The Calculation of Second Order
Polarization Energies in Atoms

The Molecular Structures of the Bromomethanes,
Boron Trimethyl, and Three Boron Trihalides

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A. Introduction. The development of the quantum mechanics
made possible a systematic attack on many problems of atomic
energy. The problem of polarization in an external field is
one to which the approximation methods of quantum mechanics
are applicable, since in cases of interest the external field
is small compared to internal atomic forces. Indeed, the
first use to which Schrödinger[1] put his newly developed first
order perturbation theory was the treatment of the first
order Stark effect in atomic hydrogen. A second order per-
turbation theory was developed independently by Epstein[2],
Wentzel[3], and Waller[4] and applied to the second order Stark
effect in hydrogen. Other treatments of hydrogen and more
complex atoms in a uniform field followed, notably by
Buckingham[5], who applied the variation method to the problem.

The more complex problem of polarization in a non-
homogeneous field has received relatively little attention.
Th. Neugebauer[6] has given an approximate treatment of ion
deformation in binary crystals, but he was not concerned
with the energy effect of the deformation.

Inasmuch as an ion in an ionic crystal is subject to
a complex electric field arising from the distribution of
positive and negative charges in its environment, knowledge
of the theory of atomic polarization in non-uniform fields
is essential to a complete understanding of crystal lattice
energies. It is with this application primarily in mind

that the following treatment is undertaken.

The method to be followed in the subsequent calculation is first to carry through as rigorous as possible a treatment for an electron in an hydrogen-like orbital, then to generalize the result by substituting an effective nuclear charge for the true nuclear charge. This method is to be sure, an approximate one, since it assumes that the field about one electron due to the rest is central, a condition obviously not fulfilled.

The expression for the hydrogen-like atom will be obtained by application of a general perturbation theory[7] which is capable of giving results which are exact (for the hydrogen-like atom) to second-order terms in the parameters describing the field. However, since filled-shell ions are of primary interest, simplifications will be made which, while not affecting the results for filled-shell ions, will destroy the rigor of the treatment for hydrogen.

B. Electrons in Hydrogen-like Orbitals

1. The Potential Field. In order to describe a potential in charge-free space, a function of spatial coordinates V (x, y, z) must satisfy Laplace's equation

$$\nabla^2 V = 0 \tag{1.1}$$

where ∇^2 is the Laplace operator. The most general solution of this equation satisfying the usual physical restrictions of boundary and continuity for charge-free space is, in polar coordinates

$$V(r, \vartheta, \varphi) = 2\sqrt{\frac{\pi}{3}} \sum_{g,h} G_{g,h} \, K_{gh}(r, \vartheta, \varphi) \tag{1.2}$$

where $K_{g,h}(r, \vartheta, \varphi)$ is a spherical harmonic function given by

$$K_{g,h}(r, \vartheta, \varphi) = r^g \Theta_{g,h}(\vartheta) \, \Omega_h(\varphi) \tag{1.3}$$

with

$$\Theta_{g,h}(\vartheta) = \left[\frac{(2g+1)}{2} \frac{(g-h)!}{(g+h)!} \right]^{\frac{1}{2}} P_g^h(\cos \vartheta) \tag{1.4}$$

$$\Omega_h(\varphi) = \frac{1}{\sqrt{p\pi}} \frac{\cos}{\sin} h\varphi \quad ; \qquad p = 2 \quad \text{for} \quad h = 0$$
$$p = 1 \quad \text{otherwise.}$$

$P_g^h(z)$ is an associated Legendre polynomial of degree g and order h, and may be calculated explicitly by means of the formula

$$P_g^h(z) = (1-z^2)^{h/2} \frac{d^h}{dz^h} \frac{1}{2^g g!} \frac{d^g}{dz^g}(z^2-1)^g \quad ; \quad P_o^o(z) = 1 \tag{1.4}$$

The set of functions $\Theta_{g,h}(\vartheta)$ are normalized and orthogonal satisfying the condition

$$\int_o