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Hartree-Fock formalism for solids. II. Application to the nearly-free-electron gas

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In this paper, Gaussian basis functions and Fourier transforms of both the Coulomb and exchange terms are employed to simplify numerical procedures in Hartree-Fock calculations for solids. A very simple set of working equations is presented, and the advantages of this particular formalism for solids are discussed. As a test of the method the nearly-free-electron gas is solved in the Hartree and Hartree-Fock approximations. In both cases excellent agreement is obtained with the well-known exact solutions if a suitable set of Gaussian basis functions is employed. On the basis of this study it is concluded that the formalism is not only practical for real solids, but yields accurate results when properly applied.

I. INTRODUCTION

In the first paper of this series (hereafter referred to as I), the exchange term in the Hartree-Fock (HF) equations for solids was Fourier transformed to take advantage of periodic properties of a perfect crystal.[1] The complicated (HF) equations which occur when a localized set of basis functions is employed were substantially simplified, with all direct lattice sums either disappearing or being replaced by reciprocal-lattice sums which are easier to handle. The Fourier transform simplifies the iterative procedure as well, and makes the time required for calculation proportional to N^2 instead of N^4 (where N is the number of orbitals employed). Thus it becomes feasible to consider solids composed of atoms with many electrons. To get the reciprocal-lattice sums in a usable form it is necessary to evaluate the Fourier transform of the exchange term by employing Gaussian basis functions. Explicit expressions for the Fourier transforms of the exchange term are given in I.

In this paper we present the full formalism for HF calculations in solids and discuss the steps necessary to implement the formalism. As a test of the formalism and the accuracy obtainable, the nearly-free-electron (NFE) gas is solved in the Hartree and Hartree-Fock approximations.

The organization of this paper is as follows. In Sec. II the present version of the HF equations is presented and discussed using the results of I. Section III applies this formalism to the NFE gas, showing how it reduces to the exact result when plane-wave basis functions are employed. Gaussian basis functions are used to solve the NFE gas in the Hartree approximation in Sec. IV, and in the HF approximation in Sec. V. Implications for real crystals are drawn in Sec. VI.

II. HARTREE-FOCK FORMALISM

The HF equations presented here are extensions of the method developed by these authors and others over the last few years to treat the Hartree and Hartree-Fock-Slater (HFS) equations in solids using linear-combination-of-atomic-orbitals (LCAO) basis functions.[2-7] In this procedure the key element is Fourier expansion of the crystal potential

$$V(\vec{r}) = \sum_n V(\vec{K}_n) e^{i\vec{K}_n\cdot\vec{r}}, \tag{2.1}$$

where $\vec{K}_n$ is restricted to a reciprocal-lattice vector. Matrix elements of the potential using localized orbitals, $\phi_i(\vec{r})$, to form the LCAO are

$$V_{ij}(\vec{k}) = \sum_n V(\vec{K}_n) S_{ij}(\vec{k}, \vec{K}_n), \tag{2.2}$$

where

$$S_{ij}(\vec{k}, \vec{K}_n) = \sum_l e^{i\vec{k}\cdot\vec{R}_l} \int \phi_i(\vec{r}) e^{i\vec{K}_n\cdot\vec{r}} \phi_j(\vec{r} - \vec{R}_l)\, d\vec{r}. \tag{2.3}$$

Here $\vec{R}_l$ is a direct lattice vector and a monatomic lattice has been assumed. These equations are discussed in Ref. 3. The advantage of the Fourier series is that $V(\vec{K}_n)$ can be related to $S_{ij}(\vec{k}, \vec{K}_n)$ at each stage of the self-consistent iterations, and $S_{ij}(\vec{k}, \vec{K}_n)$ is a matrix which can be computed once and stored. With $\phi_i(\vec{r})$ a Gaussian orbital, the calculation of S_{ij} is rapid, since simple analytic expressions are obtained. The reciprocal sum as written in (2.2) is not rapidly convergent, but procedures to handle it efficiently are available.[8]

In most studies in the past it has been necessary to treat the exchange term in the HF equations approximately by introducing a local exchange-correlation potential, e.g., the $X\alpha$ potential.[9] A large literature on this type of approximation exists.

