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Relativistic Effects in the Cohesive Energies of the Alkali Metals*

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The relativistic corrections to the cohesive energies of the alkali metals are studied from two points of view. In the first, perturbation theory is applied to the second approximation to the Dirac equation. Calculations are made for potassium and cesium. The limitations of this approach are discussed. In the second, the quantum defect method is extended to include almost all relativistic effects. A relativistic analog of Bardeen's expression for the effective mass ratio is derived. Application is made to cesium.

I. INTRODUCTION

STUDIES of electronic energy levels in solids composed of heavy atoms must include, in principle, the relativistic effects due to the motion of an electron in the strong attractive potential near any nucleus. The theory can be formulated on the basis of a relativistic self-consistent field.[1] The wave function of the N-particle system is an Nth order determinant of Dirac spinors

$$\Psi(x_1\cdots x_n)=\det U_i(x_j), \tag{1}$$

where

$$U_i(x_j)=\begin{bmatrix} u_{i1}(x_j) \\ u_{i2}(x_j) \\ u_{i3}(x_j) \\ u_{i4}(x_j) \end{bmatrix}. \tag{2}$$

The Hamiltonian for the system is

$$H=\sum_i[-c\boldsymbol{\alpha}_i\cdot\mathbf{p}_i-\beta_i mc^2+V_i+\sum_{j,\,j>i}V_{ij}]. \tag{3}$$

Here V_{ij} is the potential energy of interaction between particles i and j. We neglect the magnetic interaction of the electrons so that V_{ij} contains only the electrostatic potential energy.

$$V_{ij}=e^2/r_{ij}. \tag{4}$$

In Eq. (3), V_i is the potential energy of electron i in the field of the nuclei of the system:

$$V_i=-\sum_l Ze^2/r_{il}, \tag{5}$$

where the sum runs over all the nuclei.

The Hamiltonian is constructed to include relativistic effects due to the motion of an electron in the average field of the other electrons and the nuclei. It neglects relativistic effects in the interaction of the electrons with each other.

When wave functions of the form (1) are used, minimization of the energy of the system with respect to variation of the spinors U_i, subject to the usual conditions of orthogonality and normalization, leads to relativistic Hartree-Fock equations for these functions:

$$\begin{aligned}&(-c\boldsymbol{\alpha}_i\cdot\mathbf{p}_i-\beta_i mc^2+V_i)U_i(x_1)\\&\quad+\sum_j\left[\left(\int U_j^*(x_2)\frac{e^2}{r_{12}}U_j(x_2)d^3x_2\right)U_i(x_1)\right.\\&\quad\left.-\left(\int U_j^*(x_2)\frac{e^2}{r_{12}}U_i(x_2)d^3x_2\right)U_j(x_1)\right]=\epsilon_i U_i(x_1).\end{aligned} \tag{6}$$

In (6), ϵ_i is the energy eigenvalue; it is in the neighborhood of mc^2 for all except the most tightly bound electrons. Summation over spinor indices is implied in all integrals. These equations form the basis of the relativistic self-consistent field. Because of the complexity of these equations, there has been no adequate comparison of the results of Eq. (6) with those of the standard nonrelativistic theory.[2]

If we could regard the Coulomb and exchange terms in (6) as essentially the same as those of the nonrelativistic self-consistent field, it would be possible to treat the relativistic effects according to perturbation theory. This approach is discussed in detail in Sec. II where it is applied to potassium and cesium. Unfortunately, this simple approach is not quite valid. The screening of the nucleus by the core electrons should be more effective in a relativistic than in a nonrelativistic calculation, so that the change in the Coulomb and exchange integrals for a valence electron should tend to cancel the additional binding resulting from the rapid motion of an electron near a nucleus.

Since perturbation theory does not lead to quantitative results, it is desirable to work directly with the relativistic equation in such a way that explicit construction of a potential function is avoided. The quantum defect method offers such a possibility.[3] In Sec. III the cohesive energies of the alkali metals are discussed formally in terms of the Dirac equation for one particle in a periodic potential. We derive there a relativistic analog of the formula of Bardeen[4] for the effective mass of electrons. In Sec. IV, the corrections to the standard

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[1] B. Swirles, Proc. Roy. Soc. (London) A152, 625 (1935).

