Momentum Distribution and Charge Density in Solid-State Theory *

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We present a discussion of a number of conceptual and methodological aspects associated with the theoretical characterization and computation of charge densities and momentum distributions in solids. The main ambition has been to stress properties that both exact and approximate quantities must possess. We have also attempted to point out conceptual and computational trends which would seem to be of importance for the future of the subject.

Key words: Solid-state theory; Charge density; Momentum density; Density matrices; Hartree-Fock approximation; Density functional theory.

I. Introduction

The calculation of charge densities and momentum distributions in solids has always been of importance in solid-state theory. Despite statements to the contrary, however, band theory is not a closed field, neither conceptually nor computationally, in particular if we think of band theory not as a limited one-electron theory, but as something that at least asymptotically approaches a characterization in terms of natural spin orbitals and/or generalized overlap amplitudes. In this little review we will draw attention to some tendencies that seem to be of importance for the theoretical treatment of charge and momentum densities.

For general information about solid-state theory in general we refer to the book by Ashcroft and Mermin [1]. Symmetry plays a central rôle for our subject; here we recommend in particular the new edition of the book by Cornwell [2]. The list of references obviously has no ambition to be exhaustive, but those references that are given should provide suitable entrance channels to the various areas discussed.

In the first six of the following short sections we emphasize a number of formal aspects that although more or less discussed in the literature, should in our opinion be given more attention. In the last two sections we discuss certain aspects of the two main computational methods for calculating wave functions and thus also charge densities and momentum distributions.

II. Periodic Boundary Conditions and Discretized Momentum Space

Even though the term *periodic boundary conditions* appears in every text book of solid state theory, we should like to draw attention here to some aspects of this concept that do not seem to have received the notice they deserve. For more details concerning the present section we refer to [3].

The big difference between a finite and an extended system resides in the boundary conditions imposed on the wave functions. Wave functions for a finite system like an atom or a small molecule must tend to zero at sufficiently large distances from the system. In an extended system we require that the wave functions are different from zero throughout the whole system. The usual way of implementing that requirement is to divide space into so-called Born-von Kármán regions (BK). All *wave functions* are then required to be periodic with respect to these BKs. It is essential to distinguish this periodicity in the wave functions from another type of periodicity in the potentials that we will meet in the next section.

In one dimension periodic boundary conditions thus mean that there is a distance, $N a$, such that *all wave functions* satisfy

$$\phi(x + N a) = \phi(x). \tag{1}$$

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At this stage there is no need to write the length of a BK as a product of a typical cell length a, and a very large even integer N. Later on we will need these quantities, however, and we might just as well introduce them already here.

Given any wave function $\phi(x)$ in position space, its counterpart $\tilde{\phi}(p)$ in momentum space is given by [4]

$$\tilde{\phi}(p) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}x\, \phi(x)\, e^{-ipx} . \tag{2}$$

One can show [3] that the counterpart of a function satisfying periodic boundary conditions, (1), can be written as

$$\tilde{\phi}(p) = \frac{2\pi}{a} \tilde{\phi}_N(p) \sum_{\nu=-\infty}^{\infty} \delta\left(Np - \frac{2\pi\nu}{a}\right), \tag{3}$$

where

$$\tilde{\phi}_N(p) = \frac{1}{\sqrt{2\pi}} \int_{-Na/2}^{Na/2} \mathrm{d}x\, \phi(x)\, e^{-ipx} . \tag{4}$$

Relation (3) shows that periodic boundary conditions in position space imply a *discretization of momentum space:* the momentum-space functions vanish unless their argument is of the form

$$p = \frac{2\pi\nu}{Na}, \tag{5}$$

where ν is any positive or negative integer or zero.

