

Electron Energy Bands in Sodium

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The potential energy of a valence electron in sodium is represented by the function $V(r) = -2/r + Ae^{-\beta r}/r$. The second term, which is repulsive in character, represents the effect of the core electrons. Values for A and β are determined from spectroscopic data. Energy levels of predominantly s and p symmetry are determined at four points of the Brillouin zone.

INTRODUCTION

IN the alkali metals, one valence electron moves mostly outside of a compact core of electrons in closed shells. Beyond the core, the potential energy of the electron is $-2/r$, the Coulomb potential of the positive ion. Inside the core, the potential energy decreases, becoming $-2Z/r$ at the center (Z is the atomic number). The net effect of the core on the valence electron is nevertheless repulsive: this is manifest in that the energy of the lowest state of a valence electron in the free sodium atom is only -0.3777 Rydberg. The energy of the lowest state in a $-2/r$ potential is -1 Rydberg. The repulsive effect is due to the requirement that the valence electron wave functions be orthogonal to the wave functions of the core electrons. The orthogonality gives rise to a substantial kinetic energy of the valence electron when it is in the core.

This observation suggests that one might try to introduce a potential energy for the valence electron which would be $-2/r$ for large r , but contain a repulsive part at small r . This pseudopotential would include the effects of orthogonality of the valence electron to the core electrons, so that the lowest valence electron state is also the lowest bound state in this potential. This idea was introduced by Hellmann and Kassatotschkin,¹ who called it the combined approximation. These authors applied the method to the determination of the cohesive energies of the alkali metals. It has also been applied to the study of molecules.^{1,2}

In this paper the pseudopotential idea is applied to the computation of energy bands in sodium. The potential energy of the valence electron is expressed as

$$V(r) = -2/r + Ae^{-\beta r}/r. \quad (1)$$

The constants A and β are determined from spectroscopic data for the free atom. A plane wave method is adopted for the computation of energy levels of s and p symmetry at four points of the Brillouin zone.

QUALITATIVE JUSTIFICATION OF THE PSEUDOPOTENTIAL

The development of the quantum defect method (QDM) indicates that it is not necessary to have de-

tailed information concerning the form of the potential inside the ion in order to compute the energy levels of the valence electron in the solid, provided that the potential is Coulombic near the cell boundary.³ In the region where the potential is Coulombic, the wave function is a linear combination of the regular and irregular solutions of the Coulomb wave equation. The ratio of the coefficients in this combination is a function of energy which can be determined for energies corresponding to eigenvalues of the free atom, and extrapolated to other energies. Once the ratio is known, the wave function on the cell boundary is determined except for a multiplicative constant, and consequently the energies at which the various states ψ_k satisfy the appropriate boundary conditions can be determined.

The justification of the pseudopotential approach is that, for energies corresponding to certain eigenvalues of the free atom, the wave function is given correctly in the Coulomb region. For other energies, it gives a means of performing the extrapolation of the ratio of coefficients in the wave function in an unambiguous manner. The method can not be in principle as accurate as the QDM since, for instance, exchange effects cannot be completely represented by a potential. The principal advantage is that it permits the application of variational methods to the determination of energy levels in the solid.

It must be realized that the pseudopotential approach can be applied only to those levels of the valence electron for which there are core electron states of the same symmetry. It is only for these states that the orthogonality to the core functions gives rise to an effective repulsion. For instance, the method cannot be applied to a d state in sodium.

DETERMINATION OF THE PSEUDOPOTENTIAL PARAMETERS

The problem is to determine the pseudopotential parameters A and β from spectroscopic data. It must be expected that different values for the parameters will be obtained depending on the states used to determine them. The effect of exchange can be considered to a good approximation as giving rise to a different potential for

¹ H. Hellmann and W. Kassatotschkin, *J. Chem. Phys.* **4**, 324 (1936); *Acta Physicochim. U.R.S.S.* **5**, 23 (1936).

² H. Preuss, *Z. Naturforsch.* **102**, 365 (1955).

