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Momentum space functions for polymers

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Abstract. We present an analysis of the basic properties of momentum space functions for three-dimensional extended systems with translational symmetry in one dimension. The implications of the periodic boundary conditions in position space for the momentum space functions are carefully discussed. The advantages of applying the full line group symmetry are emphasized. We stress the simplification gained by carrying out symmetric orthonormalization in momentum space. The symmetry properties of the momentum distribution are discussed.

1. Introduction

Extended organic and inorganic chains represent an increasingly important class of materials because of a number of their properties, e.g. transport properties, non-linear optical response, dielectric behaviour and bistability [1-3], which make them interesting potential candidates for integration in many devices. Computed molecular structures, densities of electronic states, response to electric fields, etc, are usefully correlated with experimentally determined properties of existing systems. The success of such correlations serves more and more as a basis for *quantum-chemistry-aided design* of new molecular structures with improved properties. Even though the electronic properties of a system result from the behaviour of all the electrons (core and valence), it is traditionally in terms of the outer electrons that most of the above properties are understood.

Momentum space is genuinely well adapted for the description of the outer electronic states. The properties of momentum distributions and to a certain extent also momentum space wavefunctions have been studied both experimentally and theoretically for small molecules [4-9] and solids [10-22]. A number of general theoretical papers [23-29] have also appeared, and various aspects of the field have been surveyed in [8] and in [30-34]. As emphasized in a recent paper by Schneider and Bell [35] a new experimental technique now makes it possible to determine momentum densities in solids *directly*, thus allowing more precise testing of electronic structure calculations. It will be important for theoreticians to be able to extract a maximal amount of information from their calculations in order to be ready to meet that challenge.

In the case of polymers, the very valuable source of useful concepts and/or quantities that momentum space constitutes for the interpretation of their properties has

not yet been fully exploited. One reason for this lack of interest could be the apparent insensitivity of the Compton profiles with respect to the structure of the measured compounds. However, recent improvements, both experimental and theoretical [36], provide new incentives for promoting the use of momentum space concepts in the field of polymers.

The purpose of the present paper is thus to establish a solid conceptual basis and a consistent notation for the calculation of momentum space quantities related to infinite periodic chains. Polymers have similarities both to solids and to small molecules, as well as important differences from them. In order to identify these various aspects we have found it useful to study the particular properties of *momentum space wavefunctions for polymers*, as distinguished from both solids and small molecules. Therefore, particular attention is devoted to the consequences of both the basic periodic boundary conditions and the translational symmetry of the chains for the mathematical properties of momentum space Bloch states. A more complete treatment of the symmetry in polymers requires the concept of *line groups*, which are used throughout the paper. A line group consists of operations under which a one-dimensional lattice of *three-dimensional* objects is invariant. It is consequently the tool needed for symmetry adaptation of polymeric wavefunctions. Orthonormalization in momentum space is simpler than in position space and, since the symmetry adaptation must be complemented with orthonormalization, we have devoted a separate section to that topic. The paper is thus divided into three sections: symmetry aspects and boundary conditions for polymer wavefunctions in momentum space (section 2), orthogonalization in momentum space (section 3) and momentum distributions for polymers (section 4).

2. Symmetry and boundary conditions in momentum space

Symmetry represents one of the most important factors in the treatment of wavefunctions in position space and that is equally true in momentum space [8, 23–34]. Point group symmetry in momentum space has been discussed in two recent papers [37, 38] and the properties of Bloch and Wannier functions in momentum space in another paper [39]. We start with some general remarks before we proceed to the particular aspects of polymers, in this connection viewed as isolated model chains of atoms or molecules whose atomic positions can be generated through *line group* symmetry operations [40, 41]. We wish to stress that this does *not* mean a restriction to one-dimensional systems. The primary structure of a polymer can be described as a *one-dimensional lattice* of ordinary three-dimensional atoms. By convention, the repeat direction is along the z axis in position space, and the corresponding reciprocal-space direction will also be the z axis. Figure 1 shows the underlying linear one-dimensional lattice of a helical poly(propylene) chain, $-\text{[CH}_2\text{-CH(CH}_3\text{)]}_x\text{-}$, a being the translational repeat distance of the lattice. In the figure, full circles summarize the full structure of the translationally repeating pattern, i.e. three consecutive fragments A_i and B_i , which in total corresponds to nine carbon and 18 hydrogen atoms.

The basic connection between a function $\phi(\mathbf{r})$ in position space and its

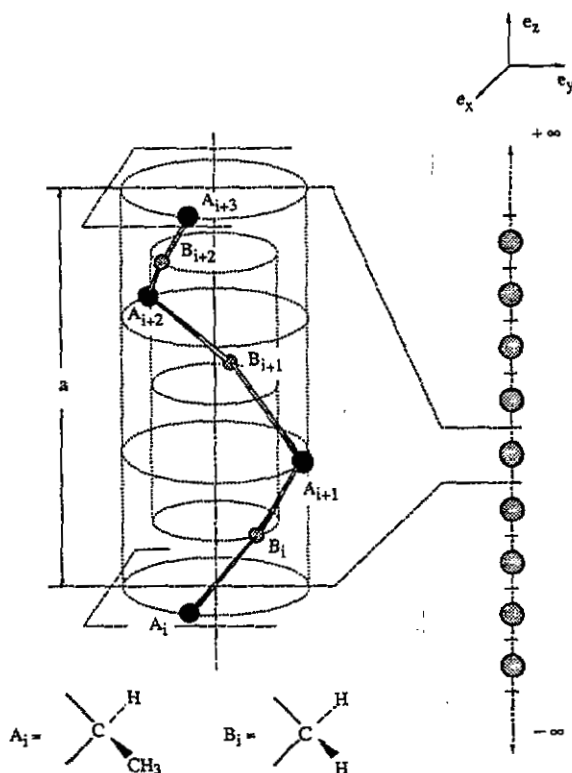


Figure 1. A schematic view of the poly(propylene) structure and illustration of the lattice parameter used to characterize translationally invariant polymers.

counterpart $\hat{\phi}(\mathbf{p})$ in momentum space is given by [42]

$$\hat{\phi}(\mathbf{p}) = (2\pi)^{-3/2} \int d\mathbf{r} \phi(\mathbf{r}) \exp(-i\mathbf{p} \cdot \mathbf{r}) \quad (2.1)$$

$$\phi(\mathbf{r}) = (2\pi)^{-3/2} \int d\mathbf{p} \hat{\phi}(\mathbf{p}) \exp(i\mathbf{p} \cdot \mathbf{r}).$$

