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Localized One-Electron States in Perfect Crystals as a Consequence of the Thermal Single-Determinant Approximation*

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A new extension of Hartree-Fock (HF) theory to nonzero temperature T, namely, the thermal single-determinant approximation (TSDA)—based on the variational principle of statistical mechanics—is applied to a model of a crystal of widely separated atoms. It is shown that, in this TSDA, one type of solution to the equations of stationarity of the free energy (TSD equations) consists of one-electron functions that are extended throughout the crystal (like Bloch functions), and another type of solution consists of localized one-electron states (particular Wannier functions), whereas it appears that in the usual, or standard, thermal HF approximation (THFA), only extended solutions are possible at finite atomic separation. (A previous argument that led to results contradictory to the latter statement is shown to be invalid.) Further, in the TSDA at $T>0$, the localized solutions give a *lower* free energy than that corresponding to the extended solutions, as well as a lower free energy than that obtained in the THFA. As far as we know, this is the first calculation in which a strictly variational requirement has rejected this class of spatially extended one-electron functions in favor of localized functions in a perfect crystal (i.e., in a system with translational symmetry).

I. INTRODUCTION

The basis of the one-electron theory of solids is the Hartree-Fock approximation. For the ground state of the system of interacting electrons this approximation gives the "best" wave function of the form of a single Slater determinant of one-electron wave functions, on the basis of the well-known minimum principle for the ground-state energy. Such an application of the ground-state variation principle, however, clearly does not lead to a prescription for the "best" excited states, even if they are also restricted to be single Slater determinants. Nevertheless, it has been customary to choose excited states as follows.

Let the occupied one-electron functions in the minimum energy determinant $D_0 \equiv D_0(\psi_1 \cdots \psi_N)$ be $\psi_1, \psi_2, \ldots, \psi_N$, which can be chosen orthonormal with no loss of generality; one can then complete the set of one-electron functions by adding $\psi_{N+1}, \psi_{N+2}, \ldots$, such that one obtains orthonormality among all functions: $(\psi_i, \psi_j) = \delta_{ij}$. By the occupation of this complete set of one-electron functions in all possible ways, one then obtains a complete orthonormal set of (determinantal) wave functions, D_ν, for the many-electron system, the additional D_ν being taken as approximate excited states. An obvious source of ambiguity in this procedure lies in the fact that there is an infinite number of essentially different ways of choosing the "excited" one-electron states $\psi_{N+1}, \psi_{N+2}, \ldots$ (if the whole space of one-particle functions has more than $N+1$ dimensions) such that they are orthogonal to the given set $\psi_1 \cdots \psi_N$. A further source of ambiguity is the well-known invariance (to within a multiplicative constant) of D_0 under a unitary transformation of the occupied states:

$$D_0(\psi_1 \cdots \psi_N) = c D_0(\psi_1' \cdots \psi_N'), \tag{1.1}$$

where

$$\psi_i' = \sum_{j=1}^{N} u_{ij} \psi_j ; \tag{1.2}$$

c is a constant of magnitude unity, and u_{ij} is any $N \times N$ unitary matrix.[1] Even though $D_0(\cdots \psi_i \cdots)$ and $D_0(\cdots \psi_i' \cdots)$ are essentially (i.e., physically) the same, as in Eq. (1.1), the determinants obtained by destroying an electron in ψ_i or in ψ_i' are essentially different; thus the set of excited states can be chosen in an infinite number of essentially different ways (for $N>1$), even for *given* $\psi_{N+1}, \psi_{N+2}, \ldots$.

Note that an immediate consequence of the ambiguity expressed by Eq. (1.1) is that minimizing the energy of a single Slater determinant can never alone lead to the conclusion that the best one-electron functions are spatially localized. For, if ψ_i were localized functions (about sites $i=1, 2, \ldots$), then one can always choose u_{ij} so that the ψ_i' are extended; that is, in the state ψ_i' there is equal probability[2] of finding an electron in ψ_1, $\psi_2, \ldots$. In other words, for any set of localized functions

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[1] There seems to be a misconception among many workers that the physical invariance (1.1) is limited somehow to systems with "filled shells" or "filled bands." In fact, there is no such limitation (nor any other limitation).

[2] There is a unity matrix for arbitrary N such that $|u_{nm}|$ is independent of n and m; namely, $u_{nm} = N^{-1/2} \exp[2\pi i(n-m)/N]$, $n, m = 1, 2, \ldots, N$.

there is an equally "good" spatially extended set (in the sense of the energy variational principle).

A common way of choosing a particular set of excited states is to choose the ψ_i to be the eigenstates of the Hartree-Fock operator (i.e., solutions to the Hartree-Fock equations with the Lagrange multiplier[3] matrix taken as diagonal). But without any further argument, this is a completely arbitrary choice in the infinite number of choices, all consistent with the ground-state variational principle.

Another way, which is not so arbitrary (in fact, no more arbitrary than the use of the ground-state variational principle), would be to use the variational principle of statistical mechanics,[4] namely, the minimum principle for the *free* energy at temperature T (see Sec. II below for details). Since the excited states do contribute to the free energy when $T>0$, this variational principle will at least be expected to make an unambiguous decision as to their nature. Formally, these "best" states are the eigenstates of the "best" statistical density operator ρ of a specific form, chosen in accordance with the free-energy variational principle. It will be convenient to describe ρ in terms of an approximate Hamiltonian $\tilde{H}$, which is to be distinguished from the exact or model Hamiltonian H.

This approach has been used[5] to provide an extension of the Hartree-Fock approximation to nonzero temperatures, as follows. In what has been called the thermal Hartree-Fock approximation (THFA), the trial density operator ρ was taken to be one corresponding to an approximate Hamiltonian which is a one-electron operator; i.e., $\tilde{H}=\sum \varepsilon_i N_i$, where N_i are the occupation-number operators for a complete orthonormal set of one-electron states ψ_i and, the ε_i are real c numbers, the ψ_i and ε_i being chosen to minimize the free energy. This conforms to the idea of a one-electron approximation and leads to the standard thermal Hartree-Fock approximation that has been used for many decades.[6] Interestingly, the zero-temperature *limit* of this theory gives just the choice of excited states described in the paragraph before the last one.

This THFA is known to give poor results in certain cases. In particular, it fails qualitatively[7,8] for a simple (single-band) model of a collection of hydrogen atoms in the limit of infinite interatomic separation. Furthermore, the choice of ρ leading to the THFA is too restrictive from the stand point of the original Hartree-Fock idea of seeking the "best" wave function for the system in the form of a single determinant, for, while all the eigenstates of a one-electron operator may be chosen to be single determinants, *one-electron operators are not the only operators with this property*. For example, an operator of the form $\sum \varepsilon_i N_i + \sum \varepsilon_{ij} N_i N_j$ would also have a complete set of single-determinantal eigenfunctions. In fact, $\tilde{H}$ would have a complete set of single-determinantal eigenfunctions if it were an *arbitrary function* $E(\cdots N_i \cdots)$ of the occupation-number operators.

Thus we are led to a new extension to nonzero temperature of the HF approximation—namely, the one-electron states ψ_i and the function $\tilde{H}=E(\cdots N_i \cdots)$ are chosen to minimize the free energy. This extension of the Hartree-Fock idea has recently been proposed[7] and described briefly[9]; it was shown[7] to overcome completely the failure of THFA for the hydrogen-atom model in the limit of infinite separation. It has been designated as the thermal single-determinant approximation (TSDA) to distinguish it from the earlier THFA.[10]

In Sec. II we review briefly[11] the main results of TSDA of a general nature and those of THFA that are of immediate interest to us here.

In Sec. III we apply TSDA and THFA to a simple and commonly used single-band model of a system of widely separated hydrogen atoms, the protons being fixed in a periodic array. In Sec. III A, the limiting case of large separation is treated, with the possible effects of the long-range nature of the Coulomb interaction on the limiting process discussed. We show that one-electron states that are *localized* around one proton satisfy the variational equations both in the TSDA and the THFA; there are also spatially *extended* one-electron functions (like running waves), which are solutions of both the TSD and the THF equations. Comparison of the free energies for the various solutions and approximations leads to the following conclusion: *The spatially extended solutions are rejected*, by the free-energy minimum principle, *in favor of the localized solutions* (for $T>0$), the absolute minimum free energy (i.e., the exact free energy) being attained only in the TSDA.

In Sec. III B, we consider in a perturbative way the case of large but not infinite separation, i.e., the case in which the overlap of the atomic orbitals is small, but nonzero. We find that in the THFA, the localized solutions for zero overlap do not form a proper zero-order set (due to removal of degeneracy) and so do not lead perturbatively to localized solutions for small overlap, whereas in TSDA, localized solutions *are* found to exist for small overlap, so that the basic conclusion of Sec. III A is not violated for large but finite separation.

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[3] See, e.g., J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., New York, 1960), Vol. II.

[4] N. David Mermin, Phys. Rev. **137**, A1441 (1965), Appendix. See also John M. Blatt, *Theory of Superconductivity* (Academic Press Inc., New York, 1964), p. 396.

[5] N. David Mermin, Ann. Phys. (N. Y.) **21**, 99 (1953); see also J. Blatt, *ibid.*, p. 403.

[6] For example, E. P. Wohlfarth, Phil. Mag. **41**, 534 (1950).

[7] T. A. Kaplan, Bull. Am. Phys. Soc. **13**, 386 (1968).

[8] T. A. Kaplan (unpublished).

[9] T. A. Kaplan, Solid-State Research Report No. DDC-AD 672961, Lincoln Laboratory, M.I.T. (1968:2), p. 53 (unpublished).

[10] This TSDA includes the most general choice of $\tilde{H}$, such that its eigenfunctions (the approximate energy eigenfunctions) are all single determinants formed from a complete orthonormal set of one-electron states. It does not include, however, the most general $\tilde{H}$ with a complete set of determinantal eigenfunctions [T. A. Kaplan and P. N. Argyres (unpublished)].

[11] For more details, see T. A. Kaplan and P. N. Argyres (unpublished).

Finally, in Sec. IV, it is shown further that for this model in the TSDA, localized solutions exist for arbitrary overlap.

In other words, the new approximation TSDA is the result of a variational procedure that leads, in the present case, to essentially different results from those of the standard thermal Hartree-Fock approximation (THFA). This is true despite the fact that both approximations are based on having approximate energy eigenstates in the form of single Slater determinants. Furthermore, the new approximation has, for the first time, given a variational procedure sufficient flexibility to allow it to choose unambiguously localized one-electron states in a situation where there is crystalline symmetry.

Localized one-electron functions in crystals, or molecules, where symmetry would appear to require extended functions, have been considered by others.[12–15] However, these wave functions have not been derived on the basis of a variational procedure.

II. THERMAL SINGLE-DETERMINANT APPROXIMATION

The idea of TSDA is as follows.[7,8,11] We consider the minimum principle of quantum statistical mechanics for a system with a Hamiltonian operator H and number of particles operator N:

$$F[\rho]\equiv \mathrm{Tr}\{\rho[H-\mu N+\beta^{-1}\ln\rho]\}\geqslant F_e. \tag{2.1}$$

Here ρ is an arbitrary Hermitian and non-negative operator with unit trace, $\beta=1/kT$, μ is the chemical potential, and F_e is the exact grand-canonical free energy for the system, namely,

$$F_e=F[\rho_e]=-\beta^{-1}\ln \mathrm{Tr}e^{-\beta(H-\mu N)}, \tag{2.2a}$$

where

$$\rho_e=e^{[-\beta(H-\mu N)]}/\mathrm{Tr}e^{[-\beta(H-\mu N)]} \tag{2.2b}$$

is the exact grand-canonical density matrix. For a system of interacting fermions, we have

$$H=\sum_{\kappa\lambda} h_{\kappa\lambda}c_\kappa{}^\dagger c_\lambda+\tfrac{1}{2}\sum_{\kappa\lambda}\sum_{\kappa'\lambda'} v_{\kappa\lambda,\kappa'\lambda'}c_\kappa{}^\dagger c_\lambda{}^\dagger c_{\lambda'}c_{\kappa'}, \tag{2.3}$$

where $|\kappa)$, $|\lambda)$, ... is any complete and orthonormal set of one-particle states, $h_{\kappa\lambda}=(\kappa|h|\lambda)$ is the matrix element of the one-particle operator h, and

$$v_{\kappa\lambda,\kappa'\lambda'}=(\kappa(1)\lambda(2)|v(1,2)|\kappa'(1)\lambda'(2))\equiv(\kappa\lambda|v|\kappa'\lambda') \tag{2.4}$$

is the matrix element of the interparticle interaction v. The TSDA consists of finding the minimum of $F[\rho]$ for a trial density matrix of the form

$$\rho=e^{\{-\beta[\tilde{H}-\mu N]\}}/\mathrm{Tr}e^{\{-\beta[\tilde{H}-\mu N]\}}, \tag{2.5a}$$

where

$$\tilde{H}=E(\cdots N_i\cdots) \tag{2.5b}$$

is any real function of the occupation number operators N_i corresponding to a complete orthonormal set of one-particle states ψ_i. Requiring stationarity of $F[\rho]$ under arbitrary variations of $E(\cdots N_i\cdots)$ and of the states ψ_i, subject to the previously stated conditions, we find[7,9,11] that the approximate Hamiltonian $E(\cdots N_i\cdots)$ is given by

$$E(\cdots N_i\cdots)=\sum_i h_{ii}N_i+\tfrac{1}{2}\sum_{ij}\hat{v}_{ij,ij}N_iN_j, \tag{2.6}$$

while the one-particle states ψ_i are determined by the system of equations (to be referred to as the TSD equations)

$$\langle N_i-N_j\rangle h_{ij}+\sum_l \hat{v}_{il,jl}\langle(N_i-N_j)N_l\rangle=0 \tag{2.7}$$

plus the condition that they form a complete orthonormal set. Here h_{ij} are the matrix elements of h in the ψ_i representation, and $\hat{v}_{il,jl}$ is the antisymmetrized matrix element

$$\hat{v}_{il,jl}\equiv v_{il,jl}-v_{il,lj}\equiv(il|\hat{v}|jl), \tag{2.8}$$

where the matrix elements of v are defined as in Eq. (2.4) but in the ψ_i representation. In addition, the angular brackets in Eq. (2.7) denote the average over the trial density matrix, i.e.,

$$\langle 0\rangle=\mathrm{Tr}\{\rho 0\}, \tag{2.9}$$

with ρ given by Eqs. (2.5) and (2.6). Actually, the stationarity condition leaves $E(\cdots N_i\cdots)$ undetermined to within an arbitrary c-number function of β and μ (which introduces no corresponding ambiguity into the free energy or anything physical), just as in the more general unrestricted case. It can be shown,[11] however, that taking this function equal to zero, as we have done in Eq. (2.6), we find for the free energy in the TSDA

$$F_{\mathrm{TSDA}}=-\beta^{-1}\ln \mathrm{Tr}e^{\{-\beta[E(\cdots N_i\cdots)-\mu N]\}}, \tag{2.10}$$

with $E(\cdots N_i\cdots)$ given by Eq. (2.6). Thus $E(\cdots N_i\cdots)$ within the TSDA plays the role of an effective Hamiltonian for the thermodynamic properties of the system.

