Compressibilities of the Alkali Metals

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As a further test of the method of Wigner and Seitz (for the calculation of the energies of the monovalent metals), the pressure variation of the compressibilities of the alkali metals is determined and compared with recent experimental results of Bridgman which extend to pressures of the order of 45,000 kg/cm³. Fröhlich's approximate analytic expression for the dependence of the energies of the alkali metals on volume suggests the following semi-empirical form:

$$W = a/v + b/v^{\frac{1}{3}} - c/v^{\frac{1}{3}}.$$

If the parameters are determined from (1) the lattice constant, (2) the energy, and (3) the compressibility (all at zero pressure), the expression gives values for the relative change in volume with pressure in close agreement with Bridgman's results. The constants so determined agree fairly well with Fröhlich's theoretical values. The pressibilities of Li and Na, as obtained from the exact and fundamental calculations of the energies in the preceding paper, are compared with the experimental values. Theoretical values for Na are in good agreement with experiment, but the corresponding values for Li are about fifteen percent too high. It is suggested that the polymorphic transition in Cs, which occurs at a pressure of about 22,000 kg/cm², is a transition from a normal body-centered to a face-centered form, resulting from the nonelectrostatic interaction energy of the ions which favors close packing.

I. INTRODUCTION

BRIDGMAN[1] has recently obtained rough experimental values of the compressibilities of a large number of the more compressible substances in the pressure range extending to about 45,000 kg/cm². Of particular theoretical interest are the results he obtained for the alkali metals. Thanks largely to the work of Wigner and Seitz,[2] it is possible to make fairly accurate calculations of a large number of properties of this particular group of metals. A calculation of the compressibility and its variation with pressure provides a very sensitive test of the general methods.

The instantaneous compressibility, K, of a metal at the absolute zero of temperature is determined from the energy, W, by means of the following equation:

$$1/K = -v(dp/dv) = v(d^2W/dv^2), \qquad (1)$$

where v is the volume of the metal and p is the pressure. Our problem is thus the calculation of the energy of a metal as a function of volume.

We have given, in the preceding paper,[3] a calculation of the energies of Li and Na. In Section III of the present paper, we discuss the compressibilities and their variation with pressure. Fröhlich[4] has given an approximate expression for the energy of an electron in its lowest state. Using the free electron value for the Fermi energy, he has determined the initial compressibilities of the alkali metals, and obtained rough agreement with experiment. A modification of Fröhlich's procedure is discussed in Section II. At the end of the paper, we give a brief discussion of the polymorphic transition in Cs, discovered by Bridgman.

II. SEMI-EMPIRICAL CALCULATION OF THE VARIATION OF THE COMPRESSIBILITY WITH PRESSURE

In the present section we assume that the energy of the metal (per atom) is the sum of the energy of an electron in its lowest state, E_0, and the Fermi energy, F. We neglect the small correction term to the interaction energy of the valence electrons (given by Eq. (29), reference) and also the nonelectrostatic interaction energy of the ions.

According to Fröhlich,[4] for values of r_s near the energy minimum (or, in the neighborhood of the normal lattice constant), the energy E_0 (in atomic units[5]) is given by the following

* Society of Fellows.
[1] P. W. Bridgman, Proc. Am. Acad. 72, 207 (1938).
[2] E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); 46, 509 (1934). E. Wigner, Phys. Rev. 46, 1002 (1934); F. Seitz, Phys. Rev. 47, 400 (1935).
[3] In the present issue. This paper will be referred to as (I).

[4] H. Fröhlich, Proc. Roy. Soc. 158A, 97 (1937); Elektronentheorie der Metalle (Berlin, 1936) p. 272.
[5] Unit of energy is the Rydberg (13.5 ev); unit of length is the Bohr radius (0.528×10⁻⁸ cm).

