

Energy Band Structure of Lithium by the Tight-Binding Method*

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The energy band structure of lithium has been calculated by the tight-binding method. The crystal potential used in the Hamiltonian is the "muffin-tin" version of the Seitz potential. Bloch functions are constructed from the $1s$, $2s$, and $2p$ Hartree-Fock functions of the free atom and are used to set up the secular equation for the energy of a given point in the Brillouin zone. The matrix elements may be expressed as the sums over the crystal lattice points of a series of multicenter integrals with varying distances between the centers of the two atomic orbitals. For the majority of the matrix elements, in order to achieve convergence, all the integrals for which the two centers are separated by less than six times the lattice constant must be included. The multicenter integrals are evaluated by the technique of Gaussian transformation and the method for computing the matrix elements of the potential energy is described. The calculated energies along the $[100]$, $[110]$, and $[111]$ axes of the Brillouin zone agree well with those calculated by a Green's-function method, by a modified plane-wave method, and by the composite-wave variational method of Schlosser and Marcus.

INTRODUCTION

ALTHOUGH the tight-binding method for studying energy bands in solids was proposed as early as in 1928,¹ detailed applications of this method to obtain band structure have hitherto been mostly of a qualitative or semiempirical nature. The immense difficulties connected with the evaluation of the multicenter integrals made it necessary to introduce certain rather strenuous approximations. For example, one of the most common approximations is to ignore all multicenter integrals except those which involve nearest neighbors,² or next-nearest neighbors.³ In some cases these integrals are treated as parameters using an interpolative scheme,⁴ while in others they are evaluated directly.⁵ It is also a common practice to omit all three-center integrals from consideration.⁶ While the approximation of neglecting all integrals except the nearest or next-nearest neighbors is applicable for core states and the d bands of some of the transition metals where overlap between neighboring orbitals is small,³ it is not valid for the general case as is demonstrated by Nran'yan⁷ for diamond and by Corbató⁸ for graphite. Thus, only qualitative results could be expected if this approximation were to be used in tight-binding calculations for crystals where there exists a substantial overlap between neighboring orbitals. Indeed, the lack of quantitative success has aroused the suspicion that the method of tight binding is incapable of providing more than a qualitative picture for crystals with strong overlap.⁹

The recent developments of the technique of numerical integration have made it possible to evaluate the multicenter integrals arising in molecular and solid-state problems by means of electronic computers. With these new devices we have performed a detailed calculation of the band structure of lithium using the method of tight binding. No approximations need be made for computing the integrals. The results of this work, as will be shown, agree very well with those obtained by the Green's-function method,¹⁰ the composite wave (CW) method,¹¹ and a method of modified plane waves (MPW).¹²

CRYSTAL POTENTIAL

The crystal potential used to form the one-electron Hamiltonian is the "muffin-tin" version of the Seitz potential¹³ as corrected by Kohn and Rostoker.¹⁴ To construct such a "muffin-tin" potential, the Wigner-Seitz cell is divided into two regions by an inscribed sphere. Within the inscribed sphere the Seitz potential is used. In the region external to the inscribed sphere but internal to the cell boundary a potential of constant value is employed, this constant being chosen equal to the average value of the Seitz potential within this region. It should be mentioned that the method of calculation presented here is not restricted to such a muffin-tin form; this particular potential was chosen so that comparison with the largest number of other methods could be made. To facilitate the numerical computation, the tabular form of the Seitz potential given by Kohn and Rostoker¹⁴ was replaced by the

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¹ F. Bloch, *Z. Physik* **52**, 555 (1928).

² G. C. Fletcher, *Proc. Phys. Soc. (London)* **A65**, 192 (1952).

³ E. F. Belding, *Phil. Mag.* **4**, 1145 (1959).

⁴ J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954).

⁵ G. C. Fletcher and E. P. Wohlfarth, *Phil. Mag.* **42**, 106 (1951).

⁶ M. Asdente and J. Friedel, *Phys. Rev.* **124**, 384 (1961).

⁷ A. A. Nran'yan, *Fiz. Tverd. Tela* **2**, 1650 (1960) [English transl.: *Soviet Phys.—Solid State* **2**, 1494 (1960)].

⁸ F. J. Corbató, in *Proceedings of the 1957 Carbon Conference* (Pergamon Press, Inc., New York, 1957), p. 173.

⁹ F. Herman, *Rev. Mod. Phys.* **30**, 102 (1958).

¹⁰ F. S. Ham, *Phys. Rev.* **128**, 82 (1962).

