

# Electron Wave Functions in Metallic Lithium

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(Received May 14, 1962)

Wave functions to order  $k^2$  are presented for electrons in metallic lithium. The calculation is an application of the cellular method. The empirical potential of Seitz was employed.

THIS paper reports the final calculation in a series of studies of wave functions of electrons in the alkali metals. Results have been reported for sodium,<sup>1</sup> potassium,<sup>2</sup> rubidium,<sup>3</sup> and cesium<sup>4</sup> in preceding papers of this series. The cellular method in the spherical approximation has been used throughout.

The wave function and energy of an electron of wave

TABLE I. The functions  $R_0$ ,  $R_1$ ,  $R_2$ , and  $Q_2$  are given as functions of  $r$ . The normalization of these functions is given in Eq. (5) of the text:  $\int_0^{r_s} R_0^2 dr = 1.000$ ;  $\int_0^{r_s} R_1^2 dr = 0.478$ ;  $\int_0^{r_s} R_0 Q_2 dr = 1.317$ ;  $\int_0^{r_s} R_2^2 dr = 1.175$ ;  $u_0(0) = 2.31$ ;  $\phi_0(0) = 0.745$ .

$r$ (au)	$R_0$	$R_1$	$R_2$	$Q_2$
0.00	0.0000	0.00000	0.000000	0.0000
0.04	0.0823	-0.00597	-0.000103	0.0265
0.08	0.1464	-0.02185	-0.000761	0.0467
0.12	0.1949	-0.450	-0.00236	0.0612
0.16	0.230	-0.732	-0.00516	0.0706
0.20	0.254	-0.1049	-0.00930	0.0753
0.24	0.269	-0.1385	-0.01482	0.0759
0.28	0.276	-0.1730	-0.0218	0.0729
0.32	0.276	-0.208	-0.0300	0.0667
0.36	0.271	-0.242	-0.0396	0.0577
0.40	0.261	-0.275	-0.0504	0.0462
0.44	0.248	-0.306	-0.0623	0.0326
0.48	0.231	-0.337	-0.0752	0.0172
0.52	0.213	-0.365	-0.0891	+0.0001
0.60	0.170	-0.416	-0.1193	-0.0380
0.68	0.123	-0.460	-0.1522	-0.0803
0.76	0.073	-0.497	-0.1871	-0.1256
0.84	+0.021	-0.525	-0.223	-0.1730
0.92	-0.031	-0.547	-0.260	-0.222
1.00	-0.082	-0.562	-0.298	-0.271
1.08	-0.133	-0.572	-0.335	-0.321
1.16	-0.182	-0.575	-0.372	-0.371
1.24	-0.230	-0.574	-0.408	-0.420
1.32	-0.277	-0.569	-0.443	-0.469
1.48	-0.364	-0.546	-0.510	-0.563
1.64	-0.445	-0.512	-0.572	-0.652
1.80	-0.519	-0.469	-0.628	-0.736
1.96	-0.587	-0.420	-0.679	-0.814
2.12	-0.650	-0.367	-0.725	-0.887
2.28	-0.708	-0.313	-0.768	-0.956
2.44	-0.763	-0.257	-0.808	-1.022
2.60	-0.814	-0.202	-0.848	-1.084
2.76	-0.864	-0.147	-0.887	-1.146
2.92	-0.913	-0.094	-0.928	-1.207
3.08	-0.961	-0.042	-0.973	-1.269
3.24	-1.011	+0.010	-1.021	-1.334
3.21	-1.001	0.000	-1.012	-1.322

<sup>1</sup> J. Callaway, Phys. Rev. **123**, 1255 (1961).

<sup>2</sup> J. Callaway, Phys. Rev. **119**, 1012 (1960).

<sup>3</sup> J. Callaway and D. F. Morgan, Phys. Rev. **112**, 334 (1958).

<sup>4</sup> J. Callaway, Phys. Rev. **112**, 1061 (1958).

vector  $\mathbf{k}$  are expanded in powers of  $k$  according to the method of Silverman.<sup>5</sup> We have

$$\psi_{\mathbf{k}} = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}, \quad (1)$$

$$u_{\mathbf{k}} = u_0 + iku_1 \cos\theta + k^2[u_2 P_2(\cos\theta) + \phi_0], \quad (2)$$

$$E(k) = E_0 + E_2 k^2 + E_4 k^4, \quad (3)$$

in which  $\theta$  is the angle between  $\mathbf{k}$  and  $\mathbf{r}$  and  $P_2$  is the second Legendre polynomial.

The equations which determine the functions  $u_0$ ,  $u_1$ , etc., and the energy parameters  $E_0$ ,  $E_2$ , and  $E_4$  are summarized in reference 4.

The functions which are tabulated in Table I are

$$R_0 = ru_0, \quad R_1 = ru_1, \quad R_2 = ru_2, \quad Q_2 = r\phi_0. \quad (4)$$

The normalization integral for  $\psi_{\mathbf{k}}$  is (to order  $k^2$ )

$$\int |\psi_{\mathbf{k}}|^2 d\tau = \int |u_{\mathbf{k}}|^2 d\tau = 4\pi[1 + k^2(\frac{1}{3}J_1 + J_2)], \quad (5)$$

in which

$$J_1 = \int_0^{r_s} R_1^2 dr, \quad J_2 = \int_0^{r_s} R_0 Q_2 dr. \quad (6)$$

This calculation was based on an empirical potential constructed by Seitz for use in a calculation of the cohesive energy of metallic lithium.<sup>6</sup> This potential yields energy levels for the free atom in good agreement with spectroscopic data, and has frequently been used in band calculations.

All calculations were made for a sphere radius  $r_s = 3.21$  atomic units (a.u.). Other details of the crystal structure are not relevant to the spherical approximation used in this calculation.

The band parameters obtained in this calculation have been given previously.<sup>7,5</sup> These results, together with the calculated cohesive energy and Knight shift parameters are summarized and discussed elsewhere.<sup>8</sup>

<sup>5</sup> R. A. Silverman, Phys. Rev. **85**, 227 (1952).

<sup>6</sup> F. Seitz, Phys. Rev. **47**, 400 (1935). The published potential contains an error. The correct potential has been given by W. Kohn and N. Rostoker, *ibid.* **94**, 1111 (1954).

<sup>7</sup> R. A. Silverman and W. Kohn, Phys. Rev. **80**, 912 (1950); **82**, 283 (1951). The values are  $E_0 = -0.6832$  Ry,  $E_2 = 0.727$ ,  $E_4 = -0.03$ .

<sup>8</sup> J. Callaway, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 99.