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Hartree-Fock density of states for extended systems

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The density of states (DOS) of extended systems, calculated at the rigorous Hartree-Fock (HF) level, can have a number of unphysical features. It is shown analytically that in partially filled band systems (crystals, thin films, polymers) the HF DOS vanishes at the Fermi energy, regardless of Fermi-surface shape. HF DOS will also vanish, in the (rare) event that an equienergetic surface S for an energy different from the Fermi energy coincides with the Fermi surface S_F. Additional features such as shoulders, peaks, or near gaps can occur at energies with surfaces S close to S_F. No HF-related zero DOS arises in filled-band extended systems. Published HF DOS are discussed. A detailed summary of expressions for crystal HF matrix elements in momentum representation is given. Their modification for thin films and polymers is indicated.

I. INTRODUCTION

Since 1969 several calculations have appeared in the literature that aim towards obtaining rigorous Hartree-Fock (HF) results for crystalline solids. These calculations differed from previous work to the extent that full, nonlocal exchange was taken into account, and that integrals were calculated accurately or approximated carefully. Because only limited basis sets were used in Bloch orbital expansions no calculation can be considered to have reached the HF limit. Nevertheless, there are indications that several have come pretty close.

Two fundamentally different approaches to rigorous HF have been used. One of these can be characterized as a configuration-space (CS) approach, since the HF matrix elements are expressed as real (or direct) lattice sums over multicenter integrals. A formulation, using Adams-Gilbert local orbitals,[1] was first given by Kunz.[2] Applications were made to the optical properties of solid rare gases,[3] alkali halides,[4] and lithium hydride.[5] The linear-combination-of-atomic-orbitals (LCAO) version of this approach was applied to diamond,[6] LiF, and Ne.[7] More recently, the CS approach was applied to some "open-shell" solids (with partially filled bands) such as calcium,[8] lithium,[9] and TiO.[10]

The other approach can be described as a momentum-space (MS) approach, because reciprocal lattice summations are used to compute HF matrix elements. First introduced by Harris and Monkhorst,[11] the MS (or Fourier) method has also been used for diamond by Mauger and Lannoo,[12] employing Slater-type orbitals for atomic basis functions. Very recently the MS approach has been analyzed by Cox and Fry[13] and Fry *et al.*[14] (hereafter referred to by FBB). Applications to properties of several simple metals have also appeared.[15]

The CS and MS formulations are totally different in their analytic and computational details, although, when carried to their limits, the two approaches are identical. We already indicated that the CS and MS methods are based on direct and reciprocal lattice summations, respectively. This difference has several consequences of great practical import. To name a few:

(i) The CS approach is most appropriate for insulating crystals, whereas the MS approach converges best for conductors.

(ii) The Madelung-type conditional convergence problem that troubles the CS method is eliminated in the MS method through a rigorous cancellation of singularities. As a result, total HF energies with the CS method can oscillate seriously with assumed unit cell cluster size (implicit in the real lattice sum truncation), whereas in the MS method these energies are stable.

(iii) The most significant difference is that the CS method requires the calculation and manipulation of horrendous numbers of many-center integrals, particularly when Gaussian-type orbitals are used. The MS method, however, allows the reductions to reciprocal lattice sums involving Fourier transforms of basis functions only. Consequently, when n orbitals occur per unit cell, the computing effort of the CS method scales like n^4, and the MS method scales more like n^2.

In physical terms one can say that the CS approaches emphasize the calculation of the *total* wave function and charge distribution, whereas the MS approach emphasizes the deviation from a uniform charge distribution and associated wave functions. It can thus be understood that the methods have different ranges of applicability.

The successes of the crystal HF calculations are based on the precise definition of the HF method. This situation allows us to draw well-founded conclusions on the correlation effects in band widths, gaps, and density of states (DOS). Moreover, and possibly most significantly, its variational character admits realistic geometry optimization. Finally, with the inclusion of proper basis functions, the method gives excellent charge distributions, with which many properties can be obtained.

Yet, the HF method has been discarded by many band theorists because of its "unphysical" aspects. They often refer to the vanishing DOS at the Fermi level in the electron gas and the enormous widening of the occupied band. Indeed, even the valence and conduction bands of alkali halides and diamond are substantially wider than those inferred from experiments.[4-8,10,12] In some instances correlation corrections have been made, and invariably the bandwidths become more "realistic."[3,8,10,16] Whether the DOS vanishes at the Fermi level in crystals with partially filled bands had not been clearly established so far. Jennison[9] and FBB[14] discuss this question, but admit that it would be difficult to see in a DOS calculation with the conventional methods.

We wish to present a rigorous proof that, indeed, the DOS at the Fermi level vanishes rigorously whenever partially filled bands occur, regardless of the shape and the connectivity of the Fermi surface. We will also show that this is the case for extended systems periodic in one or two dimensions, such as polymers and thin films. No special features are expected in the DOS for filled and empty bands, except for widening of bands and gaps near the Fermi level. Finally, we raise the warning that unphysical features might occur in the DOS as conventionally calculated. These are related to the sudden drop to zero of the DOS at the top of the Fermi sea.

The above behavior of the DOS is associated with the extensiveness of the systems. Therefore, it is not surprising that it can be most elegantly shown with the MS approach. In Sec. II we summarize the basic formulas of crystal HF in the MS representation. This enables us to most easily discuss the analytic behavior of the band energies (Sec. III). Then follows the proof that the DOS vanishes for partially filled band systems (Secs. IV and V). A discussion of its consequences can be found in Sec. VI.

II. HARTREE-FOCK IN MOMENTUM REPRESENTATION

Consider a crystalline solid with A atoms per unit cell, with nuclear charges $Z_1, Z_2, \ldots, Z_A$ and position vectors $\vec{s}_1, \vec{s}_2, \ldots, \vec{s}_A$ relative to the unit-cell origin. The unit cell volume is v_0. The lattice vectors are indicated by $\vec{R}, \vec{R}'$, etc., and the associated reciprocal lattice vectors are denoted $\vec{K}$, $\vec{K}'$, etc.

