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Nonexistence of localized Hartree-Fock eigenfunctions in periodic systems

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The question of the possible existence of localized canonical Hartree-Fock (HF) eigenfunctions in periodic systems is more subtle than has generally been recognized. The first analysis of this issue, by Kaplan and Argyres, is shown to be incomplete and thus inconclusive. We present a new argument which shows conclusively that localized canonical HF solutions cannot exist in periodic systems of physical interest. Other arguments, with varying emphasis on symmetry, intuition, and formal rigor, are also discussed. Consequences of this result for the understanding of Mott insulators will be discussed elsewhere.

I. INTRODUCTION

The question of the possible existence of localized-orbital solutions of the Hartree-Fock (HF) equations, for periodic many-electron systems, is a very fundamental one for solid-state theory. We are referring to solutions of the HF equations in which the self-consistent canonical orbitals would have localization and symmetry properties of the familiar Wannier type. Conventional wisdom would have it that HF solutions of this type are obviously impossible, because the one-electron eigenfunctions of a periodic system must satisfy Bloch's theorem. That argument is unsatisfactory, however, because the standard proof of Bloch's theorem is restricted to local potentials, whereas the exchange term of the HF potential is nonlocal. Although it is quite obvious that the standard Bloch type of solution must *always* exist, it is *not* obvious whether a Wannier type of solution might exist under some suitable circumstances. This issue was raised long ago by Seitz, in his well-known 1940 textbook.[1] The first serious attempt to settle this question was by Kaplan and Argyres.[2]

This question is a matter of considerable practical importance, in addition to its intrinsic academic interest, because of its relevance for the understanding of Mott insulators. Mott has argued for many years[3] that the valence electrons in some materials (NiO is the prime example) are localized in a phenomenological sense, and there is a variety of experimental evidence which supports this contention.[4] However, the task of developing a satisfactory theoretical explanation for this phenomenology has proven to be very difficult. If the unrestricted version of ordinary HF theory could ever give rise to localized one-electron eigenfunctions, it is quite plausible that this might lead to a simple and convenient theoretical description for Mott insulators. This provides a motivation for examining the present question very carefully. The outcome is also relevant for the understanding of quantum crystals such as solid helium, as well as for Wigner's low-density electron solid. In solid ^{3}He, for example, it is customary to regard the ^{3}He atoms as structureless spin-$\frac{1}{2}$ fermions interacting via a known two-body potential, and there is no doubt here that *some* form of physical localization is present.

For all of these reasons, we have devoted some effort towards settling this existence question. It has turned out that the problem is considerably more subtle than one might suppose. The few serious investigations that have been published have all concluded that localized HF solutions of the present type are either impossible or at least highly unlikely, in agreement with the conventional wisdom. We shall see, however, that each of the arguments to date leaves something to be desired, either by way of rigor, generality, or intuitive understanding. We shall present a new argument which exhibits all of these attributes to a reasonable degree. This finally settles the issue. Nevertheless, we shall survey the whole problem, including the previous approaches, since this leads to some insights which will prove useful elsewhere. In future papers we shall discuss several different localized-orbital descriptions,[5] all related to HF theory, which serve to explain various aspects of actual Mott insulator materials.

The main goals of this article have just been described. A secondary purpose is to respond to a recent Comment by Kaplan and Argyres.[6] In two previous publications[7,8] we mentioned that their analysis[2] had serious weaknesses, but we had provided only a very sketchy argument[8] to support this contention. In their Comment, these authors rightly point out that the disproof which we offered in Ref. 8 is incorrect. Nevertheless, we shall now demonstrate (Sec. III) that their analysis is at best an incomplete one. It does not constitute a valid nonexistence proof for the system they considered.

As mentioned already, the history of this problem dates back at least 35 years, to Seitz's textbook.[1] Seitz was persuaded that localized HF solutions *should* exist, by the following type of reasoning. For a lattice of widely spaced hydrogen atoms, it is easily seen that the *Hartree* approximation can produce localized-orbital eigenfunctions.[9] The Hartree theory differs from HF theory by the neglect of "other particle" exchange terms; the self-exchanges are retained, in effect, to compensate for the direct self-interaction terms. This cancellation of the self-interactions means that each particle experiences a much deeper potential near its own home site, where its amplitude is large and the other-particle amplitudes are small, than it does near other sites, where most of the electron density comes from other orbitals. The Hartree approximation thus allows for a direct realization of the Mott mechanism[3] for localization. At low densities the Hartree orbitals must be quite similar to the atomic orbitals, and the overlaps between near neighbors must be quite small. Consequently, if the other-particle exchange terms are now regarded as perturbative corrections to the Hartree theory, it would appear that their effect should be quite weak. This led Seitz to conclude that these exchange terms could only cause minor changes in the orbitals. Of course, the HF orbitals must be spatially orthogonal for parallel spins, in contrast to the Hartree orbitals. The "minor changes" would therefore have to include the formation of nodes near the neighboring sites (for parallel spins); thus the resulting HF orbitals should be very similar to the usual Wannier functions.