From the minimum principle (2.1) we have clearly

$$F_{\mathrm{TSDA}}\geqslant F_e \tag{2.11}$$

for *any* possible set of solutions $\{\psi_i\}$ of the TSD equations (2.7). We should point out that there are, in general, many sets of solutions $\{\psi_i\}$ to these equations, and that they give merely the stationary points of $F[\rho]$, i.e., local maxima, minima, and inflection or saddle points. The solution that makes F_{TSDA} minimum is,

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[12] W. H. Adams, J. Chem. Phys. **37**, 2009 (1962).

[13] C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. **35**, 457 (1963).

[14] P. W. Anderson, Phys. Rev. Letters **21**, 13 (1968); Phys. Rev. **181**, 25 (1969).

[15] For additional references, see N. H. March and J. C. Stoddart, Rept. Progr. Phys. **31**, 533 (1968), Part II.

of course, the "best" from the point of view of the minimum principle of statistical mechanics.[16]

The THFA can be obtained similarly from Eq. (2.1) by requiring ρ to be not only of the form (2.5) but, in addition, by restricting $E(\cdots N_i \cdots)$ to be a *linear* function of the N_i, i.e., a one-particle operator. Then, the corresponding $E(\cdots N_i \cdots)$ is found to be equal to $\sum_i \varepsilon_i N_i$, with ε_i, the THF one-electron energies, given by

$$\varepsilon_i = h_{ii} + \sum_j \hat{v}_{ij,ij}\langle N_j \rangle . \tag{2.12}$$

The average $\langle\ \rangle$ is now taken with respect to the THFA density operator, and thus $\langle N_j \rangle = f(\varepsilon_j)$, where $f(\varepsilon)$ is the Fermi-Dirac distribution function. Similarly, in the THFA, $\langle (N_i - N_j) N_l \rangle$ becomes $\langle N_i - N_j \rangle \langle N_l \rangle$, and thus Eqs. (2.7), which determined the one-particle states ψ_i, become for $i \neq j$, after the cancellation of the common factor $\langle N_i - N_j \rangle$, the off-diagonal elements of the familiar THFA equations, namely,[17]

$$h_{ij} + \sum_l \hat{v}_{il,jl}\langle N_l \rangle = \varepsilon_i \delta_{ij} . \tag{2.13}$$

Again, we may note that the minimum principle (2.1) guarantees that for any possible set of solutions ψ_i of the THF Eqs. (2.13),

$$F_{\text{THFA}} \geqslant F_e . \tag{2.14}$$

In addition, we see that if both the THF and the TSD equations for the one-particle states admit the same set $\{\psi_i\}$, then the corresponding free energies to be denoted, respectively, by $F_{\text{THFA}}\{\psi_i\}$ and $F_{\text{TSDA}}\{\psi_i\}$ satisfy the relation

$$F_{\text{THFA}}\{\psi_i\} \geqslant F_{\text{TSDA}}\{\psi_i\} \geqslant F_e . \tag{2.15}$$

Finally, denoting by $F_{\text{THFA}}{}^{\text{min}}$ and $F_{\text{TSDA}}{}^{\text{min}}$ the absolute minima in the THFA and TSDA, respectively, it is clear that

$$F_{\text{THFA}}{}^{\text{min}} \geqslant F_{\text{TSDA}}{}^{\text{min}} . \tag{2.16}$$

III. APPLICATION TO MODEL HYDROGEN CRYSTAL

In order to investigate some of the consequences of this new TSDA approximation and to examine the points where it differs from the older THFA, we apply these approximation schemes to the following simple single-band model of a crystal.[18] Consider $\mathfrak{N}$ electrons on the average moving in the field of $\mathfrak{N}$ protons, which are taken to be at sites $\mathbf{n}$, forming a fixed Bravais lattice. In addition, take the one-electron function space to be defined by requiring any one-electron function to be a linear combination of the $2\mathfrak{N}$ functions

$$a_{\mathbf{n}\sigma} \equiv a(\mathbf{r}-\mathbf{n})\alpha_\sigma = a_{\mathbf{n}}(\mathbf{r})\alpha_\sigma . \tag{3.1}$$

Here α_σ are the usual orthogonal spin functions, and $a(\mathbf{r}-\mathbf{n})$ is an "atomic" function centered at site $\mathbf{n}$ and is taken, for convenience, to be real. In numerical considerations made below, $a(\mathbf{r})$ is taken to be the hydrogen 1*s* function.

The Hamiltonian of this system is given by Eq. (2.3), where h is the kinetic energy of an electron plus its interaction with the protons, and $v(1,2)$ is the electron-electron interaction. We will also add a constant

$$C = \tfrac{1}{2} \sum{}' \frac{e^2}{|\mathbf{n}-\mathbf{m}|} ,$$

the proton-proton Coulomb energy.

We will be interested here only in the case of large separation d of the atoms. That is, we consider the overlap between $a(\mathbf{r})$ and $a(\mathbf{r}-\mathbf{n})$ to be small for $\mathbf{n} \neq 0$ and the Coulomb interaction energy $U_{\mathbf{n}}$ between electron densities $a^2(\mathbf{r})$ and $a^2(\mathbf{r}-\mathbf{n})$ to be small. However, because the latter is of long range, one has to treat it differently from the overlap if one is interested in the thermodynamic limit, $\mathfrak{N} \to \infty$, d fixed (there conceivably could be a difference depending on the order in which the limits $\mathfrak{N} \to \infty$, $d \to \infty$ are taken).

Thus we consider, in Sec. III A, two possible limiting cases: the infinite-separation limit where the Coulomb interactions $U_{\mathbf{n}}$ [defined in Eq. (3.5)] for $\mathbf{n} \neq 0$, as well as the overlaps of the atomic functions, are zero, and the zero-overlap limit, where only the overlaps vanish while $U_{\mathbf{n}} \neq 0$. In either limit, we show that both spatially localized and extended one-electron solutions ψ_i exist, whether one works in the TSDA or in the THFA. We also consider the free energies corresponding to the various cases. This leads to the following conclusion, drawn rigorously for the infinite-separation limit and sufficiently low temperatures, and plausibly for both limits and general temperatures: Namely, *the extended solutions are rejected*, by the free-energy minimum principle, *in favor of the localized solutions* (for $T > 0$), and *the lowest free energy is attained only in the* TSDA.

In Sec. III B, we consider, in a perturbative way, the effect of small but nonzero overlap. The purpose is to see if any of the solutions and, possibly, the above conclusion, are spoiled (e.g., by effects due to removal of degeneracies). We find, indeed, that in the THFA the localized solutions for zero overlap do *not* lead to localized solutions for nonzero overlap, whereas in the TSDA, localized solutions *are* found to exist for nonzero

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[16] Conditions for the local stability of solutions to the TSD equations will be discussed elsewhere (Ref. 11).

[17] The presence of the factor $\langle N_i - N_j \rangle$ when (2.7) is reduced in a one-electron theory can lead to additional solutions besides those of (2.13); it can be shown, however, that such solutions cannot yield minimum free energy. The presence of this factor, which will be discussed in more detail elsewhere (Ref. 11), can be understood in terms of the fact that (2.7) comes from variations of the states ψ_i, rather than variation directly of the density operator ρ [the latter leading to (2.13)].

[18] A brief summary of the results of this application has been presented in T. A. Kaplan and P. N. Argyres, Int. J. Quant. Chem. 3, 851 (1969). This single-band model is fairly commonly used. It was used, e.g., by Mattheiss [Phys. Rev. **123**, 1209; **123**, 1219 (1961)] in his treatment of a system of six hydrogen atoms arranged in a regular hexagonal array, and also in Refs. 7 and 8.

overlap. Also, extended solutions exist in both THFA and TSDA. Thus, making the extremely plausible assumption that the free energy for a given type of solution (if it exists for a range of overlap) is a continuous function of overlap, the conclusion of Sec. III A is established for small but nonzero overlap.

Our result, that localized solutions do not appear to exist for small overlap in the THFA, is in essential contradiction to statements existing in the literature. The error made there is pointed out in Sec. III B.

The explicit quantities appearing in the theory, which approach zero as the overlap approaches zero, are listed in the following equations, along with the existence of an upper bound expressed in the standard O notation[19]:

$$\begin{aligned} (a_{\mathrm{n}}|a_{\mathrm{n}'}) &= O(s)\,, \qquad \mathbf{n}\neq\mathbf{n}' \\ (a_{\mathrm{n}}|h|a_{\mathrm{n}'}) &= O(s)\,, \qquad \mathbf{n}\neq\mathbf{n}' \\ (a_{\mathrm{n}}a_{\mathrm{m}}|v|a_{\mathrm{n}'}a_{\mathrm{m}}) &= O(s)\,, \qquad \mathbf{n}\neq\mathbf{n}' \\ (a_{\mathrm{n}}a_{\mathrm{m}}|v|a_{\mathrm{n}'}a_{\mathrm{m}'}) &= O(s^{1+\nu})\,, \\ &\nu>0\,,\quad \mathbf{n}\neq\mathbf{n}'\,,\quad \text{and}\quad \mathbf{m}\neq\mathbf{m}' \end{aligned} \tag{3.2}$$

where s is the largest overlap integral. (The latter occurs for nearest-neighbor overlap.)

A. Limiting Cases of Large Separation

In the zero-overlap limit, all the quantities (3.2) are zero. Thus, denoting this limit by $\doteq$, one easily finds that

$$\begin{aligned} (a_{\mathrm{n}\sigma}|h|a_{\mathrm{n}'\sigma'}) &\doteq \delta_{\sigma\sigma'}\delta_{\mathrm{nn}'}(a_{\mathrm{n}\sigma}|h|a_{\mathrm{n}\sigma}) \\ &\equiv \delta_{\sigma\sigma'}\delta_{\mathrm{nn}'}\bar{h}\,, \end{aligned} \tag{3.3}$$

$$(a_{\mathrm{n}\sigma}a_{\mathrm{l}\tau}|v|a_{\mathrm{n}'\sigma'}a_{\mathrm{l}'\tau'}) \doteq \delta_{\mathrm{nn}'}\delta_{\sigma\sigma'}\delta_{\mathrm{ll}'}\delta_{\tau\tau'}U_{\mathrm{nl}}\,, \tag{3.4}$$

where

$$U_{\mathrm{nl}} \equiv \int d\mathbf{r}_1 \int d\mathbf{r}_2 v(r_{12}) a^2(\mathbf{r}_1-\mathbf{n}) a^2(\mathbf{r}_2-\mathbf{l}) = U_{\mathrm{n-l}}\,. \tag{3.5}$$

Because the states $a_{\mathrm{n}\sigma}$ are orthonormal in this limit, we can use them as a basis set for the exact model Hamiltonian (2.3), thus letting $c_{\mathrm{n}\sigma}{}^{\dagger}$ be the creation operator for the state $a_{\mathrm{n}\sigma}$, and using Eqs. (3.3) and (3.4), we have from Eq. (2.3) (adding C),

$$H \doteq \bar{h}N + \tfrac{1}{2}\sum U_{\mathrm{nn}'}(1-\delta_{\mathrm{nn}'}\delta_{\sigma\sigma'})N_{\mathrm{n}\sigma}N_{\mathrm{n}'\sigma'} + C\,. \tag{3.6}$$

In the infinite-separation limit all these relations obviously hold and, in addition, we have

$$U_{\mathrm{nn}'} = U\delta_{\mathrm{nn}'}\,. \tag{3.7}$$

We immediately see that the localized functions

$$\psi_i \rightarrow a_{\mathrm{n}\sigma} \tag{3.8}$$

are solutions to the TSD Eqs. (2.7) in these limits, since the matrix elements (3.3) and (3.4) are zero for $\mathbf{n}\sigma\neq\mathbf{n}'\sigma'$. Furthermore, the approximate Hamiltonian (2.6) corresponding to these solutions, which we denote by E_{TSDA} (loc.), is easily seen to be identical to the exact one:

$$E_{\mathrm{TSDA}}(\text{loc.}) \doteq H\,. \tag{3.9}$$

It immediately follows that the free energy in the TSDA corresponding to the localized solutions (3.8), denoted by F_{TSDA}(loc.), is the exact free energy

$$F_{\mathrm{TSDA}}(\text{loc.}) \doteq F_e\,, \tag{3.10}$$

and so, of course, all thermodynamic quantities calculated in the TSDA are exact in both limits.