We assume that the HF Bloch wave functions $|\nu\vec{k}\rangle$ can be expressed in the LCAO form

$$|\nu\vec{k}\rangle = \sum_{p} |p\vec{k}\rangle C_{p\nu}(\vec{k}), \tag{1}$$

where the basis Bloch orbitals $|p\vec{k}\rangle$ in $\vec{r}$ representation are given by

$$\langle\vec{r}\,|p\vec{k}\rangle = N^{-1/2} \sum_{\vec{R}} \exp(i\vec{k}\cdot\vec{R})\langle\vec{r}-\vec{R}\,|p\rangle \tag{2}$$

as a real lattice summation, or

$$\langle\vec{r}\,|p\vec{k}\rangle = \frac{N^{-1/2}}{v_0} \sum_{\vec{K}} \exp[i(\vec{K}+\vec{k})\cdot\vec{r}\,]\langle\vec{k}+\vec{K}\,|p\rangle \tag{3}$$

as a reciprocal lattice sum. N is the number of unit cells, and $\vec{k}$ is the Bloch vector in the Brillouin zone (BZ). $|p\rangle$ are the atomic orbitals.

The $|\nu\vec{k}\rangle$ are assumed to satisfy the orthonormality condition

$$\langle\mu\vec{k}\,|\nu\vec{k}\rangle = \delta_{\mu\nu}, \tag{4}$$

or, using Eq. (1) and the identification

$$S_{pq}(\vec{k}) \equiv \langle p\vec{k}\,|q\vec{k}\rangle, \tag{5}$$

we can write

$$\sum_{pq} C^*_{\mu p}(\vec{k})S_{pq}(\vec{k})C_{\nu q}(\vec{k}) = \delta_{\mu\nu}. \tag{6}$$

For later developments it is convenient to write $\underline{M}(\vec{k})$ for a matrix with elements $M_{pq}(\vec{k})$, and $\underline{C}_\nu(\vec{k})$ for a vector with components $C_{p\nu}(\vec{k})$. We can now compactly write, instead of Eq. (6),

$$\underline{C}^\dagger_\mu(\vec{k})\underline{S}(\vec{k})\underline{C}_\nu(\vec{k}) = \delta_{\mu\nu}. \tag{7}$$

We will need the density matrix $\underline{D}(\vec{k})$, with elements

$$D_{pq}(\vec{k}) = \sum_{\nu} n_\nu(\vec{k})C^*_{p\nu}(\vec{k})C_{q\nu}(\vec{k}). \tag{8}$$

The occupation number $n_\nu(\vec{k})$ is defined as

$$n_\nu(\vec{k}) = \begin{cases} 1, & \text{if } E_\nu(\vec{k}) \leq E_F, \\ 0, & \text{if } E_\nu(\vec{k}) > E_F, \end{cases} \tag{9}$$

where $E_\nu(\vec{k})$ and E_F are the HF band energies and Fermi energy as calculated below. Adopting a restricted HF scheme (double occupancy of the orbitals), we have the charge neutrality condition

$$\sum_{\vec{k}}^{BZ} \sum_{pq} D_{pq}(\vec{k})S_{pq}(\vec{k}) = N\left(\sum_{m=1}^{A} Z_m\right), \tag{10}$$

where the $\vec{k}$ sum is over the BZ. Using the equivalence, as $N\to\infty$,

$$\sum_{\vec{k}} \longrightarrow \frac{Nv_0}{(2\pi)^3}\int d^3k \tag{11}$$

we can equivalently write, thanks to (7) and (8),

$$2\sum_{\nu}\frac{v_0}{(2\pi)^3}\int_{\mathrm{BZ}} d^3k\, n_\nu(\vec{\mathrm{k}})=\sum_{m=1}^{A} Z_m . \tag{12}$$

The HF equations can now be cast in the form

$$[\underline{F}(\vec{\mathrm{k}})-E_\nu(\vec{\mathrm{k}})\underline{S}(\vec{\mathrm{k}})]\underline{C}_\nu(\vec{\mathrm{k}})=0 . \tag{13}$$

As usual, these equations are obtained by minimizing the HF energy with constraints of Eqs. (7) and (10) [or (12)]. Indeed, the latter condition implicitly defines the Fermi energy E_F. The Fock matrix has the following structure:

$$F_{pq}(\vec{\mathrm{k}})\equiv\langle p\vec{\mathrm{k}}\,|\hat{F}|\,q\vec{\mathrm{k}}\rangle ; \tag{14}$$

$$\hat{F}=\hat{T}+\hat{V}+\hat{C}+\hat{X} . \tag{15}$$

$\hat{T}$, $\hat{V}$, $\hat{C}$, and $\hat{X}$ are the kinetic energy, nuclear attraction, electron-electron repulsion, and exchange operators, respectively.

We are now ready to discuss the expression for the various matrix elements over the operators in $\hat{F}$. As we indicated, we introduced the momentum representation for all integrals. This was followed by an interchange of the integrations and lattice sums, wherever admissible. Subsequently, use was made of the lattice orthogonality relation; as $N\to\infty$,

$$\sum_{\vec{\mathrm{R}}}\exp(i\vec{\mathrm{Q}}\cdot\vec{\mathrm{R}})=\frac{(2\pi)^3}{v_0}\sum_{\vec{\mathrm{K}}}\delta(\vec{\mathrm{Q}}-\vec{\mathrm{K}}) . \tag{16}$$

For $\hat{V}$ and $\hat{C}$, singularities arise for $\vec{\mathrm{K}}=0$, due to the long-range nature of the Coulomb potential. A careful analysis reveals that these singularities rigorously cancel, provided that, besides charge neutrality, the unit cells have no dipole, quadrupole, or second moments.[17] (This condition is generally overlooked in conventional applications of Ewald-type lattice summations, and its nonsatisfaction can cause shifts in the band energies and total energies of the CS approach.[18]) The expressions below are therefore the remainders after this long-range cancellation. These leftovers can be interpreted as resulting from a deviation from a uniform-charge distribution.

