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Direct-space analysis of the Hartree-Fock energy bands and density of states for metallic extended systems

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The restricted Hartree-Fock equations for a crystal with at least one partially filled band are written in terms of Wannier functions. The orbital energy then contains lattice sums, whose convergence properties are of decisive importance for the analytic properties of the energy bands. In particular it is shown how the particular form of the restricted Hartree-Fock exchange operator, when applied to an extended system with Coulombic forces, leads to the well-known singularity at the Fermi energy. Our analysis makes it possible to trace the sources of this singularity for a realistic system, thus leading to a better understanding of the background for systematic improvements.

I. INTRODUCTION

Hartree-Fock calculations for metals have an inherent drawback. The orbital energy of the uppermost partially filled bands has an infinite derivative at the Fermi energy. This implies that the density of states at the Fermi energy vanishes—an unreasonable situation for a metal. For this reason band calculations for metals are usually carried out with other one-electron methods.

This singularity is easily seen if one applies the Hartree-Fock method to the homogeneous electron gas, in which case the doubly filled plane waves form exact solutions.[1] With that result for the electron gas the problem is usually dismissed and it is taken for granted that the result can be taken over to more realistic systems.

The infinity in the slope of the orbital energy at the Fermi surface is indeed a characteristic feature of the Hartree-Fock method when applied to an extended metallic system. As we will show in the present paper the singularity is the result of a combination of the long-range Coulombic force and the particular form of the exchange operator in the Hartree-Fock method. It is of definite interest to trace the sources of this singularity for a realistic system, both in order to understand it better and in order to find systematic procedures for avoiding it as well as for constructing more realistic models.

Band theory traditionally works with concepts defined in reciprocal space. The complementary view in direct space has however proven valuable in several respects in recent years.[2] If the system under consideration has translational symmetry one should ideally consider the possibility of treating a problem from both points of view. This means that one needs the properties of both Bloch and Wannier functions. The former are calculated in practically all band computations, whereas the latter ones have so far been treated more at the formal level,[3] although we now also have the possibility of calculating Wannier functions directly, without getting first the corresponding Bloch functions.[4]

The vanishing of the density of states at the Fermi level for an extended metallic system has been treated in momentum space by Monkhorst.[5] He located the singularity in the gradient of the exchange contribution, and traced its source in the step function which describes the occupation of a partially filled band. He discussed lattices in one, two, and three dimensions.

We have studied the corresponding problem as one aspect of the convergence properties of direct-space exchange lattice sums in one-dimensional lattices.[6] The long-range behavior of the many center integrals combined with the cutoff in the occupation function indeed leads to an infinite derivative of the band at the Fermi energy.

Both the previous investigations were carried out within the framework of a linear combination of atomic orbitals (LCAO) approximation. This is indeed how most of the corresponding calculations are actually carried out. It is, however, desirable to study the singularity also at a formal level independent of any approximation.

The purpose of the present paper is thus to study the analyticity properties of a partially filled band of a realistic extended system, as they follow from *direct-space* properties. Visualization and therefore interpretation is normally easier in direct space and this will make the analysis more transparent. We express the relevant quantities in terms of Wannier functions and use their localization to analyze in detail why and how the singularity appears.

The paper is organized as follows. In Sec. II we introduce the basic equations and discuss the convergence aspects of the various lattice sums which appear when band theory is expressed in terms of Wannier functions. We concentrate on the exchange part of the orbital energy and in Sec. III we calculate its gradient with respect to the

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wave vector and analyze the reasons for its singularity at the Fermi energy. Some special aspects of the derivation are discussed in the concluding section.

II. RESTRICTED HARTREE-FOCK EQUATIONS FOR CRYSTALLINE SOLIDS AND CONVERGENCE OF THEIR DIRECT LATTICE SUMS

In this section we summarize the basic formulas of the restricted Hartree-Fock method for crystalline solids (RHF-CO) and then briefly establish the convergence characteristics of the various lattice sums occurring in these equations.

A. Basic RHF-CO equations

Consider a crystalline solid with ω electrons and Ω atoms per unit cell with nuclear charges Z_g $(g=1,2,\ldots,\Omega)$ centered at position vectors $\mathbf{s}_g$ relative to the unit-cell origin. The unit-cell volume is V_{0a} and the lattice vectors are indicated by $\mathbf{m}$, $\mathbf{m}'$, and $\mathbf{m}''$. The Hartree-Fock (HF) Bloch states $\psi_\mu(\mathbf{k},\mathbf{r})$ are doubly occupied up to the Fermi energy ε_F and orthonormal, i.e.,

$$\int d\mathbf{r}\,\psi_\mu^*(\mathbf{k}',\mathbf{r})\psi_\nu(\mathbf{k},\mathbf{r})=\delta_{\mathbf{k}\mathbf{k}'}\delta_{\mu\nu}\,, \tag{1}$$

where $\mathbf{k}$ is the wave vector defined in the Brillouin zone (BZ) whose volume is $8\pi^3 V_{0b}$. Indices μ and ν are used to label the energy bands, $\varepsilon_\mu(\mathbf{k})$. The following conventions and ranges define the above quantities:

$$\mathbf{a}_i\cdot\mathbf{b}_j=\delta_{ij},\quad i,j=1,2,3 \tag{2a}$$

$$\mathbf{m}=\mathbf{a}_1 m_1+\mathbf{a}_2 m_2+\mathbf{a}_3 m_3,\quad m_i \text{ integer} \tag{2b}$$

$$\mathbf{k}=\mathbf{b}_1 k_1+\mathbf{b}_2 k_2+\mathbf{b}_3 k_3,\quad -\pi\le k_i\le\pi \tag{2c}$$

$$V_{0a}=\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)=V_{0b}^{-1}\,. \tag{2d}$$