³ F. S. Ham, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 127.

the states of different angular momentum.⁴ Consequently, it would be desirable to determine a pseudopotential for each angular momentum. The difference of the effective exchange potential between the different angular momentum states is likely to produce only a small effect in sodium as is evidenced by the success of Prokofjew in accounting for all the spectral levels on the basis of a single potential.⁵ It was believed to be sufficiently accurate in this case to determine a single potential based upon the lowest valence *s* and *p* states.

An obvious way to determine the pseudopotential parameters is to apply the variational principle. This is the procedure employed by Hellmann and Kassatotschkin.¹ The expectation value of the one-electron Hamiltonian can be calculated analytically with the pseudopotential if a simple trial function is employed. It is possible to determine the parameters by requiring that the minimum of the expectation value of the energy occur at the observed eigenvalues of two states, subject to the requirement of orthogonality. This procedure was applied to sodium. Trial functions of the form $re^{-\mu r}$ for the *s* state and $r^2e^{-\nu r}$ for the *p* state were used and yielded values of $A=5.378$, $\beta=1.448$. These values differ significantly from those quoted by Preuss.² Unfortunately, the simple trial functions are rather poor approximations to the actual wave functions for this sort of potential, and it appears that the variationally determined parameters overestimate the range and underestimate the strength of the repulsive potential quite seriously.

In order to determine the parameters more carefully, the following procedure was adopted. The wave equation was integrated numerically with a trial repulsive potential out to a radius in the region where the potential is Coulombic. The logarithmic derivative of the wave function was computed and compared with that required by the Coulomb wave equation for the given eigenvalue. The latter exact logarithmic derivative can be computed according to the procedure of Ham,³ but the following approach was found to be simpler and less subject to computational error.

It is possible to give a semiconvergent expansion in decreasing powers of r for the wave function in the Coulomb region, based on the fact that if the energy is an eigenvalue, the wave function must decrease exponentially at large r . The radial equation is

$$\frac{d^2R_l}{dr^2} + \left(E + \frac{2}{r} - \frac{l(l+1)}{r^2} \right) R_l = 0. \quad (2)$$

The expansion is

$$R_l = \exp(-W^{\frac{1}{2}}r) \sum_n a_n r^{-n}, \quad (3)$$

where $W = -E$, $s = (W)^{-\frac{1}{2}}$, and

$$a_n = [l(l+1) - (s+1-n)(s-n)] a_{n-1} / (2n\sqrt{W}). \quad (4)$$

⁴ Herman, Callaway, and Acton, Phys. Rev. **95**, 371 (1954).

⁵ W. Prokofjew, Z. Physik **58**, 255 (1929).

The first three terms of this expansion are usually sufficient to obtain a good value for the logarithmic derivative.

Given the difference between the logarithmic derivative of the wave function in the Coulomb region as computed from a set of pseudopotential parameters, and that obtained using the expansion above, it is possible to correct the parameters to bring the derivatives into reasonable coincidence. The method for doing this is closely related to a procedure given by Kambe.⁶ The radial wave equation for an energy E and potential V is

$$\frac{d^2R_l}{dr^2} + \left(E - V - \frac{l(l+1)}{r^2} \right) R_l = 0. \quad (5)$$

For the special case of $V=E=0$, we have

$$\frac{d^2P_l}{dr^2} - \frac{l(l+1)}{r^2} P_l = 0, \quad (6)$$

of which the solution is $P_l = r^{l+1}$. We multiply (5) by P_l and (6) by R_l , subtract, integrate with respect to r , and finally divide by the product $R_l P_l$. We obtain

$$\frac{1}{R_l} \frac{dR_l}{dr} - \frac{1}{P_l} \frac{dP_l}{dr} = \frac{1}{R_l(r)P_l(r)} \times \int_0^r [V(r') - E] R_l(r') P_l(r') dr'.$$

Thus for a given potential V_1 , the logarithmic derivative is

$$L_1 = \frac{1}{R_l} \frac{dR_l}{dr} = \frac{l+1}{r} + \frac{1}{R_l r^{l+1}} \times \int_0^r [V_1(r') - E] R_l(r') (r')^{l+1} dr'. \quad (7)$$