Casting the formulas in forms convenient for further discussion we have

$$S_{pq}(\vec{\mathrm{k}})=\frac{1}{v_0}\sum_{\vec{\mathrm{K}}}\langle p|\vec{\mathrm{K}}+\vec{\mathrm{k}}\rangle\langle\vec{\mathrm{K}}+\vec{\mathrm{k}}\,|q\rangle ; \tag{17}$$

$$\langle p\vec{\mathrm{k}}\,|\hat{T}|\,q\vec{\mathrm{k}}\rangle=\frac{1}{v_0}\sum_{\vec{\mathrm{K}}}\langle p|\vec{\mathrm{K}}+\vec{\mathrm{k}}\rangle\frac{(\vec{\mathrm{K}}+\vec{\mathrm{k}})^2}{2}\langle\vec{\mathrm{K}}+\vec{\mathrm{k}}\,|q\rangle ; \tag{18}$$

$$\langle p\vec{\mathrm{k}}\,|\hat{V}|\,q\vec{\mathrm{k}}\rangle=\frac{1}{{v_0}^2}\sum_{\vec{\mathrm{K}},\vec{\mathrm{K}}'}{}'\langle p|\vec{\mathrm{K}}+\vec{\mathrm{k}}\rangle V(\vec{\mathrm{K}}-\vec{\mathrm{K}}')\langle\vec{\mathrm{K}}'+\vec{\mathrm{k}}\,|q\rangle ; \tag{19}$$

with the definitions

$$V(\vec{\mathrm{Q}})=-\frac{4\pi}{Q^2}Z(\vec{\mathrm{Q}}) ; \tag{20}$$

$$Z(\vec{\mathrm{Q}})=\sum_{m=1}^{A} Z_m\exp(i\vec{\mathrm{Q}}\cdot\vec{\mathrm{s}}_m) ; \tag{21}$$

$$\langle p\vec{\mathrm{k}}\,|\hat{C}|\,q\vec{\mathrm{k}}\rangle=\frac{1}{{v_0}^2}\sum_{\vec{\mathrm{K}},\vec{\mathrm{K}}'}{}'\langle p|\vec{\mathrm{K}}+\vec{\mathrm{k}}\rangle C(\vec{\mathrm{K}}-\vec{\mathrm{K}}')\langle\vec{\mathrm{K}}'+\vec{\mathrm{k}}\,|q\rangle \tag{22}$$

with the definition

$$C(\vec{\mathrm{Q}})=\frac{2v_0}{(2\pi)^3}\int d^3k'\sum_{rs}D_{rs}(\vec{\mathrm{k}}')\times\left[\frac{1}{v_0}\sum_{\vec{\mathrm{K}}''}\langle r|\vec{\mathrm{K}}''+\vec{\mathrm{Q}}+\vec{\mathrm{k}}'\rangle\left(\frac{4\pi}{Q^2}\right)\times\langle\vec{\mathrm{K}}''+\vec{\mathrm{k}}'\,|s\rangle\right] . \tag{23}$$

Finally,

$$X_{pq}(\vec{\mathrm{k}})\equiv\langle p\vec{\mathrm{k}}\,|\hat{X}|\,q\vec{\mathrm{k}}\rangle=\frac{1}{{v_0}^2}\sum_{\vec{\mathrm{K}},\vec{\mathrm{K}}'}\langle p|\vec{\mathrm{K}}+\vec{\mathrm{k}}\rangle X(\vec{\mathrm{K}}+\vec{\mathrm{k}},\vec{\mathrm{K}}'+\vec{\mathrm{k}})\langle\vec{\mathrm{K}}'+\vec{\mathrm{k}}\,|q\rangle , \tag{24}$$

where we have used the definition

$$X(\vec{\mathrm{Q}},\vec{\mathrm{Q}}')=-\frac{v_0}{(2\pi)^3}\int d^3k'\sum_{rs}D_{rs}(\vec{\mathrm{k}}')\times\left(\frac{1}{v_0}\sum_{\vec{\mathrm{K}}''}\frac{\langle r|\vec{\mathrm{K}}''+\vec{\mathrm{Q}}-\vec{\mathrm{Q}}'-\vec{\mathrm{k}}'\rangle\langle\vec{\mathrm{K}}''-\vec{\mathrm{k}}'\,|s\rangle}{|\vec{\mathrm{K}}''+\vec{\mathrm{Q}}-\vec{\mathrm{k}}'|^2}\right) . \tag{25}$$

The primes to the $\vec{\mathrm{K}},\vec{\mathrm{K}}'$ sums of Eqs. (19) and (21) indicate the exclusion of $\vec{\mathrm{K}}=\vec{\mathrm{K}}'$. It is understood that $\vec{\mathrm{Q}}-\vec{\mathrm{Q}}'$ is a reciprocal lattice vector. Notice that the nonlocal character of $\hat{X}$ is reflected by the fact that $X(\vec{\mathrm{Q}},\vec{\mathrm{Q}}')$ is not a function of $\vec{\mathrm{Q}}-\vec{\mathrm{Q}}'$ alone.

At this point it is well to remind the reader that Eqs. (17)–(24) are not always most convenient in actual calculations. We have found various alternative expressions more conducive to exploitation of convergence characteristics.[11,17] In particular, when $|p\rangle$ and/or $|q\rangle$ are corelike orbitals, direct-lattice sums give more rapid convergence. In practice, therefore, we have used a mixture of direct and reciprocal lattice sums.[11]

The HF total energy per unit cell E_{HF} can be obtained from the expression

$$E_{\mathrm{HF}}=\frac{v_0}{(2\pi)^3}\int d^3k\left[\sum_{\nu} n_\nu(\vec{\mathrm{k}})E_\nu(\vec{\mathrm{k}}) + \sum_{pq}\left[T_{pq}(\vec{\mathrm{k}})+V_{pq}(\vec{\mathrm{k}})\right]\right]D_{pq}(\vec{\mathrm{k}})+C. \tag{26}$$

$\underline{T}$ and $\underline{V}$ are given by Eqs. (18)–(20), and C is a constant characteristic of the lattice structure and cell size

$$C=\left(\frac{1}{2}\right)\left(\frac{1}{2\pi^2}\right)\left[\frac{(2\pi)^3}{v_0}\sum_{\vec{\mathrm{K}}}{}'\frac{|Z(\vec{\mathrm{K}})|^2}{K^2}-Z^2(0)\int\frac{d^3q}{q^2}\right]. \tag{27}$$

The sum in C excludes $K=0$, and the integral is over all momentum values. This term appears when the singularity from the V contribution to (26) is balanced against that arising from the nuclear-nuclear repulsion.[17] Of course, the same condition applied to this cancellation as discussed below Eq. (16); the singularities have the same origin. The constant C can be interpreted as the electrostatic energy between the nuclei with charges Z_m and positions $\vec{\mathrm{s}}_m$ within the unit cell and a uniform compensating background of negative charge. It is easy to show that C vanishes if, in addition, the (positive) nuclear charge is spread out uniformly. This is the situation in the electron-gas model for a solid.

