Electron Wave Functions in Metallic Sodium

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

THIS paper reports a continuation of previous calculations of wave functions of electrons in the alkali metals. In preceding papers of this series, results have been reported for potassium,[1] rubidium,[2] and cesium.[3] The cellular method in the spherical approximation has been used throughout.

The wave function and energy of an electron of wave vector $\mathbf{k}$ are expanded in powers of $\mathbf{k}$ according to the method of Silverman.[4] We have

$$\psi_{\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}};$$
$$u_{\mathbf{k}}=u_0+ik\cos\theta u_1+k^2[u_2P_2(\cos\theta)+\phi_0], \quad (1)$$
$$E(k)=E_0+E_2k^2+E_4k^4, \quad (2)$$

in which P_2 is the second Legendre polynomial.

The equations which determine the functions u_0, u_1,

TABLE I. The solid-state functions R_0, R_1, R_2, and Q_2 are given as functions of r for $E_0=-0.6113$ ry. The normalization of these functions is given in Eq. (5) of the text. $\int_0^{r_s}R_0^2=1.0000$; $\int_0^{r_s}R_1^2dr=0.2093$; $\int_0^{r_s}R_0Q_2dr=1.5624_5$; $\lim_{r\to0}(R_0/r)=3.219$; $\lim_{r\to0}(Q_2/r)=3.014$.

r	R_0	R_1	R_2	Q_2	r	R_0	R_1	R_2	Q_2
0.00	0.00000	0.00000	0.00000	0.00000	0.85	−0.0878	−0.3872	−0.3622	−0.1792
0.01	0.02878	−0.00269	−0.00002	0.02694	0.90	−0.0614	−0.3559	−0.3664	−0.1464
0.02	0.05122	−0.01013	−0.00014	0.04790	0.95	−0.0342	−0.3255	−0.3683	−0.1113
0.03	0.06811	−0.02141	−0.00044	0.06356	1.00	−0.0067	−0.2963	−0.3680	−0.0747
0.04	0.08015	−0.03578	−0.00097	0.07457					
0.05	0.08802	−0.05256	−0.00180	0.08154	1.1	+0.0483	−0.2428	−0.3626	+0.0017
0.06	0.09232	−0.07120	−0.00294	0.08501	1.2	0.1021	−0.1965	−0.3525	0.0800
0.07	0.09357	−0.09119	−0.00441	0.08545	1.3	0.1537	−0.1576	−0.3395	0.1583
0.08	0.09224	−0.11213	−0.00622	0.08333	1.4	0.2028	−0.1256	−0.3250	0.2354
0.09	0.08875	−0.1337	−0.00839	0.07901	1.5	0.2492	−0.1000	−0.3099	0.3106
0.10	0.08346	−0.1555	−0.01090	0.07285	1.6	0.2929	−0.0797	−0.2949	0.3834
					1.7	0.3339	−0.0642	−0.2803	0.4533
0.12	0.06873	−0.1993	−0.01692	0.05617	1.8	0.3723	−0.0527	−0.2665	0.5201
0.14	0.05015	−0.2420	−0.02422	0.03533	1.9	0.4082	−0.0444	−0.2538	0.5836
0.16	0.02931	−0.2828	−0.03267	+0.01185	2.0	0.4417	−0.0388	−0.2424	0.6438
0.18	+0.00738	−0.3212	−0.04218	−0.01307	2.1	0.4731	−0.0352	−0.2322	0.7007
0.20	−0.01479	−0.3569	−0.05261	−0.03859	2.2	0.5025	−0.0332	−0.2234	0.7543
0.22	−0.03659	−0.3896	−0.06385	−0.06405	2.3	0.5300	−0.0324	−0.2160	0.8049
0.24	−0.05759	−0.4194	−0.07577	−0.08898	2.4	0.5559	−0.0323	−0.2099	0.8527
0.26	−0.07746	−0.4460	−0.08824	−0.11300	2.5	0.5804	−0.0327	−0.2052	0.8977
0.28	−0.09598	−0.4697	−0.10115	−0.1359	2.6	0.6037	−0.0332	−0.2017	0.9403
0.30	−0.1130	−0.4904	−0.11438	−0.1573	2.7	0.6258	−0.0337	−0.1994	0.9807
0.32	−0.1285	−0.5082	−0.1278	−0.1773	2.8	0.6471	−0.0339	−0.1982	1.0192
0.34	−0.1423	−0.5232	−0.1414	−0.1956	2.9	0.6676	−0.0338	−0.1979	1.0560
0.36	−0.1544	−0.5356	−0.1549	−0.2123	3.0	0.6876	−0.0331	−0.1985	1.0914
0.38	−0.1649	−0.5454	−0.1684	−0.2272	3.1	0.7072	−0.0319	−0.2000	1.1256
0.40	−0.1738	−0.5529	−0.1818	−0.2404	3.2	0.7265	−0.0301	−0.2021	1.1592
0.42	−0.1812	−0.5582	−0.1949	−0.2519	3.3	0.7457	−0.0277	−0.2049	1.1920
0.44	−0.1870	−0.5614	−0.2077	−0.2617	3.4	0.7650	−0.0246	−0.2083	1.225
0.46	−0.1913	−0.5628	−0.2202	−0.2698	3.5	0.7844	−0.0209	−0.2121	1.257
0.48	−0.1943	−0.5623	−0.2323	−0.2762	3.6	0.8041	−0.0168	−0.2164	1.290
0.50	−0.1960	−0.5603	−0.2440	−0.2812	3.7	0.8243	−0.0122	−0.2211	1.323
					3.8	0.8450	−0.0072	−0.2262	1.357
0.55	−0.1949	−0.5491	−0.2711	−0.2869	3.9	0.8665	−0.0021	−0.2317	1.391
0.60	−0.1873	−0.5307	−0.2949	−0.2842					
0.65	−0.1743	−0.5070	−0.3152	−0.2741	3.92	0.8709	−0.0010	−0.2329	1.3985
0.70	−0.1569	−0.4796	−0.3319	−0.2575	3.94	0.8753	0.0000	−0.2341	1.406
0.75	−0.1362	−0.4498	−0.3452	−0.2356	3.96	0.8798	+0.0010	−0.2353	1.413
0.80	−0.1129	−0.4187	−0.3552	−0.2092	3.98	0.8843	0.0021	−0.2365	1.420
					4.00	0.8888	0.0031	−0.2377	1.427