References may be found in Callaway's text[7] or a recent paper such as Ref. 9. Local exchange-correlation potentials may be handled by Eqs. (2.1) and (2.2).

In this paper we show how to treat the exchange term exactly in solids. Correlation corrections may then be included by some suitable technique based upon knowledge of the HF solutions.[10-12] From I the exchange term may be written in a form like (2.1), except a Fourier integral also appears:

$$V_{\mathrm{ex}}(\vec{r}_1, \vec{r}_2) = \sum_{\vec{K}_2} \int V_{\mathrm{ex}}(\vec{q}, \vec{q}+\vec{K}_2) \times \exp[i\vec{q}\cdot\vec{r}_1 - i(\vec{q}+\vec{K}_2)\cdot\vec{r}_2]\, d\vec{q}, \tag{2.4}$$

where $\vec{K}_2$ is a reciprocal-lattice vector. The corresponding matrix element is, from I,

$$V_{ij}^{\mathrm{ex}}(\vec{k}) = \frac{(2\pi)^3}{\Omega} \sum_{n,m} V_{\mathrm{ex}}(\vec{k}+\vec{K}_n, \vec{k}+\vec{K}_m) \times \phi_i^*(\vec{k}+\vec{K}_n)\phi_j(\vec{k}+\vec{K}_m), \tag{2.5}$$

which is a double reciprocal lattice sum. $\phi_i(\vec{k}+\vec{K}_n)$ is defined by

$$\phi_i(\vec{q}) = \int \phi_i(\vec{r}) e^{-i\vec{q}\cdot\vec{r}} d\vec{r}\,. \tag{2.6}$$

The functions $\phi_i(\vec{q})$ may be evaluated once and stored. During self-consistent iterations $V_{\mathrm{ex}}(\vec{k}+\vec{K}_n, \vec{k}+\vec{K}_m)$ changes, but it may be related to ϕ_i, ϕ_j and an error function of complex argument as shown in I, if a Gaussian basis set is used. Thus an iterative cycle is established similar to the one used extensively in Hartree and HFS LCAO calculations.[3] An important property in the practical application of this equation is the fact that only the first few terms in the reciprocal lattice expansion change during the self-consistent iterations. The complete Hamiltonian matrix element, including kinetic (K), potential (V_c), and exchange (V_{ex}) terms may be written in terms of reciprocal lattice sums as

$$H_{ij}(\vec{k}) = K_{ij}(\vec{k}) + \sum_{n} V_c(\vec{K}_n) S_{ij}(\vec{k}, \vec{K}_n) + \frac{(2\pi)^3}{\Omega} \sum_{n,m} V_{\mathrm{ex}}(\vec{k}+\vec{K}_n, \vec{k}+\vec{K}_m) \times \phi_i^*(\vec{k}+\vec{K}_n)\phi_j(\vec{k}+\vec{K}_m). \tag{2.7}$$

While no assumption has been made about form of the basis functions, rather simple expressions for K_{ij}, S_{ij}, and ϕ_i occur if Gaussian orbitals are used as the local orbitals in the LCAO. In this case analytic expressions also are obtained for $V_c(\vec{k})$ and $V_{\mathrm{ex}}(\vec{k}+\vec{K}_n, \vec{k}+\vec{K}_m)$. Equation (2.7) is the basic working equation of this procedure. The only difficulty in its application is obtaining convergence of the reciprocal lattice sums. The Ewald procedure has been used to obtain rapid convergence of the Coulomb term[8,13,14] and, with the exchange term, a similar procedure may be used, although the product ϕ_i and ϕ_j in some cases could give rapid enough convergence of the double sum as it is written. This is discussed in I and below.

The relation of this method to other HF procedures for solids has been discussed in I. The methods which are closest in spirit to this paper are those of Harris *et al.*[15] and of Mauger and Lannoo.[16] The latter authors, who recently published the HF band structure of diamond, have employed essentially the same procedures originally proposed by Harris which are based upon the use of Fourier transforms. The procedures used in this paper differ in the choice of basis functions and in the choice of which terms in the HF equations to Fourier transform. The choice made here leads to a very considerable simplification of the iterative procedures and greatly simplifies the Fourier series, so that convergence difficulties encountered in other methods are eliminated.[15]

III. NFE GAS: EXACT SOLUTION

Equation (2.7) is valid for a suitable choice of $\phi_i(\vec{r})$, possibilities being Slater orbitals, Gaussian orbitals, or some other localized orbitals. With S_{ij} and ϕ_i properly defined it is valid even for a plane wave basis. In this section it is demonstrated that the latter choice in Eq. (2.7) yields the familiar HF energies for the NFE gas.