From Eqs. (17)–(25) it should be clear that the MS formulation is really advantageous for valence and conduction bands: the $\vec{\mathrm{K}}, \vec{\mathrm{K}}'$ sums will converge fast. A few such expressions can be found in FBB.

In conventional band calculations C has been usually ignored. This is unfortunate because it is easy to compute for any lattice structure,[17] and its inclusion allows a realistic total-energy evaluation.

Finally, we wish to point out that *all* $\vec{\mathrm{K}}$ sums are accompanied by a factor $1/v_0$. This will prove important when discussing extended systems with lower dimensionality (see Sec. V).

III. AN EXPRESSION FOR $\vec{\nabla}E_\nu(\vec{\mathrm{k}})$

For our analysis of the HF DOS we need the gradient of the band energies. Starting from (13) and dropping the $\vec{\mathrm{k}}$ dependence from the expression, we get

$$(\vec{\nabla}\underline{F}-E_\nu\vec{\nabla}\underline{S})\underline{C}_\nu+(\underline{F}-E_\nu\underline{S})\vec{\nabla}\underline{C}_\nu-\vec{\nabla}E_\nu\underline{S}\,\underline{C}_\nu=0. \tag{28}$$

When we now premultiply with $\underline{C}_\nu^\dagger$; using the hermiticity of $\underline{F}, \underline{S}$ and the orthonormality condition of Eq. (7), we readily arrive at

$$\vec{\nabla}E_\nu(\vec{\mathrm{k}})=\underline{C}_\nu^\dagger(\vec{\mathrm{k}})\left[\vec{\nabla}\underline{F}(\vec{\mathrm{k}})-E_\nu(\vec{\mathrm{k}})\vec{\nabla}\underline{S}(\vec{\mathrm{k}})\right]\underline{C}_\nu(\vec{\mathrm{k}}). \tag{29}$$

This is a very compact expression indeed. It shows that no explicit variation of $\underline{C}_\nu$ needs to be considered; only variation of matrix elements matters, once the HF equations are satisfied.

IV. HF DENSITY OF STATES

The density of states (DOS), $\rho(E)$ can be obtained using a variety of mathematically equivalent, but computationally distinct formulas. For our purposes the expression

$$\rho(E)=\frac{v_0}{4\pi^3}\sum_\nu\int_S\frac{\vec{\mathrm{n}}_s\cdot d\vec{\mathrm{S}}}{|\vec{\nabla}E_\nu(\vec{\mathrm{k}}_s)|} \tag{30}$$

is convenient. The integral is over equienergetic surfaces S, with position vectors $\vec{\mathrm{k}}_s$, so that

$$E_\nu(\vec{\mathrm{k}}_s)=E \tag{31}$$

for at least one ν value. $\vec{\mathrm{n}}_s$ is the unit vector normal to S in $\vec{\mathrm{k}}_s$. $\rho(E)$ is normalized so that

$$\int_0^{E_F}\rho(E)dE=\sum_{m=1}^{A}Z_m, \tag{32}$$

with E_F the Fermi energy.

It is well known that in the electron-gas model $\rho(E_F)=0$, i.e., the DOS vanishes at the Fermi surface S_F. This is caused by a logarithmic singularity in $\vec{\nabla}E(\vec{\mathrm{k}})$ at the (spherical) S_F (see, for example, Ref. 26):

$$|\vec{\nabla}E(\vec{\mathrm{k}}_s)|\sim\ln|k_s-k_F| \text{ as } S\to S_F. \tag{33}$$

We now wish to show that a similar singularity occurs in any crystal with partially filled bands.

Our starting point is Eq. (29). Going over Eqs. (14) and (17)–(25) we notice that the $\vec{\mathrm{k}}$ dependence appears either in the basis orbital Fourier transforms or in the kernels of the sums for the $\hat{T}$ and $\hat{X}$ matrix elements. Typically Gaussian or Slater-type basis orbitals have been used; neither have Fourier transforms with singular gradients. In fact, quantum-mechanical continuity conditions mandate the $\vec{\mathrm{k}}$ dependence of Bloch functions to be "smooth" analytically. Therefore, basis functions with discontinuous $\vec{\mathrm{k}}$ behavior are to be excluded. Moreover, the factor $(\vec{\mathrm{K}}+\vec{\mathrm{k}})^2$ in Eq. (18) is obviously analytic in $\vec{\mathrm{k}}$. We thus conclude that the only possible source for a singularity in $\vec{\nabla}E_\nu(\vec{\mathrm{k}})$ is the "exchange kernel" of Eq. (25).

Let us look at this quantity more closely. Whenever

$$\vec{\mathrm{K}}''+\vec{\mathrm{Q}}=\vec{\mathrm{k}},$$

the $\vec{\mathrm{k}}'$ integrals are of the form

$$\int d^3k' \frac{f(\vec{k}')}{|\vec{k}-\vec{k}'|^2},$$

with $f(\vec{k}')$ analytic, and $\vec{k}$ and $\vec{k}'$ both within the BZ. But now we have identified a possible singularity, since the integrand diverges whenever $\vec{k}' = \vec{k}$; the analyticity in $\vec{k}$ after $\vec{k}'$ integration need not be maintained. Therefore, we can restrict our attention to $\underline{X}(\vec{k})$, and write

$$E_\nu^x(\vec{k}) = \underline{C}_\nu^\dagger(\vec{k})\underline{X}(\vec{k})\underline{C}_\nu(\vec{k}). \tag{34}$$

In order to more clearly exhibit the underlying analytic structure of E_ν^x, we recognize that, in general, the density matrix contains a sum over both filled and partially filled bands. Therefore, with regard to the $\vec{k}'$ integration domains, we can write

$$E_\nu^x(\vec{k}) = \int_{BZ} d^3k' \sum_{\vec{K}} \frac{Y_\nu^1(\vec{k},\vec{k}',\vec{K})}{|\vec{K}+\vec{k}-\vec{k}'|^2} + \int_{V_F} d^3k' \sum_{\vec{K}} \frac{Y_\nu^2(\vec{k},\vec{k}',\vec{K})}{|\vec{K}+\vec{k}-\vec{k}'|^2}. \tag{35}$$

The details of Y_ν^1 and Y_ν^2 are irrelevant for our discussion except that these quantities (i) are analytic in $\vec{k}$ and $\vec{k}'$, and (ii) cause periodicity in $\vec{k}, \vec{k}'$ space to the integrands. V_F is the volume within S_F. Both $\vec{k}'$ integrations are to be confined to (at most) the first BZ. The first integral (the filled band contribution) is over this BZ, *including* its boundary. The second integral (the partially filled-band contribution) is over a fraction thereof, V_F, *including* the boundary, the Fermi surface S_F.