In order to generalize these expressions to three dimensions, we introduce basis vectors, $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$, for the direct lattice and $\boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3$, for the reciprocal lattice, satisfying

$$\boldsymbol{a}_i \cdot \boldsymbol{b}_j = \delta_{ij} . \tag{6}$$

Instead of (1) we now require

$$\phi(\boldsymbol{r} + G\boldsymbol{a}_i) = \phi(\boldsymbol{r}), \quad i = 1, 2, 3 , \tag{7}$$

where G is a large even integer. The momentum-space counterpart of a function satisfying (7) can be written as [3]

$$\tilde{\phi}(\boldsymbol{p}) = \tilde{\phi}_G(\boldsymbol{p}) \cdot \frac{8\pi^3}{G^3 V_{0a}} \cdot \sum_{\boldsymbol{k}}^{\text{all}} \delta(\boldsymbol{p} - \boldsymbol{k}) . \tag{8}$$

Here $\tilde{\phi}_G(\boldsymbol{p})$ is defined in analogy with (4) as an integral over the BK, and

$$\boldsymbol{k} = \frac{2\pi}{G} (\boldsymbol{b}_1 \nu_1 + \boldsymbol{b}_2 \nu_2 + \boldsymbol{b}_3 \nu_3) ;$$

ν_i is any positive or negative integer or zero.

III. Translational Invariance and Translational Symmetry

Crystalline solids are characterized by *translational symmetry*. Various kinds of diffraction experiments reveal that certain quantities have the periodicity of the direct lattice or of a related lattice. In order to describe the electronic structure, the usual starting point is some kind of effective one-electron equation (see further Sects. VIII and IX) with a potential having the periodicity of the direct lattice. That implies that the effective Hamiltonian commutes with the three translation operators associated with the basis vectors:

$$[\mathbf{H}_{\text{eff}}, \mathbf{T}_i] = 0; \quad i = 1, 2, 3 . \tag{10}$$

For the translation operators we use the convention

$$\mathbf{T}_i\, \phi(\boldsymbol{r}) = \phi(\boldsymbol{r} - \boldsymbol{a}_i) . \tag{11}$$

An arbitrary lattice vector in the BK can be written as (μ_i integers),

$$\boldsymbol{m} = \boldsymbol{a}_1 \mu_1 + \boldsymbol{a}_2 \mu_2 + \boldsymbol{a}_3 \mu_3 ; \quad -\frac{G}{2} \le \mu_i < \frac{G}{2} . \tag{12}$$

The three commutation relations (10) imply that for any $\boldsymbol{m}$,

$$[\mathbf{H}_{\text{eff}}, \mathbf{T}(\boldsymbol{m})] = 0 , \tag{13}$$

where $\mathbf{T}(\boldsymbol{m})$ is the translation operator associated with the lattice vector (12).

The concept of *translational symmetry*, (13), should be carefully distinguished from that of *translational invariance*, which means that the effective Hamiltonian commutes with *the momentum operator* [5]. Translational invariance implies translational symmetry, but not vice versa [6].

The commutator (13) forces the eigenfunctions of the effective one-electron Hamiltonian to be *Bloch functions*, i.e. eigenfunctions of the translation operators, characterized by a wave vector $\boldsymbol{k}$ in the first Brillouin zone (BZ):

$$\mathbf{T}(\boldsymbol{m})\, \phi(\boldsymbol{k}; \boldsymbol{r}) = \phi(\boldsymbol{k}; \boldsymbol{r})\, e^{-i\boldsymbol{k}\cdot\boldsymbol{m}} . \tag{14}$$

These wave vectors $\boldsymbol{k}$ are of the form (9), but with the coefficients restricted to certain values:

$$\boldsymbol{k} = \frac{2\pi}{G} (\boldsymbol{b}_1 \varkappa_1 + \boldsymbol{b}_2 \varkappa_2 + \boldsymbol{b}_3 \varkappa_3); \quad -\frac{G}{2} \le \varkappa_i < \frac{G}{2} . \tag{15}$$

It is instructive to observe that, whereas the periodic boundary conditions imply non-vanishing functions in momentum space only for arguments of the form (9), the further requirement of translational symmetry restricts those wave vectors, that label the possible translation symmetry types of the wave functions, to a certain subset of (9). Momentum-space considerations help us to understand the connections between periodic boundary conditions and translational symmetry better. In position space we notice the difference between wave functions satisfying periodic boundary conditions (7), and Bloch functions (14). Bloch functions obviously also satisfy periodic boundary conditions. But whereas the potential has the periodicity of the direct lattice, the Bloch functions only change their phases when going from one cell to another one.