¹¹ H. C. Schlosser and P. M. Marcus, *Phys. Rev.* **131**, 2529 (1963); H. C. Schlosser, Ph.D. thesis, Carnegie Institute of Technology, 1960 (unpublished).

¹² E. Brown and J. A. Krumhansl, *Phys. Rev.* **109**, 30 (1958).

¹³ F. Seitz, *Phys. Rev.* **47**, 400 (1935).

¹⁴ W. Kohn and J. Rostoker, *Phys. Rev.* **94**, 1111 (1954).

following least-squares curve fit:

$$V(r) = -2.92586710r^{-1} + 2.70181570 + 1.6756787r \\ - 6.82306300r^2 + 6.83237350r^3 - 3.48727250r^4 \\ + 0.98854560r^5 - 0.14795717r^6 \\ + 0.0091263185r^7. \quad (1)$$

Unless otherwise designated, Hartree's atomic units are used for all formulas. The average value of the Seitz potential between the inscribed spheres was taken as

$$V(r) = \bar{V} = -0.3248.$$

Analogous with the work of Ham,¹⁰ we have replaced the cell boundary by that of the equivalent volume sphere in calculating \bar{V} [with $a_0 = 6.65$ atomic units (a.u.)]. For convenience of calculations, we shall introduce $V'(r)$ defined by

$$V(r) = V'(r) + \bar{V}, \quad (2)$$

so that $V'(r)$ is zero in the region between the inscribed spheres.

ENERGY-BAND CALCULATIONS

The Hartree-Fock self-consistent-field (SCF) atomic wave functions for the $1s$, $2s$, and $2p$ states of the lithium atom¹⁵ are used as the constituents of the Bloch sums. Analytic expressions were devised to fit these numerical functions,

$$\phi_{1s} = 1.91049 \exp(-2.4423r) \\ + 0.701005 \exp(-4.5531r), \\ \phi_{2s} = 0.36748 \exp(-2.222r) \\ - 0.120003r \exp(-0.6632r), \quad (3) \\ \phi_{2p_z} = x[0.107199 \exp(-0.5166r) \\ + 0.0757334 \exp(-1.9662r)], \text{ etc.}$$

The Bloch functions are then constructed in the usual manner as

$$b_{nlm}(\mathbf{k}, \mathbf{r}) = [N\Omega_{nlm}(\mathbf{k})]^{-1/2} \sum_{\mathbf{r}'} e^{i\mathbf{k} \cdot \mathbf{R}_{\mathbf{r}'}} \phi_{nlm}(\mathbf{r} - \mathbf{R}_{\mathbf{r}'}), \quad (4)$$

where N is the number of lattice sites in the crystal and the summation is carried out over all N of these sites. To find the energy band, the five Bloch functions are used as basis for the secular equation,

$$|H_{nlm, n' l' m'}(\mathbf{k}) - ES_{nlm, n' l' m'}(\mathbf{k})| = 0, \quad (5)$$

where H is the one-electron Hamiltonian

$$H = -\frac{1}{2}\nabla^2 + V(r). \quad (6)$$

The matrix elements are composed of the overlap,

¹⁵ V. Fock and M. J. Petrashen, *Physik. Z. Sowjetunion* 8, 547 (1935).

kinetic energy, and potential integrals,

$$S_{i,j}(\mathbf{k}) = \int b_i^*(\mathbf{k}, \mathbf{r}) b_j(\mathbf{k}, \mathbf{r}) d\tau \\ = [\Omega_i(\mathbf{k})\Omega_j(\mathbf{k})]^{-1/2} \sum_{\mathbf{r}} e^{i\mathbf{k} \cdot \mathbf{R}_{\mathbf{r}}} \int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r} - \mathbf{R}_{\mathbf{r}}) d\tau \\ = [\Omega_i(\mathbf{k})\Omega_j(\mathbf{k})]^{-1/2} \sum_{\mathbf{r}} e^{i\mathbf{k} \cdot \mathbf{R}_{\mathbf{r}}} \langle \phi_i(0) | \phi_j(\mathbf{R}_{\mathbf{r}}) \rangle, \\ T_{i,j}(\mathbf{k}) = \int b_i^*(\mathbf{k}, \mathbf{r}) (-\frac{1}{2}\nabla^2) b_j(\mathbf{k}, \mathbf{r}) d\tau \\ = [\Omega_i(\mathbf{k})\Omega_j(\mathbf{k})]^{-1/2} \sum_{\mathbf{r}} e^{i\mathbf{k} \cdot \mathbf{R}_{\mathbf{r}}} \langle \phi_i(0) | -\frac{1}{2}\nabla^2 | \phi_j(\mathbf{R}_{\mathbf{r}}) \rangle, \\ V_{i,j}(\mathbf{k}) = \int b_i^*(\mathbf{k}, \mathbf{r}) V'(\mathbf{r}) b_j(\mathbf{k}, \mathbf{r}) d\tau \\ = [\Omega_i(\mathbf{k})\Omega_j(\mathbf{k})]^{-1/2} \sum_{\mathbf{r}} e^{i\mathbf{k} \cdot \mathbf{R}_{\mathbf{r}}} \langle \phi_i(0) | V' | \phi_j(\mathbf{R}_{\mathbf{r}}) \rangle. \quad (7)$$