As we indicated, nonanalyticity in $\vec{k}$ can occur from $\vec{K}=0$ in Eq. (35). We therefore single out those terms and Taylor-expand Y_ν^i,

$$Y_\nu^i(\vec{k},\vec{k}',0) = Y_\nu^i(\vec{k},\vec{k},0) + (\vec{k}'-\vec{k}) \cdot [\vec{\nabla}' Y_\nu^i(\vec{k},\vec{k}',0)]_{\vec{k}'=\vec{k}} + \ldots, \quad (i=1,2). \tag{36}$$

Substituting these expressions in (35) we generate $\vec{k}'$ integrals of the form

$$I_0(V,\vec{k}) = \int_V \frac{d^3k'}{|\vec{k}-\vec{k}'|^2}, \tag{37}$$

$$\vec{I}_1(V,\vec{k}) = \int_V \frac{(\vec{k}'-\vec{k})d^3k'}{|\vec{k}-\vec{k}'|^2}, \tag{38}$$

where V is either BZ or V_F. We have now isolated the quantities that might be responsible for singularities.

V. INTEGRALS I_0 AND $\vec{I}_1$

Let us first consider I_0. We wish to apply Gauss's theorem. If $\vec{k}$ is within V we must exclude a small sphere, with volume v, radius ϵ, and surface σ, around $\vec{k}$ so as to have continuity over $(V-v)$. Writing

$$\frac{1}{|\vec{k}-\vec{k}'|^2} = \vec{\nabla}' \cdot \frac{(\vec{k}'-\vec{k})}{|\vec{k}-\vec{k}'|^2}, \tag{39}$$

we express I_0 in the form

$$I_0(V,\vec{k}) = I_0(V-v,\vec{k}) + I_0(v,\vec{k}), \tag{40}$$

or, using Gauss's theorem for the first term,

$$I_0(V-v,\vec{k}) = \int_\Sigma \frac{(\vec{k}_s-\vec{k})\cdot d\vec{S}}{|\vec{k}_s-\vec{k}|^2} + \int_\sigma \frac{(\vec{k}_\sigma-\vec{k})\cdot d\vec{\sigma}}{|\vec{k}_\sigma-\vec{k}|^2}, \tag{41}$$

Σ is the boundary to V (being either the BZ boundary or S_F). $\vec{k}_\sigma$ are the σ surface position vectors. Evaluating the integrals associated with v and σ:

$$I_0(v,\vec{k}) = \int_v \frac{d^3q}{q^2} = 4\pi\epsilon, \tag{42}$$

$$\int_\sigma \frac{(\vec{k}_\sigma-\vec{k})\cdot d\vec{\sigma}}{|\vec{k}_\sigma-\vec{k}|^2} = -\frac{1}{\epsilon}\int_\sigma d\sigma = -4\pi\epsilon. \tag{43}$$

Combining (40)–(43) we thus conclude

$$I_0(V,\vec{k}) = \int_\Sigma \frac{(\vec{k}_s-\vec{k})\cdot d\vec{S}}{|\vec{k}_s-\vec{k}|^2}. \tag{44}$$

As ϵ can be made arbitrarily small, this result also holds for $\vec{k}$ on Σ.

For $\vec{I}_1$, we can carry through a similar analysis. The result is

$$\vec{I}_1(V,\vec{k}) = \int_\Sigma \ln|\vec{k}_s-\vec{k}|\,d\vec{S}; \tag{45}$$

as before, this holds for all $\vec{k}$.

We are now ready to discuss the gradient of I_0 and I_1. Whenever $\vec{k}$ is not on Σ, i.e., $\vec{k}$ is either within or outside V, the integrands are finite and continuous in $\vec{k}$. We therefore can bring the gradient operation under the integration. For example,

$$\vec{\nabla} I_0(V,\vec{k}) = \int_\Sigma \vec{\nabla} \frac{(\vec{k}_s-\vec{k})\cdot d\vec{S}}{|\vec{k}_s-\vec{k}|^2};$$

or, using

$$\vec{q} = \vec{k}_s - \vec{k}, \tag{46}$$

we can write

$$\vec{\nabla} I_0(V,\vec{k}) = 2\int_\Sigma \frac{\vec{q}\cdot(\vec{q}\cdot d\vec{S})}{q^4} - \int_\Sigma \frac{d\vec{S}}{q^2}. \tag{47}$$

Clearly q never vanishes in this case, and we find

$$|\vec{\nabla} I_0(V,\vec{k})| < \infty, \quad \forall\, \vec{k} \notin \Sigma. \tag{48}$$

Similarly, it is easily found

$$|\vec{\nabla} I_1(V,\vec{k})| < \infty, \quad \forall\, \vec{k} \notin \Sigma. \tag{49}$$

We thus reach our first conclusion: (i) The band-energy gradient $\vec{\nabla}E_\nu(\vec{k})$ will have finite values for all $\vec{k}$ *not* on either the BZ boundary or on the Fermi surface S_F.

Now we will consider the case that $\vec{k}$ approaches a vector $\vec{k}_s$ on Σ. Because of a lack of continuity of the integrands in the surface integrals (44), (45) we cannot bring the gradient operation under the integral signs. Therefore we must proceed as follows:

We can assume, without loss of generality, that $\vec{k}$ approaches $\vec{k}_s$ so that

$$\vec{\delta}=\vec{k}-\vec{k}_s \tag{50}$$

is an infinitesimal vector parallel to $\vec{n}_s$, the unit vector normal to Σ in $\vec{k}_s$,

$$\vec{\delta}/\delta=\mp\vec{n}_s . \tag{51}$$

δ is the distance of $\vec{k}$ to Σ. The minus (plus) sign applies when $\vec{k}$ approaches $\vec{k}_s$ from within (outside). We next cast a small circle denoted by c, around $\vec{k}_s$ on Σ. Its radius ϵ is taken small enough so that Σ can be considered locally flat. We then can express I_0, I_1 as

$$I_m(V,\vec{k})=I_m^c(V,\vec{k})+[I_m(V,\vec{k})-I_m^c(V,\vec{k})] \quad (m=0,1)\,, \tag{52}$$

where

$$I_0^c(V,\vec{k})=\int_c \frac{(\vec{k}_\sigma-\vec{k})\cdot d\vec{\sigma}}{|\vec{k}_\sigma-\vec{k}|^2}\,, \tag{53}$$

$$\vec{I}_1^c(V,\vec{k})=\int_c \ln|\vec{k}_\sigma-\vec{k}|\,d\vec{\sigma}. \tag{54}$$

