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Electronic-structure studies of solids. III. Hartree-Fock band functions and energies for cubic lithium crystals*

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The authors's methods for Hartree-Fock calculations of electronic structures of solids with exact treatment of exchange are extended to systems containing inner electronic shells and are applied to body-centered-cubic and face-centered-cubic lithium crystals. The calculated structures are found stable relative to Li_2 molecules; but the omission of correlation effects and limitations of the basis set preclude a quantitative estimate of the cohesive energy. The variation of total energy with lattice spacing is quite weak, and the calculated equilibrium lattice spacings are about 20% too large. The fcc crystal is calculated to be slightly more stable than the bcc form. From the present results and those of Calais and Sperber, it is concluded that the main deficiency of both wave functions are their inflexible descriptions of lower-symmetry components such as those based on p atomic orbitals.

I. INTRODUCTION

The development of methods to calculate electronic properties of crystals has been quite different from the corresponding development for atoms and molecules. For the latter systems, quantum chemists have formulated more and more sophisticated computational techniques, at a rate which increased as better computers became available to more chemical theoreticians. As a result, chemists have at their disposal a wide variety of computational methods, ranging from semiempirical methods such as the still very popular Pariser-Parr-Pople theory[1] to *ab initio* techniques such as the Hartree-Fock[2] (HF) theory and its extension by configuration-interaction[3] and many-body theoretical methods.[4] On the other hand, progress in solid-state theory has been of a more qualitative nature. Considerable insight has been obtained into the workings of and the relationships between band-theoretical methods,[5] and the advent of big computers has enabled a drastic increase in the complexity of crystals that can be treated. Yet all crystal methods still suffer from an ill definition in a quantitative sense. Crystal potentials are obtained semitheoretically[6] or semiempirically,[7] with a concomitant uncertainty in both crystal wave functions and total energies. This uncertainty makes impossible a precise and critical discussion of exchange and correlation effects, and thereby hinders the development of improved methods.

The (rigorous) HF model for crystals has been traditionally considered by solid-state theorists as both unphysical and intractable. The physical shortcomings are mainly connected with attempts to obtain one-electron properties from the energy bands. Bandwidths and densities of states, particularly near the Fermi surface (FS) in metals, are unrealistic in the HF model. On the other hand, total HF energies should be quite useful in discussions of cohesive properties of solids and for comparing stabilities of crystalline phases. Moreover, the well-defined nature of HF calculations enables them to serve as a precise and reliable starting point for corrections beyond the independent-particle model.[8] Recently the significance and usefulness of precise HF calculations has been recognized for the description of the properties of alkali halides,[9] noble-gas crystals,[10] and diamond.[11] In the first two classes of crystals the extremely small overlap between atomic orbitals on different lattice sites simplifies enormously the computational problem without much loss of numerical rigor. The work on diamond by Euwema *et al.*[11] shows that rigorous HF calculations using clusters of unit cells are now feasible, although computing times are enormous.

We have developed a formulation of rigorous HF calculations for crystals in which the special features of the crystalline state (infinite size of system and periodicity) have been fully exploited.[12] Introduction of Fourier-transform techniques and invocation of lattice orthogonality relations reduce the crystal integrals to reciprocal-lattice summations whose terms only involve Fourier transforms of basis atomic orbitals. No approximations are necessary, and the exchange and the long-range cancellation features of the electrostatic energy are treated rigorously. The use of Fourier transforms in lattice summations is discussed in detail in the first paper of the present series (Ref. 13, hereafter referred to as I). We then applied our methods to HF calculations for all cubic atomic hydrogen crystals (Ref. 14, hereafter referred to as II). The results reported in II show that it is possible to obtain accurate HF results with a minimum of computational effort. These results also permit insight into the importance of atomiclike inhomogeneities in the HF Bloch functions, and show the effect of these inhomogeneities on the total energy and exchange potentials for hydrogen crystals.

The present paper describes an extension of our work to lithium crystals, for which it is necessary to introduce additional techniques to treat the core electrons. We have already reported some preliminary HF results for lithium,[15] but did not at that time give a full discussion of the mathematical and numerical methods involved. Sections II–IV present the HF formalism and the expressions of the quantities needed therein for systems containing localized core electrons. Section V deals with the numerical techniques and their accuracy. Sections VI and VII contain a detailed presentation of the results. A full specification of the optimized HF band functions and energies is given for the body-centered-cubic and face-centered-cubic crystal forms. A subsequent paper[16] will report the calculation of several physical quantities from these HF results.

II. BASIC FORMULATION

Consider a lattice of lithium nuclei at 0 °K, consisting of N compound unit cells with sides a. The number of nuclei per compound cell is denoted by d and their position vectors relative to the cell origin are $a\vec{s}_m$, $m = 1, \ldots, d$. In the structures to be treated here, the $\vec{s}_m$ are such that all nuclei are geometrically equivalent. The crystal also contains a total of $3Nd$ electrons. The d values and $\vec{s}_m$ vectors for the different cubic structures are given in Table I of II. The nearest-neighbor distances δ for the bcc and fcc structures are $\frac{1}{2}a\sqrt{3}$ and $\frac{1}{2}a\sqrt{2}$, respectively.

We assume a crystal HF wave function in which $2Nd$ electrons doubly occupy Nd symmetrically orthonormalized[17] 1s core orbitals $\varphi_c(\vec{r})$ centered at the lithium nuclei. The remaining Nd electrons doubly occupy $\frac{1}{2}Nd$ valence Bloch functions $|\vec{k}\rangle$, where $\vec{k}$ denotes the Bloch wave vector in reciprocal-lattice units $2\pi/a$. As in II, the $|\vec{k}\rangle$ are constructed from basis Bloch orbitals $|\vec{k}_i\rangle$ according to the formula

$$|\vec{k}\rangle = \sum_{i=1}^{M} c_i(\vec{k}) |\vec{k}_i\rangle , \tag{1}$$

where the $c_i(\vec{k})$ are coefficients which are determined by applying the HF variational condition. The $c_i(\vec{k})$ depend explicitly on $\vec{k}$ so as to permit compensation for inadequacies in the $\vec{k}$ dependence of the $|\vec{k}_i\rangle$. The $|\vec{k}_i\rangle$ are formed from valence atomic orbitals $\varphi_i(\vec{r})$ and are orthogonalized to the core orbitals:

$$|\vec{k}_i\rangle = e^{2\pi i a^{-1}\vec{k}\cdot\vec{r}} \times \sum_{\vec{\mu}} [\Phi_i(\vec{r} - a\vec{\mu}) - B_i(\vec{k})\Phi_c(\vec{r} - a\vec{\mu})] . \tag{2}$$

Throughout this paper, sums over vector indices $\vec{\mu}$, $\vec{\nu}$, or $\vec{\lambda}$ run over a simple cubic lattice of unit dimension. Thus $a\vec{\mu}$ is the origin of one of the compound unit cells of the crystal. The symbols Φ_i and Φ_c denote sums of φ_i and φ_c, respectively, over the equivalent nuclear positions within a unit cell,

$$\Phi(\vec{r}) = \sum_{m=1}^{d} \varphi(\vec{r} - a\vec{s}_m) , \tag{3}$$

and the orthogonalization condition causes $B_i(\vec{k})$ to have the value

$$B_i(\vec{k}) = \varphi_{ci}(\vec{k})/\varphi_{cc}(\vec{k}) , \tag{4}$$

where φ_{ci} and φ_{cc} are Fourier transforms of lattice sums of orbital products:

$$\varphi_{ci}(\vec{q}) = \sum_{\vec{\mu}} \langle \varphi_c(\vec{r}) | e^{2\pi i a^{-1}\vec{q}\cdot\vec{r}} | \Phi_i(\vec{r} - a\vec{\mu})\rangle , \tag{5}$$

$$\varphi_{cc}(\vec{q}) = \sum_{\vec{\mu}} \langle \varphi_c(\vec{r}) | e^{2\pi i a^{-1}\vec{q}\cdot\vec{r}} | \Phi_c(\vec{r} - a\vec{\mu})\rangle . \tag{6}$$

As we have pointed out before,[14] the form chosen for the $|\vec{k}_i\rangle$ is in the spirit of the orthogonalized-plane-wave (OPW) method. Our form has both certain advantages and disadvantages with respect to OPW functions. These characteristics are discussed in Sec. VII.

