PHYSICAL REVIEW VOLUME 112, NUMBER 4 NOVEMBER 15, 1958

Electron Wave Functions in Metallic Cesium*

JOSEPH CALLAWAY
Department of Physics, University of Miami, Coral Gables, Florida

(Received July 17, 1958)

Wave functions to order k^2 are presented for electrons in metallic cesium. The calculation is an application of the cellular method to a potential adapted from previous work of Sternheimer.

INTRODUCTION

In the course of a calculation of electron energy bands in cesium, wave functions were obtained to order k^2.[1] The value of E_4 (the coefficient of k^4 in the expansion of the energy is powers of k) obtained in this work was so large in magnitude that a thorough check of the calculations prior to publication of the wave functions seemed desirable. Consequently, the calculation was repeated employing an electronic calculating machine. The results, which are in good agreement with the previous work, are presented here.

THEORY

The wave function and energy of an electron of wave vector $\mathbf{k}$ are expanded in powers of k according to the procedure of Silverman.[2] We have, for a state of wave vector $\mathbf{k}$,

$$\psi_{\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}},\quad u_{\mathbf{k}}=u_0+ikP_1u_1+k^2(u_2P_2+\phi_0),\tag{1}$$

in which P_1 and P_2 are the first and second Legendre polynomials and the functions u_0, u_1, u_2, and ϕ_0 are radial functions. Similarly, the energy is

$$E(k)=E_0+E_2k^2+E_4k^4+\cdots.\tag{2}$$

Terms proportional to odd powers of k are absent in (2) for reasons of symmetry. Terms which have cubic, rather than spherical, symmetry may be present in the expansion of the energy, but cannot be obtained by this method.

The function u_0 which appears in (1) is the wave function of the electron whose wave vector is zero and whose energy is E_0. It satisfies the boundary condition

$$(\partial u_0/\partial r)_{r_s}=0.\tag{3}$$

The quantity r_s is the radius of the sphere whose volume equals that of the atomic cell (Ω). For u_1,

$$u_1=f_p(r)-u_0,\tag{4}$$

where f_p is a p-state solution of the radial wave equation for $E=E_0$. The boundary condition on u_1 is

$$u_1(r_s)=0.\tag{5}$$

The other functions are given by

$$u_2=\tfrac{2}{3}ru_1+\tfrac{1}{3}r^2u_0+c_df_d,\tag{6}$$

$$\phi_0=\tfrac{1}{3}ru_1+\tfrac{1}{6}r^2u_0+E_2(\partial u_0/\partial E),\tag{7}$$

in which f_d is a d-state solution of the wave equation for $E=E_0$. These functions satisfy the boundary conditions

$$(\partial u_2/\partial r)_{r_s}=(\partial\phi_0/\partial r)_{r_s}=0.\tag{8}$$

The boundary condition on u_2 determines c_d:

$$c_d\left(\frac{df_d}{dr}\right)_{r_s}=\frac{-2E_2}{r_s^2u_0(r_s)}.\tag{9}$$

The function $(\partial u_0/\partial E)$ satisfies

$$\left[-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+V-E_0\right]\frac{\partial u_0}{\partial E}=u_0,\tag{10}$$

subject to the condition that

$$\int_\Omega u_0\frac{\partial u_0}{\partial E}d\tau=0,\tag{11}$$

which implies that u_0 is normalized for all E. The boundary condition on ϕ_0 determines E_2:

$$E_2=\tfrac{1}{3}r_s^2u_0^2(r_s)\left[\frac{r}{f_p}\frac{df_p}{dr}\right]_{r_s}.\tag{12}$$