[2] The only existing relativistic self-consistent field for an atomic system is that for Cu (without exchange): A. O. Williams, Phys. Rev. 58, 723 (1940).

[3] T. S. Kuhn and J. H. Van Vleck, Phys. Rev. 79, 382 (1950); F. S. Ham in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 127.

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

quantum defect calculation due to the relativistic effects are obtained for cesium.

II. PERTURBATION THEORY

In this section we assume that the effective potential acting upon an electron in a solid is the same in both the relativistic and nonrelativistic self-consistent field calculations. We consider only the change in energy brought about by the relativistic motion of an electron in that potential. Although the basic assumption is not really justified, this approach does provide a useful estimate of the orders of magnitude of the relativistic effects. The work reported in this section has already been discussed briefly.[5]

The assumption of an unchanged potential permits us effectively to reduce Eq. (6) to the Dirac equation for one particle in a periodic potential. We can employ the second approximation to this equation for our purposes,[6]

$$E\psi=\left[\left(1-\frac{E-V}{2mc^2}\right)\frac{p^2}{2m}+V-\frac{\hbar^2}{4m^2c^2}\nabla V\cdot\nabla+\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\nabla V\times\mathbf{p})\right]\psi. \tag{7}$$

The terms

$$-\left[\left(\frac{E-V}{2mc^2}\right)\frac{p^2}{2m}+\frac{\hbar^2}{4m^2c^2}\nabla V\cdot\nabla-\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\nabla V\times\mathbf{p})\right] \tag{8}$$

may be regarded as perturbations. To determine the effect of these terms on the cohesive energies of the alkali metals, we calculate the expectation value of (8) for the valence electron both for the lowest state in the free atom and to order k^2 in the solid. To do this, we need wave functions for the solid which are correct to order k^2. We consider Bloch functions

$$\begin{aligned}\psi_{\mathbf{k}}&=e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}),\\ u_{\mathbf{k}}&=u_0+ik\cos\theta u_1+k^2(u_2P_2+\phi_0),\end{aligned} \tag{9}$$

where

$$P_2=(3\cos^2\theta-1)/2.$$

In Eq. (9) the functions u_0, u_1, u_2, and ϕ_0 are essentially those given by Silverman[7]:

$$u_1=f_P-ru_0, \tag{10}$$

where f_P is a P-state solution of the homogeneous wave equation for energy E_0 and $u_1(r_s)=0$. (Here r_s is the radius of the atomic sphere.)

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

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

$$\left[\frac{d^2}{dr^2}+\frac{2m}{\hbar^2}(E_0-V)\right]\left(r\frac{\partial u_0}{\partial E}\right)=-\frac{2m}{\hbar^2}ru_0. \tag{12}$$

If we calculate the expectation value of (8) by using these wave functions, we obtain after a straightforward but somewhat tedious calculation[8]:

$$\begin{aligned}E_k={}&E_0+\frac{\hbar^2k^2}{2m}E_2\\ &-\left\{1+k^2\left[\tfrac{1}{3}\int u_1^2r^2dr+2\int u_0\phi_0r^2dr\right]\right\}^{-1}\\ &\times\left\{\Delta E_0+\tfrac{1}{3}k^2\int u_1\left[\frac{(E_0-V)^2}{2mc^2}+\frac{\hbar^2}{4m^2c^2}\frac{dV}{dr}\frac{d}{dr}\right]\right.\\ &\times u_1r^2dr+2k^2\int u_0\frac{(E_0-V)^2}{2mc^2}\phi_0r^2dr+\frac{\hbar^2k^2}{4m^2c^2}\\ &\left.\times\int\left(\phi_0\frac{dV}{dr}\frac{du_0}{dr}+u_0\frac{dV}{dr}\frac{d\phi_0}{dr}\right)r^2dr\right\}.\end{aligned} \tag{13}$$