The transformation of a function $\phi(\mathbf{r})$ in position space under a symmetry operator \mathbf{g} of point group type (rotation, reflection or inversion) is described by

$$\mathbf{g}\phi(\mathbf{r}) = \phi(\mathbf{g}^{-1}\mathbf{r}) = \phi_{\mathbf{g}}(\mathbf{r}). \quad (2.2)$$

According to (2.1), the momentum space counterpart of the transformed function is

$$\begin{aligned} \hat{\phi}_{\mathbf{g}}(\mathbf{p}) &= (2\pi)^{-3/2} \int d\mathbf{r} \phi_{\mathbf{g}}(\mathbf{r}) \exp(-i\mathbf{p} \cdot \mathbf{r}) \\ &= (2\pi)^{-3/2} \int d\mathbf{r} \phi(\mathbf{g}^{-1}\mathbf{r}) \exp(-i\mathbf{p} \cdot \mathbf{r}). \end{aligned} \quad (2.3)$$

After changing the integration variable to $\mathbf{r}' = \mathbf{g}^{-1}\mathbf{r}$ and if \mathbf{g} is a unitary group operation, we can write (2.3) as

$$\begin{aligned} \hat{\phi}_{\mathbf{g}}(\mathbf{p}) &= (2\pi)^{3/2} \int d\mathbf{r}' \phi(\mathbf{r}') \exp[-i\mathbf{p} \cdot (\mathbf{g}\mathbf{r}')] \\ &= (2\pi)^{3/2} \int d\mathbf{r}' \phi(\mathbf{r}') \exp[-i(\mathbf{g}^{-1}\mathbf{p}) \cdot \mathbf{r}'] = \hat{\phi}(\mathbf{g}^{-1}\mathbf{p}) = \mathbf{g}\hat{\phi}(\mathbf{p}). \end{aligned} \quad (2.4)$$

Thus for point group operations the same rules hold in position and in momentum space.

2.1. Space group operations on momentum space functions

We first briefly recall the action of a space group operation on a function in momentum space and use the results as templates for developing the polymer case. Space group operations include point group operations and translations, denoted by \mathbf{R} and $\mathbf{T}(\mathbf{m})$, respectively. For a point group operation \mathbf{R} we have an expression such as (2.2) also in momentum space (cf (2.4)):

$$\mathbf{R}\hat{\phi}(\mathbf{p}) = \hat{\phi}(\mathbf{R}^{-1}\mathbf{p}). \quad (2.5)$$

If on the other hand \mathbf{g} is a translation $\mathbf{T}(\mathbf{m})$, i.e. if

$$\mathbf{g}\mathbf{r} = \mathbf{T}(\mathbf{m})\mathbf{r} = \mathbf{r} + \mathbf{m} \quad (2.6)$$

we get

$$\mathbf{T}(\mathbf{m})\hat{\phi}(\mathbf{p}) = (2\pi)^{-3/2} \int d\mathbf{r} \phi(\mathbf{r} - \mathbf{m}) \exp(-i\mathbf{p} \cdot \mathbf{r}) = \hat{\phi}(\mathbf{p}) \exp(-i\mathbf{p} \cdot \mathbf{m}). \quad (2.7)$$

This expression represents one of the essential simplifications in momentum space compared with position space; a position space translation corresponds to a phase factor in momentum space.

If the system under consideration 'has translational symmetry', i.e. if it is invariant under a group of translations that is usually taken to be of finite order by imposing periodic boundary conditions, the corresponding symmetry-adapted functions are Bloch functions $\psi(\mathbf{k}, \mathbf{r})$ characterized by a wavevector \mathbf{k} in the first Brillouin zone (BZ) [43]. The translation $\mathbf{T}(\mathbf{m})$ acting on $\psi(\mathbf{k}, \mathbf{r})$ simply changes the phase of the symmetry-adapted function in a way depending on the translation and on the wavevector:

$$\mathbf{T}(\mathbf{m})\psi(\mathbf{k}, \mathbf{r}) = \psi(\mathbf{k}, \mathbf{r} - \mathbf{m}) = \psi(\mathbf{k}, \mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{m}). \quad (2.8)$$

Equation (2.8) is known as the Bloch condition. The similarity between (2.7) and (2.8) should be noticed but not exaggerated. It is extremely important to distinguish between *momentum space* with the *coordinate* \mathbf{p} and *reciprocal space* with the *wavevector* \mathbf{k} which is related to a lattice.

For a general space group operation we use the ordinary expression $\{\mathbf{R}|\mathbf{m}\}$ [44] to denote the transformation of a vector \mathbf{r} to $\{\mathbf{R}|\mathbf{m}\}\mathbf{r} = \mathbf{R}\mathbf{r} + \mathbf{m}$. For a function in position space we then get

$$\{\mathbf{R}|\mathbf{m}\}\phi(\mathbf{r}) = \phi(\{\mathbf{R}^{-1}|\mathbf{R}^{-1}\mathbf{m}\}\mathbf{r}) = \phi(\mathbf{R}^{-1}\mathbf{r} - \mathbf{R}^{-1}\mathbf{m}). \quad (2.9)$$

For the transformation of a momentum space function under the same group operation we get with (2.1)

$$\begin{aligned} (2\pi)^{-3/2} \int d\mathbf{r} \phi(\mathbf{R}^{-1}\mathbf{r} - \mathbf{R}^{-1}\mathbf{m}) \exp(-i\mathbf{p} \cdot \mathbf{r}) \\ = (2\pi)^{-3/2} \int d\mathbf{r}' \phi(\mathbf{r}') \exp[-i(\mathbf{R}^{-1}\mathbf{p}) \cdot \mathbf{r}'] \exp(-i\mathbf{p} \cdot \mathbf{m}). \end{aligned} \quad (2.10)$$

This is a product of a phase factor due to the translational part of the space group operation and an integral which is the momentum space counterpart of the original function transformed by the point group part of the space group operation. Consequently the transformed function (2.9) under a general space group operation $\{\mathbf{R}|m\}$ corresponds in momentum space to

$$\{\mathbf{R}|m\}\hat{\phi}(\mathbf{p}) = \hat{\phi}(\mathbf{R}^{-1}\mathbf{p}) \exp(-i\mathbf{p} \cdot \mathbf{m}). \quad (2.11)$$

Comparing (2.9) and (2.11) we see that the same operator working in position space and momentum space, respectively, yields quite different results. When the space group elements work in position space, their operation corresponds directly to the intuitive meaning of the terms rotation, reflection, inversion, translation and combinations of these. In momentum space this is no longer true as soon as the space group element contains a non-zero translational part. Strictly speaking we should therefore use different notation for space group operations in position and momentum space, in order to stress that an expression such as (2.11) should be interpreted as that function in momentum space which is obtained when the space group operation $\{\mathbf{R}|m\}$ works on the position space function $\phi(\mathbf{r})$. With these reservations we shall, however, keep the same notation for space group operations whether they work in position or momentum space.