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etc., and the energy parameters E_0, E_2, and E_4 are summarized in reference 3.

The functions which are tabulated in Table I are

$$R_0=ru_0;\quad R_1=ru_1;\quad R_2=ru_2;\quad Q_2=r\phi_0. \tag{3}$$

The normalization integral[5] for ψ_k is (to order k^2):

$$\int_\Omega |\psi_k|^2 d\tau=\int |u_k|^2 d\tau=4\pi[1+k^2(\tfrac{1}{3}J_1+2J_2)], \tag{4}$$

in which

$$J_1=\int_0^{r_s} R_1^2 dr;\quad J_2=\int_0^{r_s} R_0 Q_2 dr. \tag{5}$$

In two of the previous calculations of this series,[1,2] potentials derived from self-consistent field calculations for the appropriate free atoms (supplemented by approximate exchange potentials) have been employed. In the present case, the semiempirical potential derived by Prokofjew was used.[6] This potential yields energy levels for the free atom in reasonable agreement with spectroscopic data, and has been frequently used in band calculations. Insofar as exchange and correlation effects can be included in a single potential, the calculations based on this potential are probably more accurate than those based on a self-consistent fields.

All calculations were made for a sphere radius $r_s=3.94$ (Bohr units), which is appropriate for 0°K.[7]

The band parameters computed in this way are $E_0=-0.6113$ ry; $E_2=1.0659$; $E_4=-0.153$. The values of E_0 and E_2 are in good agreement with results previously obtained by Bardeen.[8] E_4 is somewhat larger than had previously been expected,[9] and suggests that the effective mass on the Fermi surface may be greater than unity. The agreement with results of "quantum defect" calculations is also quite good, except for E_4.[10] The cohesive energy, computed in the standard way from these parameters,[9] is 27.7 kcal/mole. The experimental value is 26.0 kcal/mole.

A quantity of interest in the theory of the Knight shift[11] is

$$\xi=|\psi_F(0)|^2/|\psi_A(0)|^2,$$

where $\psi_F(0)$ is the average over the Fermi surface of the wave function at a nucleus, and $\psi_A(0)$ is similarly the value of the wave function of an electron in the free atom at the nucleus. We find from the expansion, $|\psi_F(0)|^2=0.566$. Using $|\psi_A(0)|^2=0.685$, as computed by Kjeldaas and Kohn,[12] we find $\xi=0.826$; in good agreement with the non-perturbation calculation of those authors ($\xi=0.81$) and with the earlier perturbation calculation of Townes *et al.*[13]

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