Obviously, the term in square brackets in Eq. (52) excludes $\vec{k}_s$ from the surface integral. Therefore, its gradient with respect to $\vec{k}$, as $\vec{k}\to\vec{k}_s$, will remain finite. However, this is not the case for the other term when $m=0$, as we will now show. We introduce the variable $\vec{q}$,

$$\vec{q}=\vec{k}_\sigma-\vec{k}. \tag{55}$$

If we describe the integral over c with the radial variable r, then we have

$$\vec{q}\cdot d\vec{\sigma}=\delta\, r dr d\phi\,, \tag{56}$$

$$q^2=r^2+\delta^2 . \tag{57}$$

We thus are led to

$$I_0^c(V,\vec{k})=\delta\int_0^{2\pi}d\phi\int_0^{\epsilon}\frac{r dr}{r^2+\delta^2},$$

or

$$I_0^c(V,\vec{k})=\pi[\delta\ln(\delta^2+\epsilon^2)-2\delta\ln\delta]\,. \tag{58}$$

Since $\delta=|\vec{k}-\vec{k}_s|$, we readily derive

$$\vec{\nabla}I_0^c(V,\vec{k})=\pm 2\pi\vec{n}_s\left[\ln\delta+\frac{\epsilon^2}{\delta^2+\epsilon^2}-\frac{1}{2}\ln(\delta^2+\epsilon^2)\right]. \tag{59}$$

Finally, we are prepared to take the limit $\vec{k}\to\vec{k}_s$. Doing so, Eqs. (58) and (59) immediately give (with $\epsilon>0$),

$$\lim_{\vec{k}\to\vec{k}_s} I_0^c(V,\vec{k})=0\,, \tag{60}$$

$$\lim_{\vec{k}\to\vec{k}_s}\vec{\nabla}I_0^c(V,\vec{k})=\pm\lim_{\vec{k}\to\vec{k}_s}2\pi\vec{n}_s\ln|\vec{k}-\vec{k}_s|\,. \tag{61}$$

Now, considering $\vec{I}_1^c$, we quickly get

$$I_1^c(V,\vec{k})\leqslant\left|\int\ln|\vec{k}_\sigma-\vec{k}|\,d\sigma\right|\,,$$

or, with Eqs. (35)–(57) ,

$$I_1^c(V,\vec{k})\leqslant\pi\left|(\epsilon^2+\delta^2)\ln(\epsilon^2+\delta^2)-\epsilon^2-2\delta^2\ln\delta\right|. \tag{62}$$

Furthermore,

$$|\vec{\nabla}I_1^c|=\left|\frac{dI_1^c}{d\delta}\right|,$$

or, using (62),

$$|\vec{\nabla}I_1^c(V,\vec{k})|\leqslant 2\pi\,|2\delta\ln\delta-\delta\ln(\epsilon^2+\delta^2)|\,. \tag{63}$$

Again, we take the limit $\vec{k}\to\vec{k}_s$, and we obtain

$$\lim_{\vec{k}\to\vec{k}_s} I_1^c(V,\vec{k})\leqslant\pi\epsilon^2|2\ln\epsilon-1|<\infty\,, \tag{64}$$

$$\lim_{\vec{k}\to\vec{k}_s}|\vec{\nabla}I_1^c(V,\vec{k})|=0. \tag{65}$$

Looking at Eqs. (61), (65), and remembering the role I_m^c plays in I_m [Eq. (52)] we conclude

$$\lim_{\vec{k}\to\vec{k}_s} I_0(V,\vec{k})<\infty\,; \tag{66}$$

$$\lim_{\vec{k}\to\vec{k}_s}\vec{I}_1(V,\vec{k})<\infty\,; \tag{67}$$

$$\lim_{\vec{k}\to\vec{k}_s}|\vec{\nabla}I_0(V,\vec{k})|=\lim_{\delta\to 0}|2\pi\ln\delta|\,; \tag{68}$$

$$\lim_{\vec{k}\to\vec{k}_s}|\vec{\nabla}I_1(V,\vec{k})|<\infty. \tag{69}$$

A. Singularity in $\vec{\nabla}E_\nu(\vec{k})$

Returning to the Taylor expansion (36), which gave rise to I_0 and I_1, it is clear that higher-order forms will not generate any divergences in $\vec{\nabla}E_\nu^x(\vec{k})$; the $\vec{k}'$ integrands will not be singular. Therefore, we have precisely pinpointed the singularity in $\vec{\nabla}E_\nu(\vec{k})$, and we will argue that it only occurs in partially filled band systems, with $\vec{k}$ any point $\vec{k}_F$ on the Fermi surface.

In order to see this, we first remind ourselves that the singularity in $\vec{\nabla}I_0$ emerges as a three-dimensional version of an endpoint singularity to an integral representation with singular kernel. We saw that no singular behavior was found for $\vec{k}$ away from the "endpoint", i.e., not on Σ.

Now, using the symmetry

$$D_{rs}(\vec{k}') = D_{rs}(\vec{k}' + \vec{K}'') \tag{70}$$

in Eq. (25), it is not hard to see that the first term in Eq. (35) is of the form

$$\sum_{\vec{K}''} \int_{\mathrm{BZ}} d^3k' \frac{g(\vec{K}'' + \vec{k}')}{|\vec{K}'' + \vec{k}' - \vec{k}|^2} = \int^{\infty} d^3\kappa \frac{g(\vec{\kappa})}{|\vec{\kappa} - \vec{k}|^2}.$$

There is no endpoint singularity, as this integral covers the entire reciprocal lattice. But that means that the *full* BZ integration in $E_\nu(\vec{k})$ does *not* give a singular contribution to $\vec{\nabla} E_\nu(\vec{k})$, whatever $\vec{k}$ is.

