

## Lithium Energy-Band Structure Calculations Using *Ab Initio* Pseudopotentials\*

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A recently suggested method for constructing *ab initio* pseudopotentials has been applied to Li and used to calculate the energies at high-symmetry points of the Brillouin zone for lithium metal. This potential is unique, local, and Hermitian and is much weaker than the Hartree-Fock potential. As a result of the weakness of the potential, the conduction-band orbitals are smooth in the core regions, and plane-wave expansions are found to converge rapidly. (There is no restriction that the conduction orbitals be made orthogonal to the core orbitals.) The lowest energy band has character similar to the band obtained from orthogonalized planes-wave calculations using the Seitz empirical potential.

### INTRODUCTION

SIGNIFICANT progress has been made in elucidating the electronic band structure of metals.<sup>1</sup> Although it has not been possible to carry out *ab initio*<sup>2</sup> calculations for solids, techniques have been developed for estimating the crystal potential.<sup>3-7</sup>

Once one has an approximate Hartree-Fock crystal potential in a metal, it is necessary to solve for the conduction orbitals in this potential. Orthogonality restrictions imposed by the Hartree-Fock method result in rapid oscillation of the conduction orbital near the atomic cores, so that plane-wave expansions converge extremely slowly here, requiring high momentum waves.<sup>1</sup> This behavior is incorporated in the basis set by orthogonalizing the plane waves<sup>8</sup> to the core functions. Expansion of the conduction orbitals in these orthogonalized plane waves (OPW) then converges rapidly.<sup>8,9</sup>

In recent years a different approach, using pseudopotentials,<sup>10,11</sup> has received much attention. In this approach one deals not with Hartree-Fock states but rather with pseudo-orbitals which are "smoothed" Hartree-Fock orbitals. These pseudo-orbitals are eigen-

states of a pseudopotential which is the sum of the Hartree-Fock potential and a repulsive potential. Such an approach has several distinct advantages. Since the pseudopotential is much weaker than the Hartree-Fock potential, perturbation theory may be used in describing scattering due to impurities or electron-phonon interactions.<sup>12,13</sup> In addition, since the orbitals are smooth, plane-wave expansions are rapidly convergent.<sup>10,11</sup>

However, as has long been recognized,<sup>10,12</sup> the fundamental foundation for pseudopotentials is tenuous in that the pseudopotential is not unique,<sup>14</sup> is not Hermitian,<sup>10,15</sup> and, within the Hartree-Fock framework, has not been derived from *ab initio*<sup>2</sup> calculations.

It has been shown elsewhere<sup>16</sup> that an alternative approach, the G1 method, for electronic-wave functions automatically leads to a smooth, nodeless valence

TABLE I. Band energies (Ref. 19) in hartree atomic units (Ref. 20) for the lowest state  $\Gamma_1$  in the lowest band, and for another low-lying state  $N_1'$ , calculated using basis-set sizes as indicated. The lowest energies calculated in the same way using the Seitz Fourier coefficients (Ref. 9) are included for comparison.

	Original plane-wave set	Size of reduced matrix	Lowest energy	Next lowest energy	Lowest Seitz value
$\Gamma_1$	1	1	-0.3220		-0.5011
	7	2	-0.3239		-0.5035
	19	3	-0.3275	0.7876	-0.7291
	43	4	-0.3296	0.7683	-0.8420
	51	5	-0.3296	0.7679	-0.8767
	75	6	-0.3297	0.7648	-0.9532
	123	7	-0.3297	0.7644	-1.024
$N_1'$	2	1	-0.1821		-0.1823
	6	2	-0.1852	0.7321	-0.1915
	14	3	-0.1946	0.7145	-0.2049
	16	4	-0.1973	0.7111	-0.2074
	20	5	-0.1977	0.7102	-0.2075
	24	6	-0.1986	0.7052	-0.2076
	32	7	-0.1988	0.7041	-0.2076
	36	8	-0.1990	0.7032	-0.2078
	44	9	-0.1993	0.6980	-0.2079
	52	10	-0.1993	0.6972	-0.2080

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<sup>1</sup> J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Co., New York, 1965), Vol. 2.

<sup>2</sup> By an *ab initio* wave function, we mean one obtained directly from the many-electron Schrödinger equation with no restrictions except on the functional form of the many-electron wave function (e.g., a Slater determinant or G1-type function). Thus, calculations which make use of classical approximations such as using Poisson's equation, or of such approximations as the Slater exchange approximation, we would consider to be *a priori* (not empirical) but not *ab initio*.

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TABLE II. Band energies (Ref. 19) in hartree atomic units (Ref. 20) based on G1 pseudopotentials. The two lowest values are reported for each state (Ref. 21). OPW results are included for comparison.