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approximate expression,

$$E_0 = a/r_s^3 - 3/r_s, \qquad (2)$$

where r_s is the radius of a sphere of atomic volume (s sphere). The repulsive energy is inversely proportional to the atomic volume, and the attractive energy, resulting from the interaction of the valence electrons with the positive ion, is inversely proportional to the lattice constant.

The assumptions on which this formula is based are not very clear from Fröhlich's treatment. It is not difficult to show that (2) follows if

$$\gamma = (4\pi/3)r_s^3[\psi_0(r_s)]^2 = 1, \qquad (3)$$

in other words, if the value of the wave function at the boundary of the s sphere is equal to its mean value. This relation must hold for all values of r_s for which (2) is to be applied. We would expect that (3) will be approximately satisfied if the wave function of an electron in the lowest state is fairly flat throughout most of the volume. There is reason to suppose that this will be the case for values of r_s near the actual atomic radius, since both $(d\psi_0/dr)_{r=r_s}$ and $(d^2\psi_0/dr^2)_{r=r}$ vanish when E_0 is a minimum.[6]

To derive (2) from (3), let us set $R = r\psi_0$, so that the Schrödinger equation for R (in atomic units) is:

$$d^2R/dr^2 = (V(r) - E_0)R. \qquad (4)$$

The potential $V(r)$ is that of a free (positive) ion. The boundary condition of Wigner and Seitz[2] is:

$$dR/dr = R/r \quad \text{at} \quad r = r_s. \qquad (5)$$

Both E_0 and R are functions of r_s, the point at which the boundary condition (5) is to be satisfied. Denoting derivatives with respect to r_s by a prime, we have, differentiating (4),

$$d^2R'/dr^2 = (V(r) - E_0)R' - E_0'R, \qquad (6)$$

so that, multiplying by R, integrating, and making use of (4) to eliminate $(V - E_0)RR'$, we obtain:

$$E_0' \int_0^{r_s} R^2 dr = \int_0^{r_s} [R'(d^2R/dr^2) - R(d^2R'/dr^2)]dr$$
$$= [R'(dR/dr) - R(dR'/dr)]_{r=r}. \qquad (7)$$

[6] For a discussion of this point, see N. F. Mott and H. Jones, Theory of the Properties of Metals and Alloys, (Oxford, 1936), p. 79. Values of γ for Li and Na are tabulated in (I).

Differentiating the boundary condition (5) with respect to r_s, we have:

$$[(d^2R/dr^2) + (dR'/dr)]_{r=r_s} = [R'/r]_{r=r_s}. \qquad (8)$$

Making use of this relation, we can eliminate R' from (7) and obtain

$$E_0' \int_0^{r_s} R^2 dr = [R(d^2R/dr^2)]_{r=r_s}$$
$$= [V(r_s) - E_0(r_s)]R(r_s)^2. \qquad (9)$$

We thus get the following differential equation for E_0, if condition (3) is satisfied:

$$dE_0/dr_s = (3/r_s)[V(r_s) - E_0(r_s)]. \qquad (10)$$

Fröhlich's result (Eq. (2)) is obtained by integrating (10) with $V(r_s) = -e^2/r_s$. The latter will hold for values of r_s larger than the radius of the ion core.[7]

It is, of course, impossible to tell *a priori* whether or not Fröhlich's formula will hold without making an explicit calculation of the wave functions using the actual potential of the ion, as Wigner and Seitz have done for Na and Li. Eq. (2) does give fairly good values for these metals. We will use, for comparison with the experimental data (of all the alkali metals) an expression of the form:

$$E_0 = a/r_s^3 - c/r_s, \qquad (11)$$

treating a and c as empirical constants. The value of c so obtained is then compared with the theoretical value (3) given by Eq. (2).