The overlap and kinetic-energy integrals occur frequently in molecular physics and many efficient methods of calculation have been devised.¹⁶⁻¹⁸ The potential-energy integrals are far more difficult to evaluate and it is the intractability of these potential integrals which has heretofore imposed such drastic approximations in applying the method of tight binding. We have devised a scheme for the evaluation of these potential integrals using the technique of Gaussian transformation. We first expand $V'(r)$ as defined in Eq. (2) by the Fourier series

$$V'(r) = \sum_{\mathbf{r}'} V_{\mathbf{r}'}' \cos \mathbf{K}_{\mathbf{r}'} \cdot \mathbf{r}_C, \quad (8)$$

where the summation is over all sites in the reciprocal lattice and \mathbf{r}_C is the radius vector measured from any given lattice site of the crystal. Thus the integral of $V'(r)$ between two $1s$ orbitals situated at points A and B is

$$\langle 1s(A) | V' | 1s(B) \rangle = \sum_{\mathbf{r}'} V_{\mathbf{r}'}' \langle 1s(A) | \cos \mathbf{K}_{\mathbf{r}'} \cdot \mathbf{r}_C | 1s(B) \rangle. \quad (9)$$

Upon expressing the $1s$ orbitals in a Laplace transform¹⁹ as

$$e^{-\alpha_1 r_A} = (\alpha_1/2\sqrt{\pi}) \int_0^\infty s_1^{-3/2} \exp(-\alpha_1^2/4s_1 - r_A^2 s_1) ds_1, \quad (10)$$

¹⁶ M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Tables of Molecular Integrals* (Maruzen Company Ltd., Tokyo, Japan, 1963).

¹⁷ I. Shavitt, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic Press Inc., New York, 1963), Vol. 2, p. 1.

¹⁸ M. P. Barnett, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic Press Inc., New York, 1963), Vol. 2, p. 95.

¹⁹ *Tables of Integral Transforms*, edited by A. Erdélyi (McGraw-Hill Book Company, Inc., New York, 1954).

and a similar expression for $e^{-\alpha_2 r_B}$, we have

$$\begin{aligned} \langle 1s(A) | \cos \mathbf{K}_v \cdot \mathbf{r}_C | 1s(B) \rangle \\ = (\alpha_1 \alpha_2 / 4\pi) \int_0^\infty (s_1 s_2)^{-3/2} \exp(-\frac{1}{4}\alpha_1^2/s_1 - \frac{1}{4}\alpha_2^2/s_2) \\ \times \left[\int \exp(-s_1 r_A^2 - s_2 r_B^2) \cos(\mathbf{K}_v \cdot \mathbf{r}_C) d\tau \right] ds_1 ds_2. \quad (11) \end{aligned}$$

The product of two Gaussians situated at centers A and B is proportional to a third Gaussian situated at a point D along the line AB , i.e.,

$$\begin{aligned} \exp(-s_1 r_A^2 - s_2 r_B^2) \\ = \exp[-s_1 s_2 r_{AB}^2 / (s_1 + s_2)] \exp[-(s_1 + s_2) r_D^2], \quad (12) \end{aligned}$$

where r_{AB} is the distance between the two centers, and r_D is the radius vector originated from D . The coordinates of D are related to those of A and B as