Addition of a multiple of u_0 to (11) does not affect the expectation value to order k^2. In (11), (12), and (13), E_0 is the eigenvalue of the lowest state, $-\Delta E_0$ is the expectation of (8) with the function u_0, and E_2 is the effective mass ratio m/m^*. The normalization appropriate for (13) is obtained by requiring that[9]

$$\int_0^\infty u_0^2r^2dr=1. \tag{14}$$

Equation (13) has been evaluated for potassium and cesium by using wave functions obtained in the calculation of cohesive energies in these elements.[10] If we define

$$\Delta E_k=E_k-E_0-\left(\frac{\hbar^2k^2}{2m}\right)E_2, \tag{15}$$

where E_k is given by (13), the results can be given in atomic units as follows:

for potassium,

$$\Delta E_k=-[0.00226-0.00005k^2]; \tag{16}$$

for cesium,

$$\Delta E_k=-[0.0226+0.0248k^2]. \tag{17}$$

The small coefficient of the k^2 term for potassium is apparently accidental. The change in the energy of the lowest state of a valence electron in the free atom, as computed from self-consistent field wave functions,[11] is (in atomic units)

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[5] J. Callaway, Phys. Rev. **102**, 919 (1956).

[6] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), second edition, p. 333.

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

[8] Further details are given by V. Sirounian, Master's thesis, University of Miami, 1956 (unpublished). Some negligible terms have been dropped.

[9] The normalization here is different from Eq. (5) of reference 5 where $\int_0^\infty u_0^2r^2dr=1/4\pi$ and ru_1 was written in place of our u_1.

[10] Berman, Callaway, and Woods, Phys. Rev. **101**, 1467 (1956); J. Callaway and E. L. Haase (to be published).

[11] D. R. Hartree and W. Hartree, Proc. Cambridge Phil. Soc. **34**, 550 (1938); R. M. Sternheimer (private communication).

for potassium,

$$\Delta E_a = -0.00119;$$

for cesium,

$$\Delta E_a = -0.01673. \tag{18}$$

From these results, the change in the cohesive energy is computed to be 0.33 kcal/mole in potassium and 2.41 kcal/mole in cesium. In both cases, the effect increases the binding.

There is an error resulting from the use of first-order perturbation theory applied to the second approximation to the Dirac equation as compared to the Dirac equation with the same potential. The error was estimated by comparing the results of this approach with the Dirac energy eigenvalue for the 6s state in a fictitious hydrogen-like atom with $Z=55$. The error is only 6% for that case and may be less in a more realistic example.

III. RELATIVISTIC THEORY OF THE COHESIVE ENERGY

The cohesive energies of the alkali metals are determined, as discussed by Wigner and Seitz,[12] principally from the difference of two quantities: the boundary correction and the Fermi energy. The former is found by subtracting the energy of the lowest state of a valence electron in the free atom from the energy of the corresponding lowest state. The Fermi energy can be computed if the effective mass is known.[13] The Coulomb interaction of the valence electrons can be taken into account, but the effect on the cohesive energy turns out to be small.

This picture is not changed in any essential respect by considering the relativistic motion of one electron in the field of an ion. The boundary correction is still obtained in the same manner, except that one must solve the Dirac equation [or more precisely, Eq. (6)] to determine the energies of the states of interest. The principal change comes in the calculation of the effective mass. We derive a relativistic expression for this quantity below, following the method of Silverman.[8]

We consider the Dirac equation for one particle in periodic potential:

$$(-c\boldsymbol{\alpha}\cdot\mathbf{p}-\beta mc^2+V)\psi_{\mathbf{k}}=E_k\psi_{\mathbf{k}}. \tag{19}$$

Since Bloch's theorem still holds (it is a consequence of symmetry and is independent of the form of the Hamiltonian), we write

$$\psi_{\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}, \tag{20}$$

where $u_{\mathbf{k}}$ is periodic in the lattice.