If we compare the logarithmic derivatives of functions found for two potentials at the same r , we find

$$L_1 - L_2 = \frac{1}{R_l r^{l+1}} \int_0^r [V_1(r') - E] R_l(r') (r')^{l+1} dr' - \frac{1}{R_l' r^{l+1}} \int_0^r [V_2(r') - E] R_l'(r') (r')^{l+1} dr'.$$

If the change in potential $\Delta V = V = V_1 - V_2$ is sufficiently small, we may set $R_l = R_l'$, and we have

$$L_1 - L_2 = \frac{1}{R_l r^{l+1}} \int_0^r \Delta V(r') R_l(r') (r')^{l+1} dr'. \quad (8)$$

If we know the difference in the logarithmic derivatives, we can use (8) to determine information about

⁶ K. Kambe, Phys. Rev. **99**, 419 (1958).

ΔV . Through the use of simple analytic fits to the functions R_i , it was found possible to adjust the potential using the differences between the computed and actual logarithmic derivatives for the s and p state simultaneously. After a few iterations of this procedure, the final pseudopotential parameters were chosen to be $A = 24.578$, $\beta = 2.1008$.

This potential leads to an energy for the $4S$ free-atom state of -0.1428 ry in comparison with the experimental -0.1432 ry.

BAND STRUCTURE CALCULATION

An estimate of the accuracy of the pseudopotential approach in band theory would be afforded by a comparison of energy levels calculated with the pseudopotential and those obtained using the quantum defect method. The only substance for which QDM treatment of levels away from $k=0$ has been reported is sodium.³ This is the reason for the choice of sodium as the first substance to be studied by this method.

In order to avoid the difficulties of satisfying boundary conditions on the surface of the atomic polyhedron, the orthogonalized plane wave (O.P.W.) method was chosen in preference to the cellular method for the band structure calculation. Application of the O.P.W. method is greatly simplified in this case by the fact that the effect of the core states is contained in the pseudopotential so that the orthogonalization procedure is unnecessary. Another advantage is that the simple analytic form of the potential makes possible analytic computation of the Fourier coefficients of the potential. A disadvantage is that the strong and rapidly varying repulsive potential near a nucleus gives rise to large Fourier coefficients for $k \neq 0$ and thus retards the convergence of the plane wave expansions for the states of predominantly s symmetry.

The wave function is expanded as a linear combination of symmetrized groups of plane waves chosen so as to belong to a particular representation of the group of

the wave vector. If $\psi_{\mathbf{k}}^i$ is the wave function for the i th irreducible representation of wave vector \mathbf{k} , one has

$$\psi_{\mathbf{k}}^i = \Omega_0^{-\frac{1}{2}} \sum_{\mathbf{h}} a_{\mathbf{k}+\mathbf{h}}^i \exp[i(\mathbf{k}+\mathbf{h}) \cdot \mathbf{r}]. \quad (9)$$

The sum over \mathbf{h} runs over all reciprocal lattice vectors. Ω_0 is the volume of the unit cell. Substitution of (8) into the Schrödinger equation and standard manipulations lead to the determinantal equation:

$$\det[\langle \mathbf{k}+\mathbf{h} | H | \mathbf{k}+\mathbf{h}' \rangle - E \delta_{\mathbf{h}\mathbf{h}'}] = 0. \quad (10)$$

If the Hamiltonian is written as $H = -\nabla^2 + V(\mathbf{r})$, one obtains

$$\langle \mathbf{k}+\mathbf{h} | H | \mathbf{k}+\mathbf{h}' \rangle = (\mathbf{k}+\mathbf{h})^2 \delta_{\mathbf{h}\mathbf{h}'} + V(\mathbf{h}-\mathbf{h}'), \quad (11)$$

where

$$V(\mathbf{h}-\mathbf{h}') = \Omega_0^{-1} \int \exp[-i(\mathbf{h}-\mathbf{h}') \cdot \mathbf{r}] V(\mathbf{r}) d^3r. \quad (12)$$

TABLE I. Energy levels for sodium (in Rydbergs). The order of the energy matrix diagonalized and the number of plane waves used in the expansion of the wave number are given along with the energy of each state. For comparison, the energies obtained by Ham^a using QDM, by Howarth and Jones,^b and by Von der Lage and Bethe^c are given.