Let us next consider the spatially extended functions

$$\phi_{\mathbf{k}\sigma} = \frac{1}{\sqrt{\mathfrak{N}}}\sum_{\mathrm{n}} \exp(i\mathbf{k}\cdot\mathbf{n}) a(\mathbf{r}-\mathbf{n}) \alpha_{\sigma}{}^{(n)}\,, \tag{3.11}$$

where $\alpha_{\sigma}{}^{(n)}$ is the usual pair of spin functions, but which is quantized along an axis that can vary (arbitrarily) from site to site, and where $\mathbf{k}$ is an allowed wave vector in the Brillouin zone. Straightforwardly, we find, in the zero-overlap limit,

$$(\phi_{\mathbf{k}\sigma}|\phi_{\mathbf{k}'\sigma'}) \doteq \delta_{\mathbf{kk}'}\delta_{\sigma\sigma'}\,, \tag{3.12}$$

$$(\phi_{\mathbf{k}\sigma}|h|\phi_{\mathbf{k}'\sigma'}) \doteq \delta_{\mathbf{kk}'}\delta_{\sigma\sigma'}\bar{h}\,, \tag{3.13}$$

and the antisymmetrized matrix element

$$\begin{aligned} (\phi_{\mathbf{k}\sigma}\phi_{\mathbf{k}''\sigma''}|\hat{v}|\phi_{\mathbf{k}'\sigma'}\phi_{\mathbf{k}''\sigma''}) &\doteq (1/\mathfrak{N})\delta_{\sigma\sigma'}\delta_{\mathbf{kk}'} \\ &\quad\times[U(0)-\delta_{\sigma\sigma'}U(\mathbf{k}-\mathbf{k}'')]\,, \end{aligned} \tag{3.14}$$

where

$$\begin{aligned} U(\mathbf{k}-\mathbf{k}') &\equiv \sum_{\mathbf{m}} U_{\mathrm{mn}} \exp[i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{m}-\mathbf{n})] \\ &= \mathfrak{N}(\phi_{\mathbf{k}\sigma}\phi_{\mathbf{k}'\sigma}|v|\phi_{\mathbf{k}'\sigma}\phi_{\mathbf{k}\sigma}) \end{aligned} \tag{3.15}$$

is $\mathfrak{N}$ times the exchange integral between $\phi_{\mathbf{k}\sigma}$ and $\phi_{\mathbf{k}'\sigma'}$. We see that the $\phi_{\mathbf{k}\sigma}$ are solutions to the TSD Eqs. (2.7) in both limits under consideration, since each of the matrix elements (3.12), (3.13), and (3.14) are zero for $\mathbf{k}\sigma\neq\mathbf{k}'\sigma'$. The approximate Hamiltonian (2.6) corresponding to the extended solutions $\phi_{\mathbf{k}\sigma}$, denoted by $\mathrm{E}_{\mathrm{TSDA}}$(ext.), is found, with the help of Eqs. (3.13) and (3.14), to be

$$\begin{aligned} E_{\mathrm{TSDA}}(\text{ext.}) &\doteq N\left[\bar{h}+\frac{U(0)N}{2\mathfrak{N}}\right] \\ &\quad - \frac{1}{2\mathfrak{N}}\sum U(\mathbf{k}-\mathbf{k}')n_{\mathbf{k}\sigma}n_{\mathbf{k}'\sigma}+C\,, \end{aligned} \tag{3.16}$$

where $n_{\mathbf{k}\sigma}$ is the occupation number for the state $\phi_{\mathbf{k}\sigma}$. It will prove convenient to note that Eq. (3.16) can be

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[19] N. G. DeBruijn, *Asymptotic Methods on Analysis* (North-Holland Publishing Co., Amsterdam, 1958), Chap. 1.

written

$$E_{\mathrm{TSDA}}(\mathrm{ext.}) \doteq N\left\{\bar{h}+\frac{U(0)N}{2\mathfrak{N}}-\frac{1}{2\mathfrak{N}}[U(0)-U]\right\}$$
$$-\frac{U}{2\mathfrak{N}}\sum N_{\mathbf{n}\sigma}N_{\mathbf{n}'\sigma}$$
$$+\frac{1}{2\mathfrak{N}}\sum_{\mathbf{nn}'}{}'\sum_{\sigma} U_{\mathbf{nn}'}N_{\mathbf{n}\sigma}N_{\mathbf{n}'\sigma}-G+C\,, \qquad (3.17)$$

where U, as defined by Eq. (3.7), is the Coulomb self-energy of the charge distribution $ea^2(\mathbf{r})$, and

$$G=\frac{1}{2\mathfrak{N}}\sum_{\mathbf{nn}'}{}'\sum_{\sigma}\sum_{\mathbf{m}}^{0,\mathbf{n}'-\mathbf{n}} U_{\mathbf{nn}'}c_{\mathbf{n}\sigma}{}^{\dagger}c_{\mathbf{n}+\mathbf{m},\sigma}c_{\mathbf{n}'\sigma}{}^{\dagger}c_{\mathbf{n}'-\mathbf{m},\sigma}\,, \qquad (3.18)$$

and $\sum_{\mathbf{m}}{}^{\mathbf{a},\mathbf{b}}$ means sum over $\mathbf{m}$ with $\mathbf{m}\neq\mathbf{a}$ or $\mathbf{b}$.

We shall now argue that in these limits, and for $T>0$, the free energy in the TSDA corresponding to the extended solutions (3.11), denoted by $F_{\mathrm{TSDA}}(\mathrm{ext.})$, is *greater* than $F_e[\doteq F_{\mathrm{TSDA}}(\mathrm{loc.})]$.

We first consider the *infinite-separation limit*, where $U_{\mathbf{nm}}=0$ for $\mathbf{n}\neq\mathbf{m}$. In this case, Eq. (3.15) gives $U(\mathbf{k}-\mathbf{k}')=U$; thus Eq. (3.17) becomes

$$E_{\mathrm{TSDA}}(\mathrm{ext.})=N\left(\bar{h}+\frac{UN}{2\mathfrak{N}}\right)-\frac{U}{2\mathfrak{N}}\sum N_{\mathbf{n}\sigma}N_{\mathbf{m}\sigma} \qquad \text{(inf.-sep. limit)}. \qquad (3.19)$$

Noting that

$$N_\sigma\equiv\sum_{\mathbf{n}} N_{\mathbf{n}\sigma}=\sum_{\mathbf{k}} n_{\mathbf{k}\sigma}\,, \qquad (3.20)$$

we see that Eq. (3.19) agrees with Eq. (3.16) (as it must), and can be written

$$E_{\mathrm{TSDA}}(\mathrm{ext.})=N\bar{h}+\frac{U}{\mathfrak{N}}N_{\uparrow}(N-N_{\uparrow}) \qquad \text{(inf.-sep. limit)}. \qquad (3.21)$$

Similarly, Eq. (3.6) becomes

$$H=N\bar{h}+U\sum N_{\mathbf{n}\uparrow}N_{\mathbf{n}\downarrow} \quad \text{(inf.-sep. limit)}. \qquad (3.22)$$

From these equations, it is clear that in the infinite-separation limit,

$$E_{\mathrm{TSDA}}(\mathrm{ext.})\neq H \quad \text{(inf.-sep. limit)}. \qquad (3.23)$$

For example, consider the set of states for which $N=\mathfrak{N}$. Since $U>0$, the minimum eigenvalue of (3.21) and of (3.22) is $N\bar{h}$ [attained in (3.22) for $N_{\mathbf{n}\uparrow}+N_{\mathbf{n}\downarrow}=1$, all $\mathbf{n}$]; however, the degeneracy of this ground level is two for Eq. (3.21) (the two states occurring for $N_\uparrow=0$ and $N_\uparrow=N$), whereas this degeneracy is 2^N for Eq. (3.22) (since either $N_{\mathbf{n}\uparrow}=1$, $N_{\mathbf{n}\downarrow}=0$ or $N_{\mathbf{n}\uparrow}=0$, $N_{\mathbf{n}\downarrow}=1$, for each $\mathbf{n}$, gives the minimum energy). Now there is a stronger version of the basic minimum principle (2.1), namely,[20]

$$F[\rho]>F[\rho_e]=F_e \quad \text{for} \quad \rho\neq\rho_e \quad \text{and} \quad T>0. \qquad (3.24)$$

Thus, Eq. (3.23), together with this principle, yields

$$F_{\mathrm{TSDA}}(\mathrm{ext.})>F_e[\doteq F_{\mathrm{TSDA}}(\mathrm{loc.})]\,, \quad T>0 \qquad \text{(inf.-sep. limit)}. \qquad (3.25)$$

In general, however, one must be careful about concluding that an inequality like (3.25) is significant when one is interested in the thermodynamic limit ($\mathfrak{N}\rightarrow\infty$).[21] It is possible that the difference

$$[F_{\mathrm{TSDA}}(\mathrm{ext.})-F_{\mathrm{TSDA}}(\mathrm{loc.})]\rightarrow 0$$

as $\mathfrak{N}\rightarrow\infty$ [in which case the inequality (3.25) would be felt to have lost any significance for deciding that the extended solutions are "worse" than the localized solutions], or even that $[F_{\mathrm{TSDA}}(\mathrm{ext.})-F_{\mathrm{TSDA}}(\mathrm{loc.})]/\mathfrak{N}\rightarrow 0$ (in which case the inequality would also be felt, although less strongly, to have lost its significance). This could happen, in an obvious way, if the difference between $E_{\mathrm{TSDA}}(\mathrm{ext.})$ and H occurred only in highly excited states whose energies relative to the low-lying levels $\rightarrow\infty$ as $\mathfrak{N}\rightarrow\infty$; it could also happen in more subtle ways. On the other hand, in the present case, the difference in the degeneracies of the important low-lying levels of $E_{\mathrm{TSDA}}(\mathrm{ext.})$ and H apparent from (3.21) and (3.22) (we gave the example of the ground level for $N=\mathfrak{N}$) makes it extremely reasonable that

$$[F_{\mathrm{TSDA}}(\mathrm{ext.})-F_{\mathrm{TSDA}}(\mathrm{loc.})]\mathfrak{N}^{-1}$$

remains positive as $\mathfrak{N}\rightarrow\infty$: For $T\ll U/k\approx10^5\,{}^\circ\mathrm{K}$ [the spacing between the two lowest levels for both Hamiltonians, $E_{\mathrm{TSDA}}(\mathrm{ext.})$ and H, for the case of hydrogen 1*s* orbitals], one strongly expects $F_e\sim\mathfrak{N}(\bar{h}-\mu)-\mathfrak{N}kT\ln2$ and $F_{\mathrm{TSDA}}(\mathrm{ext.})\sim\mathfrak{N}(\bar{h}-\mu)-kT\ln2$ so that the latter lies above the former by essentially $\mathfrak{N}kT\ln2$, a macroscopic and therefore significant quantity. Although we expect that most readers will not be skeptical about this reasoning—we were well convinced—we feel that we must prove the inequality (3.25) rigorously, since it is the central result of this paper. (From it follows that,

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[20] Mermin (Ref. 4, Appendix) almost proves this. Unfortunately, he omits the condition $T>0$, and it is possible to give a counterexample when that condition is omitted. Namely, suppose $H-\mu N$ has a degenerate ground level, degeneracy P; then, as $T\rightarrow0$, the eigenvalues of ρ_e approach $1/P$ for each of the ground states, and zero for all other eigenstates of $H-\mu_0N$ ($\mu\rightarrow\mu_0$ as $T\rightarrow0$). Consider a $\rho=\exp[-\beta(\tilde{H}-\mu_0N)]/\mathrm{Tr}\exp[-\beta(\tilde{H}-\mu_0N)]$, in which $\tilde{H}-\mu_0N$ has the same eigenstates as $H-\mu_0N$; its ground level is nondegenerate, and its ground state is one of the ground states of $H-\mu_0N$. Clearly, then, $F[\rho]-F[\rho_e]\rightarrow0$ as $T\rightarrow0$, but $\rho-\rho_e$ does not approach zero as $T\rightarrow0$. However, if the proviso, $T>0$, is included in the statement of the principle [as in (3.24)], then Mermin's proof appears to be valid.

[21] Care is needed even if one is interested in macroscopic systems ($\mathfrak{N}$ very large but finite). In such cases, it would seem reasonable that a significant difference in free energies would be one that is linear in $\mathfrak{N}$ over the experimentally accessible range of $\mathfrak{N}$, to an accuracy well within that which is experimentally achievable. See Appendix A for further discussion along these lines.

in the present limit, the localized solutions are preferred over the extended ones.) Hence, in Appendix A, it is shown rigorously that $F_{\mathrm{TSDA}}(\text{ext.})-F_{\mathrm{TSDA}}(\text{loc.})$ is a positive macroscopic quantity for $T>0$.

We next consider the *zero-overlap limit* $(U_{\mathbf{nm}}\neq 0)$, in which we must compare (3.6) with (3.16) or (3.17). For finite $\mathfrak{N}$ there is no problem in concluding the inequality between the free energies for the two types of solutions, Eq. (3.25), for the presence of G in (3.17) makes it clear that (3.23) holds in this limit as well, since the two Hamiltonians no longer even have the same set of eigenstates. Again, however, when $\mathfrak{N}\rightarrow\infty$, one must be careful. Following the previous argument for the infinite-separation limit, the first problem we encounter is that the nature of the ground state of H [Eq. (3.6)] for $N=\mathfrak{N}$ is not known. The *additional* terms, involving $U_{\mathbf{nm}}$ for $\mathbf{n}\neq\mathbf{m}$, would appear to be minimized, for some simple lattices (e.g., sc, bcc), when $N_{\mathbf{n}\uparrow}+N_{\mathbf{n}\downarrow}=2$ or 0 such that the nearest neighbors to sites with two electrons would have no electrons. Thus it is not obvious that the states with one electron on each atom ($N_{\mathbf{n}\uparrow}+N_{\mathbf{n}\downarrow}=1$, all $\mathbf{n}$) minimize (3.6); that they, in fact, *do* give the minimum energy is proved[22] rigorously in Appendix B. The second problem encountered is to determine the ground state of $E_{\mathrm{TSDA}}(\text{ext.})$, Eq. (3.16). For this case, it is shown rigorously in Appendix B that the minimum occurs when $n_{\mathbf{k}\uparrow}=1$, $n_{\mathbf{k}\downarrow}=0$ for all $\mathbf{k}$ in a Brillouin zone, just as for infinite separation [Eq. (3.21)]. Furthermore, this state $|n_{\mathbf{k}\uparrow}=1,\ n_{\mathbf{k}\downarrow}=0$, all $\mathbf{k}$ in BZ$)\equiv|0)$ is identical to the state $|N_{\mathbf{n}\uparrow}=1,\ N_{\mathbf{n}\downarrow}=0$, all sites $\mathbf{n}$), which is a ground state of H. Clearly, the degeneracy of this ground level of (3.16) is at least 2; the important question is whether it might approach $2^{\mathfrak{N}}$ as $\mathfrak{N}\rightarrow\infty$. It is straightforward to see that if a finite number, ν, of electron-hole creation operators $b_{\mathbf{k}'\downarrow}{}^{\dagger}b_{\mathbf{k}\uparrow}$ is applied to $|0)$, then, in the limit $\mathfrak{N}\rightarrow\infty$, the energy is increased by νU (just as in the infinite-separation limit). This suggests that the ground state is again doubly degenerate [the second ground state comes from applying $\mathfrak{N}$ operators $b_{\mathbf{k}'\downarrow}{}^{\dagger}b_{\mathbf{k}\uparrow}$ to $|0)$, which is the same as flipping all the spins in $|0)$] and that the low-T ($\ll U/k$) thermodynamics is the same as for the infinite-separation limit; in particular, it suggests that (3.25) again holds. However, this discussion leaves the possibility that, if ν is a finite fraction of $\mathfrak{N}$, additional levels might occur near the ground-state energy, approaching the latter as $\mathfrak{N}\rightarrow\infty$. This possibility is ruled out in Appendix C, where it is shown that the ground level is doubly degenerate for finite $\mathfrak{N}$, and that there is a gap Δ to the first excited level such that $\Delta\geqslant(U-U_{\mathbf{l}})(1-1/\mathfrak{N})$, where $\mathbf{l}$ is the nearest-neighbor vector in the direct lattice.