Indeed, we are now in a position to make a precise statement concerning $\vec{\nabla} E_\nu(\vec{k})$:

$$\lim_{\vec{k} \to \vec{k}_F} |\vec{\nabla} E_\nu(\vec{k})| = \lim_{\vec{k} \to \vec{k}_F} 2\pi |Y_\nu^2(\vec{k}_F, \vec{k}_F, 0) \ln |\vec{k} - \vec{k}_F||. \tag{71}$$

We have now arrived at the second and main result of this section: (ii) In partially filled band systems the gradients of *all* band energies $E_\nu(\vec{k})$ diverge logarithmically whenever $\vec{k}$ is on the Fermi surface S_F.

In filled-band systems these gradients never diverge.

B. DOS at Fermi level

It is now immediately obvious that, indeed, the DOS vanishes at the Fermi energy E_F: the surface S becomes S_F for E_F. The integral in Eq. (30) is over a zero integrand, thus giving no contribution to $\rho(E_F)$. Obviously this result holds whether S_F is either multiply connected or entirely within the BZ; the cause of the singularity is the termination of the $\vec{k}'$ integration short of the full BZ.

Our result of Sec. IV A has an interesting implication. If, for a particular $E \neq E_F$, the equienergetic surface S coincides with S_F, then the associated $\rho(E)$ will vanish as well. We are unaware of a general principle that precludes this to happen. Although it seems highly unprobable, we have to be concerned about this possibility. We will return to this point in Sec. VI.

VI. DOS FOR SYSTEMS EXTENDED IN FEWER DIMENSIONS

Polymers and thin films are extended systems (usually) periodic in one or two dimensions, respectively. HF calculations at the same rigorous level as bulk crystal work are being performed,[19] or are underway.[20] In view of our finding that the HF DOS in crystals vanishes at the Fermi level the question can be raised whether this also applies to these lower-dimensional, extended systems. After all, one can imagine these systems to physically appear if one allows one or two unit cell dimensions of a bulk crystal to increase beyond limits, keeping all relative position vectors $\vec{s}_m$ finite in length. Periodicity in these (infinite) dimensions then becomes immaterial, and we have effectively a collection of noninteracting extended systems of lower dimensionality.

Theoretically we can answer this question in two different ways. Using the MS approach, we can formulate the HF problem for polymers[19] and thin films[21] as isolated systems, exploiting the one- and two-dimensional periodicities. The Fermi surfaces are two points in polymers, and a planar curve in thin films. Instead of the three-dimensional reciprocal lattice sums, double reciprocal-space integrals and one summation appear for polymers (two summations and one integral for thin films). An analysis similar to the one given here can then be carried through.

However, a physically more appealing, albeit mathematically somewhat less rigorous approach is to start from the crystal HF formalism of Secs. II–IV, and take certain limits so as to describe the reduction of dimensionality of the system. These limits should be associated with the stretching of unit cell sizes in one (two) directions to obtain the formulas for thin films (polymers) in the HF description.

First, let us consider the transition to thin-film systems. Thereto, without loss of generality, we assume a monoclinic, three-dimensional unit cell with a parallellogram basis with area a_0 and height h. It then follows that

$$v_0 = a_0 h. \tag{72}$$

The lattice and reciprocal lattice vectors are expressible as

$$\vec{R} = \vec{R}_\parallel + \vec{R}_\perp ; \tag{73}$$

$$\vec{K} = \vec{K}_\parallel + \vec{K}_\perp , \tag{74}$$

or as a sum of vectors parallel and perpendicular to the plane of the unit cell base. The perpendicular vectors are given by

$$\vec{R}_\perp = mh\hat{z}, \quad m = 0, \pm 1, \pm 2, \ldots, \tag{75}$$

$$\vec{K}_\perp = n(2\pi/h)\hat{z}, \quad n = 0, \pm 1, \pm 2, \ldots, \tag{76}$$

if it is assumed that the unit cell base is parallel to the x-y plane.

The obvious next step is to take the limit $h \to \infty$, keeping the $\vec{s}_m$ finite. In our formulas (17)–(27) this limit has two consequences. Noticing that a factor $(1/v_0)$ is associated with each $\vec{K}$ sum, the first effect is that the $\vec{K}$ sum becomes very dense, i.e., in the limit $h\to\infty$ this becomes an integral. Indeed, we can write

$$\frac{1}{v_0}\sum_{\vec{K}} = \lim_{h\to\infty}\frac{1}{a_0 h}\sum_{\vec{K}_\parallel}\sum_{K_\perp} = \lim_{h\to\infty}\left(\frac{1}{a_0 h}\right)\sum_{\vec{K}_\parallel}\left(\frac{h}{2\pi}\right)\int_{-\infty}^{+\infty} dK_\perp ,$$

or

$$\lim_{h\to\infty}\frac{1}{v_0}\sum_{\vec{K}} = \frac{1}{2\pi a_0}\sum_{\vec{K}_\parallel}\int_{-\infty}^{+\infty} dK_\perp . \tag{77}$$

Formulas generated in this manner are identical to those obtained by a direct application of the MS approach to thin films.

The other consequence is that $\vec{k}'$ integrations reduce to integrals in the two-dimensional BZ, with $\vec{k}'\to\vec{k}'_\parallel$. More specifically

$$\lim_{h\to\infty}\frac{v_0}{(2\pi)^3}\int d^3k' = \lim_{h\to\infty}\frac{a_0 h}{(2\pi)^3}\int d^2k'_\parallel \int dk'_\perp .$$

The $k'_\perp$ integral will scale like $2\pi/h$. The occupation numbers $n_\nu(\vec{k})$ (contained in the integrands of the $\vec{k}$ integrations) will become independent of $\vec{k}_\perp$ in the limit $h\to\infty$ since its length vanishes. Therefore, we can say that in this limit, the $k'_\perp$ integral "fills up" the entire BZ width $(2\pi/h)$ in the perpendicular direction. We thus conclude that

$$\lim_{h\to\infty}\frac{v_0}{(2\pi)^3}\int d^3k' = \frac{a_0}{(2\pi)^2}\int d^2k'_\parallel . \tag{78}$$

Again, the $k'_\parallel$ integrals generated are those obtained in a "direct" slab approach; as $h\to\infty$, all $\vec{k}'$ vectors approach a vector $\vec{k}'_\parallel$ in the two-dimensional BZ.