These remarks were summarized 15 years later by Reitz,[10] with one significant difference. Reitz did not contend that the outcome was obvious; he noted that the effect of the exchange terms was problematical. Another 15 years went by before Kaplan and Argyres[2] presented the first serious attempt to settle this question. It seems remarkable to us that such a fundamental and long-standing problem did not stimulate more study, especially in view of the accelerating interest in Mott insulators during the past decade.

Unaware of these publications, we were independently led to Seitz' s argument during the course of a study of the theory of solid ^{3}He.[7] Most calculations for solid ^{3}He have been carried out with simple Gaussian orbitals to represent the motions of the individual atoms, $\phi_i \sim \exp[-\frac{1}{2}\alpha^2(\vec{r}_i - \vec{R}_i)^2]$, with the localization parameter α being determined by any one of several variational or self-consistency criteria. The resulting ϕ's turn out to have very small nearest-neighbor overlaps, $\lesssim 1\%$, so this is a system for which the Seitz argument has strong intuitive appeal. Upon reflection, we became uneasy about Seitz's conclusion (which we orginally endorsed), but we were unable to find a satisfactory analytical argument to settle the issue. For this reason, we attempted to obtain an actual localized HF solution by applying standard numerical methods to a one-dimensional model system in which the nonlocal exchange could be handled in an essentially exact manner.[7] This model had one electron per site, and was designed to simulate an infinite row of hydrogen atoms. A parallel series of calculations was done using interactions appropriate for the solid-helium problem. These two very different types of interactions led to identical conclusions. (A test of the validity of our numerical procedures is described in Sec. V.)

This attempt proved unsuccessful, but the effort turned out to be quite instructive. First, it clearly demonstrated the fallacy in the Seitz argument. In solving the differential equation, a change in the potential in one region is propagated, via the second derivative, to significantly change the function everywhere. That is, the change in the function is not as localized as the change in the potential. This has the consequence that, in the following HF iterations, the once-small perturbation may grow quite strong, and it may thereby produce a drastic change in the overall character of the solution. To provide the initial input for our HF iterations, we first obtained self-consistent localized Hartree orbitals and then orthogonalized them in the symmetric (Löwdin) manner to generate a "reasonably good" set of Wannier-like orbitals. A fully aligned (pure ferromagnetic) spin configuration was assumed. The succeeding HF iterations produced very different outputs, and it appeared that the equations were attempting to generate a Bloch-like solution. A second benefit of this experience was that the behavior of the output, for various changes in the input, suggested a physical plausibility argument for the nonexistence result.[7] We have now elaborated this experience into two distinct arguments (Secs. IV and V), focussing respectively on the roles of orthogonality and exchange. The first of these arguments is rigorous.

Following our numerical investigation, a mathematical nonexistence proof was developed by Moyer.[11] His argument (outlined in Sec. VI) was historically the first one with satisfactory rigor. Unfortunately, however, it is too formal to provide any physical insight.

It seems to us that a question as basic as the present one deserves an answer that is simple and intuitive, reasonably rigorous, and of general validity. Furthermore, it should not rely too heavily on symmetry considerations. One knows that deviations from perfect periodicity (surfaces, lattice defects, strains, certain kinds of impurities, etc.) do not drastically alter the physics of Mott insulators, so the ideal argument ought to reflect a corresponding insensitivity. Let us emphasize this point with a different example. Supposing it is demonstrated that localized HF eigenfunctions do not exist for the H_2 molecule (in its triplet state), we would like it to follow directly that this result also applies to a lithium-hydride molecule. The proof in Sec. IV is certainly the most satisfactory one in terms of these criteria. Nevertheless, the argument in Sec. V provides additional insight which is relevant for the understanding of Mott insulators.

II. FORMAL STATEMENT OF THE PROBLEM

By Hartree-Fock theory we mean the most general (unrestricted) equations that result from applying the stationary variational requirement to a single-determinant expectation value of the many-electron Hamiltonian. In practice, it is a very great convenience to require the spin orbitals of the determinant to be mutually orthogonal; otherwise the usual two-body energy expression

$$\frac{1}{2}\sum_{lm}\langle\psi_l\psi_m|v|\psi_l\psi_m\rangle - E_{\text{exchange}} \tag{2.1}$$

is replaced by one of the form

$$\sum_{jklm} C_{jklm}\langle\psi_j\psi_k|v|\psi_l\psi_m\rangle - E_{\text{exchange}}, \tag{2.2}$$

where the expression for the C's is quite complicated.[12] We therefore regard orthogonality (among same-spin orbitals) as a necessary requirement of HF theory, since we shall only consider the form (2.1).

The standard variational derivation[13] leads to a set of equations of the form

$$\mathcal{F}\varphi_m=\sum_l \lambda_{lm}\varphi_l, \tag{2.3}$$

where the λ's are Lagrange multipliers inserted to preserve orthonormality of the φ's. Here $\mathcal{F}$ is the usual one-body Fock operator, including kinetic, ionic, direct, and exchange terms. The λ elements are given by

$$\lambda_{lm}=\langle\varphi_l|\mathcal{F}|\varphi_m\rangle, \tag{2.4}$$

thanks to the assumed orthogonality of the φ's.