Thus we have carried the argument in the case of the zero-overlap limit to essentially the same point that we had for the infinite-separation limit before we reached the final rigorous argument of Appendix 1. Namely, $E_{\mathrm{TSDA}}(\text{loc.})=H$, so that the localized solutions in TSDA give the exact free energy; the ground-state energies of $E_{\mathrm{TSDA}}(\text{ext.})$ and $E_{\mathrm{TSDA}}(\text{loc.})$ are the same; the ground-state degeneracies are 2 and $2^{\mathfrak{N}}$, respectively; and there is a finite gap Δ between the first two levels of $E_{\mathrm{TSDA}}(\text{ext.})$. Hence, it is extremely plausible that for $0<T<\Delta/k$ ($\approx 10^5\,^{\circ}\mathrm{K}$), the free energy for the extended solutions exceeds that for the localized solutions by a macroscopic quantity, which is, for $kT\ll\Delta$, approximately $\mathfrak{N}kT\ln 2$. This is as far as we will carry the argument concerning localized versus extended solutions in the TSDA for the zero-overlap limit.

We now turn to the standard thermal Hartree-Fock approximation, THFA. The first question we ask is whether THFA can possibly give a lower free energy (in the present limits) than the TSDA. The answer is "no," as follows immediately from (3.10) and (2.1).

Next, one should ask if THFA can do as well as TSDA. To discuss this, we first note that the solutions of the TSD equations that we have considered [namely, the set of localized functions $a_{\mathbf{n}\sigma}$ and the set of extended functions $\phi_{\mathbf{k}\sigma}$ of (3.11)] are also solutions of the THF Eqs. (2.13) in the limits under consideration. For (2.13) with $i\neq j$, the reasons are the same as in the TSDA; Eqs. (2.13) for $i=j$ are equations for determining the one-electron energies ε_i, solutions of which necessarily exist, since (a) these are the equations for stationarity of the free energy in THFA with respect to variations of the ε_i with ψ_i fixed, and (b) the free energy is bounded from below. For the extended solutions we have, because of (2.15),

$$F_{\mathrm{THFA}}(\text{ext.})\geqslant F_{\mathrm{TSDA}}(\text{ext.})\,,\qquad(3.26)$$

and therefore, using (3.25), we conclude that the free energy in the THFA corresponding to the extended solutions cannot do as well as the TSDA.[23]

For the localized solutions, the THF Eqs. (2.13) for $i=j$, with $i\rightarrow\mathbf{n}\sigma$, become

$$\bar{h}+U\langle N_{\mathbf{n}-\sigma}\rangle+\sum_{\mathbf{n}'\neq\mathbf{n}}\sum_{\sigma'}U_{\mathbf{nn}'}\langle N_{\mathbf{n}'\sigma'}\rangle\doteq\varepsilon_{\mathbf{n}\sigma}.\qquad(3.27)$$

In the infinite-separation limit, the sum in (3.27) vanishes so that it reads

$$\bar{h}_{\infty}+U\langle N_{\mathbf{n},-\sigma}\rangle\doteq\varepsilon_{\mathbf{n}\sigma}\ \text{(inf.-sep. limit)}\,,\qquad(3.28)$$

where $\bar{h}_{\infty}=-1\,\mathrm{Ry}$. It has been shown elsewhere[8] that the minimum free energy obtainable from solutions of (3.28) is identical to the minimum free energy arising

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[22] An interesting aspect of this appendix is that it is the positive nature of the *exchange* integrals between *extended solutions* that allows the proof of this localization.

[23] In fact, we expect that in the thermodynamic limit the *equality* sign holds in (3.26). This is so partially because the method of Bogoliubov, Zubarev, and Tserkovnikov, Soviet Phys.—Doklady **2**, 535 (1957), when adapted to this problem, gives the equality. However, since the conditions for applicability of the BZT method have not been determined, there could be some doubt about this conclusion. In the special case of the infinite-separation limit, the conclusion can be established convincingly by replacing the factorials in Eq. (A1.7), by their Stirling approximation, and approximating the sum by the maximum term.

from the extended solutions of the THF equations (again in the infinite-separation limit). Thus, using (3.26), we see that $F_{\mathrm{THFA}}(\mathrm{loc.})\geqslant F_{\mathrm{TSDA}}(\mathrm{ext.})$, and therefore (3.25) gives $F_{\mathrm{THFA}}(\mathrm{loc.})>F_{\mathrm{TSDA}}(\mathrm{loc.})$. Summarizing the results of this paragraph, we have

$$\min F_{\mathrm{THFA}}>\min F_{\mathrm{TSDA}}\quad(\text{inf.-sep. limit})\,,\tag{3.29}$$

where $\min F$ means the minimum of F over all of the solutions considered here.[24]

For the zero-overlap limit, let us first assume in (3.27) that $\sum_\sigma\langle N_{\mathbf{n}\sigma}\rangle$ is independent of site **n** (which is equivalent to assuming that the thermal average charge density has the lattice periodicity). Then (3.27) becomes

$$\Big(\bar{h}+\sum_{\mathbf{n}'\neq\mathbf{n}}U_{\mathbf{n}-\mathbf{n}'}\Big)+U\langle N_{\mathbf{n},-\sigma}\rangle=\varepsilon_{\mathbf{n}\sigma}\,,\tag{3.30}$$

which is of the same form as (3.28). In fact,

$$\bar{h}+\sum_{\mathbf{n}'\neq\mathbf{n}}U_{\mathbf{n}\mathbf{n}'}=\bar{h}_\infty-\sum_{\mathbf{n}'\neq\mathbf{n}}\int a_{\mathbf{n}}(\mathbf{r})^2\times\frac{e^2}{|\mathbf{r}-\mathbf{n}'|}d\mathbf{r}+\sum_{\mathbf{n}'\neq\mathbf{n}}U_{\mathbf{n}\mathbf{n}'}\doteq\bar{h}_\infty\,,\tag{3.31}$$

since, to zero order in the overlap,

$$\int a_{\mathbf{n}}^2(r)\frac{e^2}{|\mathbf{r}-\mathbf{n}'|}d\mathbf{r}=\frac{e^2}{|\mathbf{n}-\mathbf{n}'|}=U_{\mathbf{n}\mathbf{n}'}\,.\tag{3.32}$$

In other words, for localized solutions in which the charge density has the lattice periodicity, the THF equations in the zero-overlap limit are identical to those in the infinite-separation limit. Similarly, it can be seen straightforwardly that the free energy in the case defined by {THFA, infinite-separation limit, localized solutions, periodic total charge density} is identical to that defined by {THFA, zero-overlap limit, localized solutions, periodic total charge density}. Thus, using the arguments of the preceding paragraph concerning the infinite-separation limit, we finally conclude that for $T\neq0$,

$$\min F_{\mathrm{THFA}}>\min F_{\mathrm{TSDA}}\,,\quad(\text{zero-overlap limit})\tag{3.33}$$

for all solutions considered here, with the proviso that the one-electron energies in the localized solutions (for THFA) correspond to charge densities that have the lattice periodicity.

Concerning this proviso, we add the comment that we feel intuitively that nonperiodic charge densities cannot at $T\neq0$ give a free energy in the THFA that equals $F_{\mathrm{TSDA}}(\mathrm{loc.})(=F_{\mathrm{exact}})$. This feeling is based partly on the fact that in any minimum-energy determinant the charge density must be periodic (we showed earlier in this section that $N_{\mathbf{n}\uparrow}+N_{\mathbf{n}\downarrow}=1$ all **n** is necessary and sufficient for a Slater determinant to have minimum energy). Further, we see no tendency for nonperiodic charge density solutions (if they exist in the present zero-overlap limit) to give a zero-point entropy in THFA (any more than nonperiodic spin densities have such a tendency—they definitely do *not* give a zero-point entropy in THFA[7,8] when the charge density is periodic). And of course the zero-point entropy $S_0\equiv\mathfrak{N}k\ln2$ is needed to achieve the lowering $-TS_0$ in the free energy at low T. Although this discussion does not constitute a proof, we will not pursue this question further here.

B. Case of Small Overlap

In this section we examine the possibility of finding localized solutions to the TSD and THF equations in the case of large but finite separation between the atoms, so that there is a small overlap between the atomic electron wave functions $a_{\mathbf{n}\sigma}$.

Specifically, we treat the largest overlap integral s [see Eq. (3.2)] as a small quantity and seek solutions of the TSD Eqs. (2.7) and THF Eqs. (2.13) of the form

$$\begin{aligned}\psi_{\mathbf{n}\sigma}&=a_{\mathbf{n}\sigma}+\sum_{\mathbf{n}'\sigma'}\eta_{\mathbf{n}\sigma,\mathbf{n}'\sigma'}a_{\mathbf{n}'\sigma'}\\&=\sum_{\mathbf{n}'\sigma'}(1+\eta)_{\mathbf{n}\sigma,\mathbf{n}'\sigma'}a_{\mathbf{n}'\sigma'}\,,\end{aligned}\tag{3.34}$$

where the coefficients $\eta_{\mathbf{n}\sigma,\mathbf{n}'\sigma'}$ are small (they turn out to be of first order in the small parameter s).

Note that now that the separation between the nuclei is large but finite, the atomic functions $a_{\mathbf{n}\sigma}$ in (3.34) are not orthonormal. Instead, we have

$$\begin{aligned}(a_{\mathbf{n}\sigma}|a_{\mathbf{n}'\sigma'})&=(1+S)_{\mathbf{n}\sigma,\mathbf{n}'\sigma'}\\&=\delta_{\sigma\sigma'}(\delta_{\mathbf{n}\mathbf{n}'}+s_{\mathbf{n}\mathbf{n}'})\,,\end{aligned}\tag{3.35}$$

where

$$\begin{aligned}s_{\mathbf{n}\mathbf{n}'}=s_{\mathbf{n}\mathbf{n}'}^*=s_{\mathbf{n}'\mathbf{n}}&=0 &&\mathbf{n}'=\mathbf{n}\\&=(a_{\mathbf{n}}|a_{\mathbf{n}'})=O(s)\,, &&\mathbf{n}'\neq\mathbf{n}.\end{aligned}\tag{3.36}$$

In order that the $\psi_{\mathbf{n}\sigma}$ as given by (3.34) be orthonormal, the matrices η and S must satisfy the relation

$$(1+\eta^*)(1+S)(1+\tilde{\eta})=1\,,\tag{3.37}$$

where $\tilde{\eta}$ is the transpose of η. To first order in s this gives, if we note that the matrix S is real,

$$\eta+\eta^\dagger=-S\,.\tag{3.38}$$

Thus, the Hermitian part of η is determined by the overlap matrix S. Denoting the anti-Hermitian part of η by $-P$, i.e., setting

$$\eta^\dagger-\eta=P\tag{3.39}$$

with

$$P^\dagger=-P\,,\tag{3.40}$$

we have

$$\eta=-\tfrac{1}{2}(S+P)\,.\tag{3.41}$$

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[24] Equation (3.29) illustrates the failure of the THFA discussed in Refs. 7 and 8.

It is convenient to note that the functions

$$\bar{\psi}_{\mathbf{n}\sigma}\equiv\bar{\psi}_{\mathbf{n}}\alpha_\sigma$$
$$\equiv\sum_{\mathbf{n}'}(\delta_{\mathbf{n}\mathbf{n}'}-\tfrac{1}{2}s_{\mathbf{n}\mathbf{n}'})a_{\mathbf{n}'}\alpha_\sigma \tag{3.42}$$

are orthonormal to first order, as is evident from (3.34) and (3.38) In terms of these functions, we can write (3.34) in the form

$$\psi_{\mathbf{n}\sigma}=\bar{\psi}_{\mathbf{n}\sigma}-\tfrac{1}{2}\sum_{\mathbf{n}'\sigma'}P_{\mathbf{n}\sigma,\mathbf{n}'\sigma'}a_{\mathbf{n}'\sigma'}\,. \tag{3.43}$$

We must now determine, up to order s, the matrix P so that $\psi_{\mathbf{n}\sigma}$ of (3.43) be solutions of the TSD Eqs. (2.7), and alternatively, of the THF Eqs. (2.13). It is useful for this purpose to introduce an operator $\mathfrak{F}\{\psi_l\}$ such that its matrix elements between any two one-electron states ϕ_κ, ϕ_λ is

$$(\phi_\kappa|\mathfrak{F}\{\psi_l\}|\phi_\lambda)\equiv(\phi_\kappa|h|\phi_\lambda)+\sum_l(\phi_\kappa\psi_l|\hat{v}|\phi_\lambda\psi_l)N_l, \tag{3.44}$$

where the matrix elements of v are defined by (2.8). Note that this one-electron operator $\mathfrak{F}\{\psi_l\}$, which depends on a set of states ψ_l, is also an operator in the Fock space of the system, as it involves the occupation-number operators N_l. In terms of this operator, the TSD Eqs. (2.7) can be written as

$$\langle(N_i-N_j)(\psi_i|\mathfrak{F}\{\psi_l\}|\psi_j)\rangle=0, \tag{3.45}$$

where the angular brackets denote the average over the TSDA density operator. Similarly, the THF Eqs. (2.13) can be written as

$$\langle(\psi_i|\mathfrak{F}\{\psi_l\}|\psi_j)\rangle=\varepsilon_i\delta_{ij}, \tag{3.46}$$

where now the angular brackets denote the average over the THFA density operator.