The total nonrelativistic Hamiltonian H for the system is given in Hartree atomic units (a.u.) by

$$H = \sum_{i=1}^{3Nd} (-\tfrac{1}{2}\nabla_i^2) - 3 \sum_{i=1}^{3Nd} \sum_{\vec{\mu}} \sum_{m=1}^{d} |\vec{r}_i - a\vec{\mu} - a\vec{s}_m|^{-1} + \sum_{1 \le i < j \le 3Nd} |\vec{r}_i - \vec{r}_j|^{-1} + R , \tag{7}$$

where

$$R = \frac{9d}{2a} \left(\sum_{\substack{\vec{\mu}, \vec{\mu}' \\ \vec{\mu} \ne \vec{\mu}'}} |\vec{\mu} - \vec{\mu}'|^{-1} + \sum_{\vec{\mu}, \vec{\mu}'} \sum_{m=2}^{d} |\vec{\mu} - \vec{\mu}' + \vec{s}_1 - \vec{s}_m|^{-1} \right) . \tag{8}$$

In Eq. (7) the first term is the kinetic-energy operator, and the last three terms describe electron-nuclear attraction, electron-electron repulsion, and nuclear-nuclear repulsion, respectively. With the HF wave function specified above the total energy can be written as follows:

$$E = Nd[(2T_c + 2V_c + G_{cc}) + (T_v + V_v + G_{vv}) + 2G_{cv}] + R \tag{9}$$

with

$$T_c = \langle \varphi_c(\vec{r}) | -\tfrac{1}{2}\nabla^2 | \varphi_c(\vec{r}) \rangle , \tag{10}$$

$$V_c = -3\langle \varphi_c(\vec{r}) | \sum_{\vec{\mu}} \sum_{m=1}^{d} | \vec{r} - a\vec{\mu} - a\vec{s}_m |^{-1} | \varphi_c(\vec{r}) \rangle , \tag{11}$$

$$\begin{aligned} G_{cc} = 2\sum_{\vec{\mu}} \sum_{m=1}^{d} [&\langle \varphi_c(\vec{r}_1)\varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m) | r_{12}^{-1} | \varphi_c(\vec{r}_1)\varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m) \rangle \\ &- \tfrac{1}{2}\langle \varphi_c(\vec{r}_1)\varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m) | r_{12}^{-1} | \varphi_c(\vec{r}_1 - a\vec{\mu} - a\vec{s}_m)\varphi_c(\vec{r}_2) \rangle] , \end{aligned} \tag{12}$$

$$T_v = \frac{2}{d} \int d\vec{k} \, \frac{\langle \vec{k} | -\frac{1}{2}\nabla^2 | \vec{k} \rangle}{\langle \vec{k} | \vec{k} \rangle} \tag{13}$$

$$V_v = -\frac{6}{d} \int \frac{d\vec{k}}{\langle \vec{k} | \vec{k} \rangle} \langle \vec{k} | \sum_{\vec{\mu}} \sum_{m=1}^{d} | \vec{r} - a\vec{\mu} - a\vec{s}_m |^{-1} | \vec{k} \rangle , \tag{14}$$

$$G_{vv} = \frac{2N}{d} \int d\vec{k} \, d\vec{k}' \, \frac{\langle \vec{k}\vec{k}' | r_{12}^{-1} | \vec{k}\vec{k}' \rangle - \frac{1}{2}\langle \vec{k}\vec{k}' | r_{12}^{-1} | \vec{k}'\vec{k} \rangle}{\langle \vec{k} | \vec{k} \rangle \langle \vec{k}' | \vec{k}' \rangle} , \tag{15}$$

$$\begin{aligned} G_{cv} = \frac{2}{d} \sum_{\vec{\mu}} \sum_{m=1}^{d} \int \frac{d\vec{k}}{\langle \vec{k} | \vec{k} \rangle} [&\langle \varphi_c(\vec{r}_1 - a\vec{\mu} - a\vec{s}_m), \vec{k} | r_{12}^{-1} | \varphi_c(\vec{r}_1 - a\vec{\mu} - a\vec{s}_m), \vec{k} \rangle \\ &- \tfrac{1}{2}\langle \varphi_c(\vec{r}_1 - a\vec{\mu} - a\vec{s}_m), \vec{k} | r_{12}^{-1} | \vec{k}, \varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m) \rangle] . \end{aligned} \tag{16}$$

In Eqs. (9)–(16) the subscripts c and v stand for core and valence, respectively. The T and V terms are kinetic and nuclear attraction energies, respectively, while the G terms describe electron repulsion, including exchange. Here and throughout this paper the $\vec{k}$ integrations are over the region enclosed by the Fermi surface with volume $\frac{1}{2}d$ in units $(2\pi/a)^3$.

Next we introduce the expansion of Eq. (1) for $|\vec{k}\rangle$, and we invoke the normalization condition

$$\langle \vec{k} | \vec{k} \rangle = \sum_{i,j=1}^{M} c_i^*(\vec{k}) \langle \vec{k}_i | \vec{k}_j \rangle c_j(\vec{k}) = Nd . \tag{17}$$

The "valence" terms T_v to G_{cv} then reduce to

$$T_v = \frac{2}{Nd^2} \int d\vec{k} \sum_{i,j=1}^{M} c_i^*(\vec{k}) \langle \vec{k}_i | -\tfrac{1}{2}\nabla^2 | \vec{k}_j \rangle c_j(\vec{k}) , \tag{18}$$

$$V_v = -\frac{6}{Nd^2} \int d\vec{k} \sum_{i,j=1}^{M} c_i^*(\vec{k}) \langle \vec{k}_i | \sum_{\vec{\mu}} \sum_{m=1}^{d} | \vec{r} - a\vec{\mu} - a\vec{s}_m |^{-1} | \vec{k}_j \rangle c_j(\vec{k}) , \tag{19}$$

$$G_{vv} = \frac{2}{Nd^3} \int d\vec{k} \, d\vec{k}' \sum_{i,j,m,n=1}^{M} c_i^*(\vec{k}) c_j(\vec{k}) c_m^*(\vec{k}') c_n(\vec{k}') [\langle \vec{k}_i \vec{k}'_m | r_{12}^{-1} | \vec{k}_j \vec{k}'_n \rangle - \tfrac{1}{2} \langle \vec{k}_i \vec{k}'_m | r_{12}^{-1} | \vec{k}'_n \vec{k}_j \rangle] , \tag{20}$$

$$\begin{aligned} G_{cv} = \frac{2}{Nd^2} \int d\vec{k} \sum_{i,j=1}^{M} c_i^*(\vec{k}) c_j(\vec{k}) \sum_{\vec{\mu}} \sum_{m=1}^{d} [&\langle \varphi_c(\vec{r}_1 - a\vec{\mu} - a\vec{s}_m), \vec{k}_i | r_{12}^{-1} | \varphi_c(\vec{r}_1 - a\vec{\mu} - a\vec{s}_m), \vec{k}_j \rangle \\ &- \tfrac{1}{2}\langle \varphi_c(\vec{r}_1 - a\vec{\mu} - a\vec{s}_m), \vec{k}_i | r_{12}^{-1} | \vec{k}_j, \varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m) \rangle] . \end{aligned} \tag{21}$$