The RHF-CO equations result from the minimization of the total energy under the orthonormalization constraint in Eq. (1). In the case of extended systems the charge neutrality condition,[7]

$$2\frac{V_{0a}}{8\pi^3}\int_{\mathrm{BZ}} d\mathbf{k}\sum_\mu \Theta_\mu(\mathbf{k})=\sum_{g=1}^{\Omega} Z_g=\omega\,, \tag{3}$$

must be satisfied; $\Theta_\mu(\mathbf{k})$ is the occupation function defined as

$$\Theta_\mu(\mathbf{k})=\begin{cases}1 & \text{if } \varepsilon_\mu(\mathbf{k})\le\varepsilon_F\\ 0 & \text{if } \varepsilon_\mu(\mathbf{k})>\varepsilon_F\,.\end{cases} \tag{4}$$

In this paper we discuss the properties of the restricted Hartree-Fock approximation for which the equation has the following form,

$$\mathscr{H}_{\mathrm{eff}}(1)\psi_\mu(\mathbf{k},\mathbf{r})=\varepsilon_\mu(\mathbf{k})\psi_\mu(\mathbf{k},\mathbf{r})\,, \tag{5}$$

with $\mathscr{H}_{\mathrm{eff}}(1)$, the Fock operator, written in the restricted scheme where the Bloch states are doubly filled,

$$\mathscr{H}_{\mathrm{eff}}(1)=-\tfrac{1}{2}\nabla_1^2-\sum_{\mathbf{m}}\sum_g Z_g\,|\,\mathbf{r}_1-(\mathbf{s}_g+\mathbf{m})\,|^{-1}+\int d\mathbf{r}_2\frac{(2-\mathscr{P}_{12}^r)\rho(\mathbf{r}_2,\mathbf{r}_2')}{r_{12}}\,. \tag{6}$$

In Eq. (6) $\rho(\mathbf{r},\mathbf{r}')$ is the spatial part of the Fock-Dirac density matrix,

$$\rho(\mathbf{r},\mathbf{r}')=\sum_\mu\sum_{\mathbf{k}}^{\mathrm{BZ}}\Theta_\mu(\mathbf{k})\psi_\mu(\mathbf{k},\mathbf{r})\psi_\mu^*(\mathbf{k},\mathbf{r}')=\frac{NV_{0a}}{8\pi^3}\int d\mathbf{k}\sum_\mu\Theta_\mu(\mathbf{k})\psi_\mu(\mathbf{k},\mathbf{r})\psi_\mu^*(\mathbf{k},\mathbf{r}')\,, \tag{7}$$

and $\mathscr{P}_{12}^r$ is an operator which interchanges $\mathbf{r}_1$ and $\mathbf{r}_2$.

Since we are interested in the shape of the density of states (DOS) which derives from the form of the energy bands, we now make the contents of the $\varepsilon_\mu(\mathbf{k})$'s more explicit,

$$\varepsilon_\mu(\mathbf{k})=\int d\mathbf{r}\,\psi_\mu^*(\mathbf{k},\mathbf{r})\mathscr{H}_{\mathrm{eff}}(\mathbf{r})\psi_\mu(\mathbf{k},\mathbf{r})=T_\mu(\mathbf{k})+C_\mu(\mathbf{k})+X_\mu(\mathbf{k})\,, \tag{8}$$

where $T_\mu(\mathbf{k})$, $C_\mu(\mathbf{k})$, and $X_\mu(\mathbf{k})$ are

$$T_\mu(\mathbf{k})=\int d\mathbf{r}\,\psi_\mu^*(\mathbf{k},\mathbf{r})[-\tfrac{1}{2}\nabla^2(\mathbf{r})]\psi_\mu(\mathbf{k},\mathbf{r})\,, \tag{9}$$

$$C_\mu(\mathbf{k})=\int d\mathbf{r}_1\psi_\mu^*(\mathbf{k},\mathbf{r}_1)\left[2\int d\mathbf{r}_2\frac{\rho(\mathbf{r}_2,\mathbf{r}_2)}{r_{12}}-\sum_{\mathbf{m}}\sum_g|\,\mathbf{r}_1-(\mathbf{s}_g+\mathbf{m})\,|^{-1}\right]\times\psi_\mu(\mathbf{k},\mathbf{r}_1)\,, \tag{10}$$

$$X_\mu(\mathbf{k})=-\int d\mathbf{r}_1\psi_\mu^*(\mathbf{k},\mathbf{r}_1)\int d\mathbf{r}_2\mathscr{P}_{12}^r\frac{\rho(\mathbf{r}_2,\mathbf{r}_2')}{r_{12}}\psi_\mu(\mathbf{k},\mathbf{r}_1)\,. \tag{11}$$

Our aim is to disclose as transparently as possible the mechanisms through which the characteristic properties of the HF method arise. To do so we choose to represent the Bloch states in terms of the Wannier functions which play the role of a particularly simple set of basis functions. They are defined as follows:

$$W_\mu(\mathbf{r}-\mathbf{m})=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}^{\mathrm{BZ}}\psi_\mu(\mathbf{k},\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{m}}=\frac{V_{0a}\sqrt{N}}{8\pi^3}\int d\mathbf{k}\,\psi_\mu(\mathbf{k},\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{m}}\,, \tag{12}$$

and

$$\psi_\mu(\mathbf{k},\mathbf{r})=\frac{1}{\sqrt{N}}\sum_{\mathbf{m}}W_\mu(\mathbf{r}-\mathbf{m})e^{i\mathbf{k}\cdot\mathbf{m}}\,. \tag{13}$$

