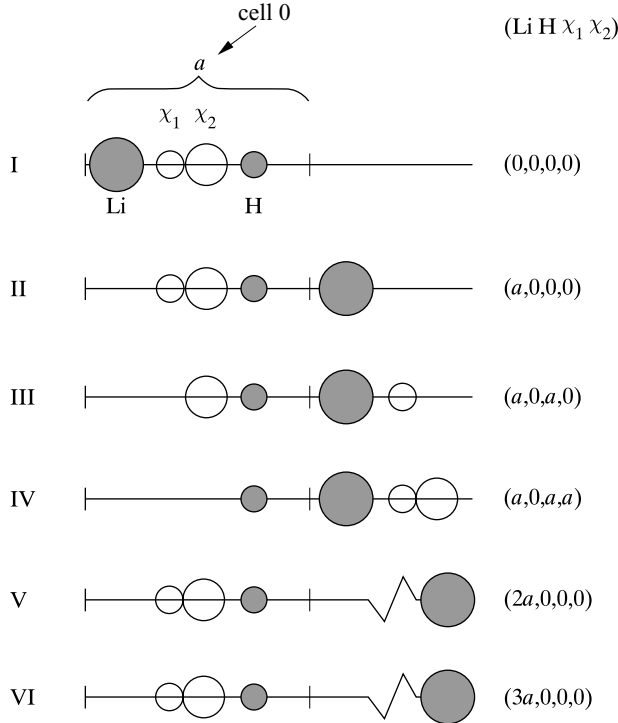


Fig. 9.22. Six different choices (I–VI) of unit cell content (motifs) for a linear chain $(\text{LiH})_\infty$. Each cell has the same length $a = 6.3676$ a.u. There are two nuclei: Li^{3+} and H^+ and two Gaussian doubly occupied $1s$ atomic orbitals (denoted by χ_1 and χ_2 with exponents 1.9815 and 0.1677, respectively) *per cell*. Motif I corresponds to a “common sense” situation: both nuclei and electron distribution determined by χ_1 and χ_2 are within the section $(0,a)$. The other motifs (II–VI) all correspond to the same unit cell $(0,a)$ of length a , but are very strange. Each motif is characterized by the symbol (ka, la, ma, na) . This means that the Li nucleus, H nucleus, χ_1 and χ_2 are shifted to the right by ka, la, ma, na , respectively. *All the unit cells with their contents (motifs) are fully justified, equivalent from the mathematical point of view, and, therefore, “legal” from the point of view of physics.* Note that the nuclear framework and the electronic density corresponding to a cell are very different for all the choices.

Use of the multipole expansion greatly improves the results and, to very good accuracy, makes them *independent of the choice of unit cell motif*.

Note that the larger the dipole moment of the unit cell the worse the results. This is understandable, because the first non-vanishing contribution in the multipole expansion is the dipole–dipole term (cf. Appendix X). Note how considerably the unit cell dependence drops after this term is switched on (a^{-3}).

The conclusion is that in the standard (i.e. short-range) calculations we should always choose the unit cell motif that corresponds to the smallest dipole moment. It seems however that such a motif is what everybody would choose using their “common sense”.

Table 9.2. Total energy per unit cell E_T in the “polymer” LiH as a function of unit cell definition (Fig. 9.22, I–V). For each choice of unit cell this energy is computed in four ways: (1) without long-range forces (long range = 0), i.e. unit cell 0 interacts with $N = 6$ unit cells on its right-hand side and N unit cells on its left-hand side; (2), (3), (4) with the long range computed with multipole interactions up to the a^{-3} , a^{-5} and a^{-7} terms. The bold figures are exact. The corresponding dipole moment μ of the unit cell (in Debyes) is also given.