We now utilize the customary perturbation expansion for $u_{\mathbf{k}}$ and E_k in terms of $\mathbf{k}$:

$$\begin{aligned} u_{\mathbf{k}}&=u_0+u_1+u_2+\cdots,\\ E_k&=E_0+E_1+E_2+\cdots, \end{aligned} \tag{21}$$

where u_i and E_i are proportional to k^i. Upon substituting (20) and (21) into (19) and collecting terms proportional to the same power of k, we have

$$(-c\boldsymbol{\alpha}\cdot\mathbf{p}-\beta mc^2+V-E_0)u_0=0, \tag{22a}$$

$$(-c\boldsymbol{\alpha}\cdot\mathbf{p}-\beta mc^2+V-E_0)u_1=(E_1+\hbar c\boldsymbol{\alpha}\cdot\mathbf{k})u_0, \tag{22b}$$

$$(-c\boldsymbol{\alpha}\cdot\mathbf{p}-\beta mc^2+V-E_0)u_2 =(E_1+\hbar c\boldsymbol{\alpha}\cdot\mathbf{k})u_1+E_2u_0. \tag{22c}$$

It is easily determined that

$$E_1=-\hbar c\int u_0^*\boldsymbol{\alpha}\cdot\mathbf{k}u_0d\tau=0. \tag{23}$$

This is a consequence of the crystal symmetry. (Summation over spinor components is implied in all integrals.)

It is now possible to solve the second of Eqs. (22) if the solution to (22a) has been obtained. A particular solution of (22b) is

$$u_1=-i(\mathbf{k}\cdot\mathbf{r})u_0. \tag{24}$$

To this must be added some multiple of a solution of the homogeneous equation in order to satisfy the boundary condition. The boundary condition in the cellular method is that an even function has zero radial derivative on the atomic sphere and that an odd function is zero on this sphere. In an alkali metal, the ground state function is almost entirely characterized by $l=0$ and $j=\frac{1}{2}$. If we take $\mathbf{k}$ along the polar axis, then the large component of u_1 is an odd function. For this large component to vanish on the atomic sphere, it is necessary to add multiples of solutions for $l=1$ and $j=\frac{1}{2}$ and $\frac{3}{2}$ (we choose $m_j=\frac{1}{2}$ for all functions). In what follows, $\varphi_{l,j}$ denotes the solutions of the homogeneous equation for a state characterized by l,j and $m_j=\frac{1}{2}$, while $g_{l,j}$ is the radial part of the large components. If we require each $\varphi_{l,j}$ to be normalized with respect to integration over solid angle, an examination of the explicit form of the function[14] shows that we must have

$$u_1=-k(r\cos\theta\varphi_{0,\frac{1}{2}}-\sqrt{2}\varphi_{1,\frac{3}{2}}-\varphi_{1,\frac{1}{2}}). \tag{25}$$

The fourth component of u_i will vanish on the atomic sphere, $r=r_s$, if

$$g_{1,\frac{3}{2}}(r_s)=g_{1,\frac{1}{2}}(r_s). \tag{26}$$

The third component will be zero when

$$r_sg_{0,\frac{1}{2}}(r_s)=2g_{1,\frac{3}{2}}(r_s)+g_{1,\frac{1}{2}}(r_s). \tag{27}$$

We now solve Eq. (22c) to determine u_2. We write (25)

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[12] 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.

[13] Terms in the series expansion of $E(k)$ of order k^4 and higher are important in detailed calculations of the cohesive energies of the heavier alkali metals, but they are disregarded in this calculation. The effects of core polarization are also neglected.

[14] H. A. Bethe in *Handbuch der Physik* (Edwards Brothers, Inc., Ann Arbor, 1943), Vol. 24, Part 1, p. 312.

in the form

$$u_1 = -i(\mathbf{k}\cdot\mathbf{r}u_0 + kv_1).$$

With this substitution, we have to solve

$$[-c\boldsymbol{\alpha}\cdot\mathbf{p} - \beta mc^2 + V - E_0]u_2 = E_2u_0 - i\hbar c\boldsymbol{\alpha}\cdot\mathbf{k}[(\mathbf{k}\cdot\mathbf{r})u_0 + kv_1]. \tag{28}$$