Now define the functions

$$R_0=ru_0,\quad R_1=ru_1,\quad R_2=ru_2,\quad Q_2=ru_0.\tag{13}$$

These functions are tabulated in Table I. The function R_0 is normalized so that

$$\int_0^{r_s}R_0^2dr=1.\tag{14}$$

In order to determine E_4, it is necessary to obtain u_3 and u_4. This has been done by Silverman, whose result is

$$E_4=\frac{2}{5}r_s^2E_2-\frac{4}{15}\frac{E_2^2}{\gamma}r_s^2\left(\frac{r}{f_d}\frac{df_d}{dr}\right)_{r_s}^{-1}\tag{15}$$

$$+\frac{\gamma E_2}{u_0(r_s)}\left[\frac{E_2}{\gamma}\left(\frac{\partial u_0}{\partial E}\right)_{r_s,E_0}-\frac{r_su_0(r_s)}{P^2(r_s)}\int_0^{r_s}P^2dr\right],\tag{16}$$

in which $P=rf_p$, $\gamma=\frac{1}{3}r_s^2u_0^2(r_s)$.

In terms of the function (13), the normalization integral for ψ_k is, to order k^2,

$$\int_\Omega|\psi_K|^2d\tau=\int_\Omega|u_K|^2d\tau=4\pi[1+k^2(\tfrac{1}{3}J_1+2J_2)],\tag{17}$$

---

* Supported by the Office of Naval Research.

[1] J. Callaway and E. L. Haase, Phys. Rev. **108**, 217 (1957).

[2] R. A. Silverman, Phys. Rev. **85**, 227 (1952).

TABLE I. Wave functions for cesium.

r (atomic units)	R_0	R_1	Q_2	R_2
0.000	0.00000	0.00000	0.00000	0.00000
0.005	0.02484	−0.01288	0.03878	0.00025
0.010	0.03594	−0.04478	0.05600	0.00186
0.015	0.03760	−0.08745	0.05831	0.00580
0.020	0.03285	−0.13476	0.05043	0.01270
0.03	+0.01276	−0.2265	+0.01768	0.03653
0.04	−0.01179	−0.2978	−0.01840	0.07395
0.05	−0.03396	−0.3392	−0.04720	0.12351
0.06	−0.05040	−0.3487	−0.06864	0.1827
0.07	−0.05590	−0.3290	−0.08097	0.2484
0.08	−0.06254	−0.2849	−0.08411	0.3175
0.09	−0.05910	−0.2220	−0.07895	0.3870
0.10	−0.05071	−0.1462	−0.06688	0.4545
0.12	−0.02403	+0.0232	−0.02837	0.5742
0.14	+0.00832	0.1882	+0.02199	0.6640
0.16	0.03937	0.3262	0.07926	0.7169
0.18	0.06469	0.4252	0.12706	0.7307
0.20	0.08200	0.4810	0.1608	0.7064
0.22	0.09060	0.4949	0.1785	0.6472
0.24	0.09088	0.4715	0.1803	0.5577
0.26	0.08386	0.4172	0.1676	0.4434
0.28	0.07092	0.3389	0.1427	0.3099
0.30	+0.05354	+0.2437	+0.1079	+0.1629
0.35	−0.00012	−0.0283	−0.0048	−0.2309
0.40	−0.05438	−0.2913	−0.1266	−0.6121
0.45	−0.09800	−0.5013	−0.2326	−0.9378
0.50	−0.12587	−0.6403	−0.3087	−1.1844
0.55	−0.13707	−0.7062	−0.3493	−1.3426
0.60	−0.13317	−0.7069	−0.3545	−1.4124
0.7	−0.09117	−0.5585	−0.2736	−1.3126
0.8	−0.02377	−0.2925	−0.1078	−0.9642
0.9	+0.04913	+0.0116	+0.0983	−0.4584
1.0	0.11491	0.3032	0.3102	+0.1269
1.1	0.1672	0.5560	0.5056	0.7349
1.2	0.2039	0.7602	0.6717	1.3279
1.4	0.2319	1.0230	0.8941	2.383
1.6	0.2110	1.1246	0.9699	3.200
1.8	0.1581	1.1172	0.9203	3.772
2.0	0.0876	1.0479	0.7789	4.138
2.2	+0.0098	0.9495	0.5765	4.346
2.4	−0.0687	0.8436	0.3378	4.446
2.6	−0.1444	0.7415	+0.0805	4.474
2.8	−0.2154	0.6484	−0.1830	4.457
3.0	−0.2809	0.5661	−0.4441	4.412
3.2	−0.3406	0.4947	−0.6968	4.352
3.4	−0.3947	0.4332	−0.9375	4.288
3.6	−0.4434	0.3799	−1.1637	4.225
3.8	−0.4872	0.3334	−1.3737	4.169
4.0	−0.5266	0.2921	−1.567	4.124
4.2	−0.5622	0.2546	−1.744	4.092
4.4	−0.5945	0.2194	−1.906	4.076
4.6	−0.6244	0.1860	−2.054	4.079
4.8	−0.6522	0.1533	−2.188	4.102
5.0	−0.6787	0.1208	−2.312	4.147
5.2	−0.7045	0.0884	−2.425	4.218
5.4	−0.7300	0.0552	−2.531	4.312
5.6	−0.7559	0.0216	−2.631	4.435
5.735	−0.7740	0.0000	−2.695	4.537