The HF equations for the valence Bloch functions are obtained by minimizing E under variation of the $c_i(\vec{k})$ and the shape of FS, subject to the scaling condition (17) and the requirement that the FS enclose a volume $\frac{1}{2}d$. Following the derivation in II, we find

$$\sum_{j=1}^{M} F_{ij}(\vec{k}) c_j(\vec{k}) = \epsilon(\vec{k}) \sum_{j=1}^{M} S_{ij}(\vec{k}) c_j(\vec{k}) , \tag{22}$$

where the Fock matrix elements $F_{ij}(\vec{k})$ are given by

$$F_{ij}(\vec{k}) = \frac{1}{Nd}\Big(\langle \vec{k}_i | -\tfrac{1}{2}\nabla^2 | \vec{k}_j\rangle - 3\langle \vec{k}_i | \sum_{\vec{\mu}} \sum_{m=1}^{d} |\vec{r} - a\vec{\mu} - a\vec{s}_m|^{-1} | \vec{k}_j\rangle$$

$$+ 2\sum_{\vec{\mu}} \sum_{m=1}^{d} [\langle \vec{k}_i, \varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m) | r_{12}^{-1} | \vec{k}_j, \varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m)\rangle$$

$$- \tfrac{1}{2}\langle \vec{k}_i, \varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m) | r_{12}^{-1} | \varphi_c(\vec{r}_1 - a\vec{\mu} - a\vec{s}_m), \vec{k}_j\rangle]$$

$$+ \frac{2}{d}\sum_{m,n=1}^{M} \int d\vec{k}'\, c_m^*(\vec{k}')c_n(\vec{k}')[\langle \vec{k}_i\vec{k}'_m | r_{12}^{-1} | \vec{k}_j\vec{k}'_n\rangle - \tfrac{1}{2}\langle \vec{k}_i\vec{k}'_m | r_{12}^{-1} | \vec{k}'_n\vec{k}_j\rangle]\Big), \quad (23)$$

and

$$S_{ij}(\vec{k}) = \frac{1}{Nd}\langle \vec{k}_i | \vec{k}_j\rangle . \quad (24)$$

For all vectors $\vec{k}_F$ on the Fermi surface, we have the additional requirement

$$\epsilon(\vec{k}_F) = \text{const.} \quad (25)$$

The scaling condition may be expressed

$$\sum_{i,j=1}^{M} c_i^*(\vec{k})c_j(\vec{k})S_{ij} = 1 . \quad (26)$$

Preparatory to the evaluation of the matrix elements we derive an alternative expression for the total energy. When Eq. (22) is satisfied and we use the definition

$$\epsilon_c = T_c + V_c + G_{cc} + G_{cv} , \quad (27)$$

we can rewrite Eq. (9) in the form

$$E = Nd\left[\epsilon_c + \frac{1}{d}\int d\vec{k}\,\epsilon(\vec{k}) + T_c + \tfrac{1}{2}T_v + \left(V_c + \tfrac{1}{2}V_v + \frac{R}{Nd}\right)\right] . \quad (28)$$

The quantity ϵ_c can be interpreted as the HF eigenvalue of the 1s-core wave function. In Ref. 16 it is used to approximate core levels and to construct a pseudopotential.

III. MATRIX ELEMENTS

As in previous work, we are able to apply Fourier-transform methods and lattice orthogonality relations to reduce most of the crystal integrals to reciprocal-lattice sums. The resulting formulas are most conveniently expressed with the aid of a few further definitions. Analogous to Eqs. (5) and (6), we introduce the Fourier transform of the lattice sum of a product of valence orbitals:

$$\varphi_{ij}(\vec{q}) = \sum_{\vec{\mu}} \langle \varphi_i(\vec{r}) | e^{2\pi i a^{-1}\vec{q}\cdot\vec{r}} | \Phi_j(\vec{r} - a\vec{\mu})\rangle . \quad (29)$$

In addition to φ_{cc} as defined in Eq. (6), we require the transform of an (unsummed) product of core orbitals:

$$\varphi_{cc}^0(\vec{q}) = \langle \varphi_c(\vec{r}) | e^{2\pi i a^{-1}\vec{q}\cdot\vec{r}} | \varphi_c(\vec{r})\rangle . \quad (30)$$

We also need the analogs of $\varphi_{ci}(\vec{q})$ and $\varphi_{ij}(\vec{q})$ after orthogonalization of the valence orbitals:

$$\psi_{ci}(\vec{k}, \vec{q}) = \varphi_{ci}(\vec{k} + \vec{q}) - B_i(\vec{k})\varphi_{cc}(\vec{k} + \vec{q}) , \quad (31)$$

$$\psi_{ij}(\vec{k}, \vec{k}', \vec{q}) = \varphi_{ij}(\vec{q}) - B_i^*(\vec{k})\varphi_{cj}(\vec{q}) - \varphi_{ci}^*(-\vec{q})B_j(\vec{k}') + B_i^*(\vec{k})B_j(\vec{k}')\varphi_{cc}(\vec{q}) . \quad (32)$$

The quantities $\vec{k}$ and $\vec{k}'$ enter Eqs. (31) and (32) through the $\vec{k}$ dependence of the orthogonalization coefficients $B_i(\vec{k})$. Introducing the structure factor $S(\vec{q})$ defined as

$$S(\vec{q}) = \sum_{m=1}^{d} e^{2\pi i\vec{q}\cdot\vec{s}_m} , \quad (33)$$

the representation of Fourier transforms involving the basis Bloch orbitals becomes

$$\langle \varphi_c(\vec{r}) | e^{2\pi i a^{-1}\vec{q}\cdot\vec{r}} | \vec{k}_i\rangle = \psi_{ci}(\vec{k}, \vec{q}) , \quad (34)$$

$$\langle \vec{k}_i | e^{2\pi i a^{-1}\vec{q}\cdot\vec{r}} | \vec{k}'_j\rangle = S(\vec{q} - \vec{k} + \vec{k}') \times \psi_{ij}(\vec{k}, \vec{k}', \vec{q} - \vec{k} + \vec{k}') \times \sum_{\vec{\lambda}} e^{2\pi i(\vec{q} - \vec{k} + \vec{k}')\cdot\vec{\lambda}} . \quad (35)$$

The lattice summation in Eq. (35) is equivalent to a sum of δ functions, and will permit the evaluation of integrals involving the variable $\vec{q}$. Analogous expressions arise in the reduction of the kinetic-energy matrix elements:

$$t_{cc} = \sum_{\vec{\mu}} \langle \varphi_c(\vec{r}) | -\tfrac{1}{2}\nabla^2 | \Phi_c(\vec{r} - a\vec{\mu})\rangle , \quad (36)$$

$$t_{ci} = \sum_{\vec{\mu}} \langle \varphi_c(\vec{r}) | -\tfrac{1}{2}\nabla^2 | \Phi_i(\vec{r} - a\vec{\mu})\rangle , \quad (37)$$

$$t_{ij} = \sum_{\vec{\mu}} \langle \varphi_i(\vec{r}) | -\tfrac{1}{2}\nabla^2 | \Phi_j(\vec{r} - a\vec{\mu})\rangle , \quad (38)$$

and

$$T_{ij}(\vec{k}) = t_{ij} - B_i^*(\vec{k})t_{cj} - t_{ci}^*B_j(\vec{k}) + B_i^*(\vec{k})B_j(\vec{k})t_{cc} . \quad (39)$$

We are now ready to present the matrix-element formulas. The overlap matrix element $S_{ij}(\vec{k})$, from Eq. (24), assumes the form

$$S_{ij}(\vec{k}) = \psi_{ij}(\vec{k}, \vec{k}, 0) . \quad (40)$$

Turning to the one-electron energy integrals, T_c needs no further reduction, while V_c can be reduced to

$$V_c = -\frac{3}{\pi a}\sum_{\vec{\nu}} \nu^{-2} S(\vec{\nu})\varphi^0_{cc}(\vec{\nu}) \ . \tag{41}$$