Unit cell	Long range	μ	$-E_T$
I	0	6.6432	6.610869
	a^{-3}	6.6432	6.612794692
	a^{-5}	6.6432	6.612794687
	a^{-7}	6.6432	6.612794674
II	0	−41.878	6.524802885
	a^{-3}	−41.878	6.612519674
	a^{-5}	−41.878	6.612790564
	a^{-7}	−41.878	6.612794604
III	0	−9.5305	6.607730984
	a^{-3}	−9.5305	6.612788446
	a^{-5}	−9.5305	6.612794633
	a^{-7}	−9.5305	6.612794673
IV	0	22.82	6.57395630
	a^{-3}	22.82	6.612726254
	a^{-5}	22.82	6.612793807
	a^{-7}	22.82	6.612794662
V	0	−90.399	6.148843431
	a^{-3}	−90.399	6.607530384
	a^{-5}	−90.399	6.612487745
	a^{-7}	−90.399	6.612774317

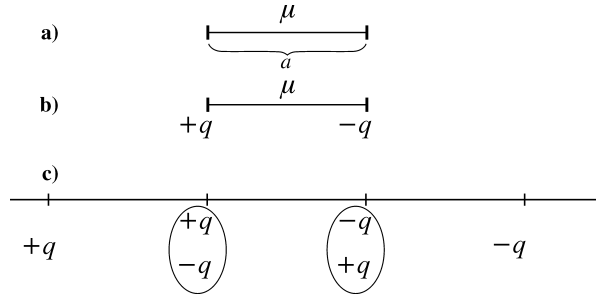
9.14.1 FIELD COMPENSATION METHOD

In a moment we will unexpectedly find a quite different conclusion. The logical chain of steps that led to it has, in my opinion, a didactic value, and contains a considerable amount of optimism. When this result was obtained by Leszek Stolarczyk and myself, we were stunned by its simplicity.

Is it possible to design a unit cell motif with a dipole moment of zero? This would be a great unit cell, because its interaction with other cells would be weak and it would decay fast with intercellular distance. We could therefore compute the interaction of a few cells like this and the job would be over: we would have an accurate result at very low cost.

There is such a unit cell motif.
Imagine we start from the concept of the unit cell with its motif (with lattice constant a). This motif is, of course, electrically neutral (otherwise the total energy

Fig. 9.23. Field compensation method. (a) the unit cell with length a and dipole moment $\mu > 0$. (b) the modified unit cell with additional fictitious charges ($|q| = \frac{\mu}{a}$) which cancel the dipole moment. (c) the modified unit cells (with $\mu' = 0$) give the original polymer, when added together.



would be $+\infty$), and its dipole moment component along the periodicity axis is equal to μ . Let us put its symbol in the unit cell, Fig. 9.23.a.

Now let us add to the motif two extra pointlike opposite charges ($+q$ and $-q$), located on the periodicity axis and separated by a . The charges are chosen in such a way ($q = \frac{\mu}{a}$) that they alone give the dipole moment component along the periodicity axis equal to $-\mu$, Fig. 9.23.b.

In this way the new unit cell dipole moment (with the additional fictitious charges) is equal to zero. Is this an acceptable choice of motif? Well, what does acceptable mean? The only requirement is that by repeating the new motif with period a , we have to reconstruct the whole crystal. What will we get when repeating the new motif? Let us see (Fig. 9.23.c).

We get the original periodic structure, because the charges all along the polymer, *except the boundaries*, have cancelled each other. Simply, the pairs of charges $+q$ and $-q$, when located at a point result in nothing.

In practice we would like to repeat just a few neighbouring unit cell motifs (a cluster) and then compute their interaction. In such case, we will observe the charge cancellation inside the cluster, but no cancellation on its boundaries (“surface”).

Therefore we get a sort of point charge distribution at the boundaries.

If the boundary charges did not exist, it would correspond to the traditional calculations of the original unit cells without taking any long-range forces into account. The boundary charges therefore play the important role of replacing the electrostatic interaction with the rest of the *infinite* crystal, by the boundary charge interactions with the cluster (“field compensation method”).

This is all. The consequences are simple.