Parameters and Integrals

$r_s = 5.735$ atomic units
$E_0 = -0.4156$ ry
$E_2 = 1.3932$
$E_4 = -3.615$

$\int_0^{r_s} R_1^2 dr = 2.0150$
$\int_0^{r_s} R_2^2 dr = 76.81$
$\int_0^{r_s} R_0 Q_2 dr = 3.186$

in which

$$J_1 = \int_0^{r_s} R_1^2 dr, \quad J_2 = \int_0^{r_s} R_0 Q_2 dr. \tag{18}$$

CALCULATIONAL DETAILS

The potential used in this calculation was adopted from one given previously by Sternheimer.[3] This potential is given in reference 1. The wave function for the 6S state in the free atom has been computed by Sternheimer using his potential.[4]

The experimental radius, r_s, in cesium varies from $r_s = 5.58$ atomic units at 0°K to 5.79 atomic units at 300°K.[5] It is not obvious what value should be chosen for r_s for the wave functions to be most useful. The value used here, $r_s = 5.735$ atomic units, is an intermediate one. An energy $E_0 = -0.4156$ Rydbergs was taken from the previous work.[1] The calculated u_0 for this energy satisfied its boundary condition at this point.

COHESIVE ENERGY AND KNIGHT SHIFT

The band parameters for $r_s = 5.735$ atomic units are $E_0 = -0.4156$, Rydbergs $E_2 = 1.3932$, and $E_4 = -3.64$. The cohesive energy, computed in the standard way[6] from these parameters, including the correlation energy according to Wigner's expression, is 22.3 kcal/mole. The experimental value of the cohesive energy is 18.8 kcal/mole. The result of this work differs from that of reference 1 in that the E_4 term has been included.

A value for the Knight-shift parameter ξ has been obtained from these wave functions as was done in reference 1:

$$\xi = |\psi_F(0)|^2 / |\psi_A(0)|^2, \tag{19}$$

in which ψ_F is the wave function for an electron on the Fermi surface, and ψ_A is the wave function for the lowest valence electron state in the free atom. We find $|\psi_F(0)|^2 = 2.89$.[7] From Sternheimer's calculation,[4] $\psi_A^2(0) = 2.6$. The ratio is $\xi = 1.1$. Benedek and Kushida find experimentally that $\xi = 1.13$.[5]

ACKNOWLEDGMENTS

Mr. A. M. Cordish and Mr. D. Bellows assisted with the numerical calculations. This work was begun while the author was a consultant to the Scientific Laboratory of the Ford Motor Company, Dearborn, Michigan. He expresses his thanks to Dr. J. Goldman, manager of the Physics Department, for his hospitality during the summer of 1957.

---

[3] R. M. Sternheimer, Phys. Rev. **78**, 235 (1950).

[4] R. M. Sternheimer (private communication).

[5] G. B. Benedek and T. Koshida, technical report No. 268, Cruft Laboratory, Harvard University, 1957 (unpublished).

[6] J. Callaway, in *Solid State Physics*, edited by F. Seitz and D. Turnbull [Academic Press, Inc., New York (to be published)], Vol. VII.

[7] The more usual normalization $\int_\Omega \psi_F^2 dT = 1$ has been used here.