Within T_v, we require

$$\langle \vec{k}_i | -\tfrac{1}{2}\nabla^2 | \vec{k}_j \rangle = Nd[T_{ij}(\vec{k}) + (2\pi^2 k^2/a^2) S_{ij}(\vec{k})] \ , \tag{42}$$

while the integral needed for V_v becomes

$$\langle \vec{k}_i | \sum_{\vec{\mu}} \sum_{m=1}^{d} |\vec{r} - a\vec{\mu} - a\vec{s}_m|^{-1} | \vec{k}_j \rangle = \frac{Nd}{\pi a}\sum_{\vec{\nu}} \nu^{-2} S(\vec{\nu}) \psi_{ij}(\vec{k}, \vec{k}, \vec{\nu}) \ . \tag{43}$$

For the two-electron integrals, we have G_{cc}, which cannot be reduced by the present method, and the following Coulomb integrals:

$$\sum_{\vec{\mu}} \sum_{m=1}^{d} \langle \vec{k}_i, \varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m) | r_{12}^{-1} | \vec{k}_j, \varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m) \rangle = \frac{Nd}{\pi a}\sum_{\vec{\nu}} \nu^{-2} S(\vec{\nu}) \psi_{ij}(\vec{k}, \vec{k}, \vec{\nu}) \varphi^0_{cc}(-\vec{\nu}) \ , \tag{44}$$

$$\langle \vec{k}_i \vec{k}'_m | r_{12}^{-1} | \vec{k}_j \vec{k}'_n \rangle = \frac{Nd}{\pi a}\sum_{\vec{\nu}} \nu^{-2} S(\vec{\nu}) \psi_{ij}(\vec{k}, \vec{k}, \vec{\nu}) \psi_{mn}(\vec{k}', \vec{k}', -\vec{\nu}) \ . \tag{45}$$

The $\vec{\nu}$ summations in Eqs. (41) and (43)–(45) each have a singular term for $\vec{\nu} = 0$. However, as discussed in I and II, these divergences cancel against each other, against that in G_{cc}, and against that arising in the Fourier representation of the nuclear-nuclear repulsion energy R:

$$R = \frac{9Nd}{2\pi a}\left(\sum_{\vec{\nu}} \nu^{-2} S(\vec{\nu}) - \int \frac{d\vec{q}}{q^2}\right). \tag{46}$$

Here and in subsequent equations integrations over $\vec{q}$ range over a full three-dimensional space. As shown previously, the nondivergent part of R is a constant whose value depends upon the lattice constant and the crystal structure, and which can be represented as the convergent difference between a divergent sum and a divergent integral. The foregoing observations lead to the conclusion that the $\vec{\nu} = 0$ term is to be omitted from the summations in Eqs. (41) and (43)–(45), and that for the cubic crystals under consideration here R should be represented as

$$R = 9NdD/2\pi a \tag{47}$$

where

$$D = -8.913\,633 \cdots + {\sum_{\vec{\nu}}}' \nu^{-2}[S(\vec{\nu}) - 1] \ , \tag{48}$$

and the prime indicates that the $\vec{\nu} = 0$ term is to be omitted from the sum.

Finally, we have the two-electron exchange integrals

$$\sum_{\vec{\mu}} \sum_{m=1}^{d} \langle \vec{k}_i, \varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m) | r_{12}^{-1} | \varphi_c(\vec{r}_1 - a\vec{\mu} - a\vec{s}_m), \vec{k}_j \rangle = \frac{Nd}{\pi a}\int \frac{d\vec{q}}{q^2} \psi_{ci}(\vec{k}, \vec{q}) \psi_{cj}(\vec{k}, -\vec{q}) \ , \tag{49}$$

$$\langle \vec{k}_i \vec{k}'_m | r_{12}^{-1} | \vec{k}'_n \vec{k}_j \rangle = \frac{Nd}{\pi a}\sum_{\vec{\nu}} \frac{S(\vec{\nu})}{|\nu + \vec{k} - \vec{k}'|^2} \psi_{in}(\vec{k}, \vec{k}', \vec{\nu}) \psi_{mj}(\vec{k}', \vec{k}, -\vec{\nu}) \ . \tag{50}$$

We are unable to reduce Eq. (49) completely to a reciprocal-lattice sum because of the lack of lattice periodicity of φ_c.

Apart from the more complicated $\vec{k}$ and $\vec{k}'$ dependence, the valence-valence Coulomb and exchange integrals [Eqs. (45) and (50)] are similar to those we found in our earlier work. From a numerical point of view the major differences are associated with the intrinsically poorer convergence of the reciprocal-lattice sums. These require some special numerical techniques which are discussed in Sec. V. The remaining integrals are not represented in our previous work, and are evaluated by methods described in Secs. IV and V.

IV. APPROXIMATIONS AND WORKING FORMULAS

The exposition of Sec. II contained no specification of the conditions determining the core orbitals in anticipation of the approximation that these orbitals be fixed in a functional form determined from studies of the Li atom and Li_2 molecule. Such studies indicate that the chemical environment has very little effect on the form of the core orbitals, and that their scales are such that the overlap of nearest-neighbor core orbitals is quite small. We therefore assumed zero differential overlap (ZDO) between cores on different nuclei. For the core wave functions we used, the actual nearest-neighboring core overlap integral is approximately 10^{-6}

for the HF equilibrium lattice parameter, and leads to an error small in comparison with the over-all accuracy of our computations. Removal of this approximation is possible, and might be necessary for systems whos inner electron shells are more diffuse.

The core ZDO approximation leads to a number of computational simplifications, of which the first is the avoidance of a need to carry out the symmetrical orthonormalization procedure. Each φ_c is therefore strictly localized at a single nucleus. As a consequence, all lattice sums involving the overlap of core orbitals reduce to single terms, and, in particular,

$$\varphi_{cc} \approx \varphi^0_{cc} \,, \tag{51}$$

$$t_{cc} \approx T_c \,, \tag{52}$$

$$G_{cc} \approx 2 \sum_{\vec{\mu}} \sum_{m=1}^{d} \langle \varphi_c(\vec{r}_1)\varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m) \,|\, r_{12}^{-1} \,|\, \varphi_c(\vec{r}_1)\varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m)\rangle - \langle \varphi_c(\vec{r}_1)\varphi_c(\vec{r}_2) \,|\, r_{12}^{-1} \,|\, \varphi_c(\vec{r}_1)\varphi_c(\vec{r}_2)\rangle \,. \tag{53}$$

Moreover, if the core orbitals are assumed spherical, the Coulombic repulsion of two core orbitals or the attraction between a core orbital and a distant nucleus can be well approximated by interactions of point charges at the orbital centers.[18] This observation has as consequences that for $\vec{\mu} + \vec{s}_m \neq 0$

$$\begin{aligned} &\langle \varphi_c(\vec{r}_1)\varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m) \,|\, r_{12}^{-1} \,|\, \varphi_c(\vec{r}_1)\varphi_c(\vec{r}_2 - a\vec{\mu} - a\vec{s}_m)\rangle \\ &\quad \approx \langle \varphi_c(\vec{r}) \,|\, |\vec{r} - a\vec{\mu} - a\vec{s}_m|^{-1} \,|\, \varphi_c(\vec{r})\rangle \\ &\quad \approx |a\vec{\mu} - a\vec{s}_m|^{-1} \,, \end{aligned} \tag{54}$$

and that, as shown in Appendix A,

$$\frac{1}{\pi a} {\sum_{\vec{\nu}}}' \nu^{-2} S(\vec{\nu}) \varphi^0_{cc}(\vec{\nu}) \approx \frac{D}{\pi a} + \langle \varphi_c(\vec{r}) \,|\, r^{-1} \,|\, \varphi_c(\vec{r})\rangle \,. \tag{55}$$

