PHYSICAL REVIEW VOLUME 112, NUMBER 2 OCTOBER 15, 1958

# Cohesive Energy and Wave Functions for Rubidium*

JOSEPH CALLAWAY AND DANIEL F. MORGAN, JR.
*Department of Physics, University of Miami, Coral Gables, Florida*

(Received June 18, 1958)

The cellular method was used to calculate the cohesive energy of rubidium. The potential was obtained from a self-consistent field for $Rb^+$ supplemented by an exchange potential. Wave functions were obtained to order $k^2$ in the solid and for the lowest valence electron state in the free atom. A value of 20.7 kcal/mole was obtained for the cohesive energy, including $k^4$ terms in the Fermi energy, but neglecting any polarization effects. The ratio of $|\psi^2(0)|$ for an electron on the Fermi surface in the metal to that for an electron in the free atom was computed and found to be in good agreement with results of the Knight shift measurements.

## INTRODUCTION

THE physical ideas underlying the calculation of the cohesive energies of the alkali metals have been reviewed by Wigner and Seitz.[1] Briefly, the cohesive energy is principally the difference between the boundary correction (which measures the difference in energy between the lowest valence electron state in the free atom and in the solid) and the Fermi energy of the electrons in the band. To this must be added a correction for the Coulomb interactions of the valence electrons. There are two differing approaches to the evaluation of the boundary correction and the Fermi energy. One is the quantum defect method,[2] in which use of an explicit potential is avoided and spectroscopic information is used directly in the determination of the electron wave functions in the solid. Alternatively, one can integrate the Schrödinger equation, using a potential obtained from a self-consistent field. The two methods generally give comparable results for the cohesive energies of the alkalis. Although the quantum defect method possesses greater intrinsic accuracy, its advantages in this respect are somewhat offset by difficulty in extrapolating the spectroscopic data to the energies of interest. Nor does it give the electron wave function throughout the cell.

We have computed the cohesive energy of rubidium using the cellular method in the spherical approximation and have determined the solid-state wave function to second order in the wave vector **k**. The calculation is based on a potential obtained from a self-consistent field, to which we have added an exchange potential. The wave function of an electron in the 5$S$ state of the free atom has also been obtained for this potential.

## DETERMINATION OF THE POTENTIAL

A self-consistent field without exchange has been obtained for $Rb^+$ by Hartree and Hartree.[3] These authors have also computed the function $2Z_p$, such that $2Z_p/r$ is the potential energy of an electron in the field of the $Rb^+$ ion. It can be expected that exchange effects are quite important in an atom as heavy as rubidium. For this reason, we have computed an approximate potential to take account of the exchange interactions of core and valence electrons in the following way:

A trial wave function was obtained for the lowest state of a valence electron in the solid by constructing the orthogonalized plane wave of $\mathbf{k}=0$.[4] The exchange potential is defined for a state whose wave function is $\psi$ as

$$V_e(r)=A(r,r')\psi(r')/\psi(r), \tag{1}$$

where $A$ is the Hartree-Fock exchange operator.[5] The exchange potential defined by (1) will have infinities where $\psi(r)$ has zeros. These infinities, which contribute nothing to the energy in an accurate treatment, were removed by a smoothing process. The resulting exchange potential roughly resembles a staircase, varying slowly in a region between nodes of $\psi(r)$ and dropping rapidly to a new level in the vicinity of a node. The final potential adopted is listed in Table I.

## CALCULATION OF THE COHESIVE ENERGY

The cohesive energy ($E_c$) is defined as follows:

$$-E_c=E_B+E_F+E_I. \tag{2}$$

$E_B$ is the boundary correction

$$E_B=E_0-E_a. \tag{3}$$

where $E_0$ is the energy of the lowest state of a valence electron in the solid and $E_a$ is the energy of the lowest state in the free atom. We obtain (all energies are given in Rydbergs)

$$E_0=-0.444, \quad E_a=-0.305.$$

$E_F$ is the Fermi energy. If the energy of a state of wave vector **k** is expanded in powers of $k$, we have

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

---

* This work was supported by the Office of Naval Research.