Let us not only kill the dipole moment, but also other multipole moments of the unit cell content (up to a maximum moment), and the resulting cell will be unable to interact electrostatically with anything. Therefore, interaction within a small cluster of such cells will give us an accurate energy per cell result.

This multipole killing (field compensation) may be carried out in several ways.⁶⁵

Application of the method is extremely simple. Imagine unit cell 0 and its neighbour unit cells (a cluster). Such a cluster is sometimes treated as a molecule and its role is to represent a bulk crystal. This is a very expensive way to describe the bulk crystal properties, for the cluster surface atom ratio to the bulk atom is much higher than we would wish (the surface still playing an important role). What is lacking is the crystal field that will change the cluster properties. In the field compensation method we do the same, but there are some fictitious charges at the cluster boundaries that take care of the crystal field. This enables us to use a smaller cluster than before (low cost) and still get the influence of the infinite crystal. The fictitious charges are treated in computations the same way as are the nuclei (even if some of them are negatively charged). However artificial it may seem, the results are far better when using the field compensation method than without it.⁶⁶

9.14.2 THE SYMMETRY OF SUBSYSTEM CHOICE

The example described above raises an intriguing question, pertaining to our understanding of the relation between a part and the whole.

There are an infinite number of ways to reconstruct the same system from parts. *These ways are not equivalent in practical calculations*, if for any reason we are unable to compute all the interactions in the system. However, if we have a theory (in our case the multipole method) that is able to compute the interactions,⁶⁷ including the long-range forces, then it turns out the final result is virtually independent of the choice of unit cell motif. This arbitrariness of choice of subsystems looks analogous to the arbitrariness of the choice of coordinate system. The final results do not depend on the coordinate system used, but still the numerical results (as well as the effort to get the solution) do.

The separation of the whole system into subsystems is of key importance to many physical approaches, but we rarely think of the freedom associated with the choice. For example, an atomic nucleus does not in general represent an elementary particle, and yet in quantum mechanical calculations we treat it as a point particle, without an internal structure and we are successful.⁶⁸ Further, in the *Bogolyubov*⁶⁹ transformation, the Hamiltonian is represented by creation and annihilation operators, each being a linear combination of the creation and annihilation

Bogolyubov
transformation

⁶⁵L. Piela, L.Z. Stolarczyk, *Chem. Phys. Letters* 86 (1982) 195.

⁶⁶Using “negative” nuclei looked so strange that some colleagues doubted receiving anything reasonable from such a procedure.

⁶⁷With controlled accuracy, i.e. we still neglect the interactions of higher multipoles.

⁶⁸This represents only a fragment of the story-like structure of science (cf. p. 60), one of its most intriguing features. It makes science operate, otherwise when considering the genetics of peas in biology we have had to struggle with the quark theory of matter.

⁶⁹Nicolai Nicolaevitch Bogolyubov (1909–1992), Russian physicist, director of the Dubna Nuclear Institute, outstanding theoretician.

operators for electrons (described in Appendix U, p. 1023). The new operators also fulfil the anticommutation rules – only the Hamiltonian contains more additional terms than before (Appendix U). A particular Bogolyubov transformation may describe the creation and annihilation of quasi-particles, such as the electron hole (and others). We are dealing with the same physical system as before, but we look at it from a completely different point of view, by considering it is composed of something else. Is there any theoretical (i.e. *serious*) reason for preferring one division into subsystems over another? Such a reason may only be of practical importance.⁷⁰

SYMMETRY WITH RESPECT TO DIVISION INTO SUBSYSTEMS

The symmetry of *objects* is important for the description of *them*, and therefore may be viewed as of limited interest. The symmetry of the laws of Nature, i.e. of the theory that describes all objects (whether symmetric or not) is much more important. This has been discussed in detail in Chapter 2 (cf. p. 61), but it seems that we did not list there a fundamental symmetry of any correct theory: the *symmetry with respect to the choice of subsystems*. *A correct theory has to describe the total system independently of what we decide to treat as subsystems.*

We will meet this problem once more in intermolecular interactions (Chapter 13). However, in the periodic system it has been possible to use, in computational practice, the symmetry described above.