Given a particular solution of (2.3) and (2.4), one knows that there exists a canonical transformation of the φ's which diagonalizes the λ matrix, converting (2.3) to the familiar eigenvalue form

$$\mathcal{F}\psi_n=\epsilon_n\psi_n\,. \tag{2.5}$$

The resulting basis $\{\psi\}$ is defined uniquely by the solution $\{\phi\}$, to within arbitrary phase factors, except in cases of degeneracy. (Recall that for a closed shell of $l\geq 1$ orbitals, the quantization axis z can be chosen arbitrarily.) These ψ's are commonly referred to as canonical eigenfunctions. Henceforth, we shall reserve the symbol ψ for canonical eigenfunctions.

These HF equations frequently have more than one physically distinct type of solution. (The subject of magnetism provides many examples of this phenomenon.) For periodic solids, a solution where the canonical ψ's have Bloch symmetry is always possible. Let us call this the Bloch canonical solution, $\{\psi_k^{\text{BC}}\}$. When this solution is expressed in terms of the corresponding Wannier orbitals, the HF equations assume the nondiagonal (noncanonical) form (2.3)–(2.4).[14] One can easily see that the λ matrix *must* be nondiagonal in this Wannier representation, because the elements λ_{lm} correspond to Fourier coefficients of the Bloch eigenvalue spectrum $\epsilon(\vec{k})$.[14] (If the λ matrix were diagonal, this would indicate that the Bloch bandwidth is strictly zero.)

In casting the Bloch canonical solution into the off-diagonal Wannier form (2.3)–(2.4), we have assumed either a filled band or a half-filled saturated ferromagnetic configuration, so that the Wannier description of the Bloch canonical solution still involves only a single determinant. We shall therefore only consider configuration where, for *each* of the spin directions, we have exactly filled or empty bands. These are the most interesting cases from the standpoint of Mott insulator theory, since a partly filled spin subband would lead to metallic screening of the HF exchange potential, and this screening would tend to suppress the Mott localization phenomenon that we are interested in.[3]

We are now ready to state the fundamental question of this article. Can the HF equations for a periodic many-electron system *ever* have a solution where the *canonical* orbitals have the symmetry and localization properties of Wannier orbitals?

Let us examine the consequences of supposing that such a "Wannier canonical" solution $\{\psi_n^{\text{WC}}\}$ does exist. Since the λ matrix for *this* Wannier basis is now strictly diagonal (by definition), we see that these Wannier orbitals are necessarily different from those corresponding to the Bloch canonical solution. In terms of the higher Bloch bands defined by the Fock operator $\mathcal{F}^{\text{BC}}$ for the Bloch canonical solution $\{\psi_k^{\text{BC}}\}$, we see that this new solution involves interband mixing. The set of higher Bloch bands forms a complete basis, and likewise for the corresponding Wannier transforms $\varphi_{\nu n}^{\text{BC}}$, where ν is an index labelling the higher bands from $\mathcal{F}^{\text{BC}}$. The canonical Wannier orbitals ψ_n^{WC} can therefore be expanded in this Bloch-canonical Wannier basis,

$$\begin{aligned}\psi_n^{\text{WC}}&=\mathfrak{N}\Big(\varphi_n^{\text{BC}}+\sum_{\nu n'}C_{n\nu n'}\,\varphi_{\nu n'}^{\text{BC}}\Big),\\ \mathfrak{N}&=\Big(1+\sum_{\nu n'}|C_{n\nu n'}|^2\Big)^{-1/2}.\end{aligned} \tag{2.6}$$

The resulting Slater determinant $\|\psi_n^{\text{WC}}\|$ is clearly a different function of $(\vec{r}_1\ldots\vec{r}_N)$ than the determinant $\|\varphi_n^{\text{BC}}\|$, so we are now dealing with a *physically different* solution. The total HF energy E^{WC} could therefore be either higher or lower than that of the familiar Bloch canonical solution E^{BC}. This raises the possibility of a sudden change of phase, if the lattice parameter were to be varied continuously. Another consequence is that the canonical transformation of $\{\psi_n^{\mathrm{WC}}\}$ to a Bloch representation gives rise to a new type of Bloch canonical solution, one which has a *strictly vanishing* bandwidth.

These rather peculiar features make it plausible that such Wannier canonical solutions cannot exist, at least not for nonmagnetic filled-band systems. On the other band, the physical localization observed in Mott insulators suggests the opposite conclusion. We see that it is unsafe, as well as logically improper, to try to settle the mathematical existence question by appealing to experimental evidence.