The Fermi energy F, expressed in atomic units, is

$$F = 2.21\alpha/r_s^2, \qquad (12)$$

where α is the effective number of free electrons per atom. If the electrons are free, α is equal to unity. In general, α may be either greater or smaller than unity, and may be a function of r_s. It is known that the value of α for Li is much less than unity, and decreases as r_s decreases, while for Na, α is slightly greater than unity and increases slowly as r_s decreases.[8] As a first approximation, we may assume that $\alpha = 1$, so that the Fermi energy will be inversely proportional to the square of the lattice constant.

[7] The author is indebted to Professor E. Wigner for a discussion of Fröhlich's formula.
[8] Tables I and II, reference (I).

Equations (11) and (12) suggest the following type of equation for the energy of an alkali metal:

$$W = A(v_0/v) + B(v_0/v)^{\frac{2}{3}} - C(v_0/v)^{\frac{1}{3}}, \quad (13)$$

where A, B, and C are independent of the volume, and v_0 is the atomic volume at zero pressure. The first and third terms come from the energy of an electron in its lowest state; the second from the Fermi energy. To determine the values of the three parameters, the following experimental data are used (all refer to 0°K and $p=0$):

(1) The lattice constant;

(2) The energy, given by the sum of the ionization potential and the atomic heat of sublimation, and

(3) The compressibility, K_0.

The values of the constants so obtained are checked in two ways. First, the empirical values of B and C are compared with the theoretical values given by Eqs. (12) and (2). The semi-empirical equation is then used to determine the change in compressibility with pressure (or, what amounts to the same thing, the relative change in volume with pressure) and the calculated values are compared with experiment.

Since the energy is a minimum when $v=v_0$ (or $p=0$) we have:

$$2C/3 = 2A + 4B/3. \quad (14)$$

The energy at zero pressure is given by:

$$-W = 2A + B. \quad (15)$$

Finally, the compressibility at zero pressure gives the relation:

$$3/K_0 = 2A + 2B/3. \quad (16)$$

To obtain (15) and (16) we have used the value of C given by Eq. (14).

Table I gives the relevant data for the calculation of A, B, and C for the alkali metals. Row (d) gives the energies, obtained from the sum of the ionization potential and the atomic heat of sublimation. The compressibilities, given in row (e) were obtained by extrapolating the experimental results, taken at room temperature, to $T=0$°K by means of the Debye equation of state, as discussed below. From the values given in these two rows, the constants A and B were determined by use of Eqs. (15) and (16); the results are given in rows (f) and (g). Row gives the values of $\frac{2}{3}C$ obtained by substituting these values of A and B into Eq. (14). Row gives the theoretical values of B as obtained from Eq. (12) under the assumption that a (free electron value). Row (k) gives the theoretical values of $\frac{2}{3}C$ obtained from Eq. (2) Fröhlich.

The empirical values of B, depending on small difference between rows (d) and (e), not at all accurate, but they are rather small all metals except Li. The anomalous value for results from the fact that α is not constant, decreases as the volume decreases. The Fermi energy cannot be expressed as a single term. is given in fair approximation in the region interest by the difference between a large positive term inversely proportional to the square of lattice constant, and a negative term inversely proportional to the volume. The negative value of B obtained for K may perhaps be explained in a similar fashion. The differences between theoretical and experimental values of B for Rb and Cs, are probably within the rather large experimental uncertainties.

A much more significant test of the theory obtained from a comparison of the empirical and theoretical values of C given in rows (i) and The agreement is good for all metals except for which the empirical value is somewhat smaller than the theoretical.

As a second (experimental) test of the semi-empirical equation (13), we compare the relative

TABLE I. Calculation of the parameters in the semi-empirical equation for the energies of the alkali metals $W=A(v_0/v)+B(v_0/v)^{2/3}-C(v_0/v)^{1/3}$. The theoretical values of B are obtained from the free electron formula for the Fermi energy; theoretical values of C are obtained from Fröhlich's formula for the energy of an electron in its lowest state. row a, 10^{-24} cm³; rows b and c, ev/atom; rows d to j, erg/atom.