The simplifications embodied in Eqs. (51)–(55) lead to considerable cancellation among the contributions to V_c and G_{cc}, and yield the nondivergent contributions

$$V_c + G_{cc} \approx -3\langle \varphi_c \,|\, r^{-1} \,|\, \varphi_c\rangle + \langle \varphi_c\varphi_c \,|\, r_{12}^{-1} \,|\, \varphi_c\varphi_c\rangle - \frac{D}{\pi a} \,, \tag{56}$$

$$V_c + \frac{R}{Nd} \approx -3\langle \varphi_c \,|\, r^{-1} \,|\, \varphi_c\rangle + \frac{3D}{2\pi a} \,. \tag{57}$$

In the present work we also assumed the valence Bloch orbitals to be built from spherically symmetric orbitals φ_i. This assumption leads to the conclusion that the Fourier transforms $\varphi_{ci}(\vec{k})$ and $\varphi_{ij}(\vec{k})$, and the coefficients $c_i(\vec{k})$, are totally symmetric under transformation of $\vec{k}$ by operations of the cubic point group. The same symmetry also applies to $\varphi_{cc}(\vec{k})$ and $S(\vec{q})$. It is therefore useful to introduce the notion of a star of vectors, consisting of the set of vectors related by the point-group operations. In the equations to follow, we let $\vec{\nu}_t$ be a representative vector from star t, $t = 1, 2, \ldots$, with the stars ordered in ascending value of ν_t (so $t = 1$ corresponds to $\vec{\nu} = 0$). We use g_t to denote the number of vectors in star t.

With the above approximations and notations, we obtain the working formula

$$\begin{aligned} F_{ij}(\vec{k}) = {} & T_{ij}(\vec{k}) + \frac{2\pi^2 k^2}{a^2} S_{ij}(\vec{k}) + 2C_{ij}(\vec{k}) - X_{ij}(\vec{k}) \\ & + \frac{1}{\pi a} \sum_{t \neq 1} g_t \frac{S(\vec{\nu}_t)}{\nu_t^2} \sum_{m,n=1}^{M} J^{ij}_{mn}(\vec{k}, \vec{\nu}_t) \\ & - \frac{1}{2\pi a} \sum_t g_t S(\vec{\nu}_t) \sum_{m,n=1}^{M} K^{ij}_{mn}(\vec{k}, \vec{\nu}_t) \,, \end{aligned} \tag{58}$$

where the quantities not previously defined are

$$V_{ij}(\vec{k}) = -\frac{1}{\pi a} \sum_{t \neq 1} g_t \frac{S(\vec{\nu}_t)}{\nu_t^2} \psi_{ij}(\vec{k}, \vec{k}, \vec{\nu}_t) \,, \tag{59}$$

$$C_{ij}(\vec{k}) = \frac{1}{\pi a} \sum_{t \neq 1} g_t \frac{S(\vec{\nu}_t)}{\nu_t^2} \psi_{ij}(\vec{k}, \vec{k}, \vec{\nu}_t) \varphi^0_{cc}(-\vec{\nu}_t) \,, \tag{60}$$

$$X_{ij}(\vec{k}) = \frac{1}{\pi a} \int \frac{d\vec{q}}{q^2} \psi^*_{ci}(\vec{k}, \vec{q}) \psi_{cj}(\vec{k}, -\vec{q}) \,, \tag{61}$$

$$J^{ij}_{mn}(\vec{k}, \vec{\nu}_t) = \frac{2}{d} \psi_{ij}(\vec{k}, \vec{k}, \vec{\nu}_t) \int d\vec{k}' \, c^*_m(\vec{k}') c_n(\vec{k}') \times \psi_{mn}(\vec{k}', \vec{k}', -\vec{\nu}_t) \,, \tag{62}$$

$$K^{ij}_{mn}(\vec{k}, \vec{\nu}_t) = \frac{2}{d} \int d\vec{k}' \, \langle |\vec{\nu}_t + \vec{k} - \vec{k}'|^{-2} \rangle_t \times c^*_m(\vec{k}') c_n(\vec{k}') \psi_{in}(\vec{k}, \vec{k}', \vec{\nu}_t) \psi_{mj}(\vec{k}', \vec{k}, -\vec{\nu}_t) \,. \tag{63}$$

In Eq. (63) the notation $\langle\,\rangle_t$ indicates the average over all $\vec{\nu}_t$ in star t. Equation (58) shows $F_{ij}(\vec{k})$ as containing inhomogeneity and plane-wave kinetic-energy contributions $T_{ij}(\vec{k})$ and $2\pi^2 a^{-2} k^2 S_{ij}(\vec{k})$, respectively, a nuclear attraction term $3V_{ij}(\vec{k})$, core-valence Coulomb and exchange terms $2C_{ij}(\vec{k})$ and $X_{ij}(\vec{k})$, and valence-valence Coulomb and exchange terms involving, respectively, J^{ij}_{mn} and K^{ij}_{mn}.

When the Hartree-Fock equations are satisfied, the total energy can be written

$$E = Nd\left(\epsilon_c + \frac{1}{d}\int \epsilon(\vec{k})\, d\vec{k} + T_{\rm tot} + V_{\rm tot}\right) , \tag{64}$$

with

$$\epsilon_c = T_c - 3\langle\varphi_c | r^{-1} | \varphi_c\rangle + \langle\varphi_c\varphi_c | r_{12}^{-1} | \varphi_c\varphi_c\rangle + \frac{1}{d}\sum_{i,j=1}^{M}\int d\vec{k}\, c_i^*(\vec{k}) c_j(\vec{k}) \times [2C_{ij}(\vec{k}) - X_{ij}(\vec{k})] - \frac{D}{\pi a} , \tag{65}$$

$$T_{\rm tot} = T_c + \frac{1}{d}\sum_{i,j=1}^{M}\int d\vec{k}\, c_i^*(\vec{k}) c_j(\vec{k}) \times \left(T_{ij}(\vec{k}) + \frac{2\pi^2 k^2}{a^2} S_{ij}(\vec{k})\right) , \tag{66}$$

$$V_{\rm tot} = -3\langle\varphi_c | r^{-1} | \varphi_c\rangle + \frac{3}{d}\sum_{i,j=1}^{M}\int d\vec{k}\, c_i^*(\vec{k}) c_j(\vec{k}) V_{ij}(\vec{k}) + \frac{3D}{\pi a} . \tag{67}$$

It remains to specify the orbitals φ_c and φ_i. For φ_c we chose a single-ζ 1s Slater-type orbital (STO) with optimized orbital exponent:

$$\varphi_c(\vec{r}) = (\zeta_c^3/\pi)^{1/2} e^{-\zeta_c r} . \tag{68}$$

A double-ζ φ_c (a linear combination of two STO's) could have been used without great additional labor, but we did not do so in the present work. For the valence orbitals φ_i we chose 2s STO's:

$$\varphi_i(\vec{r}) = (\zeta_i^5/3\pi)^{1/2} r e^{-\zeta_i r} . \tag{69}$$

With these choices of orbitals and the foregoing approximations, we find by direct integration

$$T_c = t_{cc} = \tfrac{1}{2}\zeta_c^2 , \tag{70}$$

$$\langle\varphi_c | r^{-1} | \varphi_c\rangle = \zeta_c , \tag{71}$$

$$\langle\varphi_c\varphi_c | r_{12}^{-1} | \varphi_c\varphi_c\rangle = \tfrac{5}{8}\zeta_c , \tag{72}$$

$$\varphi_{cc}^0(\vec{q}) = 16\zeta_c^4[(2\pi/a)^2 q^2 + 4\zeta_c^2]^{-2} . \tag{73}$$

V. NUMERICAL TECHNIQUES

Use of the working formulas given in Sec. IV depends upon the evaluation of the basic quantities t_{ij}, t_{ci}, $\varphi_{ij}(\vec{q})$, and $\varphi_{ci}(\vec{q})$, the use of suitable numerical integration procedures to evaluate $X_{ij}(\vec{k})$, $J_{mn}^{ij}(\vec{k}, \vec{\nu})$, and $K_{mn}^{ij}(\vec{k}, \vec{\nu})$, and the introduction of appropriate iterative techniques for determining the coefficients $c_m(\vec{k})$ and the shape of the Fermi surface.