III. ANALYSIS OF KAPLAN AND ARGYRES

Kaplan and Argyres[2] (hereafter KA) assume the existence of a Wannier canonical solution and then try to demonstrate that this leads to a logical contradiction. They consider a lattice of hydrogen atoms with very large lattice spacing, and they claim to have considered all the effects which are formally of first order in the atomic overlap integrals

$$S_{nn'} = \langle \phi_n | \phi_{n'} \rangle (1 - \delta_{nn'}) , \tag{3.1}$$

where the ϕ's are $1s$ eigenfunctions of atomic hydrogen, centered on the sites n, n'. We shall see, however, that they have overlooked some terms which are formally of the same order as those considered, so their analysis is actually incomplete.

These authors work with a "one-band model," which is to say that the various orbitals they consider are all to be approximated by linear combinations of the atomic $1s$ eigenfunctions ϕ_n. There is precisely one electron per site. We assume for simplicity that all of the spins are parallel (saturated ferromagnetic configuration), and we shall not consider the generalization of HF theory to finite temperatures (thermal HF approximation) which is what they actually worked with.

KA begin by constructing "one-band" Wannier functions,

$$\overline{\psi}_n = \phi_n - \frac{1}{2} \sum_{n'} S_{nn'} \phi_{n'} , \tag{3.2}$$

which are obviously orthonormal to order S. The overlap matrix (3.1) is symmetric, thus the most general set of reasonably well localized one-band orbital functions, orthonormal to order S, can be expressed as

$$\psi_n = \overline{\psi}_n - \frac{1}{2} \sum_{n'} P_{nn'} \phi_{n'} , \tag{3.3}$$

where P is an *antisymmetric* matrix assumed to be of order S. If this P matrix should turn out to have any elements which are of order unity (or larger), this would contradict the assumption that the ψ_n's are reasonably localized orbitals which evolve continuously from the ϕ_n's as the atoms are brought closer together, starting from infinite spacing.

According to (2.5), the canonical Wannier eigenfunctions must satisfy

$$\langle \psi_{n'} | \mathcal{F}(\{\psi\}) | \psi_n \rangle = \epsilon_n \delta_{nn'} , \tag{3.4}$$

where the self-consistent dependence of $\mathcal{F}$ upon the detailed form of the ψ's has been emphasized. Inserting the trial form (3.3) into (3.4) for $n' \neq n$, and retaining only the terms of first order in S, one readily obtains

$$\tfrac{1}{2} P_{n'n} = \frac{\langle \overline{\psi}_n | \mathcal{F}(\{\overline{\psi}\}) | \overline{\psi}_{n'} \rangle}{\epsilon_n^0 - \epsilon_{n'}^0} . \tag{3.5}$$

The ϵ_n^0's are eigenvalues appropriate for the $S = 0$ case, which means that they are all equal to the ground-state eigenvalue of an isolated hydrogen atom. The denominator of (3.5) obviously vanishes, whereas it can readily be demonstrated by explicit evaluation[6] that the numerator is nonvanishing to order S. KA conclude from this that $P_{nn'}$ *must* be far larger than $\mathcal{O}(S)$, and therefore the self-consistent ψ_n's cannot be well localized.

The flaw in this argument is that the "one-band" approximation in (3.2) and (3.3) is too crude to be trusted for such a delicate question. We saw in Sec. II that *if* a Wannier canonical solution exists, it *must* contain interband contributions of the type shown in (2.6). The off-diagonal λ terms in the Wannier representation (2.3) and (2.4) for the ordinary Bloch solution are obviously of order S, which means that the total interband correction $(\psi_n^{\mathrm{WC}} - \varphi_n^{\mathrm{BC}})$ should also be of order S. Consequently, it is *a priori* implausible that orbitals of the "one-band" form (3.3) could possibly satisfy (3.4) to order S. The nonvanishing of the numerator in (3.5), to order S, is to be expected in view of the crudeness of the assumed form for the orbitals. These remarks are not a conclusive proof (or disproof, rather), because the basis $\{\varphi_n^{\mathrm{BC}}, \varphi_{\nu n}^{\mathrm{BC}}\}$ also differs from the atomic basis by terms of order S. Nevertheless, it is clear that the possibility of significant interband contributions must be carefully investigated before any firm conclusions can be reached. As it stands, therefore, the analysis of KA is incomplete.

Let us now suppose that the hydrogen lattice is sufficiently regular so that every site posesses inversion symmetry. In this case the task of estimating the off-diagonal elements of P now amounts to asking the question "just how unsymmetrical should the symmetrical eigenfunctions ψ_n be?" Of course, KA did not require their canonical ψ_n's to be symmetrical, but it is obvious that the symmetry requirement is reasonable to impose here. We conclude that, rather than tampering with the symmetry of the $\psi_n^{\rm WC}$'s, attention should have been focussed on interband terms which are consistent with the symmetry.

IV. ORTHOGONALITY PROBLEM

We now present a rigorous argument which emerged from the numerical study[7] mentioned in the Introduction, but which has not been published previously. This argument centers around the problem of obtaining orthogonal orbitals from the HF equations. We begin with a periodic hydrogen-atom lattice in which all sites are equivalent and every site is a center of inversion symmetry (a Bravais lattice), and we consider the saturated ferromagnetic spin configuration.