$$D_i = (s_1 A_i + s_2 B_i) / (s_1 + s_2), \quad i = x, y, z. \quad (13)$$

Writing

$$\mathbf{r}_C = \mathbf{r}_D + \mathbf{r}_{CD},$$

we can perform the spatial integral in Eq. (11),

$$\begin{aligned} \int \exp(-s_1 r_A^2 - s_2 r_B^2) \cos(\mathbf{K}_v \cdot \mathbf{r}_C) d\tau \\ = \exp[-s_1 s_2 r_{AB}^2 / (s_1 + s_2)] \left\{ \cos(\mathbf{K}_v \cdot \mathbf{r}_{CD}) \right. \\ \times \int \exp[-(s_1 + s_2) r_D^2] \cos(\mathbf{K}_v \cdot \mathbf{r}_D) d\tau \\ \left. - \sin(\mathbf{K}_v \cdot \mathbf{r}_{CD}) \int \exp[-(s_1 + s_2) r_D^2] \sin(\mathbf{K}_v \cdot \mathbf{r}_D) d\tau \right\} \\ = [\pi / (s_1 + s_2)]^{3/2} \exp[-s_1 s_2 r_{AB}^2 / (s_1 + s_2)] \\ \times \cos(\mathbf{K}_v \cdot \mathbf{r}_{CD}) \exp[-\frac{1}{4} K_v^2 / (s_1 + s_2)]. \quad (14) \end{aligned}$$

By means of the substitution

$$\begin{aligned} z &= s_1 + s_2, \\ u &= s_1 / (s_1 + s_2), \\ f &= u(1-u) r_{AB}^2, \\ g &= K_v^2 + \alpha_2^2 / (1-u) + \alpha_1^2 / u, \end{aligned}$$

Eq. (11) can be simplified into²⁰

$$\begin{aligned} \langle 1s(A) | \cos \mathbf{K}_v \cdot \mathbf{r}_C | 1s(B) \rangle \\ = \frac{1}{4} \pi^{1/2} \alpha_1 \alpha_2 \int_0^1 [u(1-u)]^{-3/2} \cos(\mathbf{K}_v \cdot \mathbf{r}_{CD}) du \\ \times \int_0^\infty z^{-7/2} \exp(-fz - \frac{1}{4}g/z) dz \\ = 2\pi \alpha_1 \alpha_2 r_{AB}^3 \int_0^1 f [3(fg)^{-5/2} + 3(fg)^{-2} + (fg)^{-3/2}] \\ \times \exp[-(fg)^{1/2}] \cos(\mathbf{K}_v \cdot \mathbf{r}_{CD}) du, \quad (15) \end{aligned}$$

²⁰ See p. 145 of Ref. 19.

which is then easily evaluated by numerical methods. The potential integrals containing unnormalized Slater $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals can be obtained from the above by performing the proper partial differentiations with respect to α_1 , α_2 , A_x , A_y , A_z , B_x , B_y , B_z , e.g.,

$$\begin{aligned} \langle 2s(A) | \cos \mathbf{K}_v \cdot \mathbf{r}_C | 1s(B) \rangle \\ = \int r_A e^{-\alpha_1 r_A} \cos(\mathbf{K}_v \cdot \mathbf{r}_C) e^{-\alpha_2 r_B} d\tau \\ = -\frac{\partial}{\partial \alpha_1} \langle 1s(A) | \cos \mathbf{K}_v \cdot \mathbf{r}_C | 1s(B) \rangle, \quad (16) \end{aligned}$$

$$\begin{aligned} \langle 2p_x(A) | \cos \mathbf{K}_v \cdot \mathbf{r}_C | 1s(B) \rangle \\ = \int x_A e^{-\alpha_1 r_A} \cos(\mathbf{K}_v \cdot \mathbf{r}_C) e^{-\alpha_2 r_B} d\tau \\ = -\frac{\partial}{\partial \alpha_1} \left[\frac{1}{\alpha_1} \frac{\partial}{\partial A_x} \langle 1s(A) | \cos \mathbf{K}_v \cdot \mathbf{r}_C | 1s(B) \rangle \right]. \end{aligned}$$

In general the integrals of $\cos \mathbf{K}_v \cdot \mathbf{r}_A$ may be written in the form

$$\begin{aligned} \langle \psi^S(A) | \cos \mathbf{K}_v \cdot \mathbf{r}_A | \phi^S(B) \rangle \\ = 2\pi \sum_i \beta_i \int_0^1 \gamma_i(u) \left[\sum_{n=0}^7 \mu_{i,n} (fg)^{-\frac{1}{2}(9-n)} \right] \\ \times \exp[-(fg)^{1/2}] \{ \xi_{i,1} \cos[(1-u) \mathbf{K}_v \cdot \mathbf{r}_{AB}] \\ + \xi_{i,2} \sin[(1-u) \mathbf{K}_v \cdot \mathbf{r}_{AB}] \} du, \quad (17) \end{aligned}$$

where the summation over i may include one, two, three, or four terms depending on the orbitals ψ^S and ϕ^S . The superscript S appearing in ψ and ϕ stands for the *unnormalized* Slater-type orbitals. These integrals are then compiled together according to Eq. (9) to form the integrals of V' . The coefficients for Eq. (17) are given in Table I.