2.2. Line group operations on momentum space functions

We are now ready to specialize the above results to polymer chains. As already mentioned, in this case we shall need a special type of space group, namely the *line groups*, which characterize the symmetry of a system of three-dimensional objects with translational symmetry in one direction only. The line groups have been extensively studied in particular by Bozovic *et al* [40] but also by others [41]. References to earlier work can be found in these papers.

The general line group element is of the form

$$\{\mathbf{R}|t_{\mathbf{R}} + m\} \quad t_{\mathbf{R}} = t_{\mathbf{R}}e_z \quad m = mae_z \quad (2.12)$$

where m is an integer restricted to

$$-N/2 \leq m < N/2. \quad (2.13)$$

This defines the Born-von Kármán (BK) region of length Na , i.e. the period associated with the basic periodic boundary conditions along the z axis. The vector $t_{\mathbf{R}}$ denotes a non-primitive translation associated with the particular point group element \mathbf{R} . For symmorphic groups, all vectors $t_{\mathbf{R}}$ vanish. In non-symmorphic line groups the translations $t_{\mathbf{R}}$ are related to screw axis and glide plane symmetries.

It is essential to distinguish the BK periodicity which is imposed on the *wavefunctions* from the periodicity of the *potential* which will be introduced later and will imply that wavefunctions must satisfy the Bloch condition. The BK region is thus an infinite (in the x and y directions) slab of thickness Na . Figure 2 illustrates the two different concepts of periodicity.

Thus all functions in position space satisfy

$$\psi(\mathbf{r} - Na\mathbf{e}_z) = \psi(\mathbf{r}) \quad (2.14a)$$

$$\psi(\mathbf{r}) \rightarrow 0 \quad x \rightarrow \pm\infty \quad y \rightarrow \pm\infty. \quad (2.14b)$$

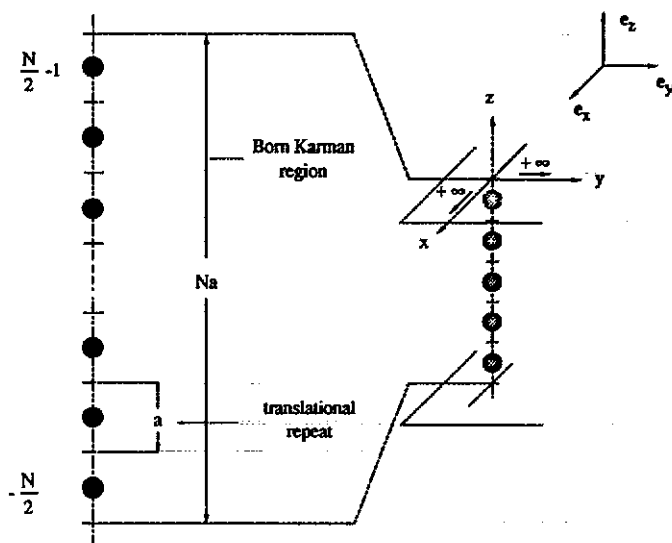


Figure 2. Sketch of the difference between the BK period which applies to wavefunctions and the translational repeat of the potential which is reflected in the electron density distribution function.

The corresponding momentum space functions have continuous arguments p_x and p_y in the x and the y directions. In the z direction the boundary condition (2.14a) leads to a *discretization in momentum space*, which implies that all momentum space functions *vanish unless* [45]

$$p_z = 2\pi\kappa_p/Na \quad (2.15)$$

where κ_p is any positive or negative integer or zero. In other words the momentum space functions $\hat{\psi}(p)$ are non-vanishing only on those (p_x, p_y) planes for which (2.15) is satisfied.

We specialize (2.11) to a line group operation of type (2.12) in order to see how a momentum space function for a polymer transforms under such an operation:

$$\{\mathbf{R}|t_{\mathbf{R}} + m\}\hat{\phi}(p) = \hat{\phi}(\mathbf{R}^{-1}p) \exp[-ip_z(t_{\mathbf{R}} + ma)]. \quad (2.16)$$

Combining this expression with (2.15) we get the following phase factor associated with non-vanishing momentum space functions:

$$\exp[-ip_z(t_{\mathbf{R}} + ma)] = \exp(-2\pi i\kappa_p t_{\mathbf{R}}/Na) \exp(-2\pi i\kappa_p m/N). \quad (2.17)$$

When the integer κ_p contains a factor N , i.e. $\kappa_p = Nn$, (2.17) reduces to

$$\exp(-2\pi int_{\mathbf{R}}/a). \quad (2.18)$$

Thus for a non-symmorphic group the line group operation (2.12) entails multiplication by a phase factor consisting of two parts. For special values of p_z corresponding to reciprocal-lattice vectors, that phase factor reduces to the complex number (2.18).

When N is very large, we can pass from summation to integration over p_z by means of

$$\frac{2\pi}{Na} \sum_{\kappa_p} \leftrightarrow \int dp_z. \quad (2.19)$$

Whichever of these operations is simplest can then be used in actual calculations. This relation is also connected with the transition from finite to infinite BK regions [45].

If a function $\psi(\mathbf{r})$ is normalized in BK, i.e. if

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-Na/2}^{Na/2} dz |\psi(\mathbf{r})|^2 = 1 \quad (2.20)$$

we have [45]

$$\int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z |\hat{\psi}(\mathbf{p})|^2 = 1 \quad (2.21)$$

for the momentum space counterpart of $\psi(\mathbf{r})$ which is obtained by integration over BK.

For a polymer, translational symmetry is present only along the z axis and, since the corresponding reciprocal-space direction is also the z axis, the k -vectors specialize to $\mathbf{k} = k\mathbf{e}_z$, k being now a wavenumber. Similarly, the notation $\mathbf{T}(m)$ for translations will be denoted as \mathbf{T}_m for polymer linear lattices. If the polymer is invariant under translation, the corresponding symmetry-adapted functions will be Bloch functions $\psi(\mathbf{k}, \mathbf{r}) = \psi(k, \mathbf{r})$ characterized by the wavenumber k in the one-dimensional first BZ. In this case also, a lattice translation \mathbf{T}_m simply changes the phase of the symmetry-adapted function in a way depending on the translation and on the wavenumber. The Bloch condition is now restricted to the z direction:

$$\mathbf{T}_m \psi(\mathbf{k}, \mathbf{r}) = \psi(\mathbf{k}, \mathbf{r} - m) = \psi(\mathbf{k}, \mathbf{r}) \exp(-i\mathbf{k} \cdot m) = \psi(\mathbf{k}, \mathbf{r}) \exp(-imak) \quad (2.22)$$

with the wavenumber k in the BZ given by

$$k = 2\pi\kappa/Na \quad -N/2 \leq \kappa < N/2 \quad -\pi/a \leq k < \pi/a. \quad (2.23)$$

Whenever convenient we shall use the wavenumber k instead of the wavevector \mathbf{k} .