When one sets out to obtain a Bloch canonical solution, the orthogonality requirement can be satisfied in an essentially trivial manner. One can simply construct the Bloch sums

$$\psi_{\vec{k}}^{\rm BS} = N^{-1/2}\left(1+\sum_n e^{i\vec{k}\cdot\vec{R}_n} S_{0n}\right)^{-1/2} \times \sum_n e^{i\vec{k}\cdot\vec{R}_n}\,\phi(\vec{r}-\vec{R}_n)\,, \qquad (4.1)$$

where the function ϕ need have only a very gross resemblance to the Wannier functions of the desired self-consistent solution. It is not necessary, for example, for the overlaps

$$S_{nm'} = \langle\phi(\vec{r}-\vec{R}_n)\,|\,\phi(\vec{r}-\vec{R}_{n'})\rangle(1-\delta_{nm'}) \qquad (4.2)$$

to vanish. In this case we see that the orthogonality feature is *completely independent* of self-consistency. This means that the numerical effort can be focussed entirely on the achievement of self-consistency.

The situation is quite different for the Wannier canonical case. Given a Hermitian Fock operator $\mathfrak{F}$, with the full lattice symmetry but not necessarily self-consistent, let us consider the set of canonical eigenfunctions which are centered on site n. Each of these orbitals will exhibit either the desired inversion symmetry, or else its opposite-parity counterpart. The site-n orbitals with a given parity will all be mutually orthogonal, thanks to the Hermiticity of $\mathfrak{F}$. There must be a similar set of inversion-symmetrical and mutually orthogonal orbitals centered on a neighboring site n', and these two sets of orbitals must be identical except for a lattice translation. The difficulty comes in attempting to establish orthogonality *between* these two corresponding sets of orbitals. The standard orthogonality proof fails here because the equivalent orbitals on sites n and n' have identical eigenvalues. The inversion symmetries of the orbitals are of no help either because these symmetries refer to different sites. We found by numerical experience[7] that self-consistent Wannier canonical solutions with inversion symmetry can be obtained, but only by sacrificing the orthogonality.

This last statement deserves some explanation, since self-consistency and orthogonality are usually regarded as synonymous in HF theory. In the numerical work referred to, the direct and exchange potential terms in $\mathfrak{F}$ were always given by the familiar expressions obtained from variation of (2.1). The subtlety here is that (2.1) itself is only valid, in the sense of being derivable from a single Slater determinant, when the input orbitals are all orthogonal; otherwise, (2.2) must be used. Even though our self-consistent solutions retained the form of HF theory, they violated the spirit (relation to a single determinant) when the orthogonality was lost.

One might suppose that the presence of the Lagrange multiplier terms in (2.3)–(2.5) should somehow suffice to ensure orthogonality, but this is not so. The purpose of introducing the Lagrange multipliers is to *preserve* orthonormality *during the variation*, assuming that the orbitals are orthogonal before the variation. If the latter assumption is not satisfied, the Lagrange multiplier technique need not produce an orthogonal output.

The lesson to be learned from these observations is the following. In the Bloch canonical case, where orthogonality can be satisfied from the outset by virtue of the translational symmetry, the attainment of self-consistency exhausts all of the available freedom. By this we mean that the 1s-band solution is unique. (We do not know of a rigorous proof for this statment, but this is certainly consistent with general experience. At any rate, there is no *continuous* degree of freedom left.) Similarly, one may expect that the self-consistency requirement will also specify a unique Wannier canonical solution. In this case, however, orthogonality amounts to a nontrivial additional requirement—the orthogonality is now a matter of dynamics instead of symmetry. After attaining self-consistency, the orbitals do not have any freedom left by which to satisfy orthogonality, so a solution possessing *both* of these properties is generally not possible.

One will observe that this argument does not rule out the possibility that there may be some special (perhaps pathological) choices of the basic one-body ("ionic") and two-body interactions for which an orthogonal and self-consistent solution can exist. However, such choices would necessarily constitute "a set of measure zero" in the parameter space of the basic interactions. These special cases would thus have a vanishing probability of being relevant for systems of physical interest. We therefore conclude that Wannier canonical solutions are *not* possible for systems of physical interest.

This argument hinges on the discreteness of the various possible Wannier canonical solutions, a feature which can be rigorously verified as follows. Let each of the desired Wannier orbitals be represented by a linear combination of a *finite* number of localized orthogonal basis functions. It is then easily seen that the Hartree-Fock formalism leads to exactly as many independent equations as there are independent free parameters to be determined. (This follows immediately from the variational formulation of HF theory.) It follows that there is no *continuous* degree of freedom left, after obtaining self-consistency, so the remarks of the preceding paragraphs are rigorously justified. Since these results are valid for any finite number of basis functions (per Wannier orbital), they must continue to hold as the basis is extended towards completeness.