For the wave functions $\psi_{\mathbf{n}\sigma}$ given by (3.43), we have to first order in s, if we denote the quantum numbers $(n\sigma)$ collectively by ν,

$$(\psi_\nu|\mathfrak{F}\{\psi_\lambda\}|\psi_{\nu'})=(\bar{\psi}_\nu|\mathfrak{F}\{\psi_\lambda\}|\bar{\psi}_{\nu'})$$
$$+\tfrac{1}{2}\sum_{\nu''}[P_{\nu''\nu}(a_{\nu''}|\mathfrak{F}\{a_\lambda\}|a_{\nu'})$$
$$-P_{\nu'\nu''}(a_\nu|\mathfrak{F}\{a_\lambda\}|a_{\nu''})], \tag{3.47}$$

where we have used (3.40). Now, however, it is easy to see from (3.44) and (3.2) that

$$(a_\nu|\mathfrak{F}\{a_\lambda\}|a_\nu{}')=e_\nu\delta_{\nu\nu'}+O(s)$$
$$\equiv[\bar{h}+\sum_{\nu''}N_{\nu''}U_{\nu\nu'}$$
$$\times(1-\delta_{\nu\nu''})]\delta_{\nu\nu'}+O(s), \tag{3.48}$$

where $\bar{h}=h_{\nu\nu}=h_{\mathbf{n}\mathbf{n}}$ is the average value of the one-electron operator h for an electron in the state $a_\nu=a_{\mathbf{n}\sigma}$ given by (3.3); $U_{\nu\nu'}=U_{\mathbf{n}\mathbf{n}'}$ is the Coulomb interaction energy of two electrons in the states $a_{\mathbf{n}}$ and $a_{\mathbf{n}'}$ in the zero-overlap limit, as given by (3.5); and N_ν denotes the occupation-number operator for the state a_ν. Note that e_ν in (3.48) is an operator in the Fock space of the system such that its average value over the THFA density operator in the zero-overlap limit is equal to the THF energy eigenvalue ε_ν given by (3.27). Also from (3.43) and (2.8) we note that, up to order s, we have

$$\sum_\lambda N_\lambda(\bar{\psi}_\nu\psi_\nu|\hat{v}|\bar{\psi}_{\nu'}\psi_\lambda)=\sum_\lambda N_\lambda(\bar{\psi}_\nu\bar{\psi}_\lambda|\hat{v}|\bar{\psi}_{\nu'}\bar{\psi}_\lambda)$$
$$-\tfrac{1}{2}(N_\nu-N_{\nu'})U_{\nu\nu'}P_{\nu'\nu}, \tag{3.49}$$

where we have made use of the anti-Hermitian character of P given by (3.40). Thus we have, up to order s,

$$(\bar{\psi}_\nu|\mathfrak{F}\{\psi_\lambda\}|\bar{\psi}_{\nu'})=(\bar{\psi}_\nu|\mathfrak{F}\{\bar{\psi}_\lambda\}|\bar{\psi}_{\nu'})$$
$$-\tfrac{1}{2}(N_\nu-N_{\nu'})U_{\nu\nu'}P_{\nu'\nu}. \tag{3.50}$$

Combining now (3.47), (3.48), and (3.50), we have, up to order s,

$$(\psi_\nu|\mathfrak{F}\{\psi_\lambda\}|\psi_{\nu'})=(\bar{\psi}_\nu|\mathfrak{F}\{\bar{\psi}_\lambda\}|\bar{\psi}_{\nu'})$$
$$-\tfrac{1}{2}[e_\nu-e_{\nu'}+(N_\nu-N_{\nu'})U_{\nu\nu'}]P_{\nu'\nu}. \tag{3.51}$$

We finally note that $(\bar{\psi}_\nu|\mathfrak{F}\{\bar{\psi}_\lambda\}|\bar{\psi}_{\nu'})$ is to be kept up to order s and that, according to (3.48), the part of order s^0 vanishes for $\nu'\neq\nu$. Furthermore, this first term of (3.51) is diagonal in the spin indices σ, σ', due to the fact that the states $\bar{\psi}_\nu=\bar{\psi}_{\mathbf{n}\sigma}$ are definite spin states, according to (3.42).

We can now determine $P_{\nu'\nu}$ so that the one-electron states $\psi_{\mathbf{n}\sigma}$ given by (3.43) are solutions to the TSD Eqs. (3.45). Since the part of (3.51) of order s^0 when multiplied by $(N_\nu-N_{\nu'})$ vanishes, the average $\langle\ \ \rangle$ in (3.45) should be taken over the TSDA density operator for zero overlap; we shall denote this by $\langle\ \ \rangle_0$. We thus obtain from (3.45) and (3.51) for $\nu=\mathbf{n}\sigma\neq\mathbf{n}'\sigma'=\nu'$

$$\tfrac{1}{2}P_{\mathbf{n}'\sigma',\mathbf{n}\sigma}$$
$$=\delta_{\sigma\sigma'}\frac{\langle(N_{\mathbf{n}\sigma}-N_{\mathbf{n}'\sigma})(\bar{\psi}_{\mathbf{n}}|\mathfrak{F}\{\bar{\psi}_\lambda\}|\bar{\psi}_{\mathbf{n}'})\rangle_0}{\langle(N_{\mathbf{n}\sigma}-N_{\mathbf{n}'\sigma})[e_{\mathbf{n}\sigma}-e_{\mathbf{n}'\sigma}+(N_{\mathbf{n}\sigma}-N_{\mathbf{n}'\sigma})U_{\mathbf{n}\mathbf{n}'}]\rangle_0}\,. \tag{3.52}$$

The denominator of (3.52) can be simplified considerably for a Bravais lattice of the sites **n**. This is not, however, important for our argument here, except that it allowed us to show that the denominator is different from zero, so that P of (3.52) has a finite value. In fact, again for a Bravais lattice, one can show that the numerator of (3.52) vanishes. We shall not demonstrate this, however, as the more general proof of the next section will make this point evident. We thus find that, to order s, the wave functions $\bar{\psi}_{\mathbf{n}\sigma}$, as given by (3.42), constitute solutions to the TSD equations. It can easily be seen that these solutions are to order s, particular Wannier functions appropriate to the Bloch states constructed from the atomic orbitals $a_{\mathbf{n}}$. In the next section we show, in fact, that for Bravais lattices, these Wannier states are solutions to the TSD equations for any amount of overlap of the atomic orbitals $a_{\mathbf{n}}$.

Let us now determine $P_{\nu'\nu}$ so that the one-electron states $\psi_{\mathbf{n}\sigma}$ given by (3.43) be solutions to the THF Eqs. (3.46). Again, since the part of (3.48) of order s^0 vanishes for $\nu'\neq\nu$, the average $\langle\ \ \rangle$ in (3.46) should now be taken over the THFA density operator for zero overlap; we shall denote this again by $\langle\ \ \rangle_0$. Recalling then that [see Eq. (3.27)]

$$\langle N_{\mathbf{n}\sigma}\rangle_0=f(\varepsilon_{\mathbf{n}\sigma}) \tag{3.53}$$

$$\varepsilon_{\mathbf{n}\sigma}=\langle e_{\mathbf{n}\sigma}\rangle_0=\bar{h}+U\langle N_{\mathbf{n},-\sigma}\rangle_0+\sum_{\mathbf{n}'\neq\mathbf{n}}U_{\mathbf{n}\mathbf{n}'}\sum_{\sigma'}\langle N_{\mathbf{n}'\sigma'}\rangle_0, \tag{3.54}$$

where $f(\varepsilon)$ is the Fermi-Dirac distribution function, we have

$$\tfrac{1}{2}P_{\mathbf{n}'\sigma',\mathbf{n}\sigma}=\delta_{\sigma\sigma'}\frac{\langle(\bar{\psi}_{\mathbf{n}}|\mathfrak{F}\{\bar{\psi}_\lambda\}|\bar{\psi}_{\mathbf{n}'})\rangle_0}{\varepsilon_{\mathbf{n}\sigma}-\varepsilon_{\mathbf{n}'\sigma}+U_{\mathbf{n}\mathbf{n}'}[f(\varepsilon_{\mathbf{n}\sigma})-f(\varepsilon_{\mathbf{n}'\sigma})]}. \tag{3.55}$$

In order to determine P, we thus need the THF energy eigenvalues $\varepsilon_{\mathbf{n}\sigma}$ for the limit of zero overlap, which are determined from Eqs. (3.53) and (3.54). We shall not attempt to investigate all possible solutions to these equations. Instead, we shall consider only solutions that give rise to a (thermal) average charge density that has the periodicity of the crystal. These are commonly used solutions of the HF equations. (If other solutions exist, they should be checked to see whether they give a free energy lower than the free energy of the solutions we consider here.) We shall show that for such solutions of the THF equations the denominator of (3.55) vanishes, while the numerator for states with the same spin does not, and thus the desired matrix $P_{\mathbf{n}\sigma\mathbf{n}'\sigma}$ does *not* exist. This will then show for the system under consideration that, although in the limit of zero overlap the THF equations do have localized solutions that yield an average charge density with the periodicity of the lattice, nevertheless for small overlap, one cannot find solutions to the THF equations of the perturbation type (3.34) that would also be localized.

In order to prove these statements, we note first that the electronic charge density operator at point $\mathbf{r}$ is, in this limited configuration model, and for zero overlap, $e\sum_{\mathbf{n}}a_{\mathbf{n}}^2(\mathbf{r})\sum_\sigma N_{\mathbf{n}\sigma}$. Thus, in the limit of zero overlap, the thermal average charge density has the periodicity of the lattice if and only if

$$\sum_\sigma\langle N_{\mathbf{n}\sigma}\rangle_0=1, \tag{3.56}$$

i.e., the average number of electrons on a site is the same for all sites, and therefore equal to one for our model. Now Eq. (3.56) and the fact that we have a Bravais lattice show that the last term of (3.54) becomes a constant K, i.e., independent of $\mathbf{n}\sigma$. Thus, for such solutions of the THF equations, the energy eigenvalues $\varepsilon_{\mathbf{n}\sigma}$ are determined from the equations

$$\varepsilon_{\mathbf{n}\sigma}=(\bar{h}+K)+Uf(\varepsilon_{\mathbf{n},-\sigma}). \tag{3.57}$$

Considering the system of Eqs. (3.57) for the same $\mathbf{n}$ and for the two values of the spin $\sigma=\pm1$, we can easily see graphically that there are at most three solutions: $\varepsilon_\sigma^{(1)}$, $\varepsilon_\sigma^{(2)}$, and $\varepsilon_\sigma^{(3)}$. Here $\varepsilon_\sigma^{(1)}\neq\varepsilon_{-\sigma}^{(1)}$, $\varepsilon_\sigma^{(1)}=\varepsilon_{-\sigma}^{(2)}$, and $\varepsilon_\sigma^{(3)}=\varepsilon_{-\sigma}^{(3)}$. It can be shown[8] that solutions (1) and (2) exist only for $kT<U/4\equiv kT^*$, in which case these solutions give the minimum free energy. Thus, for $T>T^*$, the denominator of (3.55) obviously vanishes. For $T<T^*$, the denominator again vanishes for any pair of sites $\mathbf{n}$, $\mathbf{n}'$ such that $\varepsilon_{\mathbf{n}\sigma}=\varepsilon_{\mathbf{n}'\sigma}$; since there are only two possible solutions (corresponding to having the average spin up or down), there necessarily will be some such pairs for $\mathfrak{N}>2$.

Finally, it can be checked that the numerator of (3.55) is in general, different from zero. This concludes the argument and shows that in the THFA, as applied to this single-band model, there are no localized perturbative one-electron orbitals if there is arbitrarily small overlap, at least for the case when the (thermal) average charge density has the periodicity of the crystal.

This result seems to contradict a well-known statement in the literature[25] concerning the solutions of the HF equations for the case of the hydrogen molecule, according to which both extended and localized solutions are possible for finite interatomic separation. The error in the argument cited in Ref. 25 is the neglect of the possibility that the (small) exchange term that exists for parallel spins might remove the degeneracy of the postulated localized solution. For the case of antiparallel spins, the exchange term vanishes, and therefore localized solutions are possible, as Slater[26] has noted. We note, however, that the two localized solutions are degenerate, and therefore, extended functions obtained by a unitary transformation will also be solutions. We would, therefore, expect that physical spin-dependent interactions will remove the degeneracy, allowing only these extended solutions.

IV. CASE OF FINITE OVERLAP

In this section we shall prove that when the H atoms form a simple Bravais lattice, then the TSD Eqs. (2.7), in the single-band model, are satisfied by localized one-electron orbitals, namely some Wannier functions constructed from the atomic orbitals (3.1) [$a(\mathbf{r}-\mathbf{n})$]. Explicitly, these are

$$w(\mathbf{r}-\mathbf{n})=\frac{1}{\sqrt{\mathfrak{N}}}\sum_{\mathbf{k}}\phi_{\mathbf{k}}(\mathbf{r}-\mathbf{n})=\frac{1}{\sqrt{\mathfrak{N}}}\sum_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{n}}\phi_{\mathbf{k}}(\mathbf{r}), \tag{4.1}$$

where $\phi_{\mathbf{k}}(\mathbf{r})$ are the Bloch functions constructed from

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[25] See, e.g., F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Co., New York, 1940), p. 257.

[26] J. C. Slater, Phys. Rev. **82**, 538 (1951).

the atomic orbitals $a(\mathbf{r}-\mathbf{n})$, i.e.,

$$\phi_{\mathrm{k}}(\mathbf{r})=\frac{C_{\mathrm{k}}}{\sqrt{\mathfrak{N}}}\sum_{\mathbf{n}} e^{i\mathbf{k}\cdot\mathbf{n}}a(\mathbf{r}-\mathbf{n}), \tag{4.2}$$

with C_{k} a real normalization constant. It is well known that $w(\mathbf{r}-\mathbf{n})$ is a localized function around $\mathbf{n}$. It is easy to verify that this choice of phases and the reality of $a(\mathbf{r}-\mathbf{n})$ entail the following properties for the Wannier functions:

$$w(\mathbf{r})=w(-\mathbf{r})=w(\mathbf{r})^*, \tag{4.3}$$

which will prove useful later. We shall show that the functions

$$\psi_i\rightarrow\psi_{\mathbf{n}\sigma}=w(\mathbf{r}-\mathbf{n})\alpha_\sigma\equiv w_{\mathbf{n}}(\mathbf{r})\alpha_\sigma \tag{4.4}$$

are solutions of the TSD Eqs. (2.7), by showing that each term of (2.7) is separately equal to zero.