State	Order of matrix	Number of waves	E	$E(\text{QDM})^a$	$E(\text{L.B.HJ})^{b,c}$
Γ_1	8	135	-0.597	-0.610	-0.608
N_1	16	84	-0.263	-0.287	-0.315
P_1	7	80	-0.041		-0.11
H_1	6	92	+0.193	+0.136	-0.100
N_1'	8	40	-0.316	-0.292	-0.268
P_4	8	44	-0.162		
H_{15}	8	92	-0.015	-0.018	-0.014
N_3	8	44	0.301		
N_4'	8	42	0.310		
Γ_{15}	8	86	0.632		+0.563

^a See reference 3.

^b See reference 9.

^c See reference 8.

The Fourier coefficients $V(\mathbf{h}-\mathbf{h}')$ of the potential (1) were computed in the approximation that the atomic polyhedron can be replaced by the sphere of equal volume. Calculations were based on a sphere radius⁷ $r_s = 3.94$ atomic units, believed appropriate for $T = 0^\circ\text{K}$.

The determination of the Fourier coefficients of the potential is discussed at greater length in Appendix I.

The energies of the states of predominantly s and p symmetry were determined at four symmetry points of the Brillouin zone: Γ , H , P , and N . The Brillouin zone is shown in Fig. 1. States of predominantly d (or higher l) symmetry were not considered since the pseudopotential approach cannot be applied to states for which there is no core function of like symmetry.

The energies of the states calculated are given in Table I where they are compared with the results of Ham as mentioned previously, and with those of Howarth and Jones and Von der Lage and Bethe who

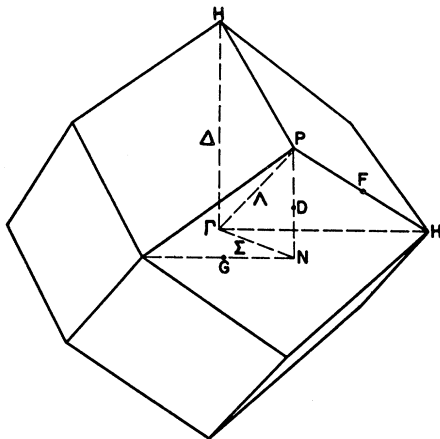


FIG. 1. Brillouin zone for the body-centered cubic lattice. Points and lines of symmetry are indicated.

⁷ G. B. Benedek and T. Kushida, Technical Report No. 268, Cruft Laboratory, Harvard University, 1957 (unpublished).

used the cellular method and the Prokofjew potential.^{8,9} The agreement is quite good although not perfect.

In comparing results we believe that the energies of the levels reported here are convergent to within 0.01 Rydberg for all states. The numerical accuracy of the cellular method calculations is difficult to assess since it is well known that point fitting of boundary condition may lead to a spread of the energy values for a given level. The calculations of Ham and Howarth and Jones were made for slightly different lattice parameters than that used here, corresponding to $r_s=3.96$ and $r_s=4.01$ atomic units, respectively. Also the previous cellular method and QDM calculations assume the potential is coulombic on the surface of the atomic cell. The potential used here has been modified so as to have zero gradient for $r=r_s$, as is discussed in the appendix.

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APPENDIX. FOURIER COEFFICIENTS OF THE POTENTIAL

In a cubic crystal, the potential must belong to the Γ_1 representation of the cubic point group. This means that the potential, if it is a function of radius only, must have zero normal derivative on the surface of the atomic sphere. Failure to satisfy this condition is equivalent to assuming the presence of a surface charge layer on the cell boundary. The potential (1) does not satisfy this condition, as has also been the case in many band calculations. It is desirable then to modify the potential so that the Fourier coefficients of the potential used in the calculation correspond to a potential with zero normal derivative on the boundary.