Effect of symmetry breaking

The distinguishing characteristic of the Wannier canonical case is the precise eigenvalue degeneracy; this is what permits self-consistency to be achieved without orthogonality. This suggest that an *arbitrarily weak* perturbation which breaks the equivalence of all sites would now lead to an orthogonal solution. We believe that this suggestion is correct, but that the resulting orthogonal self-consistent solution would be Bloch-like instead of Wannier-like. Our numerical experience revealed that the self-consistent Wannier canonical solution was extremely unstable. There is no doubt that a few iterations with this perturbation present would serve to strongly modify an initial Wannier input, and it is at least very plausible that the modifications would go in the direction of a Bloch-like canonical solution. Consequently, it appears that a weak perturbation would not enable one to evade the conclusion of the preceding paragraphs.

This conclusion follows more rigorously from the notion of physical continuity. If Bloch canonical solutions are the only orthogonal ones possible in the fully symmetrical case, a continuous deformation of the system can only lead to a continous deformation of these Bloch solutions, apart perhaps from exceptional cases constituting a set of measure zero.

It may be of interest to mention a connection with the analysis of Kaplan and Argyres. In the fully symmetrical case, we have seen that the diagonal assumption (3.4) is invalid. That is, the eigenvalue degeneracy makes it impossible to establish that the left-hand side of (3.4) is zero for $n' \neq n$. (The nonorthogonality of our self-consistent orbitals turned out to be of order S, for a reason explained in Sec. V.) In place of (3.5), therefore, we would find

$$\tfrac{1}{2}P_{n'n} = \frac{\langle \bar{\psi}_n | \mathfrak{F}(\{\bar{\psi}\} | \bar{\psi}_{n'}\rangle - \langle \psi_n | \mathfrak{F}(\{\psi\} | \psi_{n'}\rangle}{\epsilon_n^0 - \epsilon_{n'}^0} . \qquad (4.3)$$

where the $\bar{\psi}$'s and ϵ^0's now represent our self-consistent but nonorthogonal solution, and the ψ's represent some hypothetical (also not necessarily orthogonal) solution related to the $\bar{\psi}$'s by (3.3) to lowest order in S. We see that $P \equiv 0$ is not inconsistent with (4.3), since the right-hand side reduces to the indeterminate form (zero/zero) for this case. Consider, however, the effect of a weak symmetry-breaking perturbation. This perturbation enters into the "ionic potential" term in $\langle \psi_n | \mathfrak{F}(\{\psi\}) | \psi_{n'}\rangle$, and thus the numerator of (4.3) no longer vanishes. This indicates that an arbitrarily weak symmetry breaking would lead to a P matrix with large elements. This result supports the conclusion of the preceding paragraphs, since P matrix elements of order unity are required in order to express Bloch-like orbitals in a form like (3.3), that is, as localized orbitals plus corrections.

V. EFFECT OF THE EXCHANGE POTENTIAL

We have not yet dealt explicitly with the role of the exchange potential, although Seitz's argument indicates that this should be examined. The Hartree potential includes "self-exchange" terms (these are needed to cancel the "self-direct" terms), so all differences between the Hartree and HF theories must be due to the "other-particle" exchange terms. We now offer some qualitative observations about the effects of these exchange terms.[7]

A set of orthogonal Wannier canonical orbitals would have to differ from the nonorthogonal Hartree orbitals by the presence of nodes. We therefore expect that the Wannier orbitals should have more kinetic energy than the Hartree orbitals. (This orthogonality kinetic energy is a localized-orbital analog of the Fermi kinetic energy of a free-electron gas.) Since the exchange potential terms all have negative expectation values, it is not unreasonable to suppose that these terms could provide sufficient attraction to support the additional kinetic energy. We shall see, however, that the detailed form of the nonlocality makes this very unlikely.

Suppose that a Wannier canonical solution exists, and consider the wave equation for the orbital ψ_0 which is centered on "site zero." Just at the position of its first node, close to a nearest-neighbor site (call this "site one"), all local terms in the wave equation for ψ_0 will vanish. The exchange-potential term will be dominated by ψ_1, since this should be the only orbital which is large near site one, so the curvature of ψ_0 *at its node* is given by the approximate equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_0}{dx^2} \approx \psi_1(x) \int \psi_1^*(x')\psi_0(x')v(x-x')\,dx' , \qquad (5.1)$$

where we have simplified to the case of one dimension. We shall try to determine the sign of the curvature ψ_0''.