For states $i=(\mathbf{n}\sigma)$ and $j=(\mathbf{n}'\sigma')$ corresponding to different spin states, i.e., for $\sigma'\neq\sigma$, the TSD equations are satisfied, since it is seen immediately that

$$h_{\mathbf{n}\sigma,\mathbf{n}'\sigma'}\propto\hat{v}_{\mathbf{n}\sigma,l;\,\mathbf{n}'\sigma',l}\propto\delta_{\sigma\sigma'}. \tag{4.5}$$

For $\sigma'=\sigma$, however, the argument is more involved. We first prove that for any pair of Wannier functions $w_{\mathbf{n}}(\mathbf{r})$, $w_{\mathbf{n}'}(\mathbf{r})$ we have, dropping the common spin index,

$$\langle N_{\mathbf{n}}\rangle-\langle N_{\mathbf{n}'}\rangle=0. \tag{4.6}$$

[This makes the first term of the TSD Eqs. (2.7) vanish.] In order to prove (4.6), we note that for any correspondence between the states of two complete, orthonormal sets of one-electron orbitals, there exists a similarity transformation that relates the occupation number operators for the corresponding states through a unitary operator $\mathfrak{U}$. Thus, for the correspondence $w_{\mathbf{n}}\leftrightarrow w_{\mathbf{n}'}$ between the Wannier functions $w_{\mathbf{n}}$ and $w_{\mathbf{n}'}$ there exists a unitary operator $\mathfrak{U}$ such that (taking the spin of the two Wannier functions to be the same, and suppressing the common spin index),

$$N_{\mathbf{n}}=\mathfrak{U}N_{\mathbf{n}'}\mathfrak{U}^{-1}. \tag{4.7}$$

Now such a $\mathfrak{U}$ has the property

$$\mathfrak{U}E(\cdots N_{\mathbf{n}'}\cdots)\mathfrak{U}^{-1}=E(\cdots N_{\mathbf{n}}\cdots). \tag{4.8}$$

providing the correspondence $\mathbf{n}\leftrightarrow\mathbf{n}'$ is a symmetry operation of the crystal. To prove this, note that

$$\begin{aligned}\mathfrak{U}E(\cdots N_{\mathbf{n}'}\cdots)\mathfrak{U}^{-1}&=\sum_{\mathbf{n}'}h_{\mathbf{n}'\mathbf{n}'}\mathfrak{U}N_{\mathbf{n}'}\mathfrak{U}^{-1}\\&\quad+\tfrac{1}{2}\sum_{\mathbf{n}'}\sum_{\mathbf{m}'}\hat{v}_{\mathbf{n}'\mathbf{m}',\mathbf{n}'\mathbf{m}'}\mathfrak{U}N_{\mathbf{n}'}N_{\mathbf{m}'}\mathfrak{U}^{-1}\\&=\sum_{\mathbf{n}'}h_{\mathbf{n}'\mathbf{n}'}N_n\\&\quad+\tfrac{1}{2}\sum_{\mathbf{n}'}\sum_{\mathbf{m}'}\hat{v}_{\mathbf{n}'\mathbf{m}',\mathbf{n}'\mathbf{m}'}N_{\mathbf{n}}N_{\mathbf{m}},\end{aligned} \tag{4.9}$$

where $w_{\mathbf{n}}\leftrightarrow w_{\mathbf{n}'}$ and $w_{\mathbf{m}}\leftrightarrow w_{\mathbf{m}'}$ are related through the same correspondence. Taking this correspondence to be $\mathbf{n}'=\mathbf{n}+\mathbf{R}$, where $\mathbf{R}$ is a fixed vector of the Bravais lattice, we find

$$h_{\mathbf{n}'\mathbf{n}'}=h_{\mathbf{n}\mathbf{n}}, \tag{4.10}$$

$$\hat{v}_{\mathbf{n}'\mathbf{m}',\mathbf{n}'\mathbf{m}'}=\hat{v}_{\mathbf{n}\mathbf{m},\mathbf{n}\mathbf{m}}, \tag{4.11}$$

as can easily be checked. Finally, since the set $\{\mathbf{n}'\}$ is identical to the set $\{\mathbf{n}\}$, the primes in the right-hand side of (4.9) can be dropped everywhere. This proves (4.8). From (4.8) it immediately follows that

$$[\rho,\mathfrak{U}]=0, \tag{4.12}$$

where ρ is the density operator (2.5). Equation (4.6) is then easily proved, since

$$\begin{aligned}\langle N_{\mathbf{n}}\rangle&=\mathrm{Tr}\{\rho N_{\mathbf{n}}\}=\mathrm{Tr}\{\rho\mathfrak{U}N_{\mathbf{n}'}\mathfrak{U}^{-1}\}\\&=\mathrm{Tr}\{\mathfrak{U}\rho N_{\mathbf{n}'}\mathfrak{U}^{-1}\}=\mathrm{Tr}\{\rho N_{\mathbf{n}'}\}\\&=\langle N_{\mathbf{n}'}\rangle.\end{aligned}$$

We next prove that, again for any pair of Wannier functions $w_{\mathbf{n}}(\mathbf{r})$, $w_{\mathbf{n}'}(\mathbf{r})$, we have

$$\sum_{\mathbf{m}}\hat{v}_{\mathbf{n}\mathbf{m},\mathbf{n}'\mathbf{m}}\langle(N_{\mathbf{n}}-N_{\mathbf{n}'})N_{\mathbf{m}}\rangle=0. \tag{4.13}$$

To prove this, it is sufficient to show that for every $\mathbf{m}$ there is a corresponding $\mathbf{m}'$ such that the contributions of both $\mathbf{m}$ and $\mathbf{m}'$ to the left-hand side of (4.13) add up to zero. We note that the correspondence between the states $w_{\mathbf{n}}$ and $w_{\mathbf{n}'}$ can be taken to be an inversion through the midpoint 0 of the lattice vector joining $\mathbf{n}$ and $\mathbf{n}'$. Such a point can easily be seen to be a point of inversion symmetry for the Bravais lattice, and thus we may choose $\mathbf{m}'$ to be the inversion $\mathbf{m}$ through 0. It is then easy to show that

$$\hat{v}_{\mathbf{n}\mathbf{m},\mathbf{n}'\mathbf{m}}=\hat{v}_{\mathbf{n}\mathbf{m}',\mathbf{n}'\mathbf{m}'}, \tag{4.14}$$

if we use Eq. (4.3). It is then sufficient to show that

$$\langle(N_{\mathbf{n}}-N_{\mathbf{n}'})(N_{\mathbf{m}}+N_{\mathbf{m}'})\rangle=0, \tag{4.15}$$

where the correspondences $\mathbf{n}\leftrightarrow\mathbf{n}'$ and $\mathbf{m}\leftrightarrow\mathbf{m}'$ are the same, namely, an inversion through the point 0. The operator $\mathfrak{U}$ associated with the correspondence $w_{\mathbf{n}}\leftrightarrow w_{\mathbf{n}'}$ is then such that

$$N_{\mathbf{n}}=\mathfrak{U}N_{\mathbf{n}'}\mathfrak{U}^{-1}\quad\text{and}\quad N_{\mathbf{m}}=\mathfrak{U}N_{\mathbf{m}'}\mathfrak{U}^{-1}, \tag{4.16}$$

while, owing to the inversion character of the correspondence $\mathbf{n}\leftrightarrow\mathbf{n}'$,

$$\mathfrak{U}^{-1}=\mathfrak{U}. \tag{4.17}$$

In addition, it is easy to see, again using (4.3), that for this correspondence the matrix elements of h and v satisfy Eqs. (4.10) and (4.11), and thus $\mathfrak{U}$ commutes with the density matrix operator ρ, i.e., (4.12) is again satisfied. Now if we use (4.16) and (4.12), it is trivial to show that

$$\langle N_{\mathbf{n}}N_{\mathbf{m}}\rangle-\langle N_{\mathbf{n}'}N_{\mathbf{m}'}\rangle=0, \tag{4.18}$$

while

$$\langle N_{\mathbf{n}}N_{\mathbf{m}'}\rangle-\langle N_{\mathbf{n}'}N_{\mathbf{m}}\rangle=0 \tag{4.19}$$

if, in addition, (4.17) is used. Adding (4.18) and (4.19), we obtain the desired relation (4.15), which is sufficient, in conjunction with (4.14), to prove (4.13). This makes the second term of the TSD equations vanish.

Thus, Eqs. (4.13) and (4.6) show that the one-electron states $\psi_{\mathbf{n}\sigma}$ (4.4), with the orbital part given by the localized Wannier functions $w(\mathbf{r}-\mathbf{n})$, are solutions of the TSD Eqs. (2.7), for this single-band model of a system of H atoms arranged on a simple Bravias lattice of arbitrary lattice parameters.

It is worthwhile to point out that the argument presented above is primarily based on symmetry, and thus it can easily be applied to more general models.

Note that the result of this section is in complete agreement with that of the previous section, where the case of small overlap between the atomic orbitals $a_{\mathbf{n}}(\mathbf{r})$ was considered. It is easy to show that, to first order in the overlap parameter s, the Wannier functions $w_{\mathbf{n}}(\mathbf{r})$, Eq. (4.1), are identical to the $\bar{\psi}_{\mathbf{n}}$, Eq. (3.42), of the previous section, which were found to be, to order s, solutions of the TSD equations.

Finally, we observe that the same argument does not apply to the THF Eqs. (2.13). In fact, we have not been able to show whether the localized one-electron states $\psi_{\mathbf{n}\sigma}$, as given by (4.4), are solutions of the THF equations or not, although the perturbative results of the previous section suggest that they are not solutions.

APPENDIX A: PROOF THAT F_{TSDA}(ext.) $>F_{\mathrm{TSDA}}$(loc.) IN INFINITE-SEPARATION LIMIT

Let us first evaluate $F_{\mathrm{TSDA}}(\mathrm{loc.})=F_e$ in the infinite-separation limit. In this limit the Hamiltonian is given by Eq. (3.22), and the partition function is easily found to be

$$Z_e=\{1+2e^{-\beta(\bar{h}-\mu)}+e^{-\beta[2(\bar{h}-\mu)+U]}\}^{\mathfrak{N}}. \qquad \text{(A1)}$$

The chemical potential μ is determined from the condition

$$\mathfrak{N}=\langle N\rangle=(1/\beta)(\partial/\partial\mu)\ln Z_e(\beta,\mu), \qquad \text{(A2)}$$

which gives, in conjunction with (A1),

$$\mu=\bar{h}+\tfrac{1}{2}U. \qquad \text{(A3)}$$

With this value of the chemical potential, the partition function Z_e becomes

$$Z_e=2^{\mathfrak{N}}(1+e^x)^{\mathfrak{N}}, \qquad \text{(A4)}$$

where

$$x=\tfrac{1}{2}\beta U, \qquad \text{(A5)}$$

and the corresponding free energy is

$$F_e=F_{\mathrm{TSDA}}(\mathrm{loc.})=-kT\mathfrak{N}\ln 2(1+e^x). \qquad \text{(A6)}$$

For the case of the extended solutions in the TSDA, the Hamiltonian in the infinite-separation limit is given by Eq. (3.21), and thus the partition function for the exact value (A3) of the chemical potential is

$$\mathfrak{Z}\equiv Z_{\mathrm{TSDA}}(\mathrm{ext.})=\mathrm{Tr}e^{\beta U[(1/2)(N\uparrow+N\downarrow)-(1/\mathfrak{N})(N\uparrow N\downarrow)]}$$
$$=\sum_{n\uparrow=0}^{\mathfrak{N}}\sum_{n\downarrow=0}^{\mathfrak{N}}e^{\beta U[(1/2)(n\uparrow+n\downarrow)-(1/\mathfrak{N})(n\uparrow n\downarrow)]}\binom{\mathfrak{N}}{n_\uparrow}\binom{\mathfrak{N}}{n_\downarrow}, \qquad \text{(A7)}$$

where $\binom{\mathfrak{N}}{n}=\mathfrak{N}!/n!(\mathfrak{N}-n)!$. Doing one of the sums, we find

$$\mathfrak{Z}=2^{\mathfrak{N}}e^{\mathfrak{N}x/2}\sum_{n=0}^{\mathfrak{N}}\binom{\mathfrak{N}}{n}\left[\cosh\frac{x}{\mathfrak{N}}(n-\tfrac{1}{2}\mathfrak{N})\right]^{\mathfrak{N}}. \qquad \text{(A8)}$$

Considering $\mathfrak{N}$ to be even for convenience, we can write

$$\mathfrak{Z}=(2e^{x/2})^{\mathfrak{N}}S_{\mathfrak{N}}(x), \qquad \text{(A9)}$$

where

$$S_{\mathfrak{N}}(x)\equiv\sum_{l=-\frac{1}{2}\mathfrak{N}}^{\frac{1}{2}\mathfrak{N}}a_l, \qquad \text{(A10)}$$

with

$$a_l\equiv\binom{\mathfrak{N}}{\frac{1}{2}\mathfrak{N}+l}\left(\cosh\frac{xl}{\mathfrak{N}}\right)^{\mathfrak{N}}=a_{-l}. \qquad \text{(A11)}$$

To investigate the summand a_l, consider

$$g_l\equiv\frac{a_{l+1}}{a_l}=\left[\frac{\cosh(x/\mathfrak{N})(l+1)}{\cosh(xl/\mathfrak{N})}\right]^{\mathfrak{N}}\frac{(\mathfrak{N}/2)-l}{(\mathfrak{N}/2)+l+1}$$
$$=\left(\cosh\frac{x}{\mathfrak{N}}\right)^{\mathfrak{N}}\left(1+\tanh\frac{xl}{\mathfrak{N}}\tanh\frac{x}{\mathfrak{N}}\right)^{\mathfrak{N}}$$
$$\times\frac{(\mathfrak{N}/2)-l}{(\mathfrak{N}/2)+l+1}. \qquad \text{(A12)}$$

Consider first g_l at the "end point" $l=\frac{1}{2}\mathfrak{N}-1$,

$$g_{(\mathfrak{N}/2)-1}=\frac{1}{\mathfrak{N}[\cosh(x/\mathfrak{N})]^{\mathfrak{N}}[1-\tanh\frac{1}{2}x\tanh(x/\mathfrak{N}])^{\mathfrak{N}}}, \qquad \text{(A13)}$$

and then at the "central point" $l=0$,

$$g_0=\frac{a_1}{a_0}=e^{\mathfrak{N}\ln\cosh(x/\mathfrak{N})-\ln[1+(2/\mathfrak{N})]}. \qquad \text{(A14)}$$