A particular solution of this equation is

$$u_2 = E_2\left(\frac{\partial u_0}{\partial E}\right)_{E_0} - k(\mathbf{k}\cdot\mathbf{r})V_1 - \tfrac{1}{2}(\mathbf{k}\cdot\mathbf{r})^2u_0, \tag{29}$$

where $(\partial u_0/\partial E)_{E_0}$ satisfies

$$[-c\boldsymbol{\alpha}\cdot\mathbf{p} - \beta mc^2 + V - E_0]\left(\frac{\partial u_0}{\partial E}\right)_{E_0} = u_0. \tag{30}$$

Equation (30) is obtained by differentiating (22a) with respect to E and setting $E = E_0$.

The function u_2 is a solution of the Dirac equation to second order in k. We decompose this into a linear combination of functions with angular dependence appropriate to states of definite l,j, and $m_j = \frac{1}{2}$. The boundary condition which we employ is that the part of u_2 which has angular dependence appropriate for ($l=0$, $j=\frac{1}{2}$) must be such that the radial derivative of the large component is zero for $r = r_s$. This is also the boundary condition for u_0, and it clearly cannot be satisfied by adding some multiple of u_0 to u_2. Consequently, the boundary condition suffices to determine E_2.

The part of the third component of (29) belonging to $l=0$, $j=\frac{1}{2}$ is easily determined to be

$$\frac{1}{(4\pi)^{\frac{1}{2}}}\left[E_2\frac{\partial g_{0,\frac{1}{2}}}{\partial E} + k^2r(2g_{1,\frac{3}{2}} + g_{1,\frac{1}{2}}) - \frac{k^2r^2}{6}g_{0,\frac{1}{2}}\right]. \tag{31}$$

If we require this to have zero radial derivative at $r = r_s$, we obtain

$$E_2 = -\frac{k^2r_s}{3}(2g_{1,\frac{3}{2}}' + g_{1,\frac{1}{2}}')\left(\frac{\partial^2 g_{0,\frac{1}{2}}}{\partial r\partial E}\right)_{r_s,E_0}^{-1}, \tag{32}$$

where the prime indicates the derivative with respect to r. We can use (25) to write (32) in a form which is evidently independent of the normalization of all the functions:

$$E_2 = -\frac{k^2r_s^2}{3}g_{0,\frac{1}{2}}\left(\frac{\partial^2 g_{0,\frac{1}{2}}}{\partial r\partial E}\right)_{r_s,E_0}^{-1}\left(\frac{2g_{1,\frac{3}{2}}'(r_s) + g_{1,\frac{1}{2}}'(r_s)}{2g_{1,\frac{3}{2}}(r_s) + g_{1,\frac{1}{2}}(r_s)}\right). \tag{33}$$

If we introduce the functions $u_{1,\frac{3}{2}} = rg_{1,\frac{3}{2}}$, etc., a little algebra suffices to transform (33) into

$$E_2 = -\frac{k^2r_s}{3}g_{0,\frac{1}{2}}\left(\frac{\partial^2 g_{0,\frac{1}{2}}}{\partial r\partial E}\right)^{-1} \times\left[\tfrac{2}{3}\left(\frac{r_s}{u_{1,\frac{3}{2}}}\right)\frac{du_{1,\frac{3}{2}}}{dr} + \tfrac{1}{3}\left(\frac{r_s}{u_{1,\frac{1}{2}}}\right)\frac{du_{1,\frac{1}{2}}}{dr} - 1\right]. \tag{34}$$

Equation (32) is in a form suitable for use in the quantum defect method. It is nevertheless instructive to obtain an expression resembling more closely the original result of Bardeen.[4] To do this, we need to evaluate the quantity

$$\left(\frac{\partial^2 g_{0,\frac{1}{2}}}{\partial r\partial E}\right)_{r_s,E_0}.$$