The product $\psi_1^*\psi_0$ in the integrand has a sign reversal at the node, so we must determine which region dominates within the integral. If we insist on orthogonality and symmetry, we have

$$\int \psi_1^* \psi_0\, dx = \int_{\mathrm{I}} + \int_{\mathrm{II}} + \int_{\mathrm{III}} = \int_{\mathrm{II}} + 2\int_{\mathrm{III}} = 0, \qquad (5.2)$$

where the integration regions I, II, and III are indicated schematically in Fig. 1. (We are assuming the localization to be sufficiently strong that only the regions near and between the two sites contribute significantly to the integral. This is akin to the "lowest-order-in-*S*" assumption of Kaplan and Argyres.) This argument indicates that region II, with positive overlap, is far more important than region III, where $\psi_1^*\psi_0$ is negative. This strongly suggests that region II will also be the dominant one for the integral in (5.1), from which it follows that ψ_0 should have a *downwards* curvature at its node. It is intuitively fairly obvious, however, that any reasonable orthogonal Wannier-like orbital should have positive curvature at the node, or perhaps a near-vanishing curvature, but at any rate not a strong negative curvature. This argument strongly suggests that the spatial structure of the exchange potential is incompatable with the existence of a proper Wannier canonical solution, at least for "reasonable" two-body interactions.

This plausibility argument is strengthened by comparison with the Bloch canonical solution. When this solution is expressed in its Wannier representation, one obtains an equation similar to (5.1) but with the additional term $\lambda_{10}\,\varphi_1(x)$ on the right-hand side. One knows from tight-binding theory that λ_{10}, the nearest-neighbor hopping integral defined by (2.4), is a negative definite quantity. We see, therefore, that this term provides an upwards curvature tendency for φ_0, offsetting the excessive downwards influence of the exchange potential, so that the usual Wannier orbitals can now be self-consistent in the sense of (2.3)–(2.4).

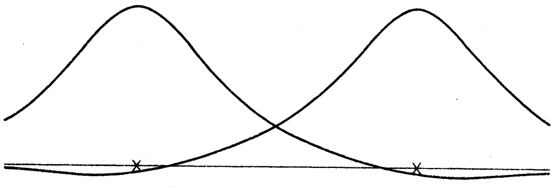

FIG. 1. Hypothetical Wannier canonical orbitals showing the regions of integration for Eqs. (5.1), (5.2). The x's represent two nearest-neighbor lattice sites.

[This usual Wannier solution *must* exist, since the equations (2.3) and (2.4) are formally equivalent to the conventional Bloch solution. Calculations including the off-diagonal λ terms are reported in Refs. 5 and 7, where localized orbitals were obtained with good orthogonality and convergence. This confirmed the validity of our numerical procedures. The orbitals in Fig. 1 are taken from one of these orthogonal solutions.]

In the numerical study mentioned in Sec. IV, the form of the self-consistent but nonorthogonal canonical orbitals also confirmed the essential soundness of this argument. These orbtials had an exaggerated negative undershoot near the neighboring sites, and correspondingly, the two nodes seen in Fig. 1 were moved closer together. This had the effect of enhancing regions I and III at the expense of region II, so that the overlap $\langle\psi_1|\psi_0\rangle$ became negative. This distortion of the orbitals has the beneficial effect, via (5.1), of eliminating the excessively negative curvature of ψ_0 near its node, an effect which is qualitatively similar to that of $\lambda_{10}\varphi_1(x)$ in the Bloch canonical case. (This relation to λ_{10} confirms that the nonorthogonality is of order *S*, as asserted in Sec. IV.)

The present argument is obviously not rigorous. Nevertheless, it is noteworthy that it does not depend on symmetry. [In (5.2), for example, the only important thing is that region II must dominate region III; the equivalence of regions I and III is not at all essential.] The argument can therefore be applied, separately and in succession, to each near-neighbor pair of orbitals with parallel spins, even in highly unsymmetrical situations such as impure or amorphous materials. It is also applicable to the types of relatively disordered spin configurations considered in Refs. 5 and 7, which we shall discuss more fully elsewhere.

VI. FORMAL NONEXISTENCE PROOF

For the sake of completeness, we shall also summarize a recent nonexistence proof by Moyer.[11] This proof also focusses on the effect of the exchange potential. It is significant because of its logical rigor. On the debit side, however, (i) it does not offer any intuitive understanding; (ii) it seems to require a high degree of symmetry; and (iii) it assumes a non-negative two-body interaction of finite range, and with an upper bound on its strength as a function of particle separation, so it is not strictly applicable for Coulomb or screened Coulomb interactions.

Moyer considers a one-dimensional closed-ring system with an even number $2N$ of equally spaced sites. He argues that if a Wannier canonical solution $\{\psi_j^{\mathrm{WC}}\}$ exists, then the particular orbital superposition

$$\Delta(x)=\left(\sum_{j=1}^{N}\psi_{2j-1}^{\mathrm{WC}}(0)\right)\left(\sum_{j=1}^{N}\psi_{2j}^{\mathrm{WC}}(x)\right)$$

$$-\left(\sum_{j=1}^{N}\psi_{2j}^{\mathrm{WC}}(0)\right)\left(\sum_{j=1}^{N}\psi_{2j-1}^{\mathrm{WC}}(x)\right) \tag{6.1}$$

must also satisfy the HF orbital equation. Taking the origin for x at one of the sites, this $\Delta(x)$ is easily seen to have certain symmetry properties, namely, $\Delta(0)=\Delta'(0)=0$, and $\Delta(-x)=\Delta(x)$. These properties are exploited to transform the integro-differential equation for Δ into a Volterra integral equation. By means of a series of inequalities, Moyer then demonstrates that $\Delta\equiv 0$ is the only possible solution unless the maximum strength of the two-body interaction within the *exchange* potential exceeds some threshold. That is, if

$$v_{\max}\equiv\max[v(x-x')]<v_c, \tag{6.2}$$

then $\Delta\equiv 0$. The expression for v_c turns out to be quite independent of the lattice spacing, provided this spacing is more than twice the range of $v(x-x')$.