A Bloch function $\hat{\psi}(k, p)$ in momentum space satisfies both the Bloch condition (2.22) and a similar relation with k replaced by p_z (cf (2.7)). This implies [39] that it vanishes unless the following relation is fulfilled between k and p_z , the momentum variable along the repeat direction:

$$p_z = k + 2\pi\nu/a \quad (2.24)$$

where ν is any positive or negative integer or zero. We thus have $\kappa_p = \kappa + N\nu$.

The two relations, (2.15) and (2.24), illustrate in an excellent way how momentum space concepts and relations complement results in position space and make their implications more visible. All momentum space counterparts of functions satisfying

the general BK boundary conditions (2.14a) vanish unless (2.15) is satisfied. The momentum space counterpart of a Bloch function vanishes for most of the values satisfying (2.15) too; it is different from zero only for those values of p_z which are related to the k labelling the Bloch function via (2.24).

The linear lattice in position space allows us to define a reciprocal lattice in the same direction:

$$K = (2\pi/a)\nu e_z \quad (2.25)$$

where ν is any positive or negative integer or zero. The values (2.24) at which a Bloch function in momentum space is different from zero can then be written

$$p_z = k + K. \quad (2.26)$$

On the other hand there is no reciprocal lattice in the x and y directions.

2.3. Symmetry-adapted wavefunctions

In a self-consistent calculation, symmetry adaptation of the basis functions is desirable not only in order to simplify the calculations but also to prevent numerical errors from yielding unsuitable solutions. Fukutome [46] has shown how the requirement that symmetry should also be self-consistent leads to a classification of possible types of solutions of Hartree-Fock equations. If on the other hand such symmetry constraints are not imposed, so-called symmetry broken solutions may appear [47]. In a restricted Hartree-Fock (RHF) calculation (called the 'time-reversal-invariant closed shell' by Fukutome) for a closed-shell polymeric system the Fock-Dirac density matrix contains complete sets of basis functions for those irreducible representations (IRs) of the line group which occur. Consequently such a Fock-Dirac matrix as well as the corresponding Fock operator commutes with all the elements of the line group. As a result the eigenfunctions of this Fock operator must transform according to IRs of the line group and in that sense the symmetry is self-consistent. The *direct* simplification due to the symmetry adaptation consists of the separation of functions associated with different IRs. For a line group this means primarily that equations for different wavenumbers k can be treated independently of each other *at a given iteration step*. All functions are mixed, however, in the Fock-Dirac matrix, which is why iterations are needed.

When an atomic orbital

$$\phi_{jm}(\mathbf{r}) = \phi_j(\mathbf{r} - mae_z) \quad (2.27)$$

of type j in the unit cell centred at $\mathbf{m} = mae_z$ is used to construct a function symmetry adapted to the translational symmetry, we get a Bloch sum

$$\eta_j(k, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{m=-N/2}^{N/2-1} \phi_{jm}(\mathbf{r}) \exp(ikma). \quad (2.28)$$

'Type j ' means both relative position in the unit cell and type of orbital. The counterpart of such a Bloch sum of atomic orbitals in momentum space is *essentially* given by the momentum space counterpart of the atomic orbital [39]:

$$\hat{\eta}_{j,N}(k, \mathbf{p}) = \sqrt{N} \hat{\phi}_j(\mathbf{p}) \delta_{p_z, k+K}. \quad (2.29)$$

Here the subscript N indicates that this momentum space Bloch function has been obtained from integration over BK [39]. Since this is the only type of Bloch function that is going to be used, we suppress this subscript from now on. The momentum space counterpart of the atomic orbital itself is given by

$$\hat{\phi}_j(\mathbf{p}) = (2\pi)^{-3/2} \int d\mathbf{r} \phi_j(\mathbf{r}) \exp(-i\mathbf{p} \cdot \mathbf{r}). \quad (2.30)$$

Apart from indicating the type of atomic orbital the subscript j can thus also denote a relative position in the unit cell. In such a case, (2.30) contains a corresponding phase factor.

The Kronecker δ in (2.29) reveals that this is a Bloch function in momentum space. The particular type of Bloch function is—as it were—concentrated in the momentum space counterpart (2.30) of the atomic orbital. Here is an interesting aspect of momentum space functions associated with translational symmetry, showing how information can be represented in a more concentrated manner in momentum space.

According to (2.16) we get with (2.27)

$$\{\mathbf{R}|t_{\mathbf{R}} + \mathbf{n}\} \hat{\eta}_j(k, \mathbf{p}) = \sqrt{N} \hat{\phi}_j(\mathbf{R}^{-1}\mathbf{p}) \delta_{\mathbf{R}^{-1}\mathbf{p}_z, k+K} \exp[-i\mathbf{p}_z(t_{\mathbf{R}} + n a)]. \quad (2.31)$$

It is instructive to recall how the same operation transforms the Bloch function in position space:

$$\begin{aligned} \{\mathbf{R}|t_{\mathbf{R}} + \mathbf{n}\} \eta_j(k, \mathbf{r}) &= \frac{1}{\sqrt{N}} \sum_{m=-N/2}^{N/2-1} \{\mathbf{R}|t_{\mathbf{R}} + \mathbf{n}\} \{1|m\} \phi_j(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{m}) \\ &= \eta_j(\mathbf{R}\mathbf{k}, \mathbf{R}^{-1}(\mathbf{r} - t_{\mathbf{R}})) \exp[-i(\mathbf{R}\mathbf{k}) \cdot \mathbf{n}]. \end{aligned} \quad (2.32)$$

The Kronecker δ in (2.31) shows that the transformed Bloch function vanishes unless

$$p_z = (\mathbf{R}\mathbf{k})_z + 2\pi\nu'/a. \quad (2.33)$$

For a line group the usual procedure for symmetry adaptation is analogous to what is done in the case of 'ordinary' space groups [40, 41, 44, 48]. One thus chooses a wavenumber k and finds the group $\mathbf{G}_0(k)$ of that wavenumber. The IRS of the line group are then obtained for each k from the IRS of $\mathbf{G}_0(k)$ and the star of k .