We thus have G^3 lattice vectors of type (12) in the BK, and the same number of wave vectors $\boldsymbol{k}$, (15), in the BZ. Since we will need that number often, we introduce the notation $G^3 = N$. The numbers

$$U(\boldsymbol{m}, \boldsymbol{k}) = \frac{1}{\sqrt{N}} e^{i\boldsymbol{k}\cdot\boldsymbol{m}} \tag{16}$$

can be seen as elements of a unitary matrix $\mathbf{U}$, of order N, thus satisfying

$$\mathbf{U}\mathbf{U}^+ = \mathbf{U}^+\mathbf{U} = \mathbf{1}\,. \tag{17}$$

Using this unitary matrix $\mathbf{U}$ we can transform a set of N Bloch functions $\phi(\boldsymbol{k}; \boldsymbol{r})$ satisfying (14) to a set of *Wannier functions*

$$W(\boldsymbol{m}; \boldsymbol{r}) = \sum_{\boldsymbol{k}}^{\mathrm{BZ}} \phi(\boldsymbol{k}; \boldsymbol{r})\, [\mathbf{U}^+]\,(\boldsymbol{k}, \boldsymbol{m})\,. \tag{18}$$

These Wannier functions are thus labeled by the direct lattice vectors $\boldsymbol{m}$. Combining (17) and (18) we get the inverse transformation

$$\phi(\boldsymbol{k}; \boldsymbol{r}) = \sum_{\boldsymbol{m}}^{\mathrm{BK}} W(\boldsymbol{m}; \boldsymbol{r})\, U(\boldsymbol{m}, \boldsymbol{k})\,. \tag{19}$$

IV. The Born-Oppenheimer Approximation

In most cases when the charge density or the momentum distribution is discussed, one probably thinks of the ground state situation or at least of a stationary state. This is obviously reflected in attempts to calculate these quantities: almost always the *Born-Oppenheimer approximation* is invoked. Generally speaking this means that the nuclei are frozen in a suitable configuration and one studies the electronic structure for that particular nuclear skeleton.

Even though that the electronic problem is formidable in itself, one should not forget that one really should solve an even more complicated many-particle problem, namely the one where both electrons and nuclei are allowed to move. The traditional way of handling that problem has been – to use a slightly provocative description – to work as if electronic structure and lattice dynamics were two separate worlds. Sooner or later they have to be combined, however, in particular when the coupling between them is non-negligible – when the *electron-phonon coupling* has to be taken into account.

A new and promising perspective on this difficult problem is offered by some recent developments due to Öhrn and Deumens [7–10]. Their starting point is the *time-dependent Schrödinger equation*, for which they construct approximate solutions by means of the *time-dependent variational principle* (TDVP), [11–13]. The key quantities of their method, END = Electron Nuclear Dynamics, are two sets of time-dependent parameters, electronic and nuclear. The electronic parameters are usually, but not necessarily, coefficients of basis orbitals. The nature of the nuclear parameters depends on the approximation level chosen. The method is capable of handling quantum mechanical nuclei; in that case one can, for example, choose nuclear parameters characterizing Gaussian wave packets for the nuclei. It is also possible to describe some or all the nuclei classically. In that case the nuclear parameters are simply the nuclear positions and momenta. The TDVP leads to a set of first-order coupled differential equations for these parameters. Computer programs already exist for solving such equations for small systems, and work on extended systems is underway.

It is to be expected that this inclusion of nuclear motion will have considerable influence on the characterization of charge densities and momentum distributions.