For t_{ij}, t_{ci}, $\varphi_{ij}(\vec{q})$, and $\varphi_{ci}(\vec{q})$ we were able, with monor modifications, to use the techniques described in II. These techniques involve the use of convolution formulas, and require knowledge of the Fourier transform $\varphi_i^T(\vec{q})$ of $\varphi_i(\vec{r})$:

$$\varphi_i^T(\vec{q}) = \left(\frac{8\delta_i^5 a^3}{3\pi^2}\right)^{1/2} \frac{3\delta_i^2 - q^2}{(\delta_i^2 + q^2)^3} , \tag{74}$$

where $\delta_i = a\zeta_i/2\pi$. The main differences from the situation described in II arise from the strong localization of φ_c. This localization and the fact that φ_c is spherical cause $\varphi_{ci}(\vec{k})$ to be nearly totally independent of the orientation of $\vec{k}$ and to depend only weakly upon the magnitude of $\vec{k}$. In fact, $\varphi_{ci}(\vec{k})$ varies only by about 10% among $\vec{k}$ values within the Fermi surface. Similar remarks apply also to $\varphi_{cc}(\vec{k})$, and therefore as well to $B_i(\vec{k})$.[15] The result is that $\varphi_{ci}(\vec{k})$, $B_i(\vec{k})$, and $\psi_{ij}(\vec{k}, \vec{k}', \vec{q})$ can be well represented by expansions in even powers of $\vec{k}$ and $\vec{k}'$, and that $J_{mn}^{ij}(\vec{k}, \vec{\nu})$ and $K_{mn}^{ij}(\vec{k}, \vec{\nu})$ can be evaluated in the same manner as we handled $Q_{mn}^{t}(\vec{k})$ in II.

When the Slater exponents ζ_i are large the quantities $\varphi_{ij}(\vec{q})$ and $\varphi_{ci}(\vec{q})$ decrease so slowly with increasing q that the reciprocal-lattice summations in the expressions for $V_{ij}(\vec{k})$ and $T_{ij}(\vec{k})$ should be extended up to stars with $\nu^2 = 500$. We found it satisfactory to calculate exactly only the $\varphi_{ij}(\vec{\nu})$ and $\varphi_{ci}(\vec{\nu})$ for $\nu^2 \leq 100$, while estimating those for $\nu^2 > 100$ from a least-squares fit to a sample of star points in that range. The fit is expedited by the fact that the $\varphi_{ij}(\vec{\nu})$ and $\varphi_{ci}(\vec{\nu})$ for large ν^2 are nearly independent of the direction of $\vec{\nu}$.

The evaluation of $X_{ij}(\vec{k})$ has no close analog in our earlier work. Noting that in the $\vec{q}$ integration shown in Eq. (61) the integrand of $X_{ij}(\vec{k})$ depends only upon $\vec{q}$ through its magnitude and upon the angle between $\vec{k}$ and $\vec{q}$, we introduced spherical coordinates with polar axis along $\vec{k}$. Integration over the azimuthal angle φ is then trivial, and we integrated over the two remaining coordinates using ten-point Lobatto quadratures. Five to six significant figures are obtained using for the q integration the two intervals $(0, 2\delta_c)$ and $(2\delta_c, \infty)$ and the respective integration variables $q/\delta_c - 1$ and $1 - 4\delta_c/q$.

In contrast to our experience in II, we were unable to obtain a satisfactory least-squares fit for the valence-band energy $\epsilon(\vec{k})$ in even powers of k and cubic harmonics. The difference is due to the large HF equilibrium lattice spacing (causing the logarithmiclike exchange term to be more important relative to the kinetic energy than it is in the hydrogen crystals) and to the extremely shallow HF energy minimum. We were able to improve the accuracy considerably by adding a simple logarithmic term in the least-squares fit. For details we refer to Appendix B.

An analysis of the accuracy of all calculated quantities and of the least-squares fitting procedures leads us to the conclusion that the HF energies and Fermi energies are obtained to an accuracy of at least five significant figures. Without removing the zero-differential-overlap approximation for the core orbitals it is unrealistic to seek a higher accuracy.

VI. RESULTS

We constructed programs to perform calculations for bcc and fcc structures, with up to four basis valence orbitals φ_i, and an organization very similar to that reported in II. Typical computing times on a Univac 1108 computer are 7.5 and 4.5 min for the bcc and fcc structures, respectively, for calculations using two basis valence orbitals and reaching convergence after two iterations. The calculations were carried to an accuracy in energies of at least one part in 10^5.

In a preliminary series of calculations we investigated the appropriacy of the choice of the screening parameter ζ_c as the best value for the Li atom.[19] We varied ζ_c in calculations with a variety of valence orbital bases, invariably finding an optimal value close to the best atom value. This result is in agreement with observations as to the optimum ζ value for the Li 1s orbital in molecules,[20] and caused us to adopt the best atom value $\zeta_c = 2.69$ in all the calculations reported here.

In Tables I and II are listed the total HF energies of bcc and fcc structures as a function of lattice spacing and the valence orbital ζ values. Table I contains results based on a single valence orbital, and indicates that at all lattice spacings its optimum ζ value lies near 0.50. In calculations based on two valence orbitals, we found the results to be quite insensitive to the ζ value of the more diffuse valence orbital, with optimum values near $\zeta = 0.50$. We therefore fixed ζ_1 at this value and obtained the results presented in Table II. We also performed calculations based on three valence orbitals, but found that addition of the third orbital yielded no significant improvement in the calculated total energy. From the data in Table II, we therefore conclude that for the bcc and fcc structures the near-HF energies are, respectively, − 7.4220 and − 7.4227 hartree, with respective optimum nearest-neighbor distances of 7.1 and 7.3 bohr. In all calculations for both bcc and fcc structures we obtained Fermi surfaces whose distortions from perfect spheres were of the order of one part in 10^5. At the optimum lattice spacings we found the virial theorem to be satisfied to an accuracy completely consistent with that of our numerical methods.

TABLE I. Total HF energies per atom E/Nd (in hartree) for bcc and fcc lithium crystals with compound cubic-lattice spacing a (in bohr), based on $\zeta_c = 2.69$ and one valence 2s Slater-type orbital with screening parameter ζ.

	bcc			fcc	
a	ζ	E/Nd	a	ζ	E/Nd
7.6	0.50	−7.41795	9.0	0.50	−7.41343
8.0	0.50	−7.41966	10.0	0.45	−7.41980
8.0	0.55	−7.41972	10.0	0.50	−7.41982
8.0	0.60	−7.41961	10.0	0.55	−7.41977
8.2	0.45	−7.41994	10.3	0.40	−7.42013
8.2	0.50	−7.42002	10.3	0.45	−7.42019
8.2	0.55	−7.41996	10.3	0.50	−7.42024
8.2	0.60	−7.41993	10.3	0.55	−7.42020
8.4	0.50	−7.41992	10.6	0.45	−7.42015
8.4	0.55	−7.41996	10.6	0.50	−7.42019
8.4	0.60	−7.41982	10.6	0.55	−7.42015
8.6	0.50	−7.41960	11.0	0.50	−7.41954
8.6	0.55	−7.41968			
8.6	0.60	−7.41959			
8.8	0.50	−7.41910			

TABLE II. Total HF energies per atom E/Nd (in hartree) for bcc and fcc lithium crystals with compound-cubic lattice spacings a (in bohr), based on $\zeta_c = 2.69$ and two 2s Slater-type orbitals. One valence orbital screening constant has been assigned the value $\zeta_1 = 0.50$ for both structures; the other valence orbital has screening constant ζ_2.