Expressed in terms of the Wannier functions $T_\mu(\mathbf{k})$, $C_\mu(\mathbf{k})$ and $X_\mu(\mathbf{k})$ become

$$T_\mu(\mathbf{k})=\sum_{\mathbf{m}}e^{i\mathbf{k}\cdot\mathbf{m}}T_{\mu\mu}^{0\mathbf{m}}\,, \tag{14}$$

with $T_{\mu\mu}^{0\mathbf{m}}$ defined as

$$T_{\mu\mu}^{0\mathbf{m}}=\int d\mathbf{r}\,W_\mu^*(\mathbf{r})[-\tfrac{1}{2}\nabla^2(\mathbf{r})]W_\mu(\mathbf{r}-\mathbf{m})\,. \tag{15}$$

The Coulombic contribution $C_\mu(\mathbf{k})$ becomes

$$C_\mu(\mathbf{k})=\sum_{\mathbf{m}} e^{i\mathbf{k}\cdot\mathbf{m}}\left[\frac{2V_{0a}}{8\pi^3}\int_{\mathrm{BZ}} d\mathbf{k}'\sum_{\mu'}\Theta_{\mu'}(\mathbf{k}')\sum_{\mathbf{m}',\mathbf{m}''} e^{i\mathbf{k}'\cdot(\mathbf{m}''-\mathbf{m}')}\langle W_\mu^0 W_{\mu'}^{\mathbf{m}'}\mid W_\mu^{\mathbf{m}} W_{\mu'}^{\mathbf{m}''}\rangle-\sum_{\mathbf{m}'}\sum_g Z_g V_{\mu\mu}^{0\mathbf{m}}(\mathbf{s}_g+\mathbf{m}')\right]$$
$$=\sum_{\mathbf{m}} e^{i\mathbf{k}\cdot\mathbf{m}} C_{\mu\mu}^{0\mathbf{m}}\ , \tag{16}$$

where a more compact notation has been introduced for the Wannier functions,

$$W_\mu^{\mathbf{m}}\equiv W_\mu(\mathbf{r}-\mathbf{m})\ , \tag{17}$$

and matrix elements,

$$V_{\mu\mu}^{0\mathbf{m}}(\mathbf{s}_g+\mathbf{m}')=\int d\mathbf{r}\, W_\mu^*(\mathbf{r})\mid \mathbf{r}-(\mathbf{s}_g+\mathbf{m}')\mid^{-1} W_\mu(\mathbf{r}-\mathbf{m})\ , \tag{18}$$

$$\langle W_\mu^0 W_{\mu'}^{\mathbf{m}'}\mid W_\mu^{\mathbf{m}} W_{\mu'}^{\mathbf{m}''}\rangle=\int d\mathbf{r}_1 d\mathbf{r}_2 W_\mu^*(\mathbf{r}_1) W_{\mu'}^*(\mathbf{r}_2-\mathbf{m}') r_{12}^{-1} W_\mu(\mathbf{r}_1-\mathbf{m}) W_{\mu'}(\mathbf{r}_2-\mathbf{m}'')\ . \tag{19}$$

The exchange contribution $X_\mu(\mathbf{k})$ is similarly obtained,

$$X_\mu(\mathbf{k})=-\sum_{\mathbf{m}} e^{i\mathbf{k}\cdot\mathbf{m}}\left[\frac{V_{0a}}{8\pi^3}\int d\mathbf{k}'\sum_{\mu'}\Theta_{\mu'}(\mathbf{k}')\sum_{\mathbf{m}',\mathbf{m}''} e^{i\mathbf{k}'\cdot(\mathbf{m}''-\mathbf{m}')}\langle W_\mu^0 W_{\mu'}^{\mathbf{m}'}\mid W_{\mu'}^{\mathbf{m}''} W_\mu^{\mathbf{m}}\rangle\right]=-\sum_m e^{i\mathbf{k}\cdot\mathbf{m}} X_{\mu\mu}^{0\mathbf{m}}\ . \tag{20}$$

B. Convergence characteristics of the lattice sums

Theories for crystalline systems involve size-related aspects in the form of lattice sums. Hereafter we identify the convergence properties of the lattice summations occurring in Eqs. (14), (16), and (20). In this discussion we assume an exponential decay with respect to $\mid\mathbf{m}\mid$ for the $W_\mu^{\mathbf{m}}$'s. However, we stress that this assumption will not affect the conclusions of this paper.

Equation (15) does not embody any particular convergence problem since the Wannier functions $W_\mu^{\mathbf{m}}$ are localized in direct space and the related matrix elements $T_{\mu\mu}^{0\mathbf{m}}$ decay exponentially with the distance $\mid\mathbf{m}\mid$ between the centers of W_μ^0 and $W_\mu^{\mathbf{m}}$.

Equation (16) requires more attention. It is more conveniently studied after a slight rewriting,

$$C_\mu(\mathbf{k})=\sum_{\mathbf{m}} e^{i\mathbf{k}\cdot\mathbf{m}}\left[\frac{2V_{0a}}{8\pi^3}\int d\mathbf{k}'\sum_{\mu'}\Theta_{\mu'}(\mathbf{k}')\sum_{\mathbf{m}',\mathbf{m}''} e^{i\mathbf{k}'\cdot\mathbf{m}''}\langle W_\mu^0 W_{\mu'}^{\mathbf{m}''}\mid W_\mu^{\mathbf{m}} W_{\mu'}^{\mathbf{m}'+\mathbf{m}''}\rangle-\sum_{\mathbf{m}'}\sum_g Z_g V_{\mu\mu}^{0\mathbf{m}}(\mathbf{s}_g+\mathbf{m}')\right] \tag{21}$$

$$=\sum_{\mathbf{m}} e^{i\mathbf{k}\cdot\mathbf{m}}\frac{2V_{0a}}{8\pi^3}\int d\mathbf{k}'\sum_{\mu'}\Theta_{\mu'}(\mathbf{k}')\sum_{\mathbf{m}'}\left[\sum_{\mathbf{m}''} e^{i\mathbf{k}'\cdot\mathbf{m}''}\langle W_\mu^0 W_{\mu'}^{\mathbf{m}'}\mid W_\mu^{\mathbf{m}} W_{\mu'}^{\mathbf{m}'+\mathbf{m}''}\rangle-\omega^{-1}\sum_g Z_g V_{\mu\mu}^{0\mathbf{m}}(\mathbf{s}_g+\mathbf{m}')\right]\ . \tag{22}$$