Consider a simple Coulomb potential in one cell:

$$V(\mathbf{r}) = -2/r. \quad (\text{A-1})$$

If we carry out the Fourier analysis of this potential according to Eq. (11) and replace the polyhedral cell by the sphere of equal volume (radius r_s), we have

$$V(\mathbf{k}) = \Omega_0^{-1} \int_{\Omega_0} e^{-i\mathbf{k}\cdot\mathbf{r}} V(\mathbf{r}) d^3r = \frac{8\pi}{k^2\Omega_0} (\cos kr_s - 1). \quad (\text{A-2})$$

The potential of Eq. (A-1) may be regarded as an approximation to that produced by a periodic array of unit point charges. To keep the average crystal potential finite, these point charges must be neutralized, for instance, by a uniform distribution of negative charge with density $1/\Omega_0$. The Fourier coefficients of the potential of this distribution are given without approximation by the formula¹⁰

$$V_c(\mathbf{k}) = -\frac{8\pi}{\Omega_0 k^2} \int_{\Omega_0} \sigma(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} d^3r, \quad (\text{A-3})$$

⁸ F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).
⁹ D. J. Howarth and H. Jones, Proc. Phys. Soc. (London) **A65**, 355 (1952).

¹⁰ J. Callaway and M. L. Glasser, Phys. Rev. **112**, 73 (1958).

TABLE II. Comparison of different potentials. The energies (in Rydbergs) of the states are given: E_I as determined from the potential whose Fourier coefficients are given by (A-5); E_{II} , from the potential with Fourier coefficients (A-6).

State	E_I	E_{II}
Γ_1	-0.597	-0.601
N_1	-0.263	
P_1	-0.041	-0.090
H_1	+0.193	+0.168
N_1'	-0.316	-0.298
P_4	-0.162	-0.145
H_{15}	-0.015	-0.060
N_3'	+0.301	+0.229
N_4'	+0.310	+0.364
Γ_{15}	+0.632	+0.592

where $\sigma(\mathbf{r})$ is the charge in each cell. For $k \neq 0$, we may neglect the uniform charge distribution, and if we set $\sigma(\mathbf{r}) = \delta(\mathbf{r})$ we have

$$V_c(\mathbf{k}) = -\frac{8\pi}{\Omega_0 k^2}. \quad (\text{A-4})$$

It will be observed that the coefficients given by (A-4) are significantly different from those given by (A-2) because of the presence of the $\cos kr_s$ term in (A-2). The $\cos kr_s$ term must be considered as spurious, arising from the failure of the potential (A-1) to possess the appropriate symmetry.

For this reason, in the computation of the Fourier coefficients of the potential (1) to be used in the band structure calculation, we have dropped the $\cos kr_s$ term and used the result (for $k \neq 0$)

$$V(\mathbf{k}) = -\frac{4\pi}{\Omega_0 k^2} \left[2 - \frac{A k^2}{\beta^2 + k^2} \right]. \quad (\text{A-5})$$

In order to make possible comparison of the results of this calculation with the cellular method results, the average crystal potential [which is $V(0)$] was computed directly from Eqs. (1) and (11) without modifications. Alteration of $V(0)$ merely displaces all levels by the same amount.

Since many of the potentials which have been employed in other band calculations are incorrect in this respect, it is of some interest to note the effect the inclusion of the spurious $\cos kr_s$ term. In Table II, the eigenvalues of the representations are given (I) for the case of the potential where Fourier coefficients are given by (A-5), and (II) for the potential for which the coefficients are given by

$$V_2(\mathbf{k}) = -\frac{4\pi}{\Omega_0 k^2} \left[2(1 - \cos kr_s) - \frac{A k^2}{\beta^2 + k^2} \right]. \quad (\text{A-6})$$

It seems that the Γ_1 level is not altered appreciably but that higher states are significantly affected.