[1] E. Wigner and F. Seitz, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 97.

[2] F. S. Ham, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 127.

[3] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A151**, 96 (1935).

[4] For a discussion of the orthogonalized plane wave method, see T. O. Woodruff, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 367.

[5] For a discussion of various methods of defining an average exchange potential, see Herman, Callaway, and Acton, Phys. Rev. **95**, 371 (1954).

The Fermi energy is

$$E_F=2.21E_2/r_s^2+5.81E_4/r_s^4. \tag{5}$$

$E_2$ and $E_4$ are determined from the formula given by Bardeen[6] and by Silverman,[7] respectively. We obtain

$$E_2=1.1814,\quad E_4=-1.28,\quad E_F=0.0860.$$

All calculations are made for $r_s=5.21$ atomic units which is close to the experimental value $r_s=5.22$ atomic units at $T=0$°K.[8] The quantity $E_I$ represents the energy of interaction of electrons in the solid. This is given approximately as

$$E_I=0.284/r_s-0.88/(r_s+7.79). \tag{6}$$

The last term, which is the correlation energy, is computed according to Wigner's formula.[9] The interaction energy $E_I$ is found to be $-0.0132$ Rydberg. From (1), the cohesive energy is obtained.

$$E_c=0.066\text{ ry}=20.7\text{ kcal/mole}.$$

The experimental cohesive energy is 18.9 kcal/mole.

It is somewhat surprising that the calculated cohesive energy exceeds the experimental result since no correction for core polarization has been included. It is possible that the magnitude of $E_4$ is somewhat too large or that Wigner's formula overestimates the magnitude of the correlation energy.

Using the quantum defect method, Brooks has obtained values for the band parameters $E_0$ and $E_2$ as follows: $E_0=-0.462$ ry, $E_2=1.101$. These values are obtained for $r_s=5.21$ atomic units by interpolation in the published results.[3] The cohesive energy obtained in this way, neglecting $E_4$, is 24.5 kcal/mole.

## WAVE FUNCTIONS

Following the procedure of Silverman,[7] we express the wave function for a state in the following way:

$$\psi_{\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}, \tag{7}$$

where $u_{\mathbf{k}}=u_0+ikP_1u_1+k^2(u_2P_2+\phi_0)$, in which $P_1$ and $P_2$ are the first and second Legendre polynomials and the functions $u_0$, $u_1$, $u_2$, and $\phi_0$ are radial functions. The function $u_0$ is the wave function of the electron whose wave vector is zero, and whose energy is $E_0$.

$$u_1=f_p(r)-u_0, \tag{8}$$

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

$$u_1(r_s)=0. \tag{9}$$

TABLE I. The solid-state functions $R_0$, $R_1$, $R_2$, and $Q_2$ defined in the text are given as functions of $r$ (in atomic units) for $E_0=-0.0444_2$ ry. The free atom function $R_a$ is given and also the function $-rV$, where $V$ is the potential used in the calculation. $E_a=-0.305$ ry.