V. Density Matrices and Form Factors

As emphasized particularly by Löwdin [14] and McWeeny [15], it is preferable to work with *reduced density matrices*, rather than many-particle wave functions [16]. Since the Hamiltonian normally contains at most two-electron operators, we need only the first and second-order reduced density matrices. For an N-electron state with the total wave function $\Psi(x_1, x_2, x_3, \dots, x_N)$, these are defined as follows with Löwdin's normalization

$$\gamma(x_1|x_1') = N \int \Psi(x_1, x_2, \dots, x_N) \cdot \Psi^*(x_1', x_2, \dots, x_N)\, dx_2, \dots, dx_N; \quad (20\,a)$$

$$\Gamma(x_1, x_2|x_1', x_2') = \frac{N(N-1)}{2} \int \Psi(x_1, x_2, x_3, \dots, x_N) \cdot \Psi^*(x_1', x_2', x_3, \dots, x_N)\, dx_3, \dots, dx_N. \quad (20\,b)$$

As usual, x denotes the combined coordinate for space and spin: $x = (\boldsymbol{r}, \zeta)$.

We write the first-order density matrix (20a) as

$$\gamma(x|x') = \gamma(\boldsymbol{r}, \zeta|\boldsymbol{r}', \zeta') = [\alpha(\zeta)\ \beta(\zeta)]\, \mathbf{Q} \begin{bmatrix} \alpha(\zeta') \\ \beta(\zeta') \end{bmatrix}. \quad (21)$$

The 2×2 matrix $\mathbf{Q}$, which is the orbital part of γ, can be written in terms of the *number density matrix* $N(\boldsymbol{r}, \boldsymbol{r}')$ and the components of the *spin density matrix vector* $\boldsymbol{S}(\boldsymbol{r}, \boldsymbol{r}')$ [17, 18]:

$$\mathbf{Q} = \mathbf{Q}(\boldsymbol{r}, \boldsymbol{r}') = \begin{bmatrix} \frac{1}{2} N(\boldsymbol{r}, \boldsymbol{r}') + S_z(\boldsymbol{r}, \boldsymbol{r}') & S_x(\boldsymbol{r}, \boldsymbol{r}') - i S_y(\boldsymbol{r}, \boldsymbol{r}') \\ S_x(\boldsymbol{r}, \boldsymbol{r}') + i S_y(\boldsymbol{r}, \boldsymbol{r}') & \frac{1}{2} N(\boldsymbol{r}, \boldsymbol{r}') - S_z(\boldsymbol{r}, \boldsymbol{r}') \end{bmatrix}. \quad (22)$$

Like wave functions, (2), density matrices also have their counterparts in momentum space. For example, the number density matrix and its counterpart are related by

$$\tilde{N}(\boldsymbol{p}, \boldsymbol{p}') = \frac{1}{8\pi^3} \int d\boldsymbol{r}\, d\boldsymbol{r}'\, N(\boldsymbol{r}, \boldsymbol{r}') \exp\{-i(\boldsymbol{p} \cdot \boldsymbol{r} - \boldsymbol{p}' \cdot \boldsymbol{r}')\}; \quad (23\,a)$$

$$N(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{8\pi^3} \int d\boldsymbol{p}\, d\boldsymbol{p}'\, \tilde{N}(\boldsymbol{p}, \boldsymbol{p}') \exp\{i(\boldsymbol{p} \cdot \boldsymbol{r} - \boldsymbol{p}' \cdot \boldsymbol{r}')\}. \quad (23\,b)$$

Similar relations hold for the components of the spin density matrix vector and for $\mathbf{Q}$.

In order to get the corresponding densities we first integrate over spin,

$$\int d\zeta\, \gamma(\boldsymbol{r}, \zeta|\boldsymbol{r}', \zeta) = \mathrm{Tr}\, \mathbf{Q} = N(\boldsymbol{r}, \boldsymbol{r}'); \quad (24\,a)$$

$$\int d\zeta\, \tilde{\gamma}(\boldsymbol{p}, \zeta|\boldsymbol{p}', \zeta) = \mathrm{Tr}\, \tilde{\mathbf{Q}} = \tilde{N}(\boldsymbol{p}, \boldsymbol{p}'); \quad (24\,b)$$