The large parentheses in Eq. (22) enclose terms which, when taken individually, lead to divergent series with respect to the index $\mathbf{m}'$. However, when combined under the charge neutrality constraint, Eq. (3), and additional conditions on first and second electric moments of the unit-cell charge distribution,[8] these terms form the well-known conditionally convergent Madelung series. This problem has been extensively discussed in the literature[8] and since we assume that all conditions for a proper convergence of the $\mathbf{m}'$ series in Eq. (22) are met, we do not consider this problem any further. The remaining two series over $\mathbf{m}$ and $\mathbf{m}''$ do not cause any problem since the terms are characterized by an exponential decay with respect to both $\mid\mathbf{m}\mid$ and $\mid\mathbf{m}''\mid$.

Equation (20) corresponds to the exchange energy contribution to $\varepsilon_\mu(\mathbf{k})$ and will be our central point of interest in this work. To make the analysis clearer we rewrite Eq. (20) as

$$X_\mu(\mathbf{k})=-\sum_{\mathbf{m}} e^{i\mathbf{k}\cdot\mathbf{m}}\frac{V_{0a}}{8\pi^3}\int d\mathbf{k}'\sum_{\mu'}\Theta_{\mu'}(\mathbf{k}')\sum_{\mathbf{m}',\mathbf{m}''} e^{-i\mathbf{k}'\cdot(\mathbf{m}+\mathbf{m}'-\mathbf{m}'')}\langle W_\mu^0 W_{\mu'}^{\mathbf{m}+\mathbf{m}'}\mid W_{\mu'}^{\mathbf{m}''} W_\mu^{\mathbf{m}'}\rangle\ . \tag{23}$$

The indices $\mathbf{m}'$ and $\mathbf{m}''$ correspond to nonproblematic lattice summations since their terms decay exponentially with respect to $\mid\mathbf{m}\mid'$ and $\mid\mathbf{m}''\mid$, respectively. The summation over m is, however, not of the exponentially decaying character. The nature of the decay is best appreciated by inserting the well-known $\mid\mathbf{m}\mid^{-1}$ asymptotic decay of $\langle W_\mu^0 W_{\mu'}^{\mathbf{m}+\mathbf{m}'}\mid W_{\mu'}^{\mathbf{m}''} W_\mu^{\mathbf{m}}\rangle$.[9,10] Indeed $\langle W_\mu^0 W_{\mu'}^{\mathbf{m}+\mathbf{m}'}\mid W_{\mu'}^{\mathbf{m}''} W_\mu^{\mathbf{m}}\rangle$ corresponds to the electrostatic energy of two interacting electron distributions, $W_\mu^*(\mathbf{r}_1) W_{\mu'}(\mathbf{r}_1-\mathbf{m}'')$ and $W_{\mu'}^*(\mathbf{r}_2-(\mathbf{m}+\mathbf{m}')) W_\mu(\mathbf{r}_2-\mathbf{m})$. At large values of $\mid\mathbf{m}\mid$ the overlap between the two distributions is negligible and the corresponding electrostatic energy decays asymptotically like $\mid\mathbf{m}\mid^{-1}$,

$$\langle W_\mu^0 W_{\mu'}^{\mathbf{m}+\mathbf{m}'}\mid W_{\mu'}^{\mathbf{m}''} W_\mu^{\mathbf{m}}\rangle\simeq P(^{0\mathbf{m}'}_{\mu\mu'}\mid^{\mathbf{m}''0}_{\mu'\mu})\mid\mathbf{m}\mid^{-1}\ ,\qquad \mid\mathbf{m}\mid \text{ large} \tag{24}$$

where $P(^{0\mathbf{m}'}_{\mu\mu'}\mid^{\mathbf{m}''0}_{\mu'\mu})$ is the product of quantities related to the charges associated with $W_\mu^*(\mathbf{r}_1) W_{\mu'}(\mathbf{r}_1-\mathbf{m}'')$ and $W_\mu^*(\mathbf{r}_2-\mathbf{m}') W_\mu(\mathbf{r}_2)$.

Let us partition $X_\mu(\mathbf{k})$ into a contribution $X_\mu^a(\mathbf{k})$, which is the partial sum over $\mid\mathbf{m}\mid\le\mid\mathbf{m}^*\mid$, and $X_\mu^b(\mathbf{k})$, the remaining contribution to $X_\mu(\mathbf{k})$ where the asymptotic decay $\mid\mathbf{m}\mid^{-1}$ constitutes a reasonable approximation to $\langle W_\mu^0 W_{\mu'}^{\mathbf{m}+\mathbf{m}'}\mid W_{\mu'}^{\mathbf{m}''} W_\mu^{\mathbf{m}}\rangle$ in the range $\mid\mathbf{m}\mid>\mid\mathbf{m}^*\mid$:

$$X_\mu(\mathbf{k})=X_\mu^a(\mathbf{k})+X_\mu^b(\mathbf{k})=X_\mu^a(\mathbf{k})-\frac{V_{0a}}{8\pi^3}\int_{\mathrm{BZ}}d\mathbf{k}'\sum_{\mu'}\Theta_{\mu'}(\mathbf{k}')\sum_{\mathbf{m}',\mathbf{m}''}e^{-i\mathbf{k}'\cdot(\mathbf{m}'-\mathbf{m}'')}P\left(\begin{smallmatrix}0m'\\ \mu\mu'\end{smallmatrix}\middle|\begin{smallmatrix}m''0\\ \mu'\mu\end{smallmatrix}\right)\sum_{\substack{\mathbf{m}\\(|\mathbf{m}|>|\mathbf{m}^*|)}}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{m}}|\mathbf{m}|^{-1}. \tag{25}$$