Our problem resembles an excerpt which I found in “*Dreams of a Final Theory*” by Steven Weinberg⁷¹ pertaining to *gauge symmetry*: “*The symmetry underlying it has to do with changes in our point of view about the identity of the different types of elementary particle. Thus it is possible to have a particle wave function that is neither definitely an electron nor definitely a neutrino, until we look at it*”. Here also we have freedom in the choice of subsystems and a correct theory has to reconstitute the description of the whole system.

An intriguing problem.

Summary

- A crystal is often approximated by an infinite crystal (*primitive*) *lattice*, which leads to the concept of the *unit cell*. By repeating a chosen atomic *motif* associated with a unit cell, we reconstruct the whole infinite crystal.
- The Hamiltonian is invariant with respect to translations by any lattice vector. Therefore its eigenfunctions are simultaneously eigenfunctions of the translation operators (Bloch theorem): $\phi_{\mathbf{k}}(\mathbf{r} - \mathbf{R}_j) = \exp(-i\mathbf{k}\mathbf{R}_j)\phi_{\mathbf{k}}(\mathbf{r})$ and transform according to the irreducible representation of the translation group labelled by the *wave vector* \mathbf{k} .

⁷⁰For example, at temperature $t < 0^\circ\text{C}$ we may solve the equations of motion for N frozen water drops and we may obtain reasonable dynamics of the system. At $t > 0^\circ\text{C}$, obtaining dynamics of the same drops will be virtually impossible.

⁷¹Pantheon Books, New York (1992), Chapter 6.

- *Bloch functions* may be treated as atomic symmetry orbitals $\phi = \sum_j \exp(ik\mathbf{R}_j)\chi(\mathbf{r} - \mathbf{R}_j)$ formed from the atomic orbital $\chi(\mathbf{r})$.
- The crystal lattice basis vectors allow the formation of the basis vectors of the *inverse lattice*.
- Linear combinations of them (with integer coefficients) determine the *inverse lattice*.
- The *Wigner–Seitz* unit cell of the inverse lattice is called the First Brillouin Zone (FBZ).
- The vectors \mathbf{k} inside the FBZ label all possible irreducible representations of the translation group.
- The wave vector plays a triple role:
 - it indicates the *direction of the wave*, which is an eigenfunction of $\hat{T}(\mathbf{R}_j)$ with eigenvalue $\exp(-ik\mathbf{R}_j)$,
 - it labels the *irreducible representations* of the translation group,
 - the longer the wave vector \mathbf{k} , the more nodes the wave has.
- In order to neglect the crystal surface, we apply the *Born–von Kármán boundary condition*: “instead of a stick-like system we take a circle”.
- In full analogy with molecules, we can formulate the SCF LCAO CO Hartree–Fock–Roothaan method (CO instead MO). Each CO is characterized by a vector $\mathbf{k} \in \text{FBZ}$ and is a linear combination of the Bloch functions (with the same \mathbf{k}).
- The orbital energy dependence on $\mathbf{k} \in \text{FBZ}$ is called the *energy band*. The stronger the intercell interaction, the wider the bandwidth (dispersion).
- Electrons occupy (besides the inner shells) the *valence bands*, the *conduction bands* are empty. The *Fermi level* is the HOMO energy of the crystal. If the HOMO–LUMO energy difference (*energy gap* between the valence and conduction bands) is zero, we have a *metal*; if it is large, we have an *insulator*; if, it is medium, we have a *semiconductor*.
- Semiconductors may be intrinsic, or *n*-type (if the donor dopant levels are slightly below the conduction band), or *p*-type (if the acceptor dopant levels are slightly above the occupied band).
- Metals when cooled may undergo what is known as the Peierls transition, which denotes lattice dimerization and band gap formation. The system changes from a metal to a semiconductor or insulator. This transition corresponds to the Jahn–Teller effect in molecules.
- Polyacetylene is an example of a Peierls transition (“dimerization”), which results in shorter bonds (a little “less–multiple” than double ones) and longer bonds (a little “more multiple” than single ones). Such a dimerization introduces the possibility of a defect separating two rhythms (“phases”) of the bonds: from “double–single” to “single–double”. This defect can move within the chain, which may be described as a solitonic wave. The soliton may become charged and in this case, participates in electric conduction (increasing it by many orders of magnitude).
- In polyparaphenylene, a soliton wave is not possible, because the two phases, quinoid and aromatic, are not of the same energy. A double defect is possible though, a bipolaron. Such a defect represents a section of the quinoid structure (in the aromatic-like chain) at the end of which we have two unpaired electrons. The electrons, when paired with extra electrons from donor dopants, or when removed by acceptor dopants, form a double ion (bipolaron), which may contribute to electric conductance.
- The band structure may be foreseen in simple cases and logically connected to the subsystem orbitals.
- To compute the Fock matrix elements or the total energy per cell, we have to calculate the interaction of cell 0 with all other cells.