The overlap integrals can be evaluated in a similar manner. Detailed discussions have been given by Shavitt.¹⁷ The kinetic-energy integrals are obtained by applying the operator

$$T = -\frac{1}{2} \nabla_B^2 = -\frac{1}{2} \left(\frac{\partial^2}{\partial B_x^2} + \frac{\partial^2}{\partial B_y^2} + \frac{\partial^2}{\partial B_z^2} \right) \quad (18)$$

to the corresponding overlap integrals. These two kinds of integrals are reduced to the general form

$$\begin{aligned} (\psi_A^S | \phi_B^S) &= 2\pi \sum_i \zeta_i \int_0^1 \eta_i(u) \\ &\times \left[\sum_{n=0}^7 \lambda_{i,n} (fG)^{-\frac{1}{2}(9-n)} \right] \\ &\times \exp[-(fG)^{1/2}] du, \quad (19) \end{aligned}$$

TABLE I. Coefficients for $\langle \psi^S(A) | \cos \mathbf{K} \cdot \mathbf{r}_A | \phi^S(B) \rangle$.

ψ^S	ϕ^S	i	β_i	$\gamma_i(u)$	$\mu_{i,0}$	$\mu_{i,1}$	$\mu_{i,2}$	$\mu_{i,3}$	$\mu_{i,4}$	$\mu_{i,5}$	$\mu_{i,6}$	$\mu_{i,7}$	$\xi_{i,1}$	$\xi_{i,2}$
1s	1s	1	$\alpha_1 \alpha_2 r_{AB}^3$	f	0	0	0	0	3	3	1	0	1	0
2s	1s	1	$\alpha_1^2 \alpha_2 r_{AB}^3$	f^2/u	0	0	15	15	6	1	0	0	1	0
		2	$-\alpha_2 r_{AB}^3$	f	0	0	0	0	3	3	1	0	1	0
2p _x	1s	1	$-\alpha_1 \alpha_2 (K_\nu)_x r_{AB}^3$	f^2	0	0	15	15	6	1	0	0	0	1
		2	$\alpha_1 \alpha_2 r_{AB} (r_{AB})_x$	f^2/u	0	0	0	0	3	3	1	0	1	0
2s	2s	1	$\alpha_1^2 \alpha_2^2 r_{AB}^5$	f^2	105	105	45	10	1	0	0	0	1	0
		2	$r_{AB}^3 K_\nu^2$	f^2	0	0	15	15	6	1	0	0	1	0
		3	$-r_{AB}^3$	f	0	0	0	0	12	12	5	1	1	0
2p _x	2s	1	$-\alpha_1 \alpha_2^2 (K_\nu)_x r_{AB}^3$	$f^3/(1-u)$	105	105	45	10	1	0	0	0	0	1
		2	$\alpha_1 \alpha_2^2 (r_{AB})_x r_{AB}^3$	f^2	0	0	15	15	6	1	0	0	1	0
		3	$\alpha_1 (K_\nu)_x r_{AB}^3$	f^2	0	0	15	15	6	1	0	0	0	1
		4	$-\alpha_1 r_{AB} (r_{AB})_x$	f^2/u	0	0	0	0	3	3	1	0	1	0
2p _x	2p _x	1	$-\alpha_1 \alpha_2 (K_\nu)_x^2 r_{AB}^3$	f^3	105	105	45	10	1	0	0	0	1	0
		2	$\alpha_1 \alpha_2 r_{AB}^3$	f^2	0	0	15	15	6	1	0	0	1	0
		3	$\alpha_1 \alpha_2 (K_\nu)_x r_{AB}^3 (r_{AB})_x$	$(2u-1)f^2$	0	0	15	15	6	1	0	0	0	1
		4	$-\alpha_1 \alpha_2 r_{AB} (r_{AB})_x^2$	f^2	0	0	0	0	3	3	1	0	1	0
2p _x	2p _y	1	$-\alpha_1 \alpha_2 r_{AB}^3 (K_\nu)_x (K_\nu)_y$	f^3	105	105	45	10	1	0	0	0	1	0
		2	$\alpha_1 \alpha_2 r_{AB}^3$	$\{[(K_\nu)_x (r_{AB})_y + (K_\nu)_y (r_{AB})_x]u - (K_\nu)_y (r_{AB})_x\} f^2$	0	0	15	15	6	1	0	0	0	1
		3	$-\alpha_1 \alpha_2 r_{AB} (r_{AB})_x (r_{AB})_y$	f^2	0	0	0	0	3	3	1	0	1	0

$$\begin{aligned}
(\psi_A^S | -\frac{1}{2} \nabla^2 | \phi_B^S) &= \pi \sum_i \omega_i \int_0^1 \eta_i(u) \\
&\times \left[\sum_{n=0}^7 \rho_{i,n} (fG)^{-\frac{1}{2}(7-n)} \right] \\
&\times \exp[-(fG)^{1/2}] du, \quad (20)
\end{aligned}$$

where

$$G = \alpha_2^2/(1-u) + \alpha_1^2/u.$$

Tables II and III list all the coefficients appearing in Eqs. (19) and (20), respectively.