Let $f_{l,j}$ be the radial function belonging to the small components of the function $\varphi_{l,j}$. The functions $f_{0,\frac{1}{2}}$ and $g_{0,\frac{1}{2}}$ satisfy the equations:

$$\begin{aligned} \frac{1}{\hbar c}[E - V(r) + mc^2]f_{0,\frac{1}{2}} &= \frac{dg_{0,\frac{1}{2}}}{dr}, \\ \frac{1}{\hbar c}[E - V(r) - mc^2]g_{0,\frac{1}{2}} &= -\frac{df_{0,\frac{1}{2}}}{dr} - \frac{2}{r}f_{0,\frac{1}{2}}. \end{aligned} \tag{35}$$

If we differentiate the first of Eqs. (35) with respect to energy and evaluate the result at $r = r_s$ and $E = E_0$ and then note that $f_{0,\frac{1}{2}}$ must vanish at r_s, we obtain

$$\frac{1}{\hbar c}[E_0 - V(r_s) + mc^2]\left(\frac{\partial f_{0,\frac{1}{2}}}{\partial E}\right)_{r_s,E_0} = \left(\frac{\partial^2 g_{0,\frac{1}{2}}}{\partial r\partial E}\right)_{r_s,E_0}. \tag{36}$$

In Eq. (36), $E_0 + V(r_s)$ is very nearly equal to mc^2 since $W = mc^2 - E_0$ is close to $V(r_s)$ for an alkali metal. To a very good approximation, we have

$$\left(\frac{\partial^2 g_{0,\frac{1}{2}}}{\partial r\partial E}\right)_{r_s,E_0} = \frac{2mc}{\hbar}\left(\frac{\partial f_{0,\frac{1}{2}}}{\partial E}\right)_{r_s,E_0}. \tag{37}$$

To obtain $(\partial f_{0,\frac{1}{2}}/\partial E)_{r_s,E_0}$, we multiply Eq. (30) by u_0^* and integrate over the atomic cell, giving

$$\int u_0^*(-c\boldsymbol{\alpha}\cdot\mathbf{p} - \beta mc^2 + V - E_0)\frac{\partial u_0}{\partial E}d\tau = \int u_0^*u_0d\tau = 1. \tag{38}$$

A straightforward calculation transforms (38) into

$$\int[(-c\boldsymbol{\alpha}\cdot\mathbf{p} - \beta mc^2 + V - E_0)u_0]^*\frac{\partial u_0}{\partial E} - \frac{\hbar c}{i}\int u_0^*\boldsymbol{\alpha}\frac{\partial u_0}{\partial E}\cdot d\mathbf{s} = 1. \tag{39}$$

The first term on the left-hand side of (39) vanishes. The other term may be evaluated by noting that $\boldsymbol{\alpha}\cdot d\mathbf{s} = \alpha_r r^2 d\Omega$ and then using an explicit representation for α_r. It turns out that

$$u_0^*\alpha_r\frac{\partial u_0}{\partial E} = \frac{1}{4\pi}\left(-if_{0,\frac{1}{2}}\frac{\partial g_{0,\frac{1}{2}}}{\partial E} + ig_{0,\frac{1}{2}}\frac{\partial f_{0,\frac{1}{2}}}{\partial E}\right). \tag{40}$$

Integration over solid angles cancels the factor $(4\pi)^{-1}$. Since $f_{0,\frac{1}{2}}(r_s)=0$,

$$-\hbar c r_s^2 g_{0,\frac{1}{2}}(r_s)\left(\frac{\partial f_{0,\frac{1}{2}}}{\partial E}\right)_{r_s,E_0}=1. \tag{41}$$

Combining (41) and (37) gives:

$$\left(\frac{\partial^2 g_{0,\frac{1}{2}}}{\partial r\partial E}\right)_{r_s,E_0}=-\frac{2m}{\hbar^2 r_s^2 g_{0,\frac{1}{2}}(r_s)}. \tag{42}$$

Upon substituting (42) into (34), we have finally

$$E_2=\frac{\hbar^2k^2}{2m}\frac{r_s u_{0,\frac{1}{2}}^2(r_s)}{3}\times\left[\frac{2}{3}\left(\frac{r}{u_{1,\frac{3}{2}}}\right)\frac{du_{1,\frac{3}{2}}}{dr}+\frac{1}{3}\left(\frac{r}{u_{1,\frac{1}{2}}}\right)\frac{du_{1,\frac{1}{2}}}{dr}-1\right]_{r_s}. \tag{43}$$

This is the result desired. It differs from the original formula of Bardeen only in that the functions are solutions of the Dirac equation and that a combination of the derivatives of the different P-state functions is used.