The orders of magnitude that we are interested in are $U\sim 10$ eV and $T\lesssim 300$°K, so that $x\gtrsim 200$. We also want $\mathfrak{N}\approx 10^{23}\cong e^{53}$. Then, clearly,

$$\tanh\tfrac{1}{2}x\sim 1. \qquad \text{(A15)}$$

Also,

$$x/\mathfrak{N}\ll 1 \qquad \text{(A16)}$$

for all except extremely small T; e.g., if $T>0.01$°K, then $x\lesssim 10^7$ and $x/\mathfrak{N}\lesssim 10^{-16}$. For definiteness we shall assume (unless stated otherwise)

$$U\sim 10\ \mathrm{eV},\quad 10^{-2}\,{}^\circ\mathrm{K}<T<300\,{}^\circ\mathrm{K}. \qquad \text{(A17)}$$

A rough idea as to Eq. (A13) is easily obtained for these orders of magnitude by putting $\cosh x/\mathfrak{N}\sim 1+x^2/2\mathfrak{N}^2$, $\tanh(x/2)\sim 1$, and $\tanh x/\mathfrak{N}\sim x/\mathfrak{N}$. Then (A13) gives

$$g_{(\mathfrak{N}/2)-1}\sim \frac{1}{\mathfrak{N}}e^{-\mathfrak{N}\ln[1+(x^2/2\mathfrak{N}^2)]-\mathfrak{N}\ln[1-(x/\mathfrak{N})]}\sim \frac{1}{\mathfrak{N}}e^{x}. \quad \text{(A18)}$$

Hence, for $\mathfrak{N}\sim 10^{23}$ and $T\lesssim 300°\mathrm{K}$, $g_{(\mathfrak{N}/2)-1}\gtrsim e^{147}=10^{63}\gg 1$. Note, however, the enormous sensitivity: If $T=600°\mathrm{K}$, and $\mathfrak{N}=10^{23}$, then $g_{(\mathfrak{N}/2)-1}\sim e^{47}\cong 10^{20}$ (instead of e^{147}). Also note that for $T<300°\mathrm{K}$, $g_{(\mathfrak{N}/2)-1}>1$ for $10^{23}\lesssim\mathfrak{N}\lesssim e^{200}$. Summarizing, we have

$$g_{(\mathfrak{N}/2)-1}>1 \text{ for conditions (A17) and } 10^{23}\lesssim\mathfrak{N}\lesssim e^{200}. \quad \text{(A19)}$$

Similarly, we find

$$g_0\sim e^{(1/2\mathfrak{N})(x^2-4)}>1 \quad \text{(A20)}$$

(with $g_0\cong 1$).

These last two results suggest that a_l increases monotonically with l for $l\geq 0$. In the remainder of this appendix, we shall assume this behavior, the rather lengthy and detailed proof being made available elsewhere.[27] With this assumption, namely,

$$a_l\leq a_{l+1} \quad \text{for} \quad l\geq 0, \quad \text{(A21)}$$

we shall obtain an expression for $\mathfrak{z}$ of the form $\mathfrak{z}_a(1+\epsilon)$, where the approximate value $\mathfrak{z}_a$ is explicit and ϵ is very small, being rigorously bounded from above.

From (A9),

$$\mathfrak{z}=(2e^{x/2})^{\mathfrak{N}}\Big[2(\cosh\tfrac{1}{2}x)^{\mathfrak{N}}+\sum_{l=-[(\mathfrak{N}/2)-1]}^{(\mathfrak{N}/2)-1}a_l\Big];$$

putting

$$\mathfrak{z}_a\equiv 2(1+e^{x})^{\mathfrak{N}}, \quad \text{(A22)}$$

we have

$$\mathfrak{z}-\mathfrak{z}_a=(2e^{x/2})^{\mathfrak{N}}\sum_{l=-(\mathfrak{N}/2)+1}^{(\mathfrak{N}/2)-1}a_l\equiv\mathfrak{z}_a\epsilon. \quad \text{(A23)}$$

Thus, because of (A21),

$$\mathfrak{z}-\mathfrak{z}_a\leqslant(2e^{x/2})^{\mathfrak{N}}(\mathfrak{N}-1)a_{(\mathfrak{N}/2)-1}\equiv\mathfrak{z}_a\bar{\epsilon}, \quad \text{(A24)}$$

where

$$\epsilon\leqslant\bar{\epsilon}\equiv\frac{(\mathfrak{N}-1)a_{(\mathfrak{N}/2)-1}}{2(\cosh\frac{1}{2}x)^{\mathfrak{N}}}=\frac{(\mathfrak{N}-1)}{2g_{(\mathfrak{N}/2)-1}}, \quad \text{(A25)}$$

the last equality following from (A11). From (A13) we have

$$\epsilon\leqslant\bar{\epsilon}=\tfrac{1}{2}\mathfrak{N}(\mathfrak{N}-1)[\cosh(x/\mathfrak{N})]^{\mathfrak{N}} \times[1-\tanh(x/2)\tanh(x/\mathfrak{N})]^{\mathfrak{N}}. \quad \text{(A26)}$$

But for $0\leq y<1$,

$$(1-y)^{\mathfrak{N}}=\exp[\mathfrak{N}(-y-\tfrac{1}{2}y^2-\tfrac{1}{3}y^3-\cdots)]\leqslant\exp(-\mathfrak{N}y).$$

Also,

$$\tanh\alpha\geqslant\alpha-(\alpha^3/3) \quad \text{for} \quad \alpha\geqslant 0 \quad \text{(A27)}$$

[proof: $g(\alpha)\equiv\tanh\alpha-\alpha+\frac{1}{3}\alpha^3$, so that $g'(\alpha)=\alpha^2-\tanh^2\alpha\geqslant 0$; also, $g(0)=0$]. Thus,

$$\begin{aligned}[1-\tanh(x/\mathfrak{N})\tanh(x/2)]^{\mathfrak{N}} &\leqslant\exp[-\mathfrak{N}\tanh(x/\mathfrak{N})\tanh(x/2)]\\ &\leqslant\exp[-(x-x^3/3\mathfrak{N}^2)\tanh(x/2)]. \quad \text{(A28)}\end{aligned}$$

Using the condition (A17), we see that $x^3/3\mathfrak{N}^2\lesssim 10^{-25}$, and $x/2\gtrsim 100$, so that to an extremely high accuracy, the last upper bound is given by $\exp(-x)$. (In fact, it is bounded by $c_1\exp(-x)$ where c_1 exceeds 1 by much less than 1%.) Further,

$$\cosh\frac{x}{\mathfrak{N}}\leqslant 1+\frac{(x/\mathfrak{N})^2}{2[1-(x/\mathfrak{N})^2]}\leqslant 1+\frac{1.001}{2}\Big(\frac{x}{\mathfrak{N}}\Big)^2,$$

so that

$$\Big(\cosh\frac{x}{\mathfrak{N}}\Big)^{\mathfrak{N}}\leqslant e^{\mathfrak{N}\ln[1+(1.001/2)(x/\mathfrak{N})^2]} \leqslant e^{(1.001/2)(x^2/\mathfrak{N})}<c_2, \quad \text{(A29)}$$

where c_2 exceeds 1 by $\ll 1\%$. Thus, using (A29) and (A28) in (A26), we finally have

$$\epsilon\leqslant\bar{\epsilon}\leqslant\tfrac{1}{2}c\mathfrak{N}^2e^{-x}\equiv c\hat{\epsilon}, \quad \text{(A30)}$$

where c exceeds 1 by $\ll 1\%$. This is the upper bound we have sought. Since $x>200$

$$\hat{\epsilon}\lesssim\tfrac{1}{2}\mathfrak{N}^2e^{-200} \quad \text{(A31)}$$

and therefore $\hat{\epsilon}\lesssim e^{-94}$ for $\mathfrak{N}\cong 10^{23}$.

We also must know that $\hat{\epsilon}$ is so small as to be experimentally "unobservable" over the experimentally accessible range of $\mathfrak{N}$. Clearly, $\mathfrak{N}$ can increase enormously and still have the right-hand side of (A31) be very small (e.g., the latter is $\sim e^{-10}$ when $\mathfrak{N}\sim 10^{41}$). On decreasing $\mathfrak{N}$ from 10^{23} we must check that $x/\mathfrak{N}\ll 1$ and $x^2/\mathfrak{N}\ll 1$ in order that c remain of order 1. But a reduction in $\mathfrak{N}$ by six orders of magnitude increases $x/\mathfrak{N}$ only to 10^{-10} so that for the conditions (A17), $x^2/\mathfrak{N}<10^{-3}$, which is still comfortably small.

The free energy for the extended solutions in the TSDA is

$$\begin{aligned}F_{\mathrm{TSDA}}(\text{ext.})&=-kT\ln\mathfrak{z}=-kT\ln\mathfrak{z}_a(1+\epsilon)\\ &=-kT\ln[2(1+e^{x})^{\mathfrak{N}}(1+\epsilon)], \quad \text{(A32)}\end{aligned}$$

where ϵ is bounded from above by a very small number, $c\hat{\epsilon}$, for $T<300°\mathrm{K}$ and $\mathfrak{N}\lesssim 10^{41}$. Comparison of (A32) with (A6) yields

$$F_{\mathrm{TSDA}}(\text{ext.})-F_e=\mathfrak{N}kT\ln 2-kT\ln 2(1+\epsilon), \quad \text{(A33)}$$

a clearly macroscopic, positive quantity, since $0\leqslant\epsilon\leqslant 1$.

Finally, we remark on the rather unconventional but physically correct considerations of this section. In the usual approach, one considers only the limit $\mathfrak{N}\to\infty$, with the expectation that there will be no observable difference between thermodynamic quantities calculated in this limit and those calculated with $\mathfrak{N}\sim 10^{23}$. In fact,

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[27] T. A. Kaplan and P. N. Argyres, Lincoln Laboratory Technical Report, M.I.T. (unpublished).

we believe this to be the case here as well. However, at least in the intermediate theoretical stages, there is a qualitative difference in the behavior of a_l, as seen from (A18), (A19) (in the limit the maximum occurs for l different from the end points $\pm\mathfrak{N}/2$, in contrast to the behavior for physical $\mathfrak{N}$ and T).

APPENDIX B: GROUND STATES OF H AND E_{TSDA}(ext.) IN ZERO-OVERLAP LIMIT

In the limit of zero overlap, the exact model Hamiltonian H is given by (3.6). We are interested here in its ground state for the total number of electrons fixed at the number of sites

$$\sum_{\mathbf{n}\sigma} N_{\mathbf{n}\sigma}=\mathfrak{N}. \tag{B1}$$

Then we can write (3.6) as

$$H=\mathfrak{N}\bar{h}+U\sum_{\mathbf{n}}(N_{\mathbf{n}}^2-N_{\mathbf{n}})+\tfrac{1}{2}\sum_{\mathbf{nm}}{}' U_{\mathbf{nm}}N_{\mathbf{n}}N_{\mathbf{m}}+C, \tag{B2}$$

where

$$N_{\mathbf{n}}\equiv N_{\mathbf{n}\uparrow}+N_{\mathbf{n}\downarrow}. \tag{B3}$$

The constraints on the N_n are given by

$$\sum N_{\mathbf{n}}=\mathfrak{N} \tag{B4}$$

and

$$N_{\mathbf{n}}=0,\ 1,\ \text{or}\ \ 2. \tag{B5}$$

With

$$N_{\mathbf{n}}=S_{\mathbf{n}}+1, \tag{B6}$$

(B4) gives

$$\sum S_{\mathbf{n}}=0 \tag{B7}$$

and (B5) becomes

$$S_{\mathbf{n}}=0,\ \pm1; \tag{B8}$$

further, (B2) is, conveniently,

$$H=\tfrac{1}{2}\sum U_{\mathbf{nm}}S_{\mathbf{n}}S_{\mathbf{m}}+E_0, \tag{B9}$$

where $E_0=-\mathfrak{N}\,\text{Ry}$, the ground-state energy of $\mathfrak{N}$ isolated hydrogen atoms.[28]

Going to the Fourier representation

$$S_{\mathbf{n}}=\frac{1}{\sqrt{\mathfrak{N}}}\sum_{\mathbf{k}} e^{(i\mathbf{k}\cdot\mathbf{n})}\sigma_{\mathbf{k}}, \tag{B10}$$

using $U_{\mathbf{nm}}=U_{\mathbf{n}-\mathbf{m}}$ plus the periodic boundary conditions, we can write (B9) as

$$H=\tfrac{1}{2}\sum_{\mathbf{k}} U(\mathbf{k})|\sigma_{\mathbf{k}}|^2+E_0, \tag{B11}$$

where $U(\mathbf{k})$ is given by (3.15). In the zero-overlap limit, (3.15) may also be written in the more familiar form

$$U(\mathbf{k}-\mathbf{k}')=\mathfrak{N}\int d\mathbf{r}d\mathbf{r}'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_{\mathbf{k}}^*(\mathbf{r})\times\phi_{\mathbf{k}'}^*(\mathbf{r}')\phi_{\mathbf{k}'}(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r}'), \tag{B12}$$

the exchange integral between the usual spatial Bloch functions

$$\phi_{\mathbf{k}}(\mathbf{r})=\mathfrak{N}^{-1/2}\sum_{\mathbf{n}}\exp(i\mathbf{k}\cdot\mathbf{n})a(\mathbf{r}-\mathbf{n}).$$

Because of (B12), we have

$$U(\mathbf{k})\geqslant 0. \tag{B13}$$

Hence, from (B11) and (B13),

$$H\geqslant E_0, \tag{B14}$$

with the minimum value attained when

$$\sigma_{\mathbf{k}}=0,\quad \text{all } \mathbf{k}. \tag{B15}$$

Thus the minimum of H occurs when $S_{\mathbf{n}}=0$, i.e., when

$$N_{\mathbf{n}}=1,\quad \text{all } \mathbf{n}. \tag{B16}$$

This is the desired result, namely that, neglecting the overlap of atomic orbitals, the minimum energy of H occurs for those states ($2^{\mathfrak{N}}$ of them) in which there is one electron at each site, even when (long-range) Coulomb interactions are included.