The above-mentioned integrals are now inserted in Eqs. (7) to obtain the matrix elements. It is interesting to examine the convergence of the summation over the crystal lattice site ν in Eqs. (7), for this is the point at which the customary nearest-neighbor approximation was introduced. For the purpose of illustration, we have

taken the matrix element $V_{2p_x, 2s'}$ with $\mathbf{k} = (2\pi/a_0) \times (0.85, 0, 0)$ as an example and truncated the summation over ν at various distances from the origin corresponding to the inclusion of more and more sites. Values of the truncated sum are shown in Table IV. As can be seen, the summation does not begin to approach convergence until all sets of equivalent atoms up to the 25th nearest neighbor have been included. We can also see a certain loss of significant figures in going from the basic integrals to the matrix elements. This difficulty was first pointed out by Parmenter,²¹ but in our case this cancellation is not serious and appears to become significant only for the higher energy bands.

RESULTS

The energy bands were calculated by solving the 5×5 secular equation with the Bloch functions as basis. All summations (over the lattice sites) in the matrix ele-

TABLE II. Coefficients for $\langle \psi^S(A) | \psi^S(B) \rangle$.

ψ^S	ϕ^S	i	ζ_i	$\eta_i(u)$	$\lambda_{i,0}$	$\lambda_{i,1}$	$\lambda_{i,2}$	$\lambda_{i,3}$	$\lambda_{i,4}$	$\lambda_{i,5}$	$\lambda_{i,6}$	$\lambda_{i,7}$
1s	1s	1	$\alpha_1 \alpha_2 r_{AB}^3$	f	0	0	0	0	3	3	1	0
2s	1s	1	$\alpha_1^2 \alpha_2 r_{AB}^3$	f^2/u	0	0	15	15	6	1	0	0
		2	$-\alpha_2 r_{AB}^3$	f	0	0	0	0	3	3	1	0
2p _x	1s	1	$\alpha_1 \alpha_2 r_{AB} (r_{AB})_x$	f^2/u	0	0	0	0	3	3	1	0
2s	2s	1	$\alpha_1^2 \alpha_2^2 r_{AB}^5$	f^2	105	105	45	10	1	0	0	0
		2	$-r_{AB}^3$	f	0	0	0	0	12	12	5	1
2p _x	2s	1	$\alpha_1 \alpha_2^2 r_{AB}^3 (r_{AB})_x$	f^2	0	0	15	15	6	1	0	0
		2	$-\alpha_1 r_{AB} (r_{AB})_x$	f^2/u	0	0	0	0	3	3	1	0
2p _x	2p _x	1	$\alpha_1 \alpha_2 r_{AB}^3$	f^2	0	0	15	15	6	1	0	0
		2	$-\alpha_1 \alpha_2 r_{AB} (r_{AB})_x^2$	f^2	0	0	0	0	3	3	1	0
2p _x	2p _y	1	$-\alpha_1 \alpha_2 r_{AB} (r_{AB})_x (r_{AB})_y$	f^2	0	0	0	0	3	3	1	0

²¹ R. H. Parmenter, Phys. Rev. **86**, 552 (1952).

TABLE III. Coefficients for $\langle \psi^S(A) | -\frac{1}{2}\nabla^2 | \phi^S(B) \rangle$.