- The interaction with neighbouring cells is calculated without approximations, while that with distant cells uses multipole expansion. Multipole expansion applied to the electrostatic interaction gives accurate results, while the numerical effort is dramatically reduced.
- In some cases (metals), we meet long-range exchange interaction, which disappears as soon as the energy gap emerges. This indicates that the Hartree–Fock method is not applicable in this case.
- The choice of unit cell motif is irrelevant from the theoretical point of view, but leads to different numerical results when the long-range interactions are omitted. By including the interactions the theory becomes independent of the division of the whole system into arbitrary motifs.

Main concepts, new terms

lattice constant (p. 431)	valence band (p. 455)
primitive lattice (p. 432)	band gap (p. 455)
translational symmetry (p. 432)	conduction band (p. 455)
unit cell (p. 432)	insulators (p. 455)
motif (p. 432)	metals (p. 455)
wave vector (p. 434)	semi-conductor (p. 455)
Bloch theorem (p. 434)	Peierls transition (p. 456)
Bloch function (p. 435)	<i>n</i> -type semiconductor (p. 458)
symmetry orbital (p. 435)	<i>p</i> -type semiconductor (p. 458)
biorthogonal basis (p. 436)	Jahn–Teller effect (p. 458)
inverse lattice (p. 436)	soliton (p. 459)
Wigner–Seitz cell (p. 438)	bipolaron (p. 459)
First Brillouin Zone (p. 438)	long-range interactions (p. 475)
Born–von Kármán boundary condition (p. 446)	multipole expansion (p. 479)
crystal orbitals (p. 450)	exchange interaction (p. 485)
band structure (p. 453)	field compensation method (p. 490)
band width (p. 454)	symmetry of division into subsystems (p. 492)
Fermi level (p. 454)	

From the research front

The Hartree–Fock method for periodic systems nowadays represents a routine approach coded in several *ab initio* computer packages. We may analyze the total energy, its dependence on molecular conformation, the density of states, the atomic charges, etc. Also calculations of first-order responses to the electric field (polymers are of interest for optoelectronics) have been successful in the past. However, non-linear problems (like the second harmonic generation, see Chapter 12) still represent a challenge. On the one hand, the experimental results exhibit wide dispersion, which partly comes from market pressure. On the other hand, the theory itself has not yet elaborated reliable techniques.

Ad futurum...

Probably there will soon be no problem in carrying out the Hartree–Fock or DFT (see Chapter 11) calculations, even for complex polymers and crystals. What will remain for a few decades is the very important problem of lowest-energy crystal packing and of solid state reactions and phase transitions. Post-Hartree–Fock calculations (taking into account

electronic correlation effects) will be more and more important. The real challenge will start in designing non-periodic materials, where the polymer backbone will serve as a molecular rack for installing some functions (transport, binding, releasing, signal transmitting). The functions will be expected to cooperate ("smart materials", cf. Chapter 15).