IV. APPLICATION OF THE QUANTUM DEFECT METHOD

Because relativistic self-consistent fields are not available for the alkali metals, it is not possible to calculate the boundary correction and the effective mass directly from the self-consistent field Eq. (6). However, we have recourse to the quantum defect method.[3] In this method, the experimental energy levels of the free atom as determined from spectroscopic data are used almost directly to circumvent the construction of the potential.

In order to apply the quantum defect method in the present instance, we note that at large r, in the region of the atomic cell where the potential energy of the valence electron is just that for a Coulomb field, $-e^2/r$, the Dirac equation can be reduced by standard procedures to the ordinary Schrödinger equation. In this region, the only relativistic effects are those pertaining to the exterior Coulomb field, which may be neglected because they are very small. For this reason, no basic modification is required in the theory of the quantum defect method. We shall, of course, expect that states of the same orbital angular momentum but of different total angular momentum j will have different energies due to the relativistic effects in the interior. Since the lowest state of a valence electron is a state of zero orbital angular momentum, which cannot be split by spin-orbit coupling, all important relativistic effects for this state are already contained in the standard calculations. In order to calculate the effective mass, we need p functions corresponding to $j=\frac{1}{2}$ and $j=\frac{3}{2}$. We must therefore obtain separate quantum defects for these states, but the calculation is otherwise unaltered.

The practical application of the quantum defect method, as discussed by Ham, depends critically on the function $\eta(E)$, which is defined at the eigenvalues of the free atom for a state of angular momentum l by

$$\pi\eta_l(E)=\arctan\left[\frac{\Gamma(n+l+1)}{n^{2l+1}\Gamma(n-l)}\cot\pi\delta_l\right], \tag{44}$$

where $E=-1/n^2$, and the quantity δ_l is determined by

$$n=m-\delta_l, \tag{45}$$

where m is an integer which increases by unity between adjacent terms of the same spectral series. The function $\eta(E)$ is supposed to vary in a slow and regular fashion with energy. This property is extremely important since it is necessary to determine η by extrapolation. The function η must be evaluated at the energy of the lowest state of a valence electron in the solid, which is considerably lower than the energy of the lowest valence state in the free atom. Once η is determined, the ratio of the coefficients of the regular and irregular Coulomb functions which compose the solid state wave function in the exterior of the cell can be determined. According to Ham,[3] we may write r times the radial wave function for a state of angular momentum l and energy E as

$$u^{l,n}(r)=\alpha(n)(z/2)J_{2l+1}{}^n(z)+\gamma(n)(z/2)N_{2l+1}{}^n(z). \tag{46}$$

Here $z=(8r)^{\frac{1}{2}}$ and J and N are certain Bessel functions discussed by Ham. The coefficients α and γ are related by

$$\alpha(n)/\gamma(n)=-\cot(\pi\eta). \tag{47}$$

Knowledge of η as a function of energy makes it possible to determine the wave function for any energy as a function of r at large r. The required Bessel functions J and N may be constructed from tables.[15] The normalization of the function is not known but only logarithmic

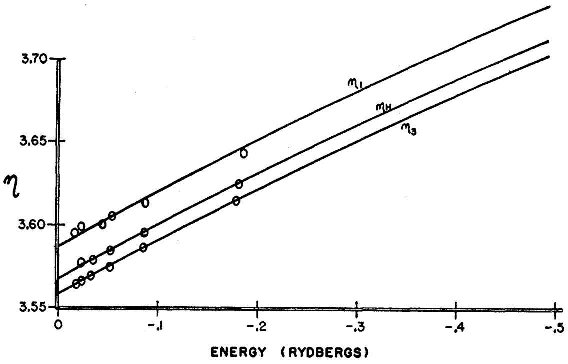

FIG. 1. Extrapolation of quantum defect method function $\eta(E)$ for cesium. The solid curves show the extrapolations used for the $l=1$ states of $j=\frac{1}{2}$ (η_1) and $j=\frac{3}{2}$ (η_3), and for the nonrelativistic (η_H) case. The circled points show the values of η obtained from experiment for the upper and lower curve, and as averaged by Ham for the middle one.