ψ^S	ϕ^S	i	ω_i	$\eta_i(u)$	$\rho_{i,0}$	$\rho_{i,1}$	$\rho_{i,2}$	$\rho_{i,3}$	$\rho_{i,4}$	$\rho_{i,5}$	$\rho_{i,6}$	$\rho_{i,7}$
1s	1s	1	$\alpha_1\alpha_2r_{AB}$	f	0	0	0	0	3	3	-1	0
2s	1s	1	$\alpha_1^2\alpha_2r_{AB}$	f^2/u	0	0	9	9	2	-1	0	0
		2	$-\alpha_2r_{AB}$	f	0	0	0	0	3	3	-1	0
2p _x	1s	1	$\alpha_1\alpha_2(r_{AB})_x/r_{AB}$	f^2/u	0	0	0	0	5	5	-1	0
2s	2s	1	$\alpha_1^2\alpha_2^2r_{AB}^3$	f^2	45	45	15	0	-1	0	0	0
		2	$-r_{AB}$	f	0	0	0	0	6	6	3	-1
2p _x	2s	1	$\alpha_1\alpha_2^2(r_{AB})_x r_{AB}$	f^2	0	0	15	15	4	-1	0	0
		2	$-\alpha_1(r_{AB})_x/r_{AB}$	f^2/u	0	0	0	0	5	5	-1	0
2p _x	2p _x	1	$\alpha_1\alpha_2r_{AB}$	f^2	0	0	15	15	4	-1	0	0
		2	$-\alpha_1\alpha_2(r_{AB})_x^2/r_{AB}$	f^2	0	0	0	0	7	7	-1	0
2p _x	2p _y	1	$-\alpha_1\alpha_2(r_{AB})_x(r_{AB})_y/r_{AB}$	f^2	0	0	0	0	7	7	-1	0

ments were carried to convergence. The calculations were performed for two values of the fundamental lattice constant $a_0=6.65$ and 6.5183 a.u. which were used in the previous works reported in the literature. Comparison of our energy values along the [100], [110], and [111] directions with Ham's calculation by a Green's-function method¹⁰ ($a_0=6.65$ a.u.) is shown in Table V, and with the results of CW¹¹ and of MPW¹² calculation is shown in Table VI. In all cases the agreement is seen to be very good.

TABLE IV. Values of truncated summation of $V_{2p_x, 2s'}$ for $k=(2\pi/a_0)(0.85, 0, 0)$, $a_0=6.65$ a.u.

Last set of nearest neighbors included in sum	Number of equivalent atoms in set	Distance from origin	Truncated sum ^a $V_{2p_x, 2s'}$
0	1	0.000	0.0000
1	8	5.759	0.8632
2	6	6.650	0.1681
3	12	9.404	-1.3572
4	24	11.028	0.8624
5	8	11.518	0.0581
6	6	13.300	-0.1877
7	24	14.493	0.8531
8	24	14.870	0.0935
9	24	16.289	-0.4678
10	24	17.277	-0.2325
11	8	17.277	-0.0746
12	12	18.809	-0.1799
13	48	19.671	0.8531
14	24	19.950	-0.0706
15	6	19.950	-0.0784
16	24	21.029	-0.1149
17	24	21.803	-0.0442
18	24	22.055	-0.0781
19	8	23.036	-0.0944
20	24	23.745	-0.0711
21	24	23.745	-0.0717
22	24	23.977	-0.0875
23	48	24.882	-0.1144
24	24	25.540	-0.1006
25	48	25.540	-0.0944
26	6	26.600	-0.0933
27	24	27.216	-0.0903
28	24	27.419	-0.0957
29	24	27.419	-0.0939
30	12	28.213	-0.0947
31	24	28.213	-0.0941

^a Since $V_{2p_x, 2s'}$ is an imaginary number, the values listed are $V_{2p_x, 2s'}/i$.

For points of high symmetry, the secular equation factorizes into smaller blocks. For example, at the Γ point only the mixing between 1s and 2s Bloch functions need be considered, whereas along the Δ line of [100] symmetry, the secular equation is a 3×3 one with 1s, 2s, and $2p_x$ basis functions. For an arbitrary point in the k space, the complete 5×5 secular equation must be solved. However, once all the basic integrals have been evaluated, the energy for any point in the Brillouin zone can be obtained as readily as that for a point of high symmetry. We have also computed the energies for points along the [221], [310], and [311] directions and the results agree well with those of Schlosser and Marcus.¹¹

To examine the effect of the 1s core on the band structure, we have calculated the energy of the Γ point using two separate approximations. The first is to completely ignore the 1s Bloch function and gives $E=-0.896$ Ry. The second is to leave out the 1s basis

TABLE V. Comparison of the energies (in rydbergs) of the conduction band of lithium calculated by the tight-binding method and by the method of Green's functions. ($a_0=6.65$ a.u.)