State	Type	Lowest solution			Second lowest solution		
		G1(exact)	G1(sph.)	OPW <sup>a</sup>	G1(exact)	G1(sph.)	OPW <sup>a</sup>
$\Gamma_1$	<i>s</i>	-0.3296	-0.3353	-0.3432	0.7683	0.8022	0.9393
$\Gamma_{16}$	<i>p</i>	0.3083	0.3085	0.3085	1.346	1.334	1.355
$\Gamma_{25}'$	<i>d</i>	0.4778	0.4196	0.427	2.178	2.142	2.175
$\Gamma_{12}$	<i>d</i>	0.5242	0.5633	0.573	1.365	1.396	1.42
$\Gamma_{25}$	<i>f</i>	0.5471	0.5680	0.578	2.330	2.384	2.425
$\Gamma_2'$	<i>f</i>	2.222	2.213	2.245	5.128	5.121	5.09
$N_1'$	<i>p</i>	-0.1990	-0.2021	-0.202	0.7032	0.7120	0.7165
$N_1$	<i>s</i>	-0.0890	-0.1001	-0.088	0.4025	0.4189	0.4355
$N_2'$	<i>p</i>	0.1515	0.1293	0.137 <sup>b</sup>	1.064	1.003	1.055 <sup>b</sup>
$N_4'$	<i>p</i>	0.2115	0.2263	0.2375 <sup>b</sup>	0.6174	0.6401	0.685 <sup>b</sup>
$N_3$	<i>d</i>	0.2841	0.2653	0.262	1.150	1.128	1.22
$N_4$	<i>d</i>	0.7198	0.7220	0.7385	1.181	1.221	1.245
$N_5$	<i>d</i>	1.092	1.087	1.105	1.650	1.646	1.675
$N_2'$	<i>f</i>	1.224	1.198	1.20	3.448	3.402	...
$H_{16}$	<i>p</i>	-0.0170	-0.0431	-0.046	0.8568	0.8949	0.8695
$H_{12}$	<i>d</i>	0.0805	0.1133	0.1135	1.754	1.785	1.76
$H_1$	<i>s</i>	0.2066	0.2104	0.2855	1.154	1.195	1.30
$H_{25}'$	<i>d</i>	0.9233	0.9095	0.92	1.824	1.785	1.855
$H_2'$	<i>f</i>	0.9535	0.8492	0.865	3.562	3.528	3.59
$H_{25}$	<i>f</i>	1.816	1.818	1.85	1.930	1.964	2.00
$P_4$	<i>p</i>	-0.0882	-0.0901	-0.0945	0.6410	0.6502	0.669
$P_1$	<i>s</i>	0.0538	0.0296	0.165	1.090	1.042	1.375
$P_3$	<i>d</i>	0.7924	0.7845	0.8015	1.756	1.748	1.785
$P_5$	<i>f</i>	0.8893	0.9089	0.930	1.738	1.758	1.825

<sup>a</sup> Glasser and Callaway (Ref. 9).

<sup>b</sup> These values may be incompletely converged.

orbital for the lithium atom and consequently a weak effective potential  $V_{\text{atom}}^{G1}$  for this orbital. This G1 potential (being Hermitian, unique, and local) possesses all of the properties required for pseudopotentials, and is derived from *ab initio* calculations.<sup>16</sup>

Making use of this *ab initio* pseudopotential, we present here the initial results of band calculations which we are carrying out on lithium metal.

### CALCULATIONS AND DISCUSSION

For the crystal potential  $V$ , we make the common approximation<sup>1,9</sup> that within any one Wigner-Seitz cell  $V = V_{\text{atom}}^{G1}$ ,<sup>17</sup> with the origin taken to be the center of the cell. Since  $V_{\text{atom}}^{G1}$  is weak, the orbitals  $\phi_k$  were expanded in simple plane waves. In this case, the solution of the G1 wave equation for  $\phi_k$  requires only the Fourier transform of  $V_{\text{atom}}^{G1}$  over the Wigner-Seitz cell.

In order to test the rapidity of convergence of the plane wave expansion, we considered the low-lying states  $\Gamma_1$  and  $N_1'$ .<sup>18</sup> All orders of the reduced matrix

<sup>17</sup> The pseudopotential derived for the 2s valence orbital of Li atom was used for the *s* symmetry states in the metal and the corresponding 2*p* potential was used for the *p*, *d*, and *f* states. Since the *s* pseudopotential is quite different from the *p* pseudopotential, it would approximate the *p* states poorly (see Ref. 1). However, the *d* and *p* potential are rather similar, so that the *p* potential leads to a good approximation for *d* states. Of course, all of these atomic pseudopotentials are spherically symmetric.