3. Orthogonalization

In a calculation using symmetry-adapted basis functions, e.g. of RHF type, the simplification obtained because of symmetry can be described by saying that the symmetry-adapted basis is *orthogonal and non-interacting* with respect to any operator that commutes with the elements of the symmetry group. The term non-interacting means that within that basis all non-diagonal matrix elements of such operators vanish. This is the situation for functions associated with *different IRS*, but there is no reason for functions transforming according to the same IR to be either orthogonal or non-interacting with respect to operators commuting with the symmetry group. In such a

case, one must solve a secular equation. The overlap between these functions must be handled in one way or another, either by means of an orthonormalization procedure or by solving a transformed secular equation.

We first notice that, for two atomic orbitals (AOs) $\phi_m(\mathbf{r})$ and $\phi_n(\mathbf{r})$ on a linear lattice, the overlap integral can be written in several ways ($m = ma e_z$; $n = na e_z$):

$$\begin{aligned} S_{mn} &= \int d\mathbf{r} \phi_m^*(\mathbf{r}) \phi_n(\mathbf{r}) = \int d\mathbf{p} \hat{\phi}_m^*(\mathbf{p}) \hat{\phi}_n(\mathbf{p}) = \int d\mathbf{p} |\hat{\phi}(\mathbf{p})|^2 \exp[ip_z a(m-n)] \\ &= \frac{2\pi}{Na} \sum_{\kappa_p=-\infty}^{\infty} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \left| \hat{\phi} \left(p_x, p_y, \frac{2\pi\kappa_p}{Na} \right) \right|^2 \\ &\quad \times \exp \left(\frac{2\pi i \kappa_p (m-n)}{N} \right). \end{aligned} \quad (3.1)$$

For a set of non-orthogonal orbitals centred on a lattice, *symmetric orthogonalization* [49–51] is the most natural procedure, with among others the property of yielding a set of functions which resemble the original ones as much as possible. The fact that in momentum space there is only one centre (cf (2.7)) implies that symmetric orthonormalization is much simpler in momentum space than in position space [52]. In position space, symmetric orthonormalization transforms a set of atomic orbitals on a lattice, $\phi(m, \mathbf{r}) = \phi_m(\mathbf{r})$, with overlap matrix \mathbf{S} , to another set

$$\varphi_m(\mathbf{r}) = \sum_{n=-N/2}^{N/2-1} \phi_n(\mathbf{r}) [\mathbf{S}^{-1/2}]_{nm} \quad (3.2)$$

i.e. a set of *multicentre functions*. In momentum space the corresponding expression is

$$\hat{\varphi}_m(\mathbf{p}) = \hat{\varphi}(\mathbf{p}) \exp(-ip_z ma) \quad (3.3)$$

with

$$\hat{\varphi}(\mathbf{p}) = \hat{\phi}(\mathbf{p}) / \sqrt{d(\mathbf{p})}. \quad (3.4)$$

Here

$$d(\mathbf{p}) = d(\mathbf{k} + \mathbf{K}) = d(\mathbf{k}) = d(k) = \sum_{m=-N/2}^{N/2-1} S_{m0} \exp(-ikma) \quad (3.5)$$

are the eigenvalues of the overlap matrix. Since $d(\mathbf{k})$ has the periodicity of the reciprocal lattice, there is for every \mathbf{p} an equivalent wavevector \mathbf{k} in the first BZ. The quantity $d(\mathbf{k})$ can also be interpreted as the normalization constant for the Bloch sum formed from the AOs $\phi_m(\mathbf{r})$ or the corresponding function in momentum space. Using (3.1) and (3.5) we have, for the unnormalized Bloch sum and its counterpart in momentum space,

$$\begin{aligned} \chi'(k, \mathbf{r}) &= \frac{1}{\sqrt{N}} \sum_m^{BK} \phi_m(\mathbf{r}) \exp(ikma) \\ \hat{\chi}'(k, \mathbf{p}) &= \sqrt{N} \hat{\phi}(\mathbf{p}) \delta_{p_z, k+K} \end{aligned} \quad (3.6)$$

and the normalization constant is

$$\begin{aligned} \int d\mathbf{r} |\chi'(k, \mathbf{r})|^2 &= \int d\mathbf{p} |\chi'(k, \mathbf{p})|^2 \\ &= \frac{2\pi}{a} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \sum_K |\hat{\phi}(p_x, p_y, k + K)|^2 = d(k). \end{aligned} \quad (3.7)$$

Thus the normalized Bloch function in momentum space is

$$\hat{\chi}(k, \mathbf{p}) = \chi'(k, \mathbf{p}) / \sqrt{d(k)} = \sqrt{N} \hat{\phi}(\mathbf{p}) \delta_{\mathbf{p}, k+K}. \quad (3.8)$$

With several AOs $\phi_{jm}(\mathbf{r})$ per unit cell, we first form normalized Bloch sums or their counterparts (cf (2.28)):

$$\hat{\chi}_j(k, \mathbf{p}) = \sqrt{N} \hat{\phi}_j(\mathbf{p}) \delta_{\mathbf{p}, k+K} = \sqrt{N} [\hat{\phi}_j(\mathbf{p}) / \sqrt{d_j(k)}] \delta_{\mathbf{p}, k+K}. \quad (3.9)$$

For different k these functions are all orthonormal and non-interacting. Functions with the same k and different subscripts j are in general *not* orthogonal, however:

$$\int d\mathbf{p} \hat{\chi}_i^*(k, \mathbf{p}) \hat{\chi}_j(k, \mathbf{p}) = d_{ij}(k). \quad (3.10)$$

We can again carry out a symmetric orthonormalization in order to obtain a set of *completely orthonormal functions*:

$$\hat{\xi}_j(k, \mathbf{p}) = \sum_i \hat{\chi}_i(k, \mathbf{p}) [\mathbf{d}(k)^{-1/2}]_{ij}. \quad (3.11)$$

Here

$$\mathbf{d}(k) = \begin{bmatrix} 1 & d_{12}(k) & d_{13}(k) & \dots \\ d_{21}(k) & 1 & d_{23}(k) & \dots \\ d_{31}(k) & d_{32}(k) & 1 & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix} \quad (3.12)$$

is the overlap matrix of the Bloch functions (3.9) for a fixed k . We see that, although the functions (3.11) are orthonormal, there is no reason for them to be non-interacting with respect to a Fock operator.

As shown in this section, symmetric orthonormalization in momentum space is a very attractive procedure, which makes it possible to concentrate on the properties of the atomic orbitals. This ought to be useful in calculations carried out directly in momentum space.