$a_0k_x/2\pi$	Energies	
	Tight-binding	Green's-function ^a
[100] Δ_1		
0.0000	-0.674	-0.681
0.2500	-0.629	-0.640
0.5000	-0.500	-0.512
0.6250	-0.407	-0.414
0.7500	-0.290	-0.294
1.0000	-0.065	-0.061
[110] Σ_1		
0.2500	-0.587	-0.598
0.3750	-0.485	-0.497
0.5000	-0.399	-0.411
[111] Δ_1		
0.1250	-0.641	-0.651
0.2500	-0.545	-0.556
0.3125	-0.478	-0.486
0.3750	-0.395	-0.400
0.5000	-0.190	-0.191

^a See Ref. 10.

TABLE VI. Comparison of the energies (in rydbergs) of the conduction band of lithium calculated by the tight-binding method and by the methods of modified plane waves and the method of composite waves. ($a_0=6.5183$ a.u.)

$a_0 k_x/2\pi$	Modified ^a plane waves	Composite ^b waves	Tight- binding ^c 5×5 secular Eq.	Simplified 4×4 using b_{2s}'	Tight- binding ^c 4×4 using b_{2s}
[100] Δ_1					
0.0	-0.683	-0.683	-0.672	-0.676	-0.896
0.2	-0.652	-0.656	-0.643	-0.642	-0.556
0.5	-0.495	-0.510	-0.494	-0.487	-0.452
0.8		-0.233	-0.223	-0.222	-0.219
0.9		-0.119	-0.106	-0.106	-0.106
1.0		-0.046	-0.044	-0.044	-0.044
[110] Σ_1					
0.1		-0.669	-0.657	-0.657	-0.508
0.3		-0.562	-0.545	-0.537	-0.451
0.5		-0.410	-0.393	-0.393	-0.393
[111] Δ_1					
0.1		-0.663	-0.650	-0.649	-0.536
0.2	-0.590		-0.587	-0.582	-0.509
0.3		-0.500	-0.485	-0.473	-0.413
0.4	-0.336	-0.358	-0.346	-0.342	-0.324
0.5	-0.175	-0.184	-0.177	-0.177	-0.177

^a See Ref. 12.

^b See Ref. 11.

^c There is a slight difference in the choice of \bar{V} used by the authors and that used in Refs. 11 and 12. An approximate perturbation-type calculation has been performed to remove this difference. It is found that using the value of \bar{V} of Schlosser and Marcus and of Brown and Krumhansl, the tight binding eigenvalues are all shifted to the negative by approximately 0.001 Ry.

function and orthogonalize the 2s Bloch sum to the 1s one, i.e.,

$$b_{2s}^{\text{orth}}(\mathbf{k}=0, \mathbf{r}) = b_{2s}(\mathbf{k}=0, \mathbf{r}) + q b_{1s}(\mathbf{k}=0, \mathbf{r}). \quad (21)$$

This gives $E = -0.6756$ Ry in very close agreement with -0.6721 Ry obtained by including the 1s function. Since there is no mixing at the Γ point between basis functions of s and p symmetry, the wave function at the Γ point corresponding to this stage of approximation is simply $b_{2s}^{\text{orth}}(\mathbf{k}=0, \mathbf{r})$. To carry this scheme of approximation outside the Γ point, one finds that the k de-

pendence of the 1s-2s and 1s-2p mixing coefficients causes considerable complication in the computations. Instead of using the properly orthogonalized 2s Bloch functions, we introduce

$$b_{2s}'(\mathbf{k}, \mathbf{r}) = [N\Omega_{2s}(\mathbf{k})]^{-1/2} \sum_{\mathbf{r}'} e^{i\mathbf{k}\cdot\mathbf{R}_r} \times [\phi_{2s}(\mathbf{r}-\mathbf{R}_{r'}) + q\phi_{1s}(\mathbf{r}-\mathbf{R}_{r'})],$$

where q has the same value as that appearing in Eq. (21). The b_{2s}' and the three b_{2p} functions then form the basis of 4×4 secular equations which yield an alternative set of energy values as shown in Table VI. Near the Γ point the deviations of this set of energies from the corresponding solutions of the 5×5 secular equation increase with \mathbf{k} since b_{2s}' is not orthogonal to b_{1s} , except for $\mathbf{k}=0$. Although one may expect to obtain better energy values using the properly orthogonalized 2s Bloch functions, the numerical computation is much simpler with $b_{2s}'(\mathbf{k}, \mathbf{r})$ which proves to be more useful from the practical standpoint. As one approaches the edges of the Brillouin zone, the band functions become more p -like and better agreements are thus found between the energy solutions of the 4×4 and of the 5×5 secular equations. Included in the last column of Table VI, are the energy solutions of the 4×4 secular equation with b_{2s} in place of b_{2s}' , neglecting the 1s core completely. The results are rather poor except near the edge of the Brillouin zone where the wave functions have primarily p character.

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