	bcc			fcc	
a	ζ_2	E/Nd	a	ζ_2	E/Nd
7.8	2.0	−7.41944	9.7	2.5	−7.42139
7.8	2.5	−7.42172	9.7	3.0	−7.42195
7.8	3.0	−7.42152	9.7	3.5	−7.42184
7.8	3.5	−7.42141			
8.0	2.5	−7.42101	10.0	2.5	−7.42211
8.0	3.0	−7.42192	10.0	3.0	−7.42263
8.0	3.5	−7.42182	10.0	3.5	−7.42240
8.2	2.5	−7.42197	10.3	2.5	−7.42227
8.2	3.0	−7.42199	10.3	3.0	−7.42266
8.2	3.5	−7.42195	10.3	3.5	−7.42219
8.4	3.0	−7.42177	10.6	2.5	−7.42199
8.4	3.25	−7.42180	10.6	3.0	−7.42258
8.4	3.5	−7.42178	10.6	3.5	−7.42220

Further details of the near-HF wave functions at the optimal lattice spacings are presented in Table III. The coefficients $B_i(\vec{k})$ and $c_i(\vec{k})$ are sufficiently independent of the orientation of $\vec{k}$ that they have been expressed as radial expansions,

$$B_i(\vec{k}) = \sum_{n=0}^{4} b_{in} k^{2n} , \tag{75}$$

$$c_i(\vec{k}) = (4\pi)^{-1/2} \sum_{n=0}^{4} c_{in} k^{2n} . \tag{76}$$

We also give the core-orbital energies ϵ_c, the energies of the bottom of the valence band $\epsilon(0)$, and the Fermi energies ϵ_F.

VII. DISCUSSION

In accordance with experiment,[21] our calculations show for both crystal structures very shallow energy minima with respect to variations in lattice spacing. However, our calculated optimum

TABLE III. Data from near-HF calculations for bcc and fcc lithium crystal at optimum lattice spacings. Energies are in hartree, distances in bohr. E/Nd = total HF energy per atom; a is the compound cubic unit cell dimension; ζ_1, ζ_2 are 2s Slater-type orbital screening parameters; ϵ_c is the core orbital energy; $\epsilon(0)$ is the energy of bottom of valence band; ϵ_F is the Fermi energy; b_{in}, c_{in} are coefficients in expansions of $B_i(\vec{k})$ and $c_i(\vec{k})$, Eqs. (75) and (76).

	E/Nd	a	ζ_1	ζ_2	ϵ_c	$\epsilon(0)$	ϵ_F
bcc	−7.4220	8.2	0.5	3.0	−2.3437	−0.2343	0.0292
fcc	−7.4227	10.3	0.5	3.0	−2.3427	−0.2353	0.0294

	n	b_{1n}	b_{2n}	c_{1n}	c_{2n}
bcc	0	0.7618	0.9126	0.8665	−0.1925
	1	-0.9763×10^{-1}	-0.1796×10^{-1}	-0.2291×10^{-3}	0.1367×10^{-1}
	2	0.1119×10^{-1}	0.5072×10^{-3}	-0.2137×10^{-2}	0.3499×10^{-1}
	3	-0.1352×10^{-2}	-0.3056×10^{-3}	0.7348×10^{-2}	−0.1369
	4	0.1559×10^{-3}	0.8437×10^{-4}	-0.1061×10^{-1}	0.2373
	n	b_{1n}	b_{2n}	c_{1n}	c_{2n}
fcc	0	0.7694	0.9156	0.8630	−0.2049
	1	-0.6247×10^{-1}	-0.1130×10^{-1}	-0.2991×10^{-3}	0.1062×10^{-1}
	2	0.4681×10^{-2}	0.3769×10^{-3}	-0.1083×10^{-3}	0.1309×10^{-1}
	3	-0.5643×10^{-3}	-0.3310×10^{-3}	0.1709×10^{-3}	-0.3587×10^{-1}
	4	0.1019×10^{-3}	0.9913×10^{-4}	-0.4221×10^{-3}	0.3999×10^{-1}

nearest-neighbor distances δ for the bcc and fcc structures, respectively, 3.7 and 3.8 Å, are considerably larger than the corresponding experimental values of 3.04 and 3.11 Å.[22] This discrepancy may in part be due to the neglect of correlation, but is also related to the fact that p orbitals were not included in the atomic valence basis. Because of the shallowness of the energy minima, the effect upon the nearest-neighbor distance can be quite large. We note that our δ value for the fcc structure is slightly larger than that for the bcc form, in agreement with experiment. Our calculations are also consistent with experimental observations that the fcc structure is stable relative to the bcc form at low temperatures.[23] However, the accuracy of the calculations is such that no importance can be attached to the calculated energy difference of about 7×10^{-4} hartree, though its magnitude agrees with pseudopotential calculations.[23]

Both the limitations of the atomic valence basis and the neglect of correlation make it impossible to infer realistic cohesive energies from our calculations. It is difficult to assess quantitatively the effect of the omission of valence p orbitals. However, we do note that the experimental cohesive energy for lithium (36.5 kcal/mole or 1.6 eV/atom) is of the same order as the correlation energy per electron pair in the same molecular or atomic orbital (about 1 eV).[24] It is therefore obvious that without accounting for correlation corrections no reliable cohesive energies can be obtained from HF energies.

Another calculated property of the Li crystals susceptible of comparison with experiment is their compressibility. A compressibility calculation requires the evaluation of the second derivative of E/Nd with respect to the lattice spacing a at the HF equilibrium spacing. It is impractical to do this analytically as the a dependence of E/Nd is very complicated. Unfortunately we cannot evaluate the compressibility numerically either, because the shallowness of the energy minimum causes E/Nd to vary too weakly. Our accuracy of five decimal spaces in E/Nd leaves no significant figures after two numerical differentiations.

The only comparably rigorous HF calculation for lithium so far published is the work by Calais and Sperber.[25] Their valence Bloch orbitals differ from ours, being of the conventional tight-binding form we considered in our initial crystal electronic-structure studies.[26] They used a double-ζ Slater-type orbital basis of 1s and 2s orbitals, thereby also differing from our work in the treatment of the core orbitals. They obtained for the bcc structure an energy of about −7.432 hartree/atom with a HF equilibrium nearest-neighbor distance close to 3.2 Å. This lattice spacing may be smaller than that we found because of the difference in $\vec{k}$ dependence of the valence Bloch orbitals.

In order to obtain further insight into the relationships between our calculations, those of Calais and Sperber, and experiment, we examined a series of HF calculations on the Li atom and the Li_2 molecule. For the atom, the ground-state single and double-ζ HF energies of, respectively, −7.41848[19] and −7.43272 hartree[27] place an upper limit estimate of 0.014 hartree on the energy improvement obtainable by change from a single-ζ to a double-ζ core (most of the improvement comes from an improved description of the 1s electrons). For the Li_2 molecule, we carried out a set of ground-state calculations with various bases as reported in Table IV. From the sixth and next-to-last lines of Table IV, we estimate an energy improvement per atom from use of a double-ζ core as 0.014 hartree. The close agreement of these figures is consistent with the expectation that the core energy should be insensitive to the atomic environment and suggests that the use of double-ζ cores would improve our crystal energies by approximately 0.014 hartree/atom. This improvement adjusts our bcc near-HF energy to -7.436 hartree/atom, in quite close correspondence with the value of Calais and Sperber.

The Li_2 calculations provide several additional pieces of information. Looking at the studies with a single core orbital and a double-ζ 2s valence basis (those comparable to our crystal calculations), we find that the optimum valence-orbital ζ values are essentially the same for Li_2 as in the crystal, and that the energy minimum occurs at an internuclear separation of 3.3 Å, about 25% larger than the experimental separation of 2.67 Å,[22] in close correspondence with the situation for the crystal (where the calculated lattice spacing is about 23% larger than experiment). We note that the Li_2 energy minimum lies above our crystal energy, indicating stability of the crystal relative to dissociation into Li_2 molecules. The calculations with double-ζ cores also indicate that the optimum lattice spacings are not affected by the core description. We also carried out some Li_2 calculations with a basis which included 2$p\sigma$ orbitals. Addition of these orbitals lowers dramatically both the HF energy and the equilibrium internuclear separation, and suggests that the lack of p orbitals may be a common fault of both our crystal wave function and that of Calais and Sperber.