	METAL	Li	Na	K	Rb	
a	Atomic Volume (v_0)	20.7	38.5	71	86	
b	Ionization Potential	5.37	5.12	4.32	4.16	
c	Heat of Sublimation[1]	1.70	1.13	0.86	0.82	
d	$-W$	11.2	9.8	8.2	7.9	
e	$3m/K$[2]	8.4	9.4	8.9	8.1	
f	A(emp.)	1.4	4.3	5.1	4.2	
g	B(emp.)	8.4	1.2	−2.1	−0.6	
h	B(theor.)	4.5	3.0	2.3	1.7	
i	$(2/3)C$(emp.)	13.9	10.3	7.5	7.6	
j	$(2/3)C$(theor.)	13.2	10.8	8.8	8.2	

[1] Bichowsky and Rossini, Thermochemistry of Chemical Substances (Reinhold, 1936).
[2] From Bridgman's data, extrapolated to $T=0$°K.

ge in volume with pressure given by the ry, with the experimental values of Bridgman. It is first necessary to extrapolate the observed values to $T=0$°K. To do this, we use Debye equation of state,[9] although it probably does not apply accurately to the alkali metals. The Debye equation is:

$$p = -(dW/dv) - 3kT(d\theta/\theta dv)D(\theta/T). \quad (17)$$

where W and v are the energy per atom and the atomic volume, respectively, and θ is the characteristic temperature. The function $D(x)$ is defined by:

$$D(x) = \frac{3}{x^3}\int_0^x \frac{\xi^3 d\xi}{e^\xi - 1}. \quad (18)$$

For small x (T large), $D(x) \cong 1$. The value of $d\theta/dv$ is obtained from Grüneisen's law:

$$3\alpha/K = -(d\theta/dv)(c_v/\theta), \quad (19)$$

in which α is the linear coefficient of thermal expansion,* K is the compressibility, and c_v is the atomic heat capacity:

$$c_v = 3k[D(\theta/T) - (\theta/T)D'(\theta/T)]. \quad (20)$$

Using (19) and (20), we have, for small values of T,

$$p = -(dW/dv) + \Delta p, \quad (21)$$

where

$$\Delta p = (3\alpha T/K)[1 - (3\theta/8T) + (1/10)(\theta/T)^2 - \cdots]. \quad (22)$$

The second term of Eq. (21), Δp, represents the pressure due to the thermal motion of the ions, which must be subtracted from the observed pressures (at room temperature) to obtain the pressure at $T=0$°K. Although this term depends on the volume, the change is probably not very great except at very high pressures. In this region, the correction term is but a small fraction of the total pressure. We have therefore assumed that Δp is independent of volume, and to determine its value we have used the values of α, K, and θ for zero pressure and room temperature. Table II gives the values of Δp for the alkalis, together with the relevant data used in

* See, for example, J. K. Roberts, Heat and Thermodynamics (Blackie, 1933).

* Not to be confused with the effective number of free electrons per atom, for which the same symbol has been used.

the calculation. The total relative change in volume due to thermal expansion from room temperature down to $T=0$°K is also given.

A plot of the relative change in volume of the different alkalis as a function of pressure is given in Fig. 1. The heavier lines represent the experimental values extrapolated to the absolute zero of temperature; the lighter lines are the theoretical values obtained from the semi-empirical formula (13). From this equation we find

$$pv_0 = y^4(y-1)[2A + \tfrac{2}{3}B + A(y-1)], \quad (21)$$

with

$$y = (v_0/v)^{\frac{1}{3}}.$$

The values of A and B which were used are given in rows (f) and (g) of Table I.

The agreement is good for all metals except Rb. Professor Bridgman informs me that the initial compressibility for this metal is less certain than for the other alkalis. The initial compressibilities were used in the determination of the parameters, so that the slopes of the theoretical curves agree with the slopes of the experimental curves at the origin. It is the shape of the curve which is important for a test of the validity of the theory. The shape is determined mainly by the factor $y^4(y-1)$ in Eq. (21). (The term $A(y-1)$ in the brackets is small.)