The *charge density* is the diagonal element of $N(\boldsymbol{r}, \boldsymbol{r}')$,

$$\varrho(\boldsymbol{r}) = N(\boldsymbol{r}, \boldsymbol{r}), \quad (25)$$

and the *momentum distribution* is the diagonal element of $\tilde{N}(\boldsymbol{p}, \boldsymbol{p})$:

$$\tilde{\varrho}(\boldsymbol{p}) = \tilde{N}(\boldsymbol{p}, \boldsymbol{p}). \quad (26)$$

An important complementary aspect of position and momentum space appears when we combine (25) with (23b) and (26) with (23a):

$$\varrho(\boldsymbol{r}) = \frac{1}{8\pi^3} \int d\boldsymbol{p}\, d\boldsymbol{p}'\, \tilde{N}(\boldsymbol{p}, \boldsymbol{p}') \exp\{i(\boldsymbol{p} - \boldsymbol{p}') \cdot \boldsymbol{r}\}; \quad (27\,a)$$

$$\tilde{\varrho}(\boldsymbol{p}) = \frac{1}{8\pi^3} \int d\boldsymbol{r}\, d\boldsymbol{r}'\, N(\boldsymbol{r}, \boldsymbol{r}') \exp\{-i\boldsymbol{p} \cdot (\boldsymbol{r} - \boldsymbol{r}')\}. \quad (27\,b)$$

Thus, in order to get the density in one space, we need the *nondiagonal elements of the density matrix* in the other space.

In experimental work, the Fourier transforms of these quantities – the *form factors* – play a major rôle:

$$F(\boldsymbol{p}) = \int \varrho(\boldsymbol{r}) \exp\{i\boldsymbol{p} \cdot \boldsymbol{r}\}; \quad (28\,a)$$

$$B(\boldsymbol{r}) = \int \tilde{\varrho}(\boldsymbol{p}) \exp\{-i\boldsymbol{p} \cdot \boldsymbol{r}\}. \quad (28\,b)$$

The "ordinary" form factor $F(\boldsymbol{p})$ as been used for a long time, whereas the reciprocal form factor, $B(\boldsymbol{r})$, has been introduced relatively recently. Its properties have been exploited in particular by Weyrich and collaborators (a rather complete bibliography can be found in [19]). We notice the interpretation of the form factors as projections of the number density matrices

$$F(\boldsymbol{p}) = \int d\boldsymbol{p}'\, \tilde{N}(\boldsymbol{p}', \boldsymbol{p}' + \boldsymbol{p}); \quad (29\,a)$$

$$B(\boldsymbol{r}) = \int d\boldsymbol{r}'\, N(\boldsymbol{r}', \boldsymbol{r}' + \boldsymbol{r}). \quad (29\,b)$$

VI. One and Many-Electron Functions

One-electron functions – spin orbitals – constitute the primary raw material both for calculations and for the interpretation of theoretical results. At the one-electron level, where the total wave function is approximated by a single determinant, we have one spin orbital per electron. Expressed in a different way, each spin orbital is occupied by one electron. At higher levels of approximation the total wave function is a more elaborate quantity and one may wonder whether the concept of one-electron function is still meaningful. The answer to this presumption is very definitely yes, and we will now sketch two different but related connections between spin orbitals and many-electron wave functions.

Löwdin has coined the term *natural spin orbital* [14, 20] for those functions $\psi_k(x)$ that diagonalize the first-order density matrix γ,

$$\gamma(x|x') = \sum_{k=1}^{\infty} \psi_k(x)\, n_k\, \psi_k^*(x'). \quad (30)$$

The eigenvalues of γ, the *occupation numbers* n_k, satisfy the relations

$$0 \leq n_k \leq 1 ; \tag{31a}$$

$$\operatorname{Tr} \gamma = \sum_{k=1}^{\infty} n_k = N , \tag{31b}$$

where N is the total number of electrons in the system. These relations are completely general, and they must be satisfied both by exact and approximate density matrices. At the independent-particle level there are only N occupation numbers different from zero, and they are all equal to one. When correlation is introduced, the occupation numbers creep below one. In principle we have an infinite number of occupation numbers different from zero, even though most of them will presumably be very close to zero.