But now we can immediately state that the results of the previous section regarding the density of states apply to thin films as well. Volume integrals become surface integrals, and surface integrals become line integrals. In particular, the divergence in $|\vec{\nabla}E_\nu(\vec{k})|$ for partially filled bands [Eq. (68)] will hold as well in the limit $h\to\infty$. Since the divergence found is related to the *distance* of $\vec{k}$ to the Fermi surface, this result should be no surprise.

By subsequently taking the limit that a two-dimensional unit cell dimension approaches infinity, we generate the formulas for polymers. *Mutatis mutandis*, we arrive at the same conclusion, namely, that in a partially filled band polymer the HF DOS vanishes at the Fermi level. No vanishing $\rho(E)$ occurs in filled band polymers. In this case the Fermi surface consists of two points.

Lest the reader is worried whether the outlined treatment concerning the DOS is sufficiently rigorous, he can convince himself by carrying out the analysis directly on isolated thin films (polymers). For the exchange terms the integrals over $K_\perp$ resulting from (77) have to be treated carefully around $K_\perp = 0$. Exclusion of a small region $[-\epsilon, \epsilon]$, with $\epsilon > 0$, will "extract" a small, pancake-shaped volume in reciprocal space around the origin, which captures the singularity. To that volume the same analysis as before can be applied, giving the same results.

To sum up then, we have arrived at the following conclusions:

(i) The HF band-energy gradients $\vec{\nabla}E_\nu(\vec{k})$ associated with systems, extended periodically in one or more dimensions and possessing partially filled bands, diverges logarithmically as $\vec{k}$ approaches a Fermi surface vector $\vec{k}_F$. No such divergence occurs for filled band systems.

(ii) The HF density of states $\rho(E)$ for such extended systems with partially filled bands vanishes at the Fermi level E_F. At any energy $E \neq E_F$ for which the equienergetic surface S [Eq. (31)] coincides with the Fermi surface S_F, $\rho(E)$ will also vanish.

In general, $\rho(E)$ will not vanish for filled band systems with E not in band gaps.

VII. DISCUSSION

The results of this paper concerning the HF DOS have a number of interesting and, in some cases, somewhat disturbing consequences for calculations already published or contemplated.

With regard to crystal HF work, in a number of cases HF DOS are presented that ought to show a vanishing $\rho(E_F)$. For example, the DOS for calcium,[22] lithium,[9] and TiO,[10] show a conspicuous absence of a zero HF DOS at E_F. In view of the computational methods used (polynomial interpolation, with or without Gaussian broadening, or a Gauss-Chebyshev method, formulated by Monkhorst and Pack[23]) it is impossible to see this behavior. Moreover, the above calculations have been performed in the CS approach. The truncation of the direct lattice sums (forced upon for practical reasons) causes the $\rho(E_F)$ to not even vanish rigorously. Yet, the intrinsic extensiveness of the systems considered *requires*, as we saw, the HF DOS to vanish. We therefore conclude that these DOS are qualitatively in error, at least near E_F, and cannot possibly be representative of the HF DOS near the Fermi level.

We also found that for an energy whose equienergetic surface S is identical to the Fermi surface S_F, the HF DOS should vanish. The occurrence of this seems highly improbable and might even be impossible. Certainly, viewing the band structure as to arise from a perturbed, nearly-free-electron (NFE) model one seems to have to rule out such coincidence. However, two remarks are in order in this connection. First, the NFE model is inappropriate for crystals with strong Bragg scattering, such as highly localized orbitals of d and f character. Fermi surfaces in transition element compounds are notoriously complicated, and the same can be expected of above surfaces S. Second, even though the coalescence of surfaces S and S_F seems improbable, they could be close. If that happens chances are that unphysical shoulders, peaks, or near gaps could appear in $\rho(E)$. The reason for this can be found in FBB [Ref. 14]. In Fig. 3 of their second paper the authors present the HF DOS for the NFE gas, both the exact curve and numerical values. Apart from the inability of the numerical method to accurately reproduce $\rho(E)$ near E_F, another unsettling observation can be made: $\rho(E)$ peaks at an energy about ($\frac{2}{3}$) the band width. This is to be contrasted with the steadily increasing Hartree $\rho(E)$, which on many counts is closer to the "correct" DOS. The kinetic energy decreases faster with decreasing electron density than the exchange energy. Therefore, we expect this prepeaking to be even more pronounced at lower electron densities. But now we have to conclude that unphysical features to the $\rho(E)$ curve can already occur for energies E with equienergetic surfaces S quite different from S_F. We saw a pre-peaking in the NFE gas model. We thus can expect shoulders, peaks, or even near gaps to occur, depending on how closely S approaches S_F and what the electron density is.

All correlation corrections have concentrated on the Fermi level DOS or the band width or band gaps. Our results indicate that with complicated band structures such as for transition element compounds, considerable attention has to be paid to the correlation problem at *all* energies. The fact that numerical inaccuracies tend to wash out these HF-caused singularities (or near singularities) is irrelevant, although expedient in practice. The point is that the theory allows for them, and therefore they should be either shown faithfully or corrected for. Unfortunately, so far no scheme has been formulated that is practical and theoretically sound.

It is even more likely that thin films and polymer HF DOS exhibit such unphysical features. In the case of thin films it is quite possible that two Fermi curves come close in shape and area. Since in polymers the Fermi surface consists of two points, there is an infinite number of energies (lying within bands) for which "S coincides with S_F." In practice, however, this is not very relevant; stable, partially filled band polymers do not occur, although a filamentary structure of equally spaced polymers of hydrogen atoms has been proposed and studied for metallic hydrogen.[19]

Summing up then, one has to be quite cautious when interpreting detailed features to $\rho(E)$ at the HF level, particularly for complicated crystals on thin films with partially filled bands.[9,10] By analogy with the widening of the HF NFE gas band width, we expect considerable exaggeration of bands and gaps near E_F. No vanishing $\rho(E)$ within bands of filled-band systems is expected.

Notwithstanding these fundamental failures to the crystal HF results we do not advocate a local approximation to exchange and correlation corrections. The work of Overhauser and others[24] has suggested that a considerable nonlocality has still to be associated with these corrections, although not as strong as "bare" exchange. The use of HF as a first approximation has many virtues: it is well defined, yields variational total energies, and gives good charge densities. Beyond that, the correlation problem for extended systems is still with us, and progress has been slow.[25]

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