There is a tendency for the theoretical curves to be slightly above the observed at the highest pressures. The nonelectrostatic interaction energy of the ions, which we have neglected, is not large enough to account for this discrepancy. The general agreement would have been better if the parameters had been adjusted to make the experimental and theoretical curves match at some high pressure, rather than to fit the initial compressibilities.

III. COMPRESSIBILITIES OF Li AND Na

It is much more desirable to have a calculation which is based on fundamental principles, so that there are no parameters to be determined from experiment. In order to determine the compressibility and its variation with pressure, it is necessary to have an accurate calculation of the energy as a function of volume. Such a calculation for Li and Na is given in the preceding paper.[2] In Fig. 2, we show the theoretical curves

of the compressibilities as a function of volume, as determined from these energy values. For comparison, experimental curves derived from Bridgman's data,[1] extrapolated to $T=0°K$, as indicated above, are also given. The abscissa gives the relative change in volume from the observed volume at zero pressure. The smallest volumes correspond to a pressure of about 40,000 kg/cm². The curves for Na are in very good agreement, but the theoretical values for Li are about 15 percent too high. The difference in the latter case is perhaps due to our neglect of terms of higher order than those in k^2 in the calculation of the Fermi energy.

The reciprocal of the compressibility is given essentially by the second derivative of the energy with respect to volume. It is interesting to note that the second derivative of the Fermi energy of Li is negative, and that the main contribution to $1 K$ comes from the energy of an electron in its lowest state, E_0. On the other hand, the second derivative of E_0 is small for Na, and the main contribution comes from the rapid increase of the Fermi energy with decreasing volume.

IV. POLYMORPHIC TRANSITION IN Cs

At ordinary pressures, the alkali metals are body centered. It is not yet known why this structure is preferred over, for example, the close packed cubic structure (face centered). Fuchs[10] has shown that, for equal atomic volume, the energies of the valence electrons in the two structures differ by only about 10^{-3} ev per electron. He attributes the face-centered structure of the noble metals (Cu, Ag and Au) to the repulsion between the closed d shells of the ions, which naturally favors the close packing. The nonelectrostatic energy of the ions in the alkali

TABLE II. *Data used in the extrapolation of Bridgman's results to* $T=0°K$.

METAL	Li	Na	K	Rb	Cs
$\alpha \times 10^6$	5.6	7.1	8.3	9.0	9.7
$(1/K) \times 10^{-2}$ (dynes/cm²)	120	58	32	23	19
θ/τ	1.5	0.6	0.40	0.29	0.20
$\rho \times 10^{-2}$ (dynes/cm²)	3.5	2.8	2.0	1.6	1.5
$\frac{v_T - v_0}{v_0}$ (calc.)	0.031	0.043	0.060	0.080	0.084

[10] K. Fuchs, Proc. Roy. Soc. A151, 585 (1935).
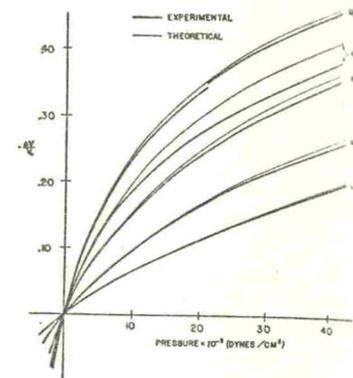

FIG. 1. Relative change in volume of alkali metals pressure. Light lines are theoretical values obtained the semi-empirical equation (13). Bridgman's experim data, extrapolated to $T=0°K$, are represented by heavy lines. The initial compressibilities have been used fix the values of the parameters in the semiempirical tion, so that the slopes of the experimental and theor curves are in agreement at the origin. The break in curve for Cs is due to a polymorphic transition.

metals (resulting both from the exchange pulsion and the van der Waals energy) will be lower in a face-centered lattice than in body-centered lattice, but this energy is so sm at ordinary pressures that it has little influe on the structure. As the volume is decrea the energy of the ions will increase relatively the energy of the valence electrons, so that would expect that at very high pressures alkali metals would take up a close pack structure. The rare gas solids are, of cou face centered, and it is likely that the alk metals are also face centered at very h pressures.