The natural spin orbitals (NSO) have the important property that they form an orthonormal set,

$$\int \psi_k^*(x)\, \psi_l(x)\, \mathrm{d}x = \delta_{kl} . \tag{32}$$

Thus given a first-order reduced density matrix for a certain state of a many electron system, we can find the corresponding natural spin orbitals and their occupation numbers. The first-order density matrix can be obtained from the total wave function or the reduced second-order density matrix. Approximations to either of these quantities can be obtained in a large number of ways. The natural spin orbitals actually provide a very efficient tool for comparing different approximations [21].

Another set of spin orbitals that are naturally associated with many-electron functions are the *generalized overlap amplitudes* (GOA) or *Dyson orbitals* [22, 23]. These are defined in terms of an exact or approximate total wave function for a certain state of an N-electron system together with all states for that system with one electron more or less. Thus we get two sets of spin orbitals, which are most easily expressed in a second-quantized formulation, using anticommuting field operators,

$$\psi(x)\, \psi^+(x') + \psi^+(x')\, \psi(x) = \delta(x - x') . \tag{33}$$

Denoting the N-electron state under consideration by $|N\rangle$, the states of the $(N-1)$-electron system by $|N-1, s\rangle$ and those of the $(N+1)$-electron system by $|N+1, s\rangle$, we define

$$g_s(x) = \langle N|\, \psi^+(x)\, |N-1, s\rangle ; \tag{34a}$$

$$f_s(x) = \langle N|\, \psi(x)\, |N+1, s\rangle . \tag{34b}$$

As has been shown by Goscinski and Lindner [23], there is an intimate but rather subtle connection between the GOA and the NSO. Combining (33) and (34), we see that the two sets of spin orbitals (34) together form a complete set:

$$\sum_{s=1}^{\infty} f_s(x)\, f_s^*(x') + \sum_{s=1}^{\infty} g_s(x)\, g_s^*(x') = \delta(x - x') . \tag{35}$$

The GOA are, however, *linearly dependent* and thus cannot be orthonormal like the NSO. The connection between them can be described by saying that, if we make a canonical orthonormalization of the set $\{g_s(x)\}$, we get the NSO, [23].

The GOA play an essential rôle for the interpretation of so-called (e, 2e) experiments [24]. It is indeed remarkable that it has been possible to design experiments which give direct access to certain properties of wave functions: the (e, 2e) experiments give information about the absolute value of the momentum counterpart of the GOA.

VII. General Forms of Bloch and Wannier Functions

In Sect. III we pointed out that the solutions of any effective one-electron equation for a system with translational symmetry must be Bloch functions, (14). The commutation relations (10) imply that Bloch functions with different wave vectors are *non-interacting with respect to the effective Hamiltonian.* The effective equation can therefore be split up in N independent partial problems. For each $\boldsymbol{k}$ we get an infinite set of solutions labeled by a *band index* μ, $\phi_\mu(\boldsymbol{k}; \boldsymbol{r})$. The N sets of solutions are orthonormal both with respect to $\boldsymbol{k}$ and μ:

$$\int \phi_\mu^*(\boldsymbol{k}'; \boldsymbol{r})\, \phi_\nu(\boldsymbol{k}; \boldsymbol{r})\, \mathrm{d}\boldsymbol{r} = \delta_{\mu\nu}\, \delta_{\boldsymbol{k}'\boldsymbol{k}} . \tag{36}$$

For each band we can form a set of Wannier functions $W_\mu(\boldsymbol{m}; \boldsymbol{r})$ using (18), which are orthogonal with respect to both $\boldsymbol{m}$ and the band index:

$$\int W_\mu^*(\boldsymbol{m}; \boldsymbol{r})\, W_\nu(\boldsymbol{n}; \boldsymbol{r})\, \mathrm{d}\boldsymbol{r} = \delta_{\mu\nu}\, \delta_{mn} . \tag{37}$$

Here we should notice that, since the phases of the Bloch functions are arbitrary, (18) only defines a family of Wannier functions. Depending on the choice of phase for the Bloch functions, the Wannier functions can be more or less localized.