Additional literature

A.A. Levin, "Vviedieniye w kvantovuyu khimiyu tverdogo tiela. Khimicheskaya svyaz i struktura energeticheskikh zon w tetrachricheskikh poluprovodnikakh", Khimija, Moscow, 1974.

This is the first textbook of solid state chemistry. The theory of periodic systems (especially semiconductors) is presented in about 230 pages.

R. Hoffmann, "Solids and Surfaces. A Chemist's View of Bonding in Extended Structures", VCH publishers, New York, 1988.

A masterpiece written by a Nobel Prize winner, one of the founders of solid state quantum chemistry. More oriented towards chemistry than Levin's book. Solid state theory was traditionally the domain of physicists, some concepts typical of chemistry as, e.g., atomic orbitals, bonding and antibonding effects, chemical bonds and localization of orbitals were usually absent in such descriptions.

J.-M. André, J. Delhalle, J.-L. Brédas, "Quantum Chemistry Aided Design of Organic Polymers", World Scientific, Singapore, 1991.

A well written book oriented mainly towards the response of polymers to the electric field.

Questions

- Bloch theorem says that:
 - $\hat{T}(\mathbf{R}_j)\phi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r})$;
 - $\phi_{\mathbf{k}}(\mathbf{r}) = \phi_{-\mathbf{k}}(\mathbf{r})$;
 - $\phi_{\mathbf{k}}(\mathbf{r}) + \phi_{-\mathbf{k}}(\mathbf{r}) = 0$;
 - $\phi_{\mathbf{k}}(\mathbf{r} - \mathbf{R}_j) = \exp(-i\mathbf{k}\mathbf{R}_j)\phi_{\mathbf{k}}(\mathbf{r})$.
- The First Brillouin Zone (\mathbf{k} stands for the wave vector, CO – for a crystal orbital):
 - represents the smallest unit cell of the primitive lattice;
 - represents the smallest motif in the crystal;
 - its interior contains only non-equivalent vectors;
 - represents a basis in the inverse cell.
- Function $\phi_{\mathbf{k}}$ corresponding to the wave vector \mathbf{k} :
 - has to satisfy the Schrödinger equation;
 - represents a wave with direction \mathbf{k} ;
 - always has $|\mathbf{k}|$ nodes;
 - represents the CO.
- Crystal orbital (\mathbf{k} is a wave vector, CO means a crystal orbital):
 - represents an arbitrary linear combination of the atomic orbitals of cell 0;
 - represents an arbitrary linear combination of the atomic orbitals of cells 0, ± 1 ;
 - with $\mathbf{k} = \mathbf{0}$ corresponds to the lowest energy in the band;
 - always corresponds to a given \mathbf{k} .
- The infinite polyacetylene chain:
 - is an electrical conductor;
 - exhibits all CC bonds of equal length;
 - if doped becomes a conductor due to soliton defects;
 - has a zero band gap.
- Band width (\mathbf{k} is a wave vector, CO means a crystal orbital) gets larger if:
 - the orbital overlap is larger;
 - the band energy is lower;
 - the CO has a larger number of nodes;
 - $|\mathbf{k}|$ is smaller.

7. A semiconductor:
a) has a large band gap; b) means a resistor; c) has a small band gap; d) conducts electric current, but only in one direction.
8. Fermi level means:
a) the electric affinity of an insulator; b) HOMO energy for the crystal; c) the mean value of the occupied band; d) the lowest energy of a band.
9. In regular polymer the dipole-quadrupole interaction is:
a) 0; b) the difference of the quadrupole-quadrupole and dipole-dipole interactions;
c) $\frac{1}{3!}$; d) the mean value of the dipole-dipole and quadrupole-quadrupole interactions.
10. The dipole moment of a unit cell in a polymer:
a) is uniquely determined if the polymer is electrically neutral; b) depends on the position of the cell with respect to cell 0; c) depends on the choice of the motif; d) is equal to 0.

Answers

1d, 2c, 3b, 4d, 5c, 6a, 7c, 8b, 9a, 10c