The metal for which the transition should ta place at lowest pressure is Cs, since it not o has the largest ion of the alkali metals, but a has the highest compressibility. Bridgman found a polymorphic transition in Cs at a pr sure of about 22,000 kg/cm². The change volume at the transition point is 0.00336 cm and the latent heat, determined from the cha in transition pressure with temperature is
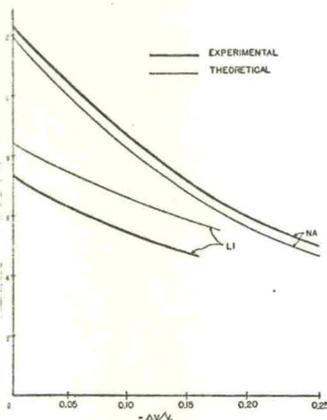
2. Compressibilities of Li and Na as a function of re. Theoretical values are obtained from direct cal- ns of the energies (given in the preceding paper); mental from Bridgman's data, extrapolated to K.

cm/g (0.2 cal./g). The small latent heat s that the difference in entropy between the phases is small.

rough test of the theory that the transition e to the nonelectrostatic energy of the ions be obtained from the change in volume at transition point. Let the free energy of the pressure phase be $F_1(v)$ that of the high ure phase be $F_2(v)$, and the corresponding mes at the transition point be v_1 and v_2. ssing the condition that the pressures of wo phases are equal at the transition point, ave, for $v_1 - v_2$ small,

$$\left[\frac{d(F_1 - F_2)}{dv}\right]_{v=v_1} = -\frac{v_1 - v_2}{v_1}\left(\frac{1}{K_1}\right)_{v=v_1}, \quad (22)$$

re K_1 is the compressibility of the low ure phase. The right-hand side may be ated from experimental data. The result is ×10⁹ dynes/cm².[11] In order to obtain a

[11] This value is for room temperature. In order to com- with theory, we should take the value at absolute zero. out a knowledge of the thermal expansion in the two

rough theoretical value for the left hand side of the equation, we will assume that the main contribution comes from the difference in the repulsive energy of the ions in the two phases. The difference in energy of the valence electrons, which presumably favors the body-centered lattice, will not change rapidly with volume, so that the derivative will be small. If we assume that the van der Waals energy of the ions varies as $1/r^6$, the difference between its values for the body-centered and face-centered structures is very small.

The exchange repulsion between the alkali ions has been estimated by Mayer and collaborators[12] from an analysis of the alkali-halide crystals. They find, for the mutual repulsive energy of two ions a distance r apart,

$$W = A_i \exp\left[(2r_i - r)/\rho\right], \quad (23)$$

where, if A_i is taken to be 1.25×10^{-12} ergs, the ionic radius $r_i = 1.455$A for the Cs ion, and $\rho = 0.345$A for all the alkali and halide ions. Using these values, we have estimated the contribution of the repulsion of the ion cores to (22) and find a value which is only about one-fifth of that observed. However, direct calculations[13] of the repulsion between the rare gas atoms He and Ne show that the energy can be given approximately by the form (23), with $\rho = 0.21$A, a value much smaller than that of the above authors. The larger value probably results from the fact that it is a kind of a mean between the values for the alkali ions and the halide ions, and the latter are probably much larger than the former. If we take $\rho = 0.21$A for the Cs ion, and take the same value for $A_i(1.25 \times 10^{-12}$ ergs) we estimate, from the lattice constant of the corresponding rare gas solid, that $r_i \sim 1.75$ -1.80A. With these values, one obtains results of about the right order of magnitude for (22).