It is instructive to consider the properties of the counterparts of Bloch and Wannier functions in momentum space [25]. Since the functions in direct space satisfy periodic boundary conditions, their counterparts must, to begin with, satisfy (8). For a Bloch function the basic transformation rule (2) gives for any direct-lattice vector $\boldsymbol{m}$

$$\tilde{\phi}(\boldsymbol{k};\boldsymbol{p}) = \exp\{i(\boldsymbol{k}-\boldsymbol{p})\cdot\boldsymbol{m}\}\,\tilde{\phi}(\boldsymbol{k};\boldsymbol{p})\,. \tag{38}$$

This implies that a Bloch function in momentum space vanishes unless the difference between its *label* $\boldsymbol{k}$ and its *argument* $\boldsymbol{p}$ is equal to a reciprocal-lattice vector (times 2π in our crystallographic normalization of (6)).

The members of a set of Wannier functions $W_\mu(\boldsymbol{m};\boldsymbol{r})$ associated with a certain band differ only in their "position" $\boldsymbol{m}$. Their counterparts in momentum space therefore only differ by a phase factor $\exp\{-i\boldsymbol{p}\cdot\boldsymbol{m}\}$:

$$\tilde{W}_\mu(\boldsymbol{m};\boldsymbol{p}) = \tilde{W}_\mu(\boldsymbol{p})\exp\{-i\boldsymbol{p}\cdot\boldsymbol{m}\}\,. \tag{39}$$

Here $\tilde{W}_\mu(\boldsymbol{p})$ is the counterpart of the Wannier function centered at the origin.

Depending on the particular procedure chosen to solve the effective one-electron equation one gets different types of Bloch and Wannier functions. It definitely would seem worthwhile to exploit the information one can gain from exploring the various counterparts of these functions in momentum space.

VIII. Hartree-Fock Renaissance

For finite systems – atoms and small molecules – the Hartree-Fock approximation provides the natural zeroth-order level, and it is the most common starting point for more eleborate calculations. For extended systems the situation is very different. There are historical reasons for this difference. Larger systems require a considerable mobilization of computational resources, and it was therefore natural to resort to various kinds os simplifications rather than trying a fully fledged Hartree-Fock calculation for a crystal. More important, however, are the methodological objections that can be raised against applying Hartree-Fock to an extended system.

Metallic systems present the worst problems. From the point of view of band theory a metal is a system with at least one partially filled band. Since for an extended system the energy levels form continuous (or quasi-continuous) bands, this means that at the Fermi level, occupied and virtual levels are degenerate. Because of the special features of the restricted Hartree-Fock (RHF) method this leads to the disastrous result that the density of states at the Fermi level vanishes. This is completely unphysical, since a system with that property cannot be called a metal.

For the favorite model system of solid-state theorists, the uniform electron gas with uniform positive background, it is easy to derive this "pathological" aspect of the RHF approximation [26]. For more realistic systems with nuclei instead of the uniform positive background it was for a long time taken for granted that similar results would hold. Monkhorst [27] seems to have been the first to *show* that this is indeed the case. More recently Delhalle and the present author have analyzed this problem in some detail and have shown that the pathological result is due to a divergent lattice sum [28] in the exchange part of the energy. The problem is thus intimately connected with the RHF approximation itself. But it is characteristic that the problem appears only for extended systems. One can sum up this analysis by saying that the unphysical results are due to an *unfortunate conjunction of three factors: Coulomb forces, extended systems and the RHF approximation.*

For nonmetallic systems – insulators and semiconductors – RHF works better. Even there it is far from ideal, however, in particular for the band structure where the calculated band gaps are far too large as compared to the experimental values. For ground-state properties like the density the situation is definitely brighter.