At this point it is convenient to separate the energy bands into a set of fully occupied ones, i.e., occupied over the entire BZ, and a set of partially occupied bands. For reasons of simplicity and without loss of generality we consider only one partially occupied band denoted by the subscript μ_F, and μ_0 filled bands. The points where the occupation stops are denoted by $\mathbf{k}_F$ and define the Fermi surface (FS) enclosing the Fermi volume (FV). Again for convenience we will assume that FV contains the origin of the $\mathbf{k}$ space. It should be stressed that more complicated situations can equally well be treated within the approach developed here. $X_\mu(\mathbf{k})$ now reads as

$$X_\mu(\mathbf{k})=X_\mu^a(\mathbf{k})-\frac{V_{0a}}{8\pi^3}\sum_{\mathbf{m},\mathbf{m}',\mathbf{m}''}e^{i\mathbf{k}\cdot\mathbf{m}}|\mathbf{m}|^{-1}\int_{\mathrm{BZ}}d\mathbf{k}'e^{-i\mathbf{k}'\cdot(\mathbf{m}+\mathbf{m}'+\mathbf{m}'')}\left[\sum_{\mu'=1}^{\mu_0}\Theta_{\mu'}(\mathbf{k}')P\left(\begin{smallmatrix}0m'\\ \mu\mu'\end{smallmatrix}\middle|\begin{smallmatrix}m''0\\ \mu'\mu\end{smallmatrix}\right)+\Theta_{\mu_F}(\mathbf{k}')P\left(\begin{smallmatrix}0m'\\ \mu\mu_F\end{smallmatrix}\middle|\begin{smallmatrix}m''0\\ \mu_F\mu\end{smallmatrix}\right)\right]. \tag{26}$$

We can now concentrate our discussion on $X_\mu^b(\mathbf{k})$ since $X_\mu^a(\mathbf{k})$ is a finite sum over $\mathbf{m}$ and as such does not deserve any attention as to its convergence characteristics.

In the case of the occupied bands, i.e., $\mu'=1,2,\ldots,\mu_0$, $\Theta_{\mu'}(\mathbf{k}')=1$ over the entire BZ and the corresponding integrals over $\mathbf{k}'$ reduce to

$$\frac{V_{0a}}{8\pi^3}\int_{\mathrm{BZ}}d\mathbf{k}'\sum_{\mu'=1}^{\mu_0}e^{-i\mathbf{k}'\cdot(\mathbf{m}+\mathbf{m}'-\mathbf{m}'')}=\mu_0\delta_{0,\mathbf{m}+\mathbf{m}'-\mathbf{m}''}\,. \tag{27}$$

Thus the summation $\mathbf{m}$ is limited by the Kronecker condition, $\delta_{0,\mathbf{m}+\mathbf{m}'-\mathbf{m}''}$, and the other two summations, i.e., over $\mathbf{m}'$ and $\mathbf{m}''$, by the exponentially decaying terms. Accordingly no convergence problem arises from the occupied band contributions.

The situation is different in the case of the partially filled band μ_F. Here $\Theta_{\mu_F}(\mathbf{k}')$ is 1 $\forall\mathbf{k}'\in\mathrm{FV}$ and zero elsewhere. The topology of the Fermi surface (FS) can be quite complex and a general treatment would be somewhat counterintuitive to start with. Therefore we consider the Fermi volume in the form of an oblique parallelepiped with its faces parallel to the faces of the BZ as illustrated in Fig. 1. The corresponding volume is totally determined given the following relation:

$$-k_{F_j}\le k_j\le k_{F_j},\quad j=1,2,3 \tag{28}$$

with $0<k_{F_j}<\pi$ for partially filled band systems. The k' integration in Eq. (26) for the partially filled band can now be written as

$$\frac{V_{0a}}{8\pi^3}\int_{\mathrm{FV}}d\mathbf{k}'e^{-i\mathbf{k}'\cdot\mathbf{n}}=\frac{1}{8\pi^3}\prod_{j=1}^{3}\int_{-k_{F_j}}^{k_{F_j}}e^{-ik_j'n_j}=\frac{1}{\pi^3}\prod_{j=1}^{3}\frac{\sin(k_{F_j}n_j)}{n_j}\,, \tag{29}$$

where $\mathbf{n}=\mathbf{m}+\mathbf{m}'-\mathbf{m}''$. Let us denote by $K_\mu^{b_0}(\mathbf{k})$ and $K_\mu^{b_F}(\mathbf{k})$ the contributions to $X_\mu^b(\mathbf{k})$ from the occupied and the partially filled band, respectively. The explicit form of $K_\mu^{b_F}(\mathbf{k})$ is

$$K_\mu^{b_F}(\mathbf{k})=-\frac{V_{0a}}{8\pi^3}\int_{\mathrm{FV}}d\mathbf{k}'\sum_{\mathbf{m},\mathbf{m}',\mathbf{m}''}e^{-i\mathbf{k}'\cdot(\mathbf{m}+\mathbf{m}'-\mathbf{m}'')}e^{i\mathbf{k}\cdot\mathbf{m}}P\left(\begin{smallmatrix}0m'\\ \mu\mu_F\end{smallmatrix}\middle|\begin{smallmatrix}m''0\\ \mu_F\mu\end{smallmatrix}\right)|\mathbf{m}|^{-1}\,, \tag{30}$$