| $r$ | $R_0$ | $R_1$ | $R_2$ | $Q_2$ | $R_a$ | $-rV(r)$ |
|---|---|---|---|---|---|---|
| 0.000 | 0.00000 | 0.00000 | 0.000000 | 0.00000 | 0.00000 | 74.000 |
| 0.005 | 0.02488 | −0.00589 | 0.000045 | 0.03076 | 0.02055 | 72.136 |
| 0.010 | 0.04071 | −0.02142 | 0.000341 | 0.05027 | 0.03362 | 70.879 |
| 0.015 | 0.04927 | −0.04380 | 0.001098 | 0.06070 | 0.04069 | 69.404 |
| 0.020 | 0.05207 | −0.07075 | 0.002485 | 0.06392 | 0.04300 | 67.999 |
| 0.03 | 0.04535 | −0.13125 | 0.007646 | 0.05477 | 0.03745 | 65.385 |
| 0.04 | 0.02850 | −0.1919 | 0.016536 | 0.03267 | 0.02353 | 63.007 |
| 0.05 | +0.00698 | −0.2459 | 0.02949 | +0.00450 | +0.00576 | 60.740 |
| 0.06 | −0.01550 | −0.2892 | 0.04656 | −0.02500 | −0.01281 | 58.572 |
| 0.07 | −0.03654 | −0.3200 | 0.06762 | −0.05272 | −0.03018 | 56.495 |
| 0.08 | −0.05469 | −0.3378 | 0.09238 | −0.07673 | −0.04517 | 54.550 |
| 0.09 | −0.06914 | −0.3430 | 0.12048 | −0.09591 | −0.05711 | 52.728 |
| 0.10 | −0.07958 | −0.3366 | 0.15147 | −0.10976 | −0.06573 | 51.106 |
| 0.12 | −0.08850 | −0.2937 | 0.2202 | −0.12132 | −0.07309 | 48.094 |
| 0.14 | −0.08335 | −0.2206 | 0.2946 | −0.11345 | −0.06882 | 45.428 |
| 0.16 | −0.06741 | −0.1288 | 0.3708 | −0.09022 | −0.05565 | 42.992 |
| 0.18 | −0.04421 | −0.0281 | 0.4455 | −0.05618 | −0.03648 | 40.768 |
| 0.20 | −0.01696 | +0.0733 | 0.5159 | −0.01569 | −0.01396 | 38.685 |
| 0.22 | +0.01164 | 0.1695 | 0.5798 | +0.02750 | +0.00967 | 36.743 |
| 0.24 | 0.03952 | 0.2563 | 0.6354 | 0.07036 | 0.03269 | 34.877 |
| 0.26 | 0.06514 | 0.3309 | 0.6817 | 0.10696 | 0.05386 | 33.112 |
| 0.28 | 0.08750 | 0.3920 | 0.7182 | 0.14642 | 0.07231 | 31.455 |
| 0.30 | 0.10596 | 0.4389 | 0.7444 | 0.1769 | 0.08754 | 29.920 |
| 0.35 | 0.13371 | 0.4973 | 0.7659 | 0.2258 | 0.11040 | 26.671 |
| 0.40 | 0.13646 | 0.4826 | 0.7282 | 0.2354 | 0.11257 | 23.975 |
| 0.45 | 0.11900 | 0.4137 | 0.6395 | 0.2107 | 0.09803 | 21.719 |
| 0.50 | 0.08729 | 0.3093 | 0.5098 | 0.1594 | 0.07170 | 19.730 |
| 0.55 | 0.04697 | 0.1851 | 0.3489 | 0.0895 | 0.03828 | 17.992 |
| 0.60 | +0.00278 | 0.0534 | +0.1662 | +0.0086 | +0.00167 | 16.482 |
| 0.70 | −0.08386 | −0.1997 | −0.2340 | −0.1636 | −0.06995 | 13.863 |
| 0.80 | −0.1552 | −0.4108 | −0.6431 | −0.3229 | −0.12867 | 11.830 |
| 0.90 | −0.2047 | −0.5686 | −1.0322 | −0.4522 | −0.1691 | 10.363 |
| 1.00 | −0.2318 | −0.6748 | −1.3847 | −0.5444 | −0.1907 | 9.360 |
| 1.10 | −0.2383 | −0.7360 | −1.6905 | −0.5980 | −0.1950 | 8.479 |
| 1.20 | −0.2276 | −0.7608 | −1.9455 | −0.6152 | −0.1848 | 7.710 |
| 1.4 | −0.1688 | −0.7357 | −2.3067 | −0.5579 | −0.1333 | 6.467 |
| 1.6 | −0.0950 | −0.6553 | −2.5047 | −0.4178 | −0.0580 | 5.511 |
| 1.8 | −0.0092 | −0.5535 | −2.5689 | −0.2245 | +0.0252 | 4.649 |
| 2.0 | +0.0777 | −0.4525 | −2.5420 | −0.0056 | 0.1064 | 4.008 |
| 2.2 | 0.1601 | −0.3630 | −2.4598 | +0.2205 | 0.1807 | 3.293 |
| 2.4 | 0.2359 | −0.2896 | −2.3547 | 0.4431 | 0.2464 | 2.906 |
| 2.6 | 0.3044 | −0.2322 | −2.2445 | 0.6560 | 0.3032 | 2.718 |
| 2.8 | 0.3658 | −0.1886 | −2.1370 | 0.8555 | 0.3510 | 2.561 |
| 3.0 | 0.4202 | −0.1560 | −2.0374 | 1.0394 | 0.3902 | 2.436 |
| 3.2 | 0.4685 | −0.1318 | −1.9491 | 1.2075 | 0.4215 | 2.337 |
| 3.4 | 0.5114 | −0.1136 | −1.8741 | 1.3601 | 0.4456 | 2.258 |
| 3.6 | 0.5498 | −0.0994 | −1.8136 | 1.4983 | 0.4632 | 2.197 |
| 3.8 | 0.5846 | −0.0876 | −1.7685 | 1.6236 | 0.4751 | 2.152 |
| 4.0 | 0.6165 | −0.0768 | −1.7384 | 1.7375 | 0.4819 | 2.117 |
| 4.2 | 0.6462 | −0.0661 | −1.7238 | 1.8417 | 0.4844 | 2.089 |
| 4.4 | 0.6747 | −0.0550 | −1.7244 | 1.9387 | 0.4831 | 2.068 |
| 4.6 | 0.7024 | −0.0427 | −1.7396 | 2.0301 |  |  |
| 4.8 | 0.7301 | −0.0297 | −1.7710 | 2.1175 | 0.4713 | 2.041 |
| 5.0 | 0.7583 | −0.0157 | −1.8177 | 2.2027 |  |  |
| 5.2 | 0.7876 | −0.0010 | −1.8794 | 2.2877 | 0.4503 | 2.018 |
| 5.211 | 0.7893 | 0.0000 | −1.8831 | 2.2927 |  |  |

