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Abstract. — Results preliminary to exact Hartree-Fock calculations for cubic lithium crystals are obtained by a method recently developed by the authors. The Is core orbitals have thus far been treated as non-overlapping and fixed, but this limitation is not inherent to the method. The valence electrons are assigned to doubly-occupied Bloch orbitals orthogonalized to the core functions. All energy contributions are evaluated exactly. The results are qualitatively in accord with experimental data on the lithium crystal, and indicate the practicality of complete Hartree-Fock calculations at favorable computation times.

Introduction. — We have recently presented a method for calculating the total energy, band energies, Bloch orbitals, and the Fermi surface for simple crystals at the exact Hartree-Fock (HF) level [1]. The HF Bloch orbitals are built using atomic orbitals in a manner intermediate between the linear-combination-of-atomic-orbitals (LCAO) and orthogonalized-plane-wave (OPW) methods. A main feature of our formulation is the reduction of all integrals over Bloch orbitals to reciprocal-lattice summations, which we obtain from the original integrals by use of Fourier representation formulas and lattice orthogonality relations. The terms in the lattice sums involve Fourier transforms of the atomic orbitals used and are therefore simple to evaluate for any of the usual choices of atomic basis functions. The result is that we obtain tractable expressions for all the energy quantities needed for HF calculations, including the exact exchange energy [2].

In our previous work we applied our methods to atomic hydrogen crystals with cubic symmetry [3], [4]. In this communication we present preliminary calculations for cubic lithium crystals, which illustrate new features associated with the presence of cores of inner-shell electrons. As we indicate later in this paper, we proceed by describing the core electrons in ordinary space while continuing to use a reciprocal-space description of the valence electrons.

Theory. — We assume the total HF wavefunction of the Li crystal to be built up from doubly-occupied 1s core orbitals $\phi_{1s}$ and doubly-occupied valence Bloch orbitals $| k \rangle$. In this preliminary study, we approximate the core orbitals by 1s Slater-type orbitals (STO's) localized at the lithium nuclei, and further assume that these STO's could be assigned the screening parameter (Slater exponent) $\xi = 2.7$ found optimum for atomic lithium. Experience in atomic and molecular HF calculations indicates that the 1s orbital is little affected by the atomic environment, and that the approximation made here will result in a nearly uniform displacement of all calculated energies. We also assume zero differential overlap between core orbitals on different nuclei. This assumption is well justified, as the overlap integral between nearest neighbors at the normal experimental separation of about 6 bohr is approximately $10^{-3}$. It should be emphasized that the above-described approximations are not essential to our method of calculation and will be removed when necessary to obtain the accuracy desired.

In line with our earlier work on atomic hydrogen...
crystals, we take the valence Bloch orbital for wave vector \( k \) in the form

\[
|k > = \sum_{j=1}^{M} c_j(k) |k_j > ,
\]

(1)

where the \( c_j(k) \) are determined by applying the HF condition. The \( c_j(k) \) are explicitly indicated to depend upon \( k \), as the \( k \) dependence of the \( |k_j > \) may not suffice for the HF wavefunction. The HF condition also defines the set of \( k \) values for which the orbitals \( |k_j > \) are occupied, i.e., it determines the Fermi surface.

The \( |k_j > \) are basis Bloch orbitals formed from valence atomic orbitals \( \phi_j(r - R_\mu) \) centered at the nuclear locations \( R_\mu \), with admixtures of the core orbitals \( \phi_{c\nu}(r - R_\mu) \) as needed to make each \( |k_j > \) orthogonal to all core orbitals. The form we use for \( |k_j > \) is

\[
|j > = e^{ik \cdot r} \sum_{\mu} [\phi_j(r - R_\mu) - B_j(k) \phi_{1s}(r - R_\mu)] ,
\]

(2)

where the summation runs over all nuclear locations \( R_\mu \). The orthogonality condition causes \( B_j(k) \) to be given by

\[
B_j(k) = \frac{\sum_{\mu} <\phi_{1s}(r)|e^{ik \cdot r}|\phi_j(r - R_\mu)>}{\sum_{\mu} <\phi_{1s}(r)|e^{ik \cdot r}|\phi_{1s}(r - R_\mu)>}
\]

(3)

the last equality resulting from the zero-differential-overlap assumption for \( \phi_{1s} \).

Equation (2) shows that the \( |k_j > \) have been chosen to be plane waves of wave vector \( k \), modulated by lattice sums of atomic orbitals \( \phi_j \) and \( \phi_{1s} \). This choice of the \( |k_j > \) is in the spirit of the OPW method [5], as may be more clearly seen if we use Fourier representation theory to rewrite eq. (2) as a reciprocal-lattice sum. With the aid of lattice orthogonality relations, eq. (2) can be brought to the form

\[
|k_j > = \sum_{q} e^{i(q - k) \cdot r} [\phi_{jT}(q_v) - B_j(k) \phi_{1sT}(q_v)],
\]

(4)

where the summation is over the points \( q_v \), reciprocal to the nuclear locations \( R_\mu \), and the superscripts « \( T \) » designate the Fourier transforms of the functions so labelled. The main difference between our present procedures and those of the usual OPW calculations is that our independent variational quantities are the coefficients of the atomic orbitals \( \phi_p \) rather than the coefficients of individual plane waves. Our procedure may be expected to be advantageous to the extent that atomic orbitals are superior to uniformity as a starting point for describing the HF electron distribution.