Due to the difficulties in estimating the difference between the energies of the valence electrons in the two different structures, and also to the difficulty in estimating the interaction energy of

phases, the change with temperature cannot be determined, but it is probably not very great. As we are interested only in the order of magnitude, we use the room-temperature value.

[12] M. Born and J. E. Mayer, Zeits. f. Physik 75, 1 (1932); M. Huggins and J. E. Mayer, J. Chem. Phys. 1, 643 (1933).
[13] J. C. Slater, Phys. Rev. 32, 349 (1928) (He); W. E. Bleik and J. E. Mayer, J. Chem. Phys. 2, 252 (1934) (Ne).

the ions, one cannot be certain, but it does seem probable that the transition in Cs is from a body centered to a more close packed structure, which is probably face centered.

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Electronic Structure of the First Row Hydrides

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Stehn's formulae for the energies of the first row hydrides, BH to FH, in terms of Heitler-London exchange integrals have been applied to more recent data. The empirically derived values for the integrals are now smooth functions of the atomic number, Z. They are also considered as functions of the internuclear distance, r_e, and taken in conjunction with data on BeH, and with the facts that r_e and the force-constant, k, are smooth functions of Z, but invariant to electronic excitation, the results show that it is $2s^2 - 1s$ exchange that predominates in fixing the internuclear distance and force-constant. On the contrary, the dissociation energies cannot be expected to be smoothly dependent on Z, r_e or k. The heat of dissociation of NH is calculated by Stehn's formulae, after interpolating one exchange integral.

INTRODUCTION

PRESENT theories of heats of dissociation of molecules with more than four electrons are quite crude, and any correlation between theory and experiment, even for the simplest molecules would have value in giving theoretical thermo chemistry a better quantitative basis. Stehn[1] made a considerable contribution in deriving formulae for the energies of the first row hydrides, BH, CH, NH, OH, FH, in terms of exchange and Coulomb integrals which can be determined empirically and tested for self-consistency. Since his publication new data have appeared, and in this paper the integrals are recalculated. The three classes of integrals are now smooth functions of the atomic number, and combined with facts known about the internuclear distances and force-constants give a more detailed picture of the orbitals in these molecules.

REDETERMINATION OF THE INTEGRALS

Stehn applied the usual Heitler-London theory, building the molecules from a hydrogen $1s$ electron and various configurations of the heavy atom, to obtain expressions for the electronic

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[1] J. R. Stehn, J. Chem. Phys. **5**, 186 (1937).

energy

$$W = A + a_1 B + a_2 K + a_3 J_\pi + a_4 J_\sigma,$$

where A is the atomic level of the heavy a into which the molecule adiabatically de poses, B is an atomic exchange integral, K exchange of the hydrogen $1s$ electron wi electrons plus Coulomb terms, J_σ and J_σ exchange with π or σp electrons. The a's numerical coefficients of the matrix eleme Stehn noticed that the internuclear distance mains practically the same in all excited state any one molecule, so that the J's and K re the same, permitting simultaneous equations them to be set up and solved. In this applicat then the principal defect of the Heitler-Lo method, that of nonorthogonality, cancels but other corrections, such as higher order te destroy the linearity of Eq. (1).

DISCUSSION OF THE DATA

The excitation energies ν_{mol} and ν_{atom} usually known quite accurately, and some the J integrals can be calculated from them But a complete solution also depends on one sociation energy, which is invariably the wea datum. However, for any one molecule only

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energy need be known, by virtue of the known cycle connecting upper and lower dissociation energies, D_e' and D_e'',

$$\nu_{mol} + D_e' = \nu_{atom} + D_e''. \qquad (2)$$

The literature on the dissociation energies of series of hydrides has been investigated roughly. In our calculations we have not used approximate D's, e.g., from the formula $\frac{1}{4} x_e \omega_e$, or from extrapolation to the limiting vibrational quantum numbers, but only those ained from dissociation through rotation, ch gives an upper *and a lower* limit to D_e, (CH), or from thermal data, (OH, FH).