| $r$ | $R_a$ | $-rV(r)$ |
|---|---|---|
| 5.6 | 0.4233 | 2.000 |
| 6.0 | 0.3927 | 2.000 |
| 6.4 | 0.3604 |  |
| 6.8 | 0.3276 |  |
| 7.2 | 0.2953 |  |
| 7.6 | 0.2643 |  |
| 8.0 | 0.2350 |  |
| 8.4 | 0.2078 |  |
| 9.2 | 0.1601 |  |
| 10.0 | 0.1213 |  |
| 10.8 | 0.0907 |  |
| 11.6 | 0.0669 |  |
| 12.4 | 0.0489 |  |
| 13.2 | 0.0354 |  |
| 14.8 | 0.0180 |  |
| 16.4 | 0.0089 |  |
| 18.0 | 0.0044 |  |
| 19.6 | 0.0021 |  |
| 21.2 | 0.0010 |  |
| 22.8 | 0.0005 |  |
| 24.4 | 0.0002 |  |
| 26.0 | 0.0001 |  |

$\int R_1^2dr=0.67854$

$\int R_2^2dr=18.209$

$\int R_0Q_2dr=2.7628$

---

[6] J. Bardeen, J. Chem. Phys. **6**, 367 (1938).

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

[8] G. B. Benedek and T. Kushida, Technical Report No. 268, Cruft Laboratory, Harvard University, 1957 (unpublished).

[9] E. P. Wigner, Phys. Rev. **46**, 1002 (1934). An error in this formula is corrected by D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 367.