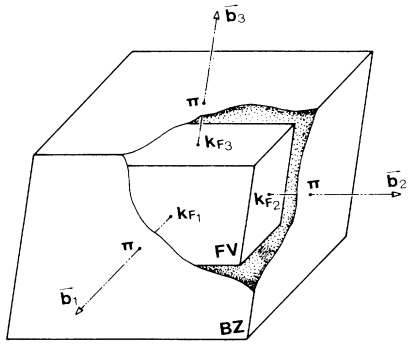

FIG. 1. Graphical illustration of a Fermi volume (FV) included in the Brillouin zone (BZ). The FV is an oblique parallelepiped with its faces parallel to those of the BZ.

and integrating over the Fermi volume, we get

$$K_\mu^{b_F}(\mathbf{k})=-\frac{1}{\pi^3}\sum_{\mathbf{m}',\mathbf{m}''}P\left(\begin{smallmatrix}0m'\\ \mu\mu_F\end{smallmatrix}\middle|\begin{smallmatrix}m''0\\ \mu_F\mu\end{smallmatrix}\right)\sum_{\mathbf{m}}e^{i\mathbf{k}\cdot\mathbf{m}}|\mathbf{m}|^{-1}\times g(\mathbf{m},\mathbf{m}',\mathbf{m}'',\mathbf{k}_F)\,, \tag{31}$$

where

$$g(\mathbf{m},\mathbf{m}',\mathbf{m}'',\mathbf{k}_F)=\frac{\sin[k_{F_1}(m_1+m_1'-m_1'')]}{m_1+m_1'-m_1''}\times\frac{\sin[k_{F_2}(m_2+m_2'-m_2'')]}{m_2+m_2'-m_2''}\times\frac{\sin[k_{F_3}(m_3+m_3'-m_3'')]}{m_3+m_3'-m_3''}\,. \tag{32}$$

Here, contrary to the filled-band case, there is no Kronecker condition, Eq. (27), to assign limits to the $\mathbf{m}$ summation whereas we still have exponential decay with respect to the other two, i.e., $\mathbf{m}'$ and $\mathbf{m}''$. Thus as a consequence of the $\mathbf{k}'$ integration, the exchange contributions originating from the partially filled band will be obtained from slowly convergent series. Taken in absolute value, the terms of the $\mathbf{m}$ series decay like $|\mathbf{m}|^{-2}$ which is enough to guarantee an absolute convergence to this series for each of its components, i.e., $j=1$, 2, and 3. Notice that intermediate cases of partial occupation can easily be accounted for. For instance if the faces of FV in one of the directions $\mathbf{b}_j$, e.g., $j=1$, coincide with those of BZ, i.e., $k_{F_1}=\pi$, it is easily found from Eq. (32) that a Kronecker condition $\delta_{0,m_1+m_1'-m_1''}$ is obtained in place of $\sin[k_{F_1}(m_1+m_1'+m_1'')]/(m_1+m_1'+m_1'')$. Then a decay analogous to the one obtained in the case of the fully occupied BZ prevails for the direction $\mathbf{b}_1$. Similarly if two sets of faces, e.g., corresponding to directions $\mathbf{b}_1$ and $\mathbf{b}_2$, come into coincidence with those of BZ then $\delta_{0,m_1+m_1'-m_1''}\cdot\delta_{0,m_2+m_2'-m_2''}$ replaces

$$\sin[k_{F_1}(m_1+m_1'-m_1'')]\sin[k_{F_2}(m_2+m_2'-m_2'')]/[(m_1+m_1'-m_1'')\cdot(m_2+m_2'-m_2'')] .$$

The absolute convergence of the series secures bounded contributions to $X_\mu(\mathbf{k})$ and thus to $\varepsilon_\mu(\mathbf{k})$. However, in the case of partial occupation, the slowly decaying series impart a peculiar behavior to the *shape* of the energy bands which is dramatically reflected in the density-of-states function at the Fermi energy E_F. This forms the subject of the next section.

Before proceeding to this analysis it is worthwhile to indicate how to deal with more general shapes of the Fermi surfaces. Just like in the integral calculus of functions of several variables the volume of integration can be divided into arbitrarily small parallelepipeds obtained by drawing parallels to the $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ axes. These elemental volumes correspond to discontinuous fragments of the continuous function $\Theta_\mu(\mathbf{k}')$. Inside the Fermi surface $\Theta_\mu(\mathbf{k}')=1$, and the continuity of this function is restored in FV by the side-by-side assembly of these parallelepipeds up to the Fermi surface. The analysis performed above on a single large parallelepiped can be made for each of the small ones, and the sum of a large number of arbitrary small parallelepipeds will correspond to the integration in Eq. (29) where FS can assume complicated shapes. The basic conclusion obtained in the case of a Fermi volume in the form of a single large parallelepiped with its faces parallel to the faces of BZ thus holds true.