TABLE IV. HF energies per lithium atom E (in hartree) for the Li_2 molecule, with different valence orbital basis sets and internuclear distances R (in bohr). Except for the last three lines of the table, the 1s core orbitals are single Slater-type orbitals with $\zeta_c = 2.69$. The last three lines describe a calculation with a double-ζ 1s basis with $\zeta_{c1} = 2.4331$, $\zeta_{c2} = 4.5177$. Screening parameters ζ_1 and ζ_2 refer to 2s Slater-type orbitals and ζ_3 refers to a 2$p\sigma$ orbital.

R	ζ_1	ζ_2	ζ_3	E
5.5	0.50	3.0	···	−7.3992
6.0	0.40	3.0	···	−7.3830
6.0	0.50	3.0	···	−7.4003
6.0	0.65	3.0	···	−7.3988
6.25	0.50	2.0	···	−7.4003
6.25	0.50	3.0	···	−7.4004
6.25	0.50	4.0	···	−7.4003
6.5	0.50	3.0	···	−7.4001
5.5	0.50	4.0	0.5	−7.4203
6.25	0.50	4.0	0.5	−7.4175
6.0	0.50	3.0	···	−7.4142
6.25	0.50	3.0	···	−7.4143
6.5	0.50	3.0	···	−7.4141

The agreement in energy between our work and that of Calais and Sperber, coupled with the disagreement in calculated lattice spacing, is an indication that the two wave functions are overly restricted to similar extents, but in different ways. From the tight-binding viewpoint, the Calais-Sperber wave function contains no p orbitals, while our wave function can be thought of as a mixture of all angular symmetries with predetermined coefficients whose values are not optimum. Alternatively, from a modulated-plane-wave approach, our wave function is purely of s local character while the Calais-Sperber function is a fixed admixture of all symmetries. The essence of the matter is that neither function contains the full flexibility needed for an optimum representation of the electronic structure. However, the tight-binding function does have one useful property not shared by the modulated plane waves, namely, that its periodicity in $\vec{k}$ leads to better behavior near the boundaries of the Brillouin zone.

There are several possibilities for removing the deficiencies in our wave functions. One consists of the inclusion of p orbitals in the valence basis. Another alternative is to introduce plane-wave expansions in place of our present wave functions. This alternative would be equivalent to an OPW method, but with exact treatment of exchange and long-range electrostatic cancellations. If wave functions such as those found here are used as starting points, it can become practical to obtain HF convergence with a plane-wave formulation. Work along these lines is in progress.[28] Both the approaches outlined in this paragraph have the advantage that they improve the behavior as $\vec{k}$ approaches the Brillouin-zone boundary. A possible disadvantage of the plane-wave expansions is the inefficiency in their representation of sharp spatial inhomogeneities such as the Coulomb cusps at the atomic nuclei.

APPENDIX A: PROOF OF EQ. (55)

An understanding of the content of Eq. (55) may be obtained by introducing a Fourier-representation formula for $\langle \varphi_c(\vec{r}) | r^{-1} | \varphi_c(\vec{r}) \rangle$:

$$\langle \varphi_c | r^{-1} | \varphi_c \rangle = \frac{1}{\pi a} \int \varphi^0_{cc}(\vec{q}) q^{-2} \, d\vec{q} \,, \tag{A1}$$

which means that Eq. (55) is equivalent to

$$\frac{1}{\pi a}\left(\sum_{\vec{\nu}}{}' \nu^{-2} S(\vec{\nu})\varphi^0_{cc}(\vec{\nu}) - \int \varphi^0_{cc}(\vec{q})q^{-2}\,d\vec{q}\right) \approx \frac{D}{\pi a}. \qquad \text{(A2)}$$

This equality holds exactly for a point-charge array, for which $\varphi^0_{cc}(\vec{q}) = 1$.

The methods presented in I indicate that the left-hand side of Eq. (A2) describes the potential at a lattice point due to charge distributions $|\varphi_c|^2$ at all other lattice points plus that of a compensating uniform background of opposite charge. Since we are presently approximating the interactions of $|\varphi_c|^2$ on different centers by those of point charges, we have justified Eq. (A2), and hence Eq. (55).

APPENDIX B: NUMERICAL FIT TO $\epsilon(\vec{k})$

As indicated in Sec. V, we found it desirable to fit $\epsilon(\vec{k})$ to a formula containing a logarithmic term as well as a series of terms involving powers of k and cubic harmonics. The form we used was chosen for its applicability when the Fermi surface is nearly spherical, and may be written

$$\epsilon(\vec{k}) \approx \sum_u \sum_{p \geq l_u} \epsilon'_{pu} k^{2p} T_u(\Omega) - \frac{k_F^2 - k^2}{ak} \ln\left|\frac{k_F + k}{k_F - k}\right| , \qquad \text{(B1)}$$

where $k_F = (3d/8\pi)^{1/3}$ is the radius the Fermi surface would have if spherical, a is the compound lattice constant, T_u ($u \geq 1$) is the uth completely symmetrical cubic harmonic (in ascending order of l_u, its angular-momentum quantum number), Ω refers to the angular coordinates of $\vec{k}$, and the ϵ'_{pu} are coefficients to be adjusted for best fit. The ϵ'_{pu} were determined by the methods described in Sec. V of II, and yielded an over-all fit to $\epsilon(\vec{k})$ accurate to at least five significant figures.

To use Eq. (B1), we require the integral of $\epsilon(\vec{k})$ over the volume within the Fermi surface. Letting $\bar{k}(\Omega)$ refer to the radial coordinate of the Fermi surface in the direction Ω, and introducing the expansion

$$\bar{k}(\Omega) = \sum_u f_u T_u(\Omega) , \qquad \text{(B2)}$$

we find for slightly nonspherical Fermi surfaces

$$\int \epsilon(\vec{k})\,d\vec{k} = \sum_u \sum_{p \geq l_u} \epsilon'_{pu} \frac{(4\pi)^{1/2}}{2p+3} (\underline{\mathrm{E}}^{2p+3})_{u1} - \frac{4\pi}{a}\left[\tfrac{1}{2}k_F^3 \underline{\mathrm{E}}_{11} - \tfrac{1}{6}k_F(\underline{\mathrm{E}}^3)_{11}\right] , \qquad \text{(B3)}$$

where $\underline{\mathrm{E}}$ is a matrix of elements

$$E_{uv} = \sum_u f_w D_{uvw} , \qquad \text{(B4)}$$

and D_{uvw} is the Clebsch-Gordan coefficient connecting three completely symmetric cubic harmonics.[14]

In obtaining Eq. (B3) we have integrated Eq. (B1) first over the radial coordinate k, and have then substituted the expansion for $\bar{k}(\Omega)$ and performed the angular integration. The last term of Eq. (B1) was handled using

$$\int_0^{\bar{k}} k(k_F^2 - k^2) \ln\left|\frac{k_F + k}{k_F - k}\right| dk = -\left(\frac{k_F^2 - \bar{k}^2}{2}\right)^2 \ln\left|\frac{k_F + \bar{k}}{k_F - \bar{k}}\right| + \tfrac{1}{2}k_F^3\bar{k} - \tfrac{1}{6}k_F\bar{k}^3 . \qquad \text{(B5)}$$

In the present calculations, the logarithmic term on the right-hand side of Eq. (B5) is negligible to one part in 10^7 and has therefore been omitted from the analysis leading to Eq. (B3).

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