The other functions are given by

$$u_2=\tfrac{2}{3}ru_1+\tfrac{1}{3}r^2u_0+c_df_d, \tag{10}$$

$$\phi_0=\tfrac{1}{3}ru_1+\tfrac{1}{6}r^2u_0+E_2(\partial u_0/\partial E), \tag{11}$$

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

$$(\partial u_2/\partial r)_{r_s}=(\partial\phi_0/\partial r)_{r_s}=0. \tag{12}$$

The boundary conditions on $u_2$ determines $c_d$:

$$c_d\left(\frac{df_d}{dr}\right)_{r_s}=\frac{-2E_2}{r_su_0(r_s)}. \tag{13}$$

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

$$\left[\frac{-1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+V-E_0\right]\frac{\partial u_0}{\partial E}=u_0, \tag{14}$$

subject to the condition

$$\int u_0\frac{\partial u_0}{\partial E}d\tau=0, \tag{15}$$

which implies that $u_0$ is normalized for all $E$. The boundary condition on $\phi_0$ determines $E_2$ which appears in Eq. (4) to be

$$E_2=\frac{r_s^3}{2}u_0^2(r_s)\left[\frac{r}{f_p}\frac{df_p}{dr}\right]_{r_s}. \tag{16}$$

Now define functions

$$R_0=ru_0,\quad R_1=ru_1,\quad R_2=ru_2,\quad Q_2=r\phi_0. \tag{17}$$

These functions are tabulated in Table I. The function $R_a$ which is $r$ times the radial part of the free atom wave function is also given.

## THE KNIGHT SHIFT

The shift of the nuclear magnetic resonance line in metallic rubidium (as composed with nonmetallic rubidium) has been measured.[8,10] This shift gives a value for $\langle|\psi_F(0)|^2\rangle$, where $\psi_F$ is the wave function of an electron on the Fermi surface and $\langle\ \rangle$ symbolizes an average over the Fermi surface. In order to deduce a value for $\langle|\psi_F(0)|^2\rangle$ from the experimental data, it is necessary to know the spin paramagnetic susceptibility. The spin susceptibility of rubidium has not been measured. The value used in interpreting the experiments is computed from a formula of Pines. At room temperature and atmospheric pressure Benedek and Kushida find $\langle|\psi_F(0)|^2\rangle=2.32$. A value for $|\psi_A(0)|^2$, where $\psi_A$ is the wave function of the valence electron in the free atom, has been obtained from observed hyperfine splittings: $|\psi_A(0)|^2=2.337$. The ratio $\xi$, defined as

$$\xi=\langle|\psi_F(0)|^2\rangle/|\psi_A(0)|^2, \tag{18}$$

is thus found to be 0.993.

The cell radius in rubidium is at room temperature in 5.31 atomic units, about 2% larger than at $T=0$. From the measurements of Benedek and Kushida[10] it is possible to obtain a value for $\xi$ at a cell radius equal to that used in these calculations ($r_s=5.21$ atomic units). In doing this, we neglect the explicit temperature dependence of the Knight shift. The value of $\xi$ for $r_s=5.21$ atomic units is then found to be $\xi=1.03$.

A theoretical estimate of $\xi$ can be made by using the wave function previously calculated. Assuming the Fermi surface to be spherical with $k_f^2=0.136$, we obtain $|\psi_F(0)|^2=2.162$. The free atom function gives $|\psi_A(0)|^2=1.965$. The ratio $\xi$ is then 1.10. The agreement is quite gratifying considering the crudeness of the assumptions involved. In particular it is not obvious that an expansion of $\psi_{\mathbf{k}}$ in powers of $k$ should converge readily on the Fermi surface.

## ACKNOWLEDGMENTS

This work was begun while one author, (J.C.) was a consultant at 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.

---

[10] W. D. Knight, in *Solid State Physics*, edited by F. Seitz, and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 93.