III. HARTREE-FOCK DENSITY OF STATES

The inverse of the absolute value of the orbital energy gradient with respect to the wave vector $\mathbf{k}$ is a measure of the availability of one-electron states contributed by the band at the corresponding energy. It enters directly in the expression of $n_\mu(E)$, the density-of-states function for energy band $\varepsilon_\mu(\mathbf{k})$, which is found most convenient for our analysis:

$$n_\mu(E)=\frac{V_{0a}}{4\pi^3}\int\frac{\mathbf{n}_S\cdot d\mathbf{S}}{|\nabla_{\mathbf{k}}\varepsilon_\mu(\mathbf{k})|} . \tag{33}$$

The integral is carried out over isoenergetic surfaces S with position vector $\mathbf{k}_S$ so that $\varepsilon_\mu(\mathbf{k}_S)=E$, $\mathbf{n}_S$ is a unit vector normal to S. The total density of states is obtained by summing (33) over the bands,

$$N(E)=\sum_\mu n_\mu(E) , \tag{34}$$

and is such that

$$\int_{-\infty}^{\varepsilon_F} N(E)dE=\sum_g^{\Omega} Z_g , \tag{35}$$

where ε_F is the Fermi energy.

To understand the peculiarities of the HF density of states the gradient of the energy bands $\nabla_{\mathbf{k}}\varepsilon_\mu(\mathbf{k})$ and its constituents $[\nabla_{\mathbf{k}}T_\mu(\mathbf{k})$, $\nabla_{\mathbf{k}}C_\mu(\mathbf{k})$, and $\nabla_{\mathbf{k}}X_\mu(\mathbf{k})]$ will now be analyzed.

The gradients of the kinetic, $\nabla_{\mathbf{k}}T_\mu(\mathbf{k})$, and Coulombic $\nabla_{\mathbf{k}}C_\mu(\mathbf{k})$, contribution obtained by performing the partial differentiations with respect to $\mathbf{k}$ on Eqs. (14) and (16), respectively, can be expressed as well-behaved trigonometric series, i.e.,

$$\nabla_{\mathbf{k}}T_\mu(\mathbf{k})=\sum_{j=1}^{3}\left[\sum_{\mathbf{m}} im_j e^{i\mathbf{k}\cdot\mathbf{m}}T_{\mu\mu}^{0\mathbf{m}}\right]\mathbf{b}_j , \tag{36}$$

and

$$\nabla_{\mathbf{k}}C_\mu(\mathbf{k})=\sum_{j=1}^{3}\left[\sum_{\mathbf{m}} im_j e^{i\mathbf{k}\cdot\mathbf{m}}C_{\mu\mu}^{0\mathbf{m}}\right]\mathbf{b}_j . \tag{37}$$

The terms in the above series are exponentially decaying due to $T_{\mu\mu}^{0\mathbf{m}}$ and $C_{\mu\mu}^{0\mathbf{m}}$. In the case of fully occupied bands this also holds true for $\nabla_{\mathbf{k}}X_\mu(\mathbf{k})$, but in the case of partially-filled-band systems a different situation establishes. This is best illustrated starting from Eq. (25) whose gradient we write as,

$$\nabla_{\mathbf{k}}X_\mu(\mathbf{k})=\nabla_{\mathbf{k}}X_\mu^a(\mathbf{k})+\nabla_{\mathbf{k}}X_\mu^b(\mathbf{k}) . \tag{38}$$

$\nabla_{\mathbf{k}}X^a(k)$ yields finite trigonometric sums in each of the components of the gradient and therefore no particular problem arises. $\nabla_{\mathbf{k}}K_\mu^{b_0}(\mathbf{k})$, the part of $\nabla_{\mathbf{k}}X_\mu^b(k)$ corresponding to the fully occupied bands is characterized by an exponential decay due to the action of the Kronecker condition in Eq. (27) and behaves qualitatively like $\nabla_{\mathbf{k}}T_\mu(\mathbf{k})$ and $\nabla_{\mathbf{k}}C_\mu(\mathbf{k})$. The last part, $\nabla_{\mathbf{k}}K_\mu^{b_F}(\mathbf{k})$, behaves differently and is analyzed hereafter.

After differentiation, the expression for $\nabla_{\mathbf{k}}K_\mu^{b_F}(k)$ is

$$\nabla_k K_\mu^{b_F}(\mathbf{k})=\pi^{-3}\sum_{\mathbf{m}',\mathbf{m}''} P\left(\begin{smallmatrix}0\mathbf{m}'\\ \mu\mu_F\end{smallmatrix}\middle|\begin{smallmatrix}\mathbf{m}''0\\ \mu_F\mu\end{smallmatrix}\right)\left[\sum_{\mathbf{m}} im_1\,|\,\mathbf{m}\,|^{-1}e^{i\mathbf{k}\cdot\mathbf{m}}g(\mathbf{m},\mathbf{m}',\mathbf{m}'',\mathbf{k}_F)\mathbf{b}_1+\sum_{\mathbf{m}} im_2\,|\,\mathbf{m}\,|^{-1}e^{i\mathbf{k}\cdot\mathbf{m}}g(\mathbf{m},\mathbf{m}',\mathbf{m}'',\mathbf{k}_F)\mathbf{b}_2\right.$$
$$\left.+\sum_{\mathbf{m}} im_3\,|\,\mathbf{m}\,|^{-1}e^{i\mathbf{k}\cdot\mathbf{m}}g(\mathbf{m},\mathbf{m}',\mathbf{m}'',\mathbf{k}_F)\mathbf{b}_3\right],\quad |\,\mathbf{m}\,|>|\,\mathbf{m}^*\,|\ . \tag{39}$$