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[15] F. S. Ham, Office of Naval Research Technical Report No. 204, Cruft Laboratory, Harvard University, 1954 (unpublished).

derivatives, which are independent of normalization, are required.

We have determined the effective mass of electrons in cesium by using Eq. (34) and the quantum defect method. The function η was calculated for p states of $j=\frac{1}{2}$ and $j=\frac{3}{2}$ from spectroscopic data.[16] It is exhibited in Fig. 1 which shows both the points determined from the experimental eigenvalues and the extrapolations used. It can easily be seen that there is a large amount of uncertainty in the extrapolation procedure. This uncertainty detracts from the accuracy of the quantum defect method. For the purposes of comparison of relativistic and nonrelativistic calculations, it seems desirable to extrapolate all the functions in the same way. There is no fundamental justification for such a procedure, but no better one has been found. Ham's values were fitted with a quadratic expression using the method of least squares, and the other curves were required to be parallel to it. The values of the coefficients of the least-squares quadratic are given in Table I.

TABLE I. Least squares quadratic extrapolation of $\eta(E)$. The coefficients a, b, and c in the expression $\eta=a-bE+cE^2$ are given, as determined by a least-squares fit to the spectroscopic data. The coefficients proposed by Ham are also given.

	Nonrelativistic	$j=1/2$	$j=3/2$	Ham
a	3.5680	3.5883	3.5586	3.5696
b	0.3329	0.3329	0.3329	0.3019
c	−0.0747	−0.0747	−0.0747	0.0479

The so-called nonrelativistic coefficients are determined from the values of η given by Ham,[3] which were obtained from an average of the components of the spectral doublet. Ham, however, proposed a different extrapolation scheme. The coefficients in the extrapolating polynomial used by Ham are also given in Table I. The difference is a measure of the uncertainty in extrapolation.

TABLE II. Results for cesium: effective mass and cohesive energy.

$z_s=(8r_s)^{\frac{1}{2}}$	E_2 (rel.) $=m/m^*$	E_2 (nonrel.)	ΔE_c (kcal/mole)
6.0	1.5307	1.5413	−0.36
6.5	1.2200	1.2182	−0.04
7.0	1.1216	1.1232	−0.03

The energy E_0 for which the wave functions and their derivatives are required was taken from the work of Brooks,[17] as was the quantity

$$\gamma=\frac{r_s}{3}g_{0,\frac{1}{2}}(r_s)\left(\frac{\partial^2 g_{0,\frac{1}{2}}}{\partial r\partial E}\right)^{-1}_{r_s,E_0}. \tag{48}$$

This is legitimate since the relativistic effects are already included in the ground state function. The p state functions and their derivatives were evaluated according to the procedures discussed. The effective mass computed according to (34) is given in Table II together with that computed from the nonrelativistic extrapolation according to the standard formula. The same three values of the radius of the atomic sphere employed by Brooks were used. The nonrelativistic effective mass values quoted here are different from his. The changes in the cohesive energy can be computed directly from these effective masses and are quite small—considerably smaller than the residual experimental and theoretical uncertainties.

The small size of the change in the effective mass, as compared with that given by Eq. (17), reveals the competition between the increased attraction and the more effective screening discussed in the introduction. The separate effects are sizable, but the cancellation is nearly complete. Relativistic effects will probably be of more numerical significance in a calculation of the value of the wave function at the nucleus, which is required in the theory of the Knight shift.

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[16] H. R. Kratz, Phys. Rev. **75**, 1844 (1948).

[17] H. Brooks, Phys. Rev. **91**, 1027 (1953).