<sup>18</sup> For a bcc lattice,  $\Gamma$ ,  $H$ ,  $P$ , and  $N$  represent, respectively, the reciprocal vectors  $(a/2\pi)\mathbf{k} = (0,0,0)$ ,  $(1,0,0)$ ,  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , and  $(\frac{1}{2}, \frac{1}{2}, 0)$ .

were considered up to the set based on 123 and 52 plane waves, respectively. These energies are reported in Table I. We see that the plane-wave expansion does indeed lead to rapid convergence for the G1 functions, whereas in the Hartree-Fock case it shows extremely slow convergence for the  $\Gamma_1$  state. In Table II we report the calculated energies<sup>19,20</sup> for many of the lower states<sup>21</sup> at the center ( $\Gamma$ ) and at several points on the surface of the Brillouin zone ( $N, H, P$ ).<sup>18</sup> These values are compared to those for an OPW calculation<sup>9</sup> utilizing the empirical Seitz potential.<sup>4</sup> We see that the G1 energies and those obtained from OPW's agree to about 10% in most cases, indicating that either method yields a qualitatively correct band structure. However, the G1 results are based on *ab initio* pseudopotentials and lead to smooth conduction orbitals and, as such, are more likely to be useful for scattering calculations and other considerations.<sup>12,13</sup>

In the past, it has been a common practice to calculate the Fourier transforms over the Wigner-Seitz cell by assuming the bcc cell to be spherical.<sup>9</sup> Although this greatly simplifies the calculations, we have found the resulting coefficients to often be in poor agreement with the exact values (obtained by numerical integration<sup>22</sup>) as is shown in Table III. We note several cases (e.g.,  $n^2 = 4, 8, 10, 14, 18$ ) in which the spherical-cell approximation leads to sizeable errors in the Fourier coefficients. Since the spherical approximation was used

TABLE III. Fourier coefficients<sup>a</sup> for the *s* and *p* potentials<sup>b</sup> as calculated exactly using the spherical approximation

$n^2$	$(a/2\pi)\mathbf{K}$	Exact	Spherical <i>s</i>	Exact <i>p</i>	Spherical <i>p</i>
0	(0,0,0)	-0.32197	-0.32342	-0.49122	-0.48996
2	(1,1,0)	0.01957	0.01435	-0.08086	-0.08611
4	(2,0,0)	0.02427	0.04861	-0.04328	-0.01832
6	(2,1,1)	0.01888	0.02101	-0.02945	-0.02734
8	(2,2,0)	0.01223	0.00165	-0.02425	-0.03514
10	(3,1,0)	0.00658	0.00191	-0.03214	-0.03075
12	(2,2,2)	0.00287	0.00197	-0.02021	-0.02103
14	(3,2,1)	0.00142	0.00574	-0.01717	-0.01285
16	(4,0,0)	0.000765	0.00624	-0.01456	-0.00900
18	(3,3,0)	-0.000557	0.00366	-0.01358	-0.00902
18	(4,1,1)	-0.000768	0.00366	-0.01334	-0.00902
20	(4,2,0)	-0.00157	-0.000324	-0.01196	-0.01102
22	(3,3,2)	-0.00185	-0.00401	-0.01096	-0.01311
24	(4,2,2)	-0.00274	-0.00633	-0.01070	-0.01412
26	(4,3,1)	-0.000888	-0.00701	-0.00999	-0.01368
26	(5,1,0)	-0.00107	-0.00701	-0.01010	-0.01368

<sup>a</sup> Defined by  $V_{FT}(\mathbf{K}) = (1/\Omega_0)\Omega_0 e^{i\mathbf{K}\cdot\mathbf{r}} V(r) dr$ , where  $\Omega_0$  is the atomic volume and  $\mathbf{K}$  is a reciprocal-lattice vector.

<sup>b</sup> All values are in hartree atomic units (Ref. 20).

<sup>19</sup> We have used a lattice constant of  $a = 6.575a_0$  corresponding to an atomic volume of  $142.12068a_0^3$  (see Ref. 16).

<sup>20</sup> The units used throughout are hartree atomic units; thus the unit of energy is the hartree or 27.2107 eV.

<sup>21</sup> A basis set of 43 plane waves was used in the calculations of these energies. This corresponds to using all reciprocal-lattice vectors up to  $(a/2\pi)\mathbf{K} = (2,1,1)$ .

<sup>22</sup> A Riemann integration was performed under the exact surface. For choosing the optimum integration points, we used the technique of H. Conroy, J. Chem. Phys. 47, 5307 (1967).

in the OPW calculation on lithium, we have also included in Table II the energies corresponding to the use of this approximation for the G1 potential.

#### SUMMARY

We have found that band calculations using *ab initio* pseudopotentials on lithium metal are simple and lead

to reasonable energies. The resulting conduction orbitals are smooth and may be useful for considering various properties of metals. Because the orbitals are smooth, plane-wave expansions are found to converge rapidly. Band calculations to further characterize the electron-band structure of lithium for points within the Brillouin zone are currently in progress.