4. Momentum distributions

The momentum distribution for an electronic system is given by the diagonal element of the first-order density matrix $\delta(\mathbf{p}, \zeta; \mathbf{p}', \zeta')$, in momentum space, which depends on both the momentum coordinates \mathbf{p}, \mathbf{p}' and the spin coordinates ζ, ζ' . In the general

case that quantity consists of a *number-density matrix* $\hat{\mathbf{N}}(\mathbf{p}, \mathbf{p}')$ and a *spin-density matrix vector* $\hat{\mathbf{S}}(\mathbf{p}, \mathbf{p}') = e_x \hat{S}_x(\mathbf{p}, \mathbf{p}') + e_y \hat{S}_y(\mathbf{p}, \mathbf{p}') + e_z \hat{S}_z(\mathbf{p}, \mathbf{p}')$ [53]:

$$\hat{\delta}(\mathbf{p}, \zeta; \mathbf{p}', \zeta') = [\alpha(\zeta), \beta(\zeta)] \times \begin{bmatrix} \frac{1}{2}\hat{\mathbf{N}}(\mathbf{p}, \mathbf{p}') + \hat{S}_z(\mathbf{p}, \mathbf{p}') & \hat{S}_x(\mathbf{p}, \mathbf{p}') - i\hat{S}_y(\mathbf{p}, \mathbf{p}') \\ \hat{S}_x(\mathbf{p}, \mathbf{p}') + i\hat{S}_y(\mathbf{p}, \mathbf{p}') & \frac{1}{2}\hat{\mathbf{N}}(\mathbf{p}, \mathbf{p}') - \hat{S}_z(\mathbf{p}, \mathbf{p}') \end{bmatrix} \begin{bmatrix} \alpha(\zeta') \\ \beta(\zeta') \end{bmatrix}. \quad (4.1)$$

When the spin-density matrix vanishes, we have

$$\hat{\delta}(\mathbf{p}, \zeta; \mathbf{p}', \zeta') = \frac{1}{2}\hat{\mathbf{N}}(\mathbf{p}, \mathbf{p}')(\alpha\alpha' + \beta\beta'). \quad (4.2)$$

The momentum distribution is then given by

$$\hat{\rho}(\mathbf{p}) = \hat{\mathbf{N}}(\mathbf{p}, \mathbf{p}). \quad (4.3)$$

The same expression for the momentum distribution is obtained in the general case, and thus with a non-vanishing spin density, from

$$\hat{\rho}(\mathbf{p}) = \int d\zeta \hat{\delta}(\mathbf{p}, \zeta; \mathbf{p}, \zeta). \quad (4.4)$$

The spin density consists of the three components

$$\hat{S}_x(\mathbf{p}) = \hat{S}_x(\mathbf{p}, \mathbf{p}) \quad \hat{S}_y(\mathbf{p}) = \hat{S}_y(\mathbf{p}, \mathbf{p}) \quad \hat{S}_z(\mathbf{p}) = \hat{S}_z(\mathbf{p}, \mathbf{p}). \quad (4.5)$$

Both (4.4) and (4.5) are accessible experimentally [36, 54].

The various components of the first-order density matrix (4.1) can be expressed in terms of the natural spin orbitals and the occupation function [53] for the state under consideration. Closely related to the natural orbitals are the so-called generalized overlap amplitudes (GOAs), which provide an example of still another quantity available experimentally. The absolute values of the momentum space counterparts of the GOAs are in fact measured in (*e, 2e*) experiments [54].

4.1. Symmetry properties of momentum distributions

If the total wavefunction is approximated by a single determinant, the occupation function is a step function. Even with this limitation it is possible, however, to conceive of a wealth of determinants of different kinds [46, 55]. If we further restrict ourselves to what is usually called the RHF approximation, all the occupied orbitals are doubly filled and can be chosen real [46], which implies that

$$\hat{\mathbf{N}}^*(\mathbf{p}, \mathbf{p}') = \hat{\mathbf{N}}(-\mathbf{p}, -\mathbf{p}'). \quad (4.6)$$

It is practical to let the term RHF include one more condition, namely that the number-density matrix $\mathbf{N}(\mathbf{r}, \mathbf{r}')$ is invariant under those unitary operators \mathbf{g} which constitute the spatial symmetry group \mathbf{G} of the system. In such a case we have

$$\mathbf{g}\mathbf{N}(\mathbf{r}, \mathbf{r}')\mathbf{g}^\dagger = \mathbf{N}(\mathbf{g}^{-1}\mathbf{r}, \mathbf{g}^{-1}\mathbf{r}') = \mathbf{N}(\mathbf{r}, \mathbf{r}') \quad (4.7)$$

or, expressed in a slightly different way,

$$\mathbf{gN}(\mathbf{r}, \mathbf{r}') = \mathbf{N}(\mathbf{r}, \mathbf{r}')\mathbf{g}. \quad (4.8)$$

Here operators to the right of the density matrix thus work on the primed coordinates. For the electronic density $\rho(\mathbf{r}) = \mathbf{N}(\mathbf{r}, \mathbf{r})$ this implies that

$$\mathbf{g}\rho(\mathbf{r}) = \rho(\mathbf{g}^{-1}\mathbf{r}) = \rho(\mathbf{r}) \quad (4.9)$$

which is what should be expected for 'normal' systems.

In order to see what this means for the number-density matrix in momentum space we introduce symmetry-adapted orbitals $\psi_j^{(\alpha)}(\mathbf{r})$ for the system under consideration—atom, molecule, polymer or solid—assumed to be invariant under the group \mathbf{G} . Such orbitals are characterized by the relations

$$\mathbf{g}\psi_j^{(\alpha)}(\mathbf{r}) = \sum_{i=1}^{l_\alpha} \psi_i^{(\alpha)}(\mathbf{r})\Gamma_{ij}^{(\alpha)}(\mathbf{g}) \quad \mathbf{g} \in \mathbf{G} \quad j = 1, 2, 3, \dots, l_\alpha. \quad (4.10)$$

Here l_α is the dimension of an IR $\Gamma^{(\alpha)}$ of \mathbf{G} , and $\Gamma_{ij}^{(\alpha)}(\mathbf{g})$ is the ij th element of the matrix representing \mathbf{g} in that IR. The restrictions associated with the term RHF now mean that the number-density matrix contains *complete sets of partners* of each IR which is occupied:

$$\mathbf{N}(\mathbf{r}, \mathbf{r}') = \sum_{\alpha}^{\text{occ}} \sum_{j=1}^{l_\alpha} \psi_j^{(\alpha)}(\mathbf{r})\psi_j^{(\alpha)*}(\mathbf{r}'). \quad (4.11)$$

Thus, if the IR $\Gamma^{(\alpha)}$ is present in the sum (4.11), *all* the l_α functions $\psi_j^{(\alpha)}(\mathbf{r})$ must be included in that sum, in order for it to represent an RHF number-density matrix. The summation over α includes the possibility that an IR can appear more than once. In such a case we assume that the corresponding orbitals have been orthonormalized. Otherwise a more general form of the first-order density matrix must be used [56]. Combining (4.10) and (4.11) we see that (4.7) is satisfied.