Intuitively, one expects that as the lattice spacing increases, it should become easier and easier for localization to occur, but this is not what the analysis indicates. In the limit of asymptotically large lattice spacing, Mott's argument[3] suggests that an arbitrarily weak $v(x-x')$ could still produce the sort of bound state involved in a Wannier canonical solution. (The strength of the one-body "ionic" potential term is assumed to remain finite.) In this case, however, Moyer's necessary threshold strength v_c will exceed any intuitively plausible value by an arbitrarily large factor. He therefore concludes that Wannier canonical solutions are not possible in the low-density regime.

It is noteworthy that this argument rules out the possibility of a "set of measure zero" of exceptional cases which was mentioned in Sec. IV, for interactions which satisfy Moyer's criteria, at least for the low-density regime. Outside of this regime, however, it is difficult to reach any conclusion at all because the formal mathematics does not correspond to any clear physical picture.

VII. SUMMARY AND CONCLUSIONS

A new and rigorous argument for the nonexistence of localized canonical HF eigenfunctions has been presented, and all previously published arguments which we are aware of have been reviewed. In contrast to the generally prevailing opinion, no sound argument for this nonexistence result has been available until quite recently.

The pioneering analysis of Kaplan and Argyres was shown in Sec. III to have some serious weaknesses. Most importantly, it overlooks some terms which are formally of the same order as those considered explicitly. It also focusses on a possible lack of inversion symmetry, even in situations where it is entirely reasonable to impose this symmetry from the outset. Nevertheless, a modified version of their argument was found to be useful (end of Sec. IV).

Sections IV and V discussed the nonorthogonal but self-consistent localized solutions which we had previously obtained numerically for a highly symmetrical (and precisely degenerate) model system. It was proven (Sec. IV) that *orthogonal* solutions with otherwise similar features cannot exist, except perhaps for parameter choices constituting a set of measure zero. Even if they exist (which is not clear), such exceptional cases would have vanishing probability of being physically relevant. Furthermore, it was shown that an arbitrarily weak degeneracy-breaking perturbation would suffice to destroy our special nonorthogonal solution.

Section V focussed on the effect of the exchange interaction between neighboring localized orbitals. A plausibility argument suggests that the spatial structure of the HF exchange potential is inherently unsuited to support a Wannier canonical solution. This argument is noteworthy because it can readily be applied to unsymmetrical situations.

Moyer's argument, historically the first one with an acceptable degree of rigor, was discussed in Sec. VI. Unfortunately, his proof is too formal to provide any physical insight, and the Coulomb potential does not satisfy the conditions assumed for the interaction.

In later papers we shall draw upon this experience as we discuss several different localized-orbital descriptions which are useful for explaining the behavior of Mott insulators.

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[1] F. Seitz, *Modern Theory of Solids* (McGraw-Hill, New York, 1940), p. 251.

[2] T. A. Kaplan and P. N. Argyres, Phys. Rev. B 1, 2457 (1970); see Sec. III B.

[3] N. F. Mott, Philos. Mag. 6, 287 (1961), and references therein.

[4] D. Adler and J. Feinleib, Phys. Rev. B 2, 3112 (1970).

[5] One of these descriptions is presented in Refs. 7 and 8; see also B. H. Brandow, J. Solid State Chem. 12, 397 (1975).

[6] T. A. Kaplan and P. N. Argyres, Phys. Rev. B 11, 1775 (1975).

[7] B. H. Brandow, Ann. Phys. (N.Y.) 74, 112 (1972); see Appendix C.

[8] B. H. Brandow, AIP Conf. Proc. 18, 702 (1974).

[9] This orbital localization feature of the Hartree approximation has been exploited in studies of solid helium [L. N. Nosanow, Phys. Rev. 146, 120 (1966)] and of the Wigner electron solid [F. W. de Wette, Phys. Rev. 135, A287 (1964); B. Pietrass, Phys. Status Solidi 24, 571 (1967)].

[10] J. R. Reitz, Solid State Phys. 1, 1 (1955); see p. 13.

[11] K. Moyer, Phys. Rev. B 9, 3555 (1974).

[12] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Vol. I, Appendix 9.

[13] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. II, Chap. 17.

[14] G. F. Koster, Phys. Rev. 89, 67 (1953); G. Parzen, Phys. Rev. 89, 237 (1953); L. A. Girifalco, Phys. Rev. 179, 616 (1959).