details

error in D for CH or NH will not change the values J_π or J_σ, which are obtained from the ν's. The atom is reliable, so K of CH is a good point, Fig. 1. is not enough data for the evaluation of all three als in the case of BH. However, if J_σ of BH is to fit in with J_σ of C, N, OH, then J_π automatically in with J_π of C, N, OH, and K will fit with the CH and OH. Since J_σ and J_π of NH fall smoothly their respective curves, we can expect to interpolate NH.

ere is no value for the heat of dissociation of NH; the appendix we show this interpolated value of K ably very good.

heat of dissociation of FH can only be obtained the help of thermochemical data. Three investigators a heat of formation of $+63.0$ kcal. To get the ation energy of FH, the dissociation energy of F_2 needed. This has been evaluated as -62.6 kcal. anck's method from the onset of continuous absorp-n the spectrum.[3] This value can be verified from oscopic constants[4] as follows:

e upper state of F_2, $^1\Pi$, has an $\omega_e = 837$ cm^{-1} and monicity $x_e \omega_e = 140$. The formula $\omega_e^2/4 x_e \omega_e$ gives a of D_e that is usually too high, but the absolute in this case is very small, of the order of magnitude itself, 0.155 ev. Mulliken[5] has shown that the state dissociates into normal atoms. Hence the ation energy of the lower state, D_e'',(which cannot ably determined by $\omega_e''^2/4 x_e'' \omega_e''$), is $D_e' + \nu_{mol}$ $5 + 2.575 = 2.73$ ev or 63 kcal, as above. The D_e HF then is 6.35 ev.

rkpatrick and Salant[6] obtained bands with high

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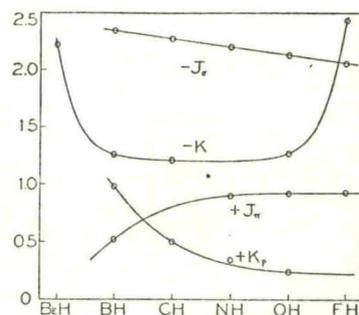E. Kirkpatrick and E. O. Salant, Phys. Rev. **48**, 945

FIG. 1. Values in electron volts of the exchange integrals J_π and J_σ, the total Coulomb terms plus $2s^2 - 1s$ exchange K, and the $2p - 1s$ Coulomb term K_p, as functions of the atomic number.

vibrational quantum numbers in the infra-red, and extrapolated to get $D_e'' = 6.1$ ev.[7]

DISCUSSION OF THE INTEGRALS

The solutions obtained for J_σ, J_π, and K are plotted against the atomic number Z in Fig. 1, and against the internuclear distance in Fig. 2. The principal remark is that the integrals are fairly constant for the series and that the curves are quite smooth. The values for K especially have become less erratic than in Stehn's figure, and show less variation. The fact that fairly constant values are obtained, even though the internuclear distance has changed markedly (from a constriction of the wave functions with increasing Z) shows that overlapping occurs to nearly the same extent and in the same relative positions.

The integral J_σ is large, as to be expected. As will be shown below the equilibrium distance is fixed by $2s^2 - 1s$ interchange. The minimum of J_σ is beyond this point, because the radius, and also the maximum value, of a $2p$ electron in a "dumbbell" orbital is larger than that of the $2s$ electron. The relative positions of the minima of $1s - 2s$ and $1s - 2p$ exchange can also be

[7] Landolt-Börnstein, *Tabellen*, Vol. 3, p. 2873, state thermochemical data gives $D_e'' = 120$ kcal. or 5.2 ev, but this probably was old thermal data, ibid. Vol. 2, p. 1489, uncorrected for polymerization, ibid., Vol. 3, p. 2746 and also Bichowski and Rossini, reference 2.