Because of these negative aspects, RHF has for many years not been considered a viable method for solids, in particular not for metals. As will be discussed in the next section, another reason for this has been the existence of a very attractive alternative method. In view of this long purgatory for RHF it is rather surprising now to witness what must be called a renaissance for Hartree-Fock. A sign of this renaissance is the fact that recently a whole special issue of the *International Journal of Quantum Chemistry* was published that is devoted to *"Hartree-Fock based correlation treatments for extended systems"* [29].

Thus the point of this "renaissance" is by no means to stop at the RHF level. In particular for metals, but also for other systems, it is imperative to include correlation. And one of the most important points in starting out with RHF is just that it provides a well-defined zeroth-order level, from which one can proceed to include correlation corrections in a systematic manner.

Before leaving this section on Hartree-Fock a few words should be said about General Hartree-Fock (GHF) [17, 30]. Using symmetry arguments, Fukutome has developed a classification scheme for single determinants, in which the various classes are characterized with respect to the properties of the number density matrix and the spin density matrix vector (cf. Sect. V). In this scheme, RHF constitutes one out of eight classes. Now when more accurate methods are being developed for doing explicit RHF calculations one can expect similar progress for the other Fukutome classes. A thorough exploitation of the GHF concept for extended systems can be expected to produce very interesting results for certain aspects of the correlation problem.

IX. Density Functional Theory

With the Hohenberg-Kohn theorem [31] the cornerstone was laid for an important alternative to Hartree-Fock. According to this theorem there exists a universal functional of the density that represents the total energy in the ground state of a many-electron system. Out of this theorem has grown a very powerful method that has made it possible to link theory and experiment for extended systems in a so far unknown way. Even though Hohenberg and Kohn "only" proved an existence theorem it has been possible to build up approximations that have made it possible to construct effective one-electron equations, which are also relatively easy to solve for a large number of realistic systems. The result has been an explosion of calculations and theoretical work, which has indeed marked the last three decades. There is an enormous literature on this subject, and most of it can be found in the recently published book by Kryachko and Ludeña [32]. Among the references we also include a recent survey paper by two of the most active practitioners in the field [33]. Density functionals are presumably connected with density matrices, as discussed in [16].

Density functional theory provided something that RHF was unable to supply: a reasonably realistic zeroth-order approximation level also for metals. The whole approach is completely different from that of RHF, and the disadvantages of RHF sketched in the previous section are circumvented. This does not mean, however, that all is good and well. Since the exact functional is unknown, an approximate one must be constructed. The most commonly used Local Density Approximation (LDA) derives its name from the assumption that one can use locally the same form of the so-called exchange-correlation potential that one knows from the theory of the homogeneous electron gas. That assumption has worked much better than one had any reason to expect, but it obviously has its limitations. Perhaps the main limitation with density functional theory as a whole is the lack of methods to develop a systematic set of improvements of the original starting point.

A way around that problem is to combine the practical aspects of the density functional method with rigorous many-body theory. Several theoreticians have used density functional calculations as a starting point for constructing the self-energy operator [34, 35], and this appears to be a very promising approach.

X. Conclusion

In this rhapsody of concepts and methods we have chosen to stress certain conceptual aspects. The developments of explicit computational procedures is obviouly essential. However, it does not hurt to stop for a while to check whether perhaps in the rapid development some aspects may have been overlooked. The combination of formal requirements that must be imposed on the quantities to be calculated represents important possibilities for checking the internal consistency of the results, both mathematically, physically and numerically.

It is hardly necessary to point out the importance of momentum space. It is not enough, however, to calculate the momentum distribution or the reciprocal form factor. Bloch and Wannier functions are just as interesting in momentum space as in position space, not least now when it is getting possible to determine certain properties of the wave functions experimentally.

If the natural spin orbitals and/or the generalized overlap amplitudes of a system in a particular state are known to some accuracy, we also know the charge density and the momentum distribution. There are many ways – direct and indirect – of obtaining NSOs and GOAs. From that point of view there are many encouraging signs both on the Hartree-Fock and the density functional horizon.

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