Using the calculational methods reported in earlier work, we are able to reduce all quantities appearing in the Hartree-Fock equations and in the expression for the total energy to reciprocal-lattice summations and single-center core-orbital integrals. Details of the computations will be provided in a fuller presentation when more complete results have been obtained.

**Results.** — We have carried out preliminary calculations for lithium crystals in simple cubic (sc) and body-centered cubic (bcc) lattices, at a variety of lattice spacings. We have not yet completed studies using several valence orbitals \( \phi_j \). The work to be reported here is based on the use of a single 2s STO \( \phi_j \) with the Slater-rule screening parameter \( \zeta = 0.65 \). While the quantitative results must be regarded as highly tentative by virtue of our initial approximations and limitations, our present results nevertheless suffice to reveal three features which will be relevant to more complete and accurate calculations.

To start, we note that the orthogonalization factor \( B_j(k) \) is found to be essentially independent of the orientation of \( k \) and to depend only weakly upon the magnitude of \( k \), varying only of the order of 10 % over the occupied part of the Brillouin zone. This behavior is illustrated by the data in Table I, calculated for the sc structure. The extremely weak \( k \) direction dependence of \( B_j(k) \) is clearly caused by the spherical symmetry of the core orbitals in combination with the cubic symmetry of the lattice. These facts and the fact that the core orbitals are confined to only a small fraction of the cell volume are responsible for the weak dependence of \( B_j(k) \) on the magnitude of \( k \). This behavior of \( B_j(k) \) is very fortunate from a practical point of view, as it enables the introduction of numerical simplifications when \( B_j(k) \) is expanded in crystal harmonics and powers of \( k \).

**Table I**

**Variation of orthogonalization factor \( B_j(k) \) for sc lithium crystal as a function of \( k \) vector. Parameters: Lattice spacing \( a = 5.1 \) bohr; 1s core STO exponent = 2.7; 2s valence STO exponent = 0.65. (Vectors \( k \) are specified by length \( k \) in units of \( 2\pi/a \) and by reciprocal lattice direction components \( [uvw] \).)**

<table>
<thead>
<tr>
<th>( k ) [uvw]</th>
<th>( B_j(k) )</th>
<th>( k ) [uvw]</th>
<th>( B_j(k) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 [100]</td>
<td>0.660 779</td>
<td>1/7 [111]</td>
<td>1.070 942</td>
</tr>
<tr>
<td>1.0 [110]</td>
<td>0.660 753</td>
<td>2/7 [111]</td>
<td>1.036 761</td>
</tr>
<tr>
<td>1.0 [111]</td>
<td>0.660 748</td>
<td>3/7 [111]</td>
<td>0.982 922</td>
</tr>
<tr>
<td>1.0 [210]</td>
<td>0.660 764</td>
<td>4/7 [111]</td>
<td>0.913 568</td>
</tr>
<tr>
<td>1.0 [211]</td>
<td>0.660 753</td>
<td>5/7 [111]</td>
<td>0.833 552</td>
</tr>
</tbody>
</table>

A second preliminary observation of some interest is based on the approximate total energy per atom \( (E/N) \) as a function of the lattice scale. In Table II we present \( E/N \) values for bcc lattices as a function of the lattice parameter \( a \). These data indicate an energy
Table II

Total HF energies per atom $E/N$ (in hartrees) as function of unit cell dimension $a$ (in bohrs) for bcc lithium crystal. $E/N$ is calculated using one 1s core STO and one 2s valence STO per lattice site with respective Slater exponents 2.7 and 0.65.

<table>
<thead>
<tr>
<th>$a$</th>
<th>$E/N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6</td>
<td>-7.4205</td>
</tr>
<tr>
<td>7.8</td>
<td>-7.4216</td>
</tr>
<tr>
<td>8.0</td>
<td>-7.4223</td>
</tr>
<tr>
<td>8.2</td>
<td>-7.4226</td>
</tr>
<tr>
<td>8.4</td>
<td>-7.4226</td>
</tr>
<tr>
<td>8.6</td>
<td>-7.4223</td>
</tr>
</tbody>
</table>

minimum of approximately $-7.423$ hartree, at an $a$ value of about 8.3 bohr, which corresponds to a nearest-neighbor separation of 7.2 bohr. These values may be compared with those for the Li$_2$ molecule, which with the atomic orbitals used here has a calculated minimum energy per atom of $-7.421$ hartree at an internuclear separation of 5.35 bohr [6]. The corresponding Li atom wavefunction yields an energy of $-7.418$ hartree [7]. The present calculations thus already predict the lithium crystal to be energetically stable with respect to dissociation either into Li$_2$ molecules or into Li atoms. This result is in contrast to our earlier finding that atomic hydrogen crystals are not even predicted at the HF level to be stable with respect to dissociation into hydrogen atoms. The calculated nearest-neighbor separations in the bcc crystal are correctly found to be larger than the internuclear separation calculated correspondingly for the Li$_2$ molecule, but are about 25% greater than the experimental bcc value (5.75 bohr) [8]. This discrepancy is indicative both of the crudeness of the present calculations and of the omission of electron correlation.

We close with an observation relating to computation time. Because the time-consuming aspects of these calculations are basically the same as for corresponding studies in which the core electrons are absent, we find computation times which differ by only a small amount from those for atomic hydrogen crystals at similar levels of approximation. More specifically, the sc calculations reported here require approximately 3 minutes each on a Univac 1108 computer, while the bcc calculations each require about 1 minute.

Acknowledgment. — We are indebted to Dr. J. M. Ziman for an illuminating discussion of the relationship between our procedure and the OPW method.

References