We now wish to show that the minimum value of E_{TSDA}(ext.), Eq. (3.16), for $N=\mathfrak{N}$ occurs for $n_{\mathbf{k}\uparrow}=1$, $n_{\mathbf{k}\downarrow}=0$, all $\mathbf{k}$. Writing

$$n_{\mathbf{k}\sigma}=\tfrac{1}{2}(1+s_{\mathbf{k}\sigma}), \tag{B17}$$

we see that $\sum_{\mathbf{k}\sigma} n_{\mathbf{k}\sigma}=\mathfrak{N}$ gives

$$\textstyle\sum_{\mathbf{k}\sigma} s_{\mathbf{k}\sigma}=0, \tag{B18}$$

and that $n_{\mathbf{k}\sigma}=0$, 1 means

$$s_{\mathbf{k}\sigma}=\pm1. \tag{B19}$$

Putting (B17) into (3.16) and using (B18) plus the remark in Ref. 28 gives, in the zero-overlap limit,

$$\begin{aligned}E_{\text{TSDA}}(\text{ext.})&=E_0+\tfrac{1}{4}\mathfrak{N}U-\frac{1}{8\mathfrak{N}}\sum_{\mathbf{kk}'\sigma}U(\mathbf{k}-\mathbf{k}')s_{\mathbf{k}\sigma}s_{\mathbf{k}'\sigma}\\&\equiv E_0+\tfrac{1}{4}\mathfrak{N}U-\tfrac{1}{8}Q.\end{aligned} \tag{B20}$$

Thus our problem is to find the maximum of

$$Q=\frac{1}{\mathfrak{N}}\sum_{\mathbf{kk}'\sigma}U(\mathbf{k}-\mathbf{k}')s_{\mathbf{k}\sigma}s_{\mathbf{k}'\sigma} \tag{B21}$$

subject to the constraints

$$s_{\mathbf{k}\sigma}{}^2=1 \tag{B22}$$

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[28] Putting (B6) into (B2) and using (B7) and (B9) yields

$$\begin{aligned}E_0=\mathfrak{N}\bar{h}+C+\tfrac{1}{2}\mathfrak{N}\textstyle\sum' U_{\mathbf{nm}}&=\mathfrak{N}(a_{\mathbf{n}}|p^2/2m-e^2/|\mathbf{r}-\mathbf{n}|\,|a_{\mathbf{n}})\\&\quad-\mathfrak{N}\textstyle\sum'(a_{\mathbf{n}}|e^2/|\mathbf{r}-\mathbf{m}|\,|a_{\mathbf{n}})+(\mathfrak{N}/2)\sum' U_{\mathbf{nm}}\\&\quad+(\mathfrak{N}/2)\textstyle\sum' e^2/|\mathbf{n}-\mathbf{m}|.\end{aligned}$$

In the zero-overlap limit, the last three terms cancel exactly, and thus $E_0=\mathfrak{N}\bar{h}_\infty$.

and

$$\sum_{\mathbf{k}\sigma} s_{\mathbf{k}\sigma}=0. \tag{B23}$$

Clearly,

$$Q\leqslant \frac{1}{\mathfrak{N}}\sum_{\mathbf{kk}'\sigma}\ \operatorname*{Max}_{s_{\mathbf{k}\sigma},s_{\mathbf{k}'\sigma}}\ U(\mathbf{k}-\mathbf{k}')s_{\mathbf{k}\sigma}s_{\mathbf{k}'\sigma}, \tag{B24}$$

where the maximum is taken subject to (B22), but ignoring (B23). Thus,

$$Q\leqslant \frac{1}{\mathfrak{N}}\sum_{\mathbf{kk}'\sigma} U(\mathbf{k}-\mathbf{k}'), \tag{B25}$$

the last step following the fact that $U(\mathbf{k})\geqslant 0$. Furthermore, the upper bound (B25) on Q *is reached* by a set of $s_{\mathbf{k}\sigma}$, which satisfy all the constraints, namely,

$$s_{\mathbf{k}\uparrow}=1,\quad s_{\mathbf{k}\downarrow}=-1,\quad \text{all } \mathbf{k}. \tag{B26}$$

It now follows that the maximum of Q, $Q_{\max}$, subject to the constraints (B22) *and* (B23), is

$$Q_{\max}=2\mathfrak{N}^{-1}\sum_{\mathbf{kk}'} U(\mathbf{k}-\mathbf{k}')=2\mathfrak{N}U, \tag{B27}$$

and this is reached when, corresponding to (B26),

$$n_{\mathbf{k}\uparrow}=1 \quad\text{and}\quad n_{\mathbf{k}\downarrow}=0. \tag{B28}$$

Thus, putting (B27) into (B20), we see that the ground-state energy of the approximate Hamiltonian in TSDA for the extended solutions is

$$[E_{\mathrm{TSDA}}(\text{ext.})]_{\min}=E_0, \tag{B29}$$

the same as the ground-state energy of H, and a ground state is $|n_{\mathbf{k}\uparrow}=1,\ n_{\mathbf{k}\downarrow}=0,\ \text{all }\mathbf{k})\equiv|0)$. We note that it *was necessary* to transform the $n_{\mathbf{k}\sigma}$ to the $s_{\mathbf{k}\sigma}$ in order to have applied successfully the approach embodied in (B24). The same approach applied directly to the sum in (3.16) would give

$$\begin{aligned}\sum U(\mathbf{k}-\mathbf{k}')n_{\mathbf{k}\sigma}n_{\mathbf{k}'\sigma}\leqslant \sum \max[U(\mathbf{k}-\mathbf{k}')n_{\mathbf{k}\sigma}n_{\mathbf{k}'\sigma}]&\\ =2\sum U(\mathbf{k}-\mathbf{k}')&;\end{aligned}$$

but the last expression is reached only when $n_{\mathbf{k}\uparrow}=n_{\mathbf{k}\downarrow}=1$, all $\mathbf{k}$, which *violates* the constraint $\sum_{\mathbf{k}\sigma} n_{\mathbf{k}\sigma}=\mathfrak{N}$ and thus does not allow one to draw the desired conclusion (B27) plus the surrounding sentence.

APPENDIX C: EXISTENCE OF AN ENERGY GAP FOR E_{TSDA}(ext.) IN ZERO-OVERLAP LIMIT

We consider here the approximate Hamiltonian E_{TSDA}(ext.), Eq. (3.16), in the basis of its eigenstates, so that the $n_{\mathbf{k}\sigma}$ are 0 or 1, this being equivalent to (B20), with the $s_{\mathbf{k}\sigma}$ being -1 or 1. We shall show that there are exactly two eigenstates with the minimum energy, and that there is a finite gap between this and the next higher energy even in the limit $\mathfrak{N}\to\infty$.

In terms of the Fourier transform $x_{\mathbf{n}\sigma}$ of $s_{\mathbf{k}\sigma}$,

$$s_{\mathbf{k}\sigma}=\frac{1}{\sqrt{\mathfrak{N}}}\sum_{\mathbf{n}} e^{-i\mathbf{k}\cdot\mathbf{n}}x_{\mathbf{n}\sigma}, \tag{C1}$$

(B21) becomes

$$Q=\sum_{\mathbf{n}\sigma} |x_{\mathbf{n}\sigma}|^2 U_{\mathbf{0n}}. \tag{C2}$$

Note that $\sum_{\mathbf{k}} s_{\mathbf{k}\sigma}{}^2=\mathfrak{N}$ is equivalent to

$$\sum_{\mathbf{n}}|x_{\mathbf{n}\sigma}|^2=\mathfrak{N}, \tag{C3}$$

defining two "spheres," $\mathcal{S}_\sigma$, one in the space of variables $x_{1\uparrow}$, $x_{2\uparrow}$, …, the other in space $x_{1\downarrow}$, $x_{2\downarrow}$, …, such that any point satisfying (B22) must lie on the appropriate one of these spheres. Putting

$$Q_\sigma=\sum_{\mathbf{n}} |x_{\mathbf{n}\sigma}|^2 U_{\mathbf{0n}}, \tag{C4}$$

we see that

$$Q_\sigma\leqslant U\sum_{\mathbf{n}} |x_{\mathbf{n}\sigma}|^2$$

($U\geqslant U_{\mathbf{0n}}$). Hence,

$$\max_{P_\sigma\epsilon\mathcal{S}_\sigma} Q_\sigma=\mathfrak{N}U\equiv Q_{\sigma 0}, \tag{C5}$$

where the maximum is over all points $P_\sigma\equiv(x_{1\sigma},x_{2\sigma},\ldots)$ lying on $\mathcal{S}_\sigma$. Thus the maximum of $Q=Q_\uparrow+Q_\downarrow$ over all pairs $P_\uparrow$, $P_\downarrow$ such that $P_\uparrow\epsilon\mathcal{S}_\uparrow$ and $P_\downarrow\epsilon\mathcal{S}_\downarrow$ is $2\mathfrak{N}U$. Noting that this value is attained by a set of $x_{n\sigma}$ such that (B22) and (B23) are satisfied (namely, $x_{\mathbf{0}\uparrow}=\sqrt{\mathfrak{N}}=-x_{\mathbf{0}\downarrow}$, $x_{\mathbf{n}\sigma}=0$ all $\mathbf{n}\neq 0$), we have an alternate to the proof already given (Appendix B) that this state gives the minimum energy of E_{TSDA}(ext.) [see Eq. (B27)]. Now, however, we can go further and say something about the next highest value of E_{TSDA}(ext.).

Consider the constraint C:

$$\sum_{\mathbf{n}\neq\mathbf{0}} |x_{\mathbf{n}\sigma}|^2=c,\quad |x_{\mathbf{0}\sigma}|^2=\mathfrak{N}-c, \tag{C6}$$

with, of course, $0\leqslant c\leqslant\mathfrak{N}$. Clearly, any point satisfying (C6) will lie on the "sphere" $\mathcal{S}_\sigma$ [i.e., will satisfy (C3)]. Further, for any point satisfying (C6), we have

$$\begin{aligned}Q_\sigma&=(\mathfrak{N}-c)U+\sum_{\mathbf{n}\neq\mathbf{0}} |x_{\mathbf{n}\sigma}|^2 U_{\mathbf{0n}}\\ &\leqslant \mathfrak{N}U-(U-U_{\mathbf{01}})c\equiv Q_{mc},\end{aligned} \tag{C7}$$

where $\mathbf{1}$ is a nearest-neighbor vector of the direct lattice (we have used the fact that for zero overlap $U_{\mathbf{0n}}=e^2/|\mathbf{n}|$, which decreases with $|\mathbf{n}|$). Hence, Q_{mc} *monotonically decreases* with increasing c. But

$$x_{\mathbf{0}\sigma}=\frac{1}{\sqrt{\mathfrak{N}}}\sum_{\mathbf{k}} s_{\mathbf{k}\sigma},$$

so that for points satisfying (B22), i.e., $s_{\mathbf{k}\sigma}{}^2=1$, the possible values of $\sqrt{\mathfrak{N}}x_{0\sigma}$ are $\mathfrak{N}$, $\mathfrak{N}-2$, $\mathfrak{N}-4$, ..., $-\mathfrak{N}$, with corresponding values

$$c=0,4\left(1-\frac{1}{\mathfrak{N}}\right),\ \ldots,\ 4l\left(1-\frac{l}{\mathfrak{N}}\right),\ \ldots\,. \qquad \text{(C8)}$$

Thus the maximum of Q_σ over all points satisfying (B22), namely, $\mathfrak{N}U=Q_{\sigma 0}$ [see Eq. (C5)], is achieved at two and only two such points, namely, $x_{0\sigma}=\pm\sqrt{\mathfrak{N}}$, $x_{\mathbf{n}\sigma}=0$ for all $\mathbf{n}\neq 0$. Further, using (C7) and (C8), we see that $Q_{\sigma 1}$, the second largest value of Q_σ satisfying (B22), must satisfy

$$Q_{\sigma 0}-Q_{\sigma 1}\geqslant (U-U_{01})4(1-1/\mathfrak{N})\,. \qquad \text{(C9)}$$

It now follows readily that the difference, $E_{\text{gap}}(\geqslant 0)$, between the lowest and the next-lowest values of (B20), subject to the constraints (B22) and (B23), must satisfy

$$E_{\text{gap}}\geqslant (U-U_{01})(1-1/\mathfrak{N})\,, \qquad \text{(C10)}$$

which is, of course, finite as $\mathfrak{N}\to\infty$.

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Calculations of the Intensity of X-Ray Diffuse Scattering Produced by Point Defects in Cubic Metals*

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We have calculated isointensity profiles for the diffuse x-ray scattering associated with certain types of defects in Cu, Al, Na, K, Li, and a theoretical model lattice. These profiles were computed for high-symmetry planes very close to reciprocal-lattice points of the $(S, 0,0)$, $(S,S,0)$, and (S,S,S) type. Both cubic and double-force defects were treated. The calculations were done using a technique presented by Kanzaki for the theoretical model lattice. Kanzaki's general conclusion that cubic defects produce leminiscate profiles and that double-force defects produce ellipsoidal profiles is confirmed for all the material studied. Our profiles for the model lattice agree with those obtained by Kanzaki, except for the profiles due to a double-force defect near an (S,S,S) reciprocal-lattice point.

I. INTRODUCTION

WHEN a defect is introduced into a crystal, it causes the atoms of the host lattice to become displaced from their perfect lattice sites to new equilibrium positions. These strain-field effects produce an associated change in the crystal volume, a change in its macroscopic electrical resistivity, and a diffuse x-ray scattering superimposed on the Bragg peaks of the normal lattice. Of these three effects, the last contains the most detailed information about the structure of the defect and can be used to discriminate between point defects and defect aggregates.

Kanzaki[1] presented a method for calculating the isointensity contours of the x-ray diffuse scattering associated with certain classes of defects. In particular, he applied the method to defects in an fcc model lattice, the elastic constants of which satisfied the constraint that $C_{11}=2C_{12}=2C_{44}$. The technique used in performing these calculations is an application of the method of lattice statics.[2–4] This method is based on the Fourier transformation of the direct-space equilibrium equations for a lattice containing N host atoms and one defect, which is taken to be at the center of the crystal. Periodic boundary conditions are imposed across the face of the crystal, and this can be shown to be equivalent to solving the problem for a superlattice of defects with one defect in each supercell. Each supercell contains N atoms. The Fourier transformation reduces the $3N\times 3N$ matrix of direct-space equilibrium equations to N-independent 3×3 matrix equations, each of which determines one of the Fourier amplitudes of the displacement field. Each of these equations is readily soluble and one then determines the direct-space displacements by Fourier inversion. However, as we show, this technique is particularly suited to the study of diffuse x-ray scattering, since it is the Fourier amplitudes themselves which enter directly into the relevant equations. In the present paper, we are only concerned, as was Kanzaki, with the diffuse scattering in the immediate vicinity of the Bragg peaks, and this enables us to use the lattice-statics equations appropriate to

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