The NFE gas is defined as a collection of N electrons in a volume V in which a uniform positive background charge is assumed and a periodic potential is defined by the use of infinitesimal charges at each bravais lattice site. The latter serve to define the direct lattice vectors $\vec{R}_l$ and the associated reciprocal lattice vectors $\vec{K}_n$. As a result of the lattice structure, energy becomes periodic in the reciprocal lattice. Bloch's theorem must be satisfied for a finite lattice translation, and multiple energy bands appear, usually described in the reduced zone scheme.[17] The Fourier transform of the total Coulomb interaction for an electron is simply

$$V(\vec{K}_n) = V_0 \delta_{\vec{K}_n, 0}, \tag{3.1}$$

where V_0 may be taken to be zero. The Fourier transform of the exchange term is not so simple. With a plane-wave basis it may be computed directly from the density matrix (see I)

$$V'_{\text{ex}}(\vec{q}_1,\vec{q}_2)=\frac{-e^2}{(2\pi)^6}\int\frac{\rho(\vec{r}_1,\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}e^{-i\vec{q}_1\cdot\vec{r}_1+i\vec{q}_2\cdot\vec{r}_2}\,d\vec{r}_1\,d\vec{r}_2$$

$$=\frac{-e^2}{(2\pi)^6}\frac{1}{V}\sum_{\vec{k}\,\text{occ.}}\int\frac{e^{i\vec{k}_1\cdot(\vec{r}_1-\vec{r}_2)}}{|\vec{r}_1-\vec{r}_2|}$$

$$\times\, e^{-\vec{q}_1\cdot\vec{r}_1+i\vec{q}_2\cdot\vec{r}_2}\,d\vec{r}_1\,d\vec{r}_2, \tag{3.2}$$

where V is the volume of the crystal. Shifting the origin for the $\vec{r}_1$ integration to $\vec{r}_2$,

$$V'_{\text{ex}}(\vec{q}_1,\vec{q}_2)=\frac{-e^2}{(2\pi)^6}\frac{1}{V}\sum_{\vec{k}\,\text{occ.}}\int d\vec{r}_1\frac{e^{i(\vec{k}-\vec{q}_1)\cdot\vec{r}_1}}{r_1}$$

$$\times\int d\vec{r}_2 e^{i(\vec{q}_2-\vec{q}_1)\cdot\vec{r}_2}$$

$$=\frac{-e^2}{(2\pi)^3}\frac{\delta(\vec{q}_1,\vec{q}_2)}{V}\sum_{\vec{k}\,\text{occ.}}\int d\vec{r}_1\frac{e^{i(\vec{k}-\vec{q}_1)\cdot\vec{r}_1}}{r_1}$$

$$=-\frac{e^2}{(2\pi)^3}\frac{\delta(\vec{q}_1,\vec{q}_2)}{V}\sum_{\vec{k}\,\text{occ.}}\frac{4\pi}{|\vec{k}-\vec{q}_1|^2}. \tag{3.3}$$

The sum over $\vec{k}$ may be computed by converting it to an integral. The result is[18]

$$\sum_{\vec{k}\,\text{occ.}}\frac{4\pi}{|\vec{k}-\vec{q}_1|^2}=\frac{Vk_F}{\pi}F\left(\frac{q_1}{k_F}\right), \tag{3.4}$$

where k_F is the magnitude of the Fermi wave vector and

$$F(x)\equiv 1+[(1-x^2)/x]\ln|(1+x)/(1-x)|. \tag{3.5}$$

Thus,

$$V'_{\text{ex}}(\vec{q}_1,\vec{q}_2)=\frac{-e^2}{(2\pi)^3}\delta(\vec{q}_1-\vec{q}_2)\frac{k_F}{\pi}F\left(\frac{q_1}{k_F}\right). \tag{3.6}$$