Since it is the modulus of $\nabla_k\varepsilon_\mu(\mathbf{k})$ which enters the definition of $n_\mu(E)$ in Eq. (33) it is sufficient to concentrate on the behavior of one component of $\nabla_k K_\mu^{b_F}(\mathbf{k})$ at $k=k_F$ to disclose the peculiar behavior of $N(\varepsilon_F)$. To further simplify the identification of the pathology we select $\mathbf{m}'$ and $\mathbf{m}''$ such that $\mathbf{m}'-\mathbf{m}''=0$. Thus consider the component of $\nabla_k K_\mu^{b_F}(\mathbf{k})$ at $\mathbf{k}=\mathbf{k}_F$ along $\mathbf{b}_1$, i.e.,

$$\pi^{-3}P\left(\begin{smallmatrix}0\mathbf{m}'\\ \mu\mu_F\end{smallmatrix}\middle|\begin{smallmatrix}\mathbf{m}'0\\ \mu_F\mu\end{smallmatrix}\right)\sum_{\substack{m_1\\(|m_1|>|m_1^*|)}} im_1 e^{ik_{F_1}m_1}\frac{\sin(k_{F_1}m_1)}{m_1}\left[\sum_{m_2,m_3}|\,\mathbf{m}\,|^{-1}e^{ik_{F_2}m_2}e^{ik_{F_3}m_3}\frac{\sin(k_{F_2}m_2)}{m_2}\frac{\sin(k_{F_3}m_3)}{m_3}\right], \tag{40}$$

which owing to the parity of $|\,\mathbf{m}\,|^{-1}$ with respect to positive and negative values of m_1 can be rewritten as

$$-\frac{2}{\pi}P\left(\begin{smallmatrix}0\mathbf{m}'\\ \mu\mu_F\end{smallmatrix}\middle|\begin{smallmatrix}\mathbf{m}'0\\ \mu_F\mu\end{smallmatrix}\right)\sum_{m_1>m_1^*}^{\infty}\sin^2(k_{F_1}m_1)\left[\sum_{m_2,m_3}|\,\mathbf{m}\,|^{-1}e^{ik_{F_2}m_2}e^{ik_{F_3}m_3}\frac{\sin(k_{F_2}m_2)}{m_2}\frac{\sin(k_{F_3}m_3)}{m_3}\right]. \tag{41}$$

The modulus $|\,\mathbf{m}\,|^{-1}$ decays like m_1^{-1} with respect to m_1 and, since k_{F_1} is such that $0<k_{F_1}<\pi$ for a partially filled band along the direction $\mathbf{b}_1$, $\sin^2(k_{F_1}m_1)$ is always a nonvanishing positive quantity. The m_1 summation is thus of the form $\sum_{n=u}^{\infty}f(n)n^{-1}$ where $f(n)$ and u have positive values, and diverges logarithmically.

This unbounded contribution of $\nabla_k K_\mu^{b_F}(\mathbf{k}_F)$ to $\nabla_k\varepsilon_\mu(\mathbf{k}_F)$ forces the density-of-states function to vanish identically at the Fermi energy ε_F.

The treatment of more general Fermi surfaces can be generalized by applying the above analysis to the infinitesimally small parallelepipeds constituting the Fermi volume as indicated in the previous section.

Monkhorst[5] was the first to prove, in reciprocal space, the unphysical features of the RHF density of states for extended systems with partially filled bands. Here, by adopting a direct space perspective at a level independent of representations by particular basis sets, e.g., LCAO, we have derived a companion proof to the one by Monkhorst.

An advantage of the direct-space approach is to provide a particularly simple and clearcut disclosure of the mechanism through which the pathology arises. The vanishing of the RHF DOS at the Fermi energy results from the combination of two effects: the discontinuity in the population function $\Theta_\mu(\mathbf{k})$ in BZ and the long-range nature of the Coulomb interactions. They combine into slowly decaying series which vary quickly near $\mathbf{k}_F$ and where their derivatives (gradients) diverge logarithmically. These series enter the expression for energy bands and are responsible for the huge broadening of the RHF bands in metals.

Degeneracy and near-degeneracy between occupied and unoccupied one-electron states can lead to various types of instabilities. Such problems are presently subject to numerous studies especially in the field of quasi-one-dimensional systems. In that context a particularly interesting advantage of the direct-space analysis is that it relates naturally to large but finite clusters and chains where such problems can gradually build up.[11]

IV. CONCLUDING REMARKS

For the electron gas the doubly filled plane waves form exact—thus self-consistent—solutions to the RHF equations. The corresponding Wannier functions are not exponentially decaying and the Bloch functions are nonanalytic in $\mathbf{k}$ space. In the present paper we have studied the implications of stronger analytic conditions. In spite of using exponentially decaying Wannier functions (the most favorable case), the conjunction of partial occupation and Coulombic interaction yields a pathological density of states. In cases when the Wannier functions decrease less rapidly (e.g., like $1/|\,m\,|$) the two sums over $\mathbf{m}'$ and $\mathbf{m}''$ in (26) will also converge less rapidly, but the analysis will still yield the pathological density of states. The electron gas treated by means of the Wannier functions corresponding to the plane waves provides an illustration of this case.

It should be noticed that we have not discussed the nature of the self-consistent solutions of the original problem (5). It can be anticipated that with appropriate constraints to prevent the system from undergoing symmetry breaking (instabilities) the true Bloch states (Wannier functions) for this system will not be analytic (exponentially decaying). Thus the pathological behavior of the bands and the density of states will —*a fortiori*—show up in this case too.

One puzzling result of this work is that the singular behavior is not restricted to the partially filled band(s). Thus unphysical features can in principle occur at energies lower than ε_F depending on the coupling between outer and inner states. We are presently investigating this problem both by model computations and formal analyses since it suggests that distortions can be driven not only by the uppermost electrons as traditionally believed but also the inner ones, which can have important implications for electron correlations and vibronic coupling.

By means of the analysis presented in the present paper we have shown how the pathological aspects of the bands at the Fermi level are inextricably connected with the re-

stricted Hartree-Fock approximation. An important aspect of the correlation problem is thus to correct this pathological behavior, and it will be an interesting task to study how and to what extent various procedures which take the correlation into account can alleviate the problem by restoring the analyticity.

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