The momentum space counterpart of $\psi_j^{(\alpha)}(\mathbf{r})$ is

$$\hat{\psi}_j^{(\alpha)}(\mathbf{p}) = (2\pi)^{-3/2} \int d\mathbf{r} \psi_j^{(\alpha)}(\mathbf{r}) \exp(-i\mathbf{p} \cdot \mathbf{r}). \quad (4.12)$$

When $\psi_j^{(\alpha)}(\mathbf{r})$ is symmetry adapted in the sense of (4.10), so is $\hat{\psi}_j^{(\alpha)}(\mathbf{p})$. Consequently we also have

$$\mathbf{g}\hat{\mathbf{N}}(\mathbf{p}, \mathbf{p}') = \hat{\mathbf{N}}(\mathbf{p}, \mathbf{p}')\mathbf{g} \quad (4.13)$$

and for the momentum distribution (4.3)

$$\mathbf{g}\hat{\rho}(\mathbf{p}) = \hat{\rho}(\mathbf{g}^{-1}\mathbf{p}) = \hat{\rho}(\mathbf{p}). \quad (4.14)$$

If \mathbf{G} is a line group, we have from (2.16)

$$\{\mathbf{R}|t_{\mathbf{R}} + m\} \hat{\psi}_j^{(\alpha)}(\mathbf{p}) = \hat{\psi}_j^{(\alpha)}(\mathbf{g}^{-1}\mathbf{p}) \exp[-ip_z(t_{\mathbf{R}} + ma)] \quad (4.15)$$

which means that

$$\{R|t_R + m\} \hat{N}(p, p') \{R|t_R + m\}^+ = R \hat{N}(p, p') R^+. \quad (4.16)$$

This implies that symmetry adaptation of the momentum distribution primarily means that the momentum distribution is invariant under the *point group part* of the line group. The translational symmetry shows up in another way in momentum space, however. In order to see how, we must specify the meaning of the superscript α for a line group.

The IRS of a line group are primarily characterized by the wavenumber k (equation (2.23)) in the BZ. For a given k they are further specified by a particular IR of $G_0(k)$, the group of that particular k . We therefore replace the general notation used so far (cf (4.10)) by $\psi_j^{(\alpha)}(k, r)$, where now α refers to an IR of $G_0(k)$. The number-density matrix can then be written

$$\hat{N}(p, p') = \sum_{k, \alpha} \sum_{j=1}^{l_\alpha} \psi_j^{(\alpha)}(k, p) \psi_j^{(\alpha)*}(k, p') \quad (4.17)$$

and we note that the summation over k includes both $+k$ and $-k$.

When the Bloch functions—the final solutions of the RHF problem—are expressed as linear combinations of AOs

$$\psi_j^{(\alpha)}(k, r) = \sum_{\mu} \hat{\eta}_{j\mu}^{(\alpha)}(k, r) c_{\mu}(k) \quad (4.18a)$$

their momentum space counterparts can be written as (cf (2.28) and (2.29))

$$\hat{\psi}_j^{(\alpha)}(k, p) = \sum_{\mu} \hat{\eta}_{j\mu}^{(\alpha)}(k, p) c_{\mu}(k). \quad (4.18b)$$

The basis functions are thus of type (2.29) and symmetry adapted to *the group of the wavenumber k* :

$$\hat{\eta}_{j\mu}^{(\alpha)}(k, p) = \sqrt{N} \hat{\phi}_{j\mu}^{(\alpha)}(p) \delta_{p, k+K}. \quad (4.19)$$

Thus there is an important distinction between the basis functions in (4.18a) that are symmetry adapted to the full line group, and those used in momentum space, (4.18b), which are symmetry adapted to the group of the particular wavevector k . By combining (4.16)–(4.19) we can make the point group symmetry of the momentum distribution clearly visible. Care is needed however, since the IRS $\Gamma^{(\alpha)}$ of $G_0(k)$ depend on k .

It is reasonable to ask whether it is possible to see from any features of the function (4.3) if it is the momentum distribution of a polymer or of some other system. In the polymer case we have drawn attention to some of these features in the present paper. The special role of the z axis reveals the existence of a lattice in that direction. The contents of each unit cell are reflected in the composition of the momentum distribution from contributions that are symmetry adapted to the point group part of the line group and its subgroups.

4.2. Form factors

In studies of the electron density $\rho(\mathbf{r}) = \mathbf{N}(\mathbf{r}, \tau)$, the *form factor*

$$F(\mathbf{p}) = \int d\mathbf{r} \rho(\mathbf{r}) \exp(-i\mathbf{p} \cdot \mathbf{r}) \quad (4.20)$$

which can also be written as

$$F(\mathbf{p}) = \int d\mathbf{p}' \hat{\mathbf{N}}(\mathbf{p}' + \mathbf{p}, \mathbf{p}') \quad (4.21)$$

plays an essential role.

Similarly it is customary [57-60] to use the *reciprocal form factor*

$$B(\mathbf{r}) = \int d\mathbf{p} \hat{\rho}(\mathbf{p}) \exp(i\mathbf{p} \cdot \mathbf{r}) \quad (4.22)$$

in analyses of momentum space experiments. Combining (4.3), (4.22) and the basic connection between momentum space and position space, we get

$$B(\mathbf{r}) = \int d\mathbf{r}' \mathbf{N}(\mathbf{r}' + \mathbf{r}, \tau) \quad (4.23)$$

which allows us to interpret the reciprocal form factor as the autocorrelation function of the number-density matrix in position space.

When the momentum distribution is invariant under the point group part of the line group (cf (4.14) and (4.16)), (4.22) implies that this also holds for the reciprocal form factor

$$\mathbf{R}B(\mathbf{r}) = \int d\mathbf{p} \hat{\rho}(\mathbf{p}) \exp[i\mathbf{p} \cdot (\mathbf{R}^{-1}\mathbf{r})] = B(\mathbf{r}). \quad (4.24)$$

Thus the reciprocal form factor $B(\mathbf{r})$ reflects the symmetry of the point group part of the line group.

5. Concluding remarks

In this paper we have analysed in some detail the properties of momentum space functions for a polymer from the point of view of boundary conditions, symmetry and orthogonalization. The differences in the implications of the periodic boundary conditions on the one hand and the translational symmetry on the other hand have been stressed. The advantages in using the full line group symmetry are emphasized. The results of the present paper should be useful for all momentum space applications to polymers and will hopefully lead to an increased interest in this important aspect of the electronic structure of such systems.

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References

- [1] Chemla D S and Zyss J (eds) 1987 *Nonlinear Optical Properties of Organic Molecules and Crystals* (New York: Academic)
- [2] Todd Jarvis M 1985 *Emerging Technologies* No 9
- [3] André J-M, Delhalle J and Brédas J-L 1991 *Quantum Chemistry Aided Design of Organic Polymers* (Singapore: World Scientific)
- [4] Whangbo M H, Smith V H Jr and von Niessen W 1974 *Chem. Phys.* **6** 282
- [5] Braun-Keller E and Epstein I R 1976 *Chem. Phys. Lett.* **40** 215
- [6] Snyder L S and Weber T A 1978 *J. Chem. Phys.* **68** 2974
- [7] Kaijser P, Smith V H Jr and Thakkar A J 1980 *Mol. Phys.* **41** 1143
- [8] Brion C E 1986 *Int. J. Quantum Chem.* **29** 1397, and references therein
- [9] Defranceschi M 1987 *Chem. Phys.* **115** 349
- [10] Manninen S, Paakkari T, Aikala O and Mansikka K 1973 *J. Phys. C: Solid State Phys.* **6** L410
- [11] Aikala O, Mansikka K, Ekström L and Berggren K-F 1973 *Phil. Mag.* **28** 997
- [12] Aikala O, Jokela V and Mansikka K 1973 *J. Phys. C: Solid State Phys.* **6** 1116
- [13] Euwema R N, Wepfer G G, Surratt G T and Wilhite D L 1974 *Phys. Rev. B* **9** 5249
- [14] Schülke W 1977 *Phys. Status Solidi* **b** **82** 229
- [15] Seth A and Ellis D E 1977 *J. Phys. C: Solid State Phys.* **10** 181
- [16] Zunger A and Freeman A J 1977 *Phys. Rev. B* **15** 5049
- [17] Schülke W and Kramer B 1979 *Acta Crystallogr. A* **35** 953
- [18] Aikala O 1979 *J. Phys. C: Solid State Phys.* **12** L581, and references therein
- [19] Pattison P, Hansen N K and Schneider J R 1981 *Chem. Phys.* **59** 231
- [20] Mijnaerends P E 1983 *Positron Solid-State Physics* vol 83 (Corso, Bologna: Società Italiana di Fisica) and references therein
- [21] Pettitt B M, Matcha R L and Ramirez B I 1983 *J. Chem. Phys.* **79** 2913, and references therein
- [22] March N H 1986 *Int. J. Quantum Chem. Symp.* **20** 367, and references therein
- [23] Thomas M W 1972 *Mol. Phys.* **23** 571
- [24] Thakkar A J, Simas A M and Smith V H Jr 1980 *Mol. Phys.* **41** 1153
- [25] Thakkar A J, Simas A M and Smith V H Jr 1981 *Chem. Phys.* **63** 175
- [26] Koga T and Morita M 1982 *Theor. Chim. Acta* **61** 73
- [27] Simas A M, Smith V H Jr and Kaijser P 1984 *Int. J. Quantum Chem.* **25** 1035
- [28] Thakkar A J 1986 *Int. J. Quantum Chem.* **23** 227
- [29] Tanner A C 1988 *Chem. Phys.* **123** 241
- [30] Epstein I R 1975 *Theoretical Chemistry (Physical Chemistry Series 2)* vol 1, ed A D Buckingham and C A Coulson (London: Butterworths)
- [31] Williams B (ed) 1977 *Compton Scattering* (New York: McGraw Hill)
- [32] Kaijser P and Smith V H Jr 1977 *Adv. Quantum Chem.* **10** 37
- [33] Moore J H, Tossel J A and Coplan M A 1982 *Acc. Chem. Rec.* **15** 192
- [34] Kryachko E S and Koga T 1985 *Adv. Quantum Chem.* **17** 97, especially pp 174-96
- [35] Schneider J R and Bell F 1992 *Europhys. News* **23** 10
- [36] Weyrich W (ed) 1992 *Proc. 10th Sagamore Conf. (Konstanz, Germany, 1991)*; *Z. Naturf.* at press
- [37] Defranceschi M and Berthier G 1990 *J. Physique* **51** 2791
- [38] Gadre S R, Limaye A C and Kulkarni S U 1991 *J. Chem. Phys.* **94** 8040
- [39] Calais J L 1988 *Coll. Czech. Chem. Commun.* **53** 1890
- [40] Bozovic N, Bozovic I B and Damjanovic M 1985 *J. Phys. A: Math. Gen.* **18** 923, and references therein
- [41] Koch W and Seelig F F 1987 *Int. J. Quantum Chem.* **32** 249
- [42] Dirac P A M 1958 *The Principles of Quantum Mechanics* 4th edn (London: Oxford University Press) p 94

- [43] Brillouin L 1953 *Wave Propagation in Periodic Structures* 2nd edn (New York: Dover)
- [44] Cornwell J F 1969 *Group Theory and Electronic Bands in Solids* (Amsterdam: North Holland)
- [45] Calais J L and Weyrich W to be published
- [46] Fukutome H 1981 *Int. J. Quantum Chem.* **20** 955, and references therein
- [47] For a recent survey see Paldus J 1990 *Selfconsistent Field Theory and Applications (Studies in Physical and Theoretical Chemistry)* vol 70, ed R Carbó and M Klobukowski p 1
- [48] Calais J L 1985 *Int. J. Quantum Chem. Symp.* **19** 655
- [49] Löwdin P-O 1947 *Ark. Mater. Fys. Astron.* **A** 35 1
- [50] Löwdin P-O 1956 *Adv. Phys.* **5** 1
- [51] Löwdin P-O 1970 *Adv. Quantum Chem.* **5** 185
- [52] Calais J L 1989 *Int. J. Quantum Chem.* **35** 735
- [53] Calais J L and Deihalle J 1988 *Phys. Scr.* **38** 746
- [54] Weigold E and McCarty I E 1991 *Rep. Prog. Phys.* **54** 789
- [55] Calais J L 1985 *Adv. Quantum Chem.* **17** 225
- [56] Löwdin P-O 1955 *Phys. Rev.* **97** 1490
- [57] Weyrich W 1978 *Habilitationsschrift* Darmstadt
- [58] Pattison P and Weyrich W 1979 *J. Phys. Chem. Solids* **40** 213
- [59] Pattison P and Schneider J R 1980 *Acta Crystallogr.* **A** 36 390
- [60] Pattison P, Hansen N K and Schneider J R 1984 *Acta Crystallogr.* **B** 40 38