In general $V_{\text{ex}}(\vec{q}_1,\vec{q}_2)$ is defined by

$$V'_{\text{ex}}(\vec{q}_1,\vec{q}_2)=\sum_{\vec{K}_2}V_{\text{ex}}(\vec{q}_1,\vec{q}_2)\delta(\vec{q}_2-\vec{q}_1-\vec{K}_2), \tag{3.7}$$

so that in the case of the NFE gas,

$$V_{\text{ex}}(\vec{k}+\vec{K}_n,\vec{k}+\vec{K}_m)=-\frac{e^2}{(2\pi)^3}F\left(\frac{|\vec{k}+\vec{K}_n|}{k_F}\right)\delta_{\vec{K}_n,\vec{K}_m}. \tag{3.8}$$

To evaluate the Hamiltonian matrix elements in (2.7) for the NFE gas, one writes the ϕ's as plane waves, with N the number of unit cells in the crystal,

$$\phi_{\vec{k}}(\vec{r})=(1/V^{1/2}N^{1/2})e^{i\vec{k}\cdot\vec{r}}, \tag{3.9}$$

$$\phi_{\vec{k}}(\vec{k}+\vec{K}_n)=(V^{1/2}/N^{1/2})\delta_{\vec{K}_n,0}. \tag{3.10}$$

Using the above results and replacing $\vec{k}$ by $\vec{k}+\vec{K}_i$, where $\vec{k}$ is now restricted to the first zone and $\vec{K}_i$ is a reciprocal-lattice vector, Eq. (2.7) becomes, in atomic units,

$$H_{ij}=\left[|\vec{k}+\vec{K}_i|^2-\frac{2k_F}{\pi}F\left(\frac{|\vec{k}+\vec{K}_i|}{k_F}\right)\right]\delta_{ij}, \tag{3.11}$$

which is the exact result for the NFE gas: The Hamiltonian is diagonal with this choice of basis functions. This was to be expected, and is a simple test of the HF formalism. Surprisingly, this test has not been used on other HF procedures. In the next sections this test is applied to Eq. (2.7) using Gaussian basis functions.

IV. NFE GAS: GAUSSIAN-HARTREE SOLUTION

A more interesting application of Eq. (2.7) occurs when a Gaussian basis set is chosen. In a real crystal the plane-wave set, although mathematically complete, does not form a very useful set because of the rate of convergence of the plane-wave expansion. Even in a metal, wave functions of an electron contain rapid variations which cannot be reproduced by a tractable number of plane waves. While there is no proof of completeness for Gaussian LCAO basis functions, there is sufficient evidence to suggest that a manageable number can be used, in insulators, or metals, to obtain energy bands in agreement with other techniques and in reasonable agreement with experiment.[19-21] Experience with HF equations in atoms and molecules shows that Gaussian orbitals may be used in variational procedures to obtain accurate energies for bound states, but in solids this question has not been settled completely for the conduction states.

In this section a typical Gaussian LCAO basis is tested by applying it to compute the energy bands of the NFE gas in the Hartree approximation. The exact solution is just the first term in Eq. (3.11). Using Gaussians and the Hartree approximation only the first term in Eq. (2.7) appears. A face-centered-cubic lattice is assumed here with a lattice constant of 7.592 a.u. The Gaussian orbitals and contractions are listed in Table I. These wave functions and lattice constant may be simultaneously scaled by an arbitrary amount to obtain any desired lattice constant without affecting the results here.

Kinetic energy integrals with the basis in Table I were already available from a previous calculation for a LiF crystal.[22] The basis contains not only orbitals localized on lattice sites (Li origin), but also off-lattice-site orbitals (F sites in this case), and it results in 34 × 34 Hamiltonian and overlap matrices. No orbitals of d symmetry were included at this time.

The results of this calculation are shown in Tables II and III. Except for the highest conduction

TABLE I. Gaussian orbitals. The contraction coefficients C multiply the normalized Gaussian orbitals, $N_i e^{-\alpha r^2}$, where α is the orbital exponent in reciprocal atomic units in column 2, and N_i is the normalization factor. Orbitals labeled "Li" are placed on lattice sites, while orbitals labeled "F" are placed at fluorine sites in a LiF fcc lattice.

Orbital type	Orbital exponent	C_1	C_2	C_3	C_4	C_5
Li *s*	3 184.467 10	0.001 482				
	480.512 66	0.011 447				
	108.863 25	0.059 942				
	30.289 479	0.245 798				
	9.641 514	0.758 958				
	3.391 556	0.0	1.0			
	1.272 029	0.0		1.0		
	0.5	0.0			1.0	
	0.2	0.0				1.0
Li *p*	2.0	1.0				
	1.0		1.0			
	0.5			1.0		
	0.2				1.0	
F *s*	37 736.000	0.000 221	−0.000 140			
	5 867.079 1	0.001 640	−0.001 065			
	1 332.467 9	0.008 735	−0.005 719			
	369.858 66	0.036 662	−0.023 829			
	117.129 69	0.123 661	−0.086 204			
	40.302 86	0.311 407	−0.233 185			
	14.898 01	0.443 441	−0.477 358			
	5.877 74	0.222 868	−0.303 661			
	1.626 76	0.0	0.0	1.0		
	0.61	0.0	0.0		1.0	
	0.23	0.0	0.0			1.0
F *p*	1 024.080 2	0.011 242				
	23.794 387	0.080 741				
	7.495 459	0.311 642				
	2.763 871	0.706 619				
	1.099 056	0.0	1.0			
	0.45	0.0		1.0		
	0.20	0.0			1.0	

TABLE II. Hartree-NFE energy levels in units of $(2\pi/a)^2$. Column 1 gives the $\vec{k}$ vector along the Δ axis. Column 2 gives exact energies. The remaining columns are eigenvalues obtained with various combinations of the Gaussian basis of Table I. Column 3 includes all basis contractions, column 4 excludes the last orbital of each symmetry in Table I, column 5 excludes all but the two longest ranged orbitals of each type and column 6 includes only lithium site orbitals, keeping only the two longest-ranged orbitals of *s* and *p* symmetry.

		$(a/2\pi)^2E$			
$(4a/\pi)\vec{k}$	Exact	34×34	26×26	16×16	8×8
(0, 0, 0)	0.000 00	0.002 93	0.999 97	0.008 19	0.032 39
(1, 0, 0)	0.015 63	0.018 28	0.991 24	0.230 80	0.045 74
(2, 0, 0)	0.062 50	0.065 02	0.977 14	0.069 18	0.088 38
(3, 0, 0)	0.140 63	0.143 23	0.982 29	0.147 04	0.165 04
(4, 0, 0)	0.250 00	0.252 70	1.024 48	0.256 28	0.278 54
(5, 0, 0)	0.390 63	0.393 31	1.109 75	0.396 73	0.429 49
(6, 0, 0)	0.562 50	0.565 06	1.236 69	0.568 35	0.616 76
(7, 0, 0)	0.765 63	0.768 07	1.400 16	0.771 22	0.834 23
(8, 0, 0)	1.000 00	1.002 24	1.551 68	1.004 76	1.006 27

TABLE III. Comparison of exact and Gaussian-Hartree-NFE energy bands at points along the Δ axis. $\vec{k}$ vectors are given in units of $\pi/4a$. The first five levels are given in units of $(2\pi/a)^2$.

	(0,0,0)			(2,0,0)			(6,0,0)			(8,0,0)	
	Exact	GH		Exact	GH		Exact	GH		Exact	GH
Γ_1	0.0000	0.0029	Δ_1	0.0625	0.0650	Δ_1	0.5623	0.5651	x_4'	1.0000	1.0022
Γ_1	3.0000	3.0009	Δ_1	2.5625	2.5630	Δ_1	1.5625	1.5642	x_1	1.0000	1.0029
Γ_{15}	3.0000	2.9999	Δ_5	2.5625	2.6514	Δ_1	2.0625	2.0627	x_5'	2.0000	2.0013
Γ_{15}	4.0000	3.9997	Δ_1	3.0625	3.0873	Δ_5	2.0625	2.0676	x_1	2.0000	2.0021
Γ_1	4.0000	4.2888	Δ_5	4.0625	4.0665	Δ_5	4.5623	4.6749	x_4'	5.0000	4.9980

bands listed, where the finite size of the LCAO basis becomes important, the largest errors occurred in Δ_5 bands which contain important contributions from d-like orbitals. Otherwise the energies are accurate to about 3 parts in 1000. The errors are systematic, so that energy differences are accurate to another significant figure. Table II shows energies obtained for the lowest NFE band for several different basis sets constructed by deleting selected orbitals from Table I. Results worth commenting upon are: (i) the corelike orbitals made small, but significant contributions to the energy eigenvalues, (ii) the off-lattice-site orbitals were significant in improving the energies for the fcc NFE gas, and (iii) the 26 × 26 matrix which eliminated all the longest-ranged Gaussian orbitals of each symmetry gave poor results. For the 34 × 34 matrix comparable accuracy was obtained for the first four NFE bands. Beyond that the limited size of the basis became important. However, it is clear that the Gaussian LCAO method is capable of yielding energies for conduction-like electrons to the accuracy desired for modern band calculations (or for comparison with experiment) if an appropriate set of Gaussian basis functions is employed. Since Gaussians work well for both localized (atomic) states and free-electron states in solids, it appears that they form an ideal set for real crystals which contain both. It is important, then, to see if this same conclusion may be made when the solid state exchange term is included.

V. NFE GAS: GAUSSIAN HF SOLUTION

The formalism of Sec. II provides the means of checking Gaussians in solid state HF calculations. Equation (2.7) is the relation needed. Two approaches to implementing this equation are possible.

One method would be to assume some starting Gaussian LCAO expansion for the occupied states, perhaps an OAP approximation (see I), compute $V_{ex}(\vec{k}_1, \vec{k}_2)$ from I using Gaussians and iterate to self-consistency. This would provide a useful test of the stability of the self-consistent cycles.

Another, easier method was employed here. The exact result for $V_{ex}(\vec{k}_1, \vec{k}_2)$ obtained in Sec. III was inserted into Eq. (2.7), but otherwise Gaussians were used. In this case there was no need to iterate, since the starting potential was self-consistent. Properties of the NFE gas simplify Eq. (2.7), reducing the exchange term to a single reciprocal lattice sum. This sum was performed using the exact value of $V_{ex}(\vec{k}+\vec{K}_n, \vec{k}+\vec{K}_n)$ given by (2.13) and using the Gaussians to compute $\phi_i(\vec{k}+\vec{K}_n)$. The latter are tabulated in the Appendix. This sum converged readily for the Gaussian basis functions employed here. Unlike the Coulomb term, this sum was slow to converge only for core-core orbital contributions, which were not significant in the NFE gas. In particular, core-conduction terms, which are so troublesome in the Coulomb sum, converged rapidly here because they involved products $\phi_i^*(\vec{k}+\vec{K}_n)\phi_j(\vec{k}+\vec{K}_n)$ instead of $S_{ij}(\vec{k}, \vec{K}_n)$. Only 180 reciprocal-lattice vectors were summed to obtain the exchange term. The kinetic-energy matrix elements were summed to as many as 75 stars of direct lattice vectors for some elements for each point $\vec{k}$ used in the fcc Brillouin zone. A comparable amount of work was required for each term in the NFE Hamiltonian.

Figure 1 shows the Hartree-Fock band structure obtained with the basis of 34 Gaussian orbitals. A Fermi sphere radius was chosen corresponding to one electron per lattice site, 0.6469 reciprocal atomic units in this case. With this choice of Fermi radius, the Fermi surface lies entirely within the first band: there is no contact with the Brillouin zone boundary. The Gaussian-Hartree-Fock (GHF) band structure compares favorably with the exact Hartree-Fock bands, except, as before, where d-orbital symmetries become important. These orbitals can be included without difficulty in this formalism, but were not part of our starting basis set. Table IV contains some of the GHF en-

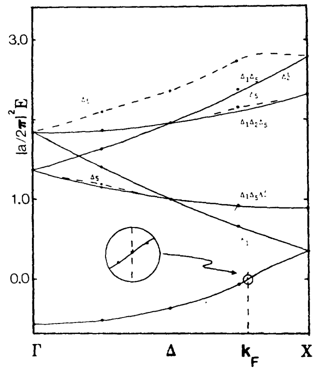

FIG. 1. fcc NFE-Hartree-Fock energy bands. Solid curves are the exact bands; the points plotted were obtained by the Gaussian procedure discussed in Sec. II. The inset shows the first band near the Fermi vector on the scale expanded 5:1.

ergies compared to exact HF energies, showing an accuracy comparable to the Gaussian-Hartree results. It is thus concluded that Gaussian orbitals may also be employed to treat accurately the exchange term in the HF equations.

A property of the NFE gas which is of special interest is the behavior of the energy and density of states in the vicinity of the Fermi surface. To find how well the GHF method reproduces this behavior, additional points along the Δ axis in the vicinity of k_F were obtained. No loss of accuracy occurred near k_F with the Gaussian basis. These points are shown in the inset in Fig. 1 which is magnified 5 : 1. The point at which $\nabla_k E$ becomes singular can be estimated from the curves in both exact and GHF bands. This behavior is responsible for the vanishing of the density of states at the Fermi energy. According to reasoning by Herring,[23] this will occur in a real solid in the HF approximation if the Fermi surface is spherical. This fact is often used in an argument against the use of uncorrelated HF theory in metallic solids. For nonspherical energy surfaces it is not clear to these authors that the argument still follows. It is interesting to find what a numerical calculation of the density of states for the NFE gas using the GHF method yields, since this will give insight into a similar study for a real metal, where the Fermi surface is not so simple.

Figures 2 and 3 show the Hartree and Hartree-Fock densities of states obtained using the analytic tetrahedron method.[24] In these calculations the irreducible portion of the Brillouin zone was divided into 6912 equal-volume tetrahedrons by assigning the point X to be (24, 0, 0); for smaller grid sizes oscillations appeared which were related to the finite grid size. The contribution of each tetrahedron to the density of states was computed for the first energy band only. Since this required calculation of energy bands at a large number of points in the Brillouin zone, the exact expressions were used to "interpolate" between computed GHF values. On the scale of these diagrams the exact and GHF energies were identical for the first band, so this procedure saved computer time without prejudicing the results. But, as a consequence, this calculation serves more as a test of the analytic tetrahedron method than the GHF results.

Figure 2 shows good agreement with the analytic results of the NFE density of states in the Hartree approximation, where the function is slowly varying ($E^{1/2}$). On the other hand, the HF density of states in Fig. 3, which contains a rapid variation near the Fermi energy, is not reproduced so well for this grid size. The HF density of states can be reproduced more accurately by sampling more, smaller tetrahedrons in the vicinity of the Fermi surface,[25] but this requires knowledge of the location of the Fermi surface in order to make the sampling. For the NFE (spherical) Fermi surface this is easy to do, but for a complicated Fermi surface this may be a nontrivial task requiring very substantial computer time and necessitating some type of interpolation of energies. It is concluded that, in a real solid with a nonspherical Fermi surface, the zero of the density of states at the Fermi energy, if it exists, could easily be overlooked in a numerical calculation. This may be seen by comparing the dashed curve in Fig. 3.

TABLE IV. Comparison of exact and Gaussian-Hartree-Fock-NFE energy bands along the Δ axis. Units are the same as Table III.

	(0,0,0)			(2,0,0)			(6,0,0)			(8,0,0)	
	Exact	GHF		Exact	GHF		Exact	GHF		Exact	GHF
Γ_1	−1.2024	−1.1992	Δ_1	−1.0980	−1.0952	Δ_1	−0.1350	−0.1322	x_4'	0.7129	0.7152
Γ_{15}	2.9147	2.9146	Δ_1	2.4619	2.4621	Δ_1	1.3909	1.3927	x_1	0.7129	0.7159
Γ_1	2.9147	2,9157	Δ_5	2.4619	2.5526	Δ_1	1.9357	1.9359	x_5'	1.8689	1.8702
Γ_{15}	3.9368	3.9365	Δ_1	2.9791	3.0042	Δ_5	1.9357	1.9408	x_1	1.8689	1.8710
Γ_1	3.9368	4.2272	Δ_5	4.0003	4.0044	Δ_5	4.5073	4.6208	x_4'	4.9498	4.9478

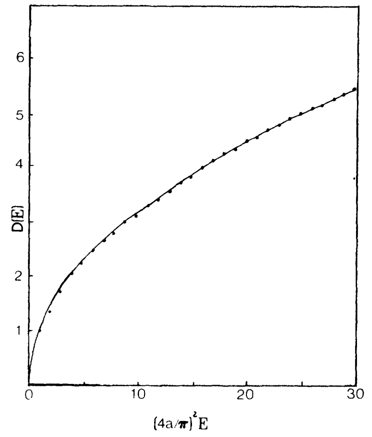

FIG. 2. Hartree density of states for the NFE gas. The solid curve gives the exact result; the points were obtained with the GHF bands using the analytic tetrahedron method and a cubic grid of 1505 points in $\frac{1}{48}$ of the Brillouin zone. The density of states is given in units of $(2m/\hbar^2)\times(V/8\pi a)$, where V is the crystal volume. On this scale the density of states at the point X is 8.

VI. CONCLUSION

In this paper a Hartree-Fock formalism has been presented and tested by applying it to one of the few three-dimensional problems in solid state physics for which exact solutions are known: the nearly-free-electron gas. It is concluded that the formalism is both simple and practical, and it is found to yield accurate NFE energy bands when a reasonable set of Gaussian orbitals is chosen. Depending upon the accuracy desired, a fairly small basis set may be employed. In this paper no special effort was made to optimize the orbitals, but good energy eigenvalues were obtained. No tests of the Gaussian wave functions which resulted have been performed, such as charge density or susceptibility calculations. Tests of the wave functions and variation of nonlinear Gaussian parameters are reserved for future studies, and should be performed in view of the conclusions drawn by Kari *et al.* in atomic calculations.[26] As far as the energy bands are concerned it appears, on the basis of this study and results of atomic GHF calculations, the Gaussian-Hartree-Fock procedures should be powerful enough to yield good energy bands for real crystals. A real crystal will require more extensive calculation for the first iteration of the HF equation, but use of the overlapping atomic potential model simplifies the procedures, as discussed in I.

The fact that "localized" basis sets are able to treat conduction states in the NFE gas or a real solid can be traced to the formation of the LCAO.

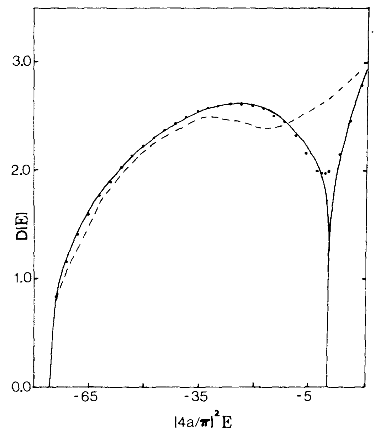

FIG. 3. Hartree-Fock density of states for the NFE gas. The solid curve is the exact result. The dashed curve was obtained with a cubic grid of 89 points, while the unconnected points were obtained with a grid of 1505 points in $\frac{1}{48}$ of the Brillouin zone. Units are the same as Fig. 2.

As an LCAO, the Gaussian functions are not localized, but satisfy Bloch's theorem. The variational freedom needed for the basis set is satisfied by choosing a variety of Gaussians which can be made to overlap in such a way as to accurately reproduce the true Bloch function in a single unit cell. In this way the Gaussian LCAO can be made to simulate even a plane wave solution of the NFE gas.

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APPENDIX A

For Gaussian orbitals the functions $\phi_i(\vec{q})$ of Eq. (2.6) may be computed easily. Including normalization factors, the s and p orbitals are

$$\phi_s(\vec{r}) = (2\alpha_s/\pi)^{3/4} e^{-\alpha_s r^2} \tag{A1}$$

and

$$\phi_{p_x}(\vec{r}) = -ix(128\alpha_p^5/\pi^3)^{1/4} e^{-\alpha_p r^2}, \tag{A2}$$

where a phase factor has been introduced to make the fcc LCAO sp matrix elements real. Inserting these orbitals into (2.6) yields

$$\phi_s(\vec{q}) = (2\pi/\alpha_s)^{3/4} e^{-q^2/4\alpha_s}, \tag{A3}$$

$$\phi_{p_x}(\vec{q}) = -\frac{q_x}{2}(128\pi^3/\alpha_p^5)^{1/4} e^{-q^2/4\alpha_p}. \tag{A4}$$

Similar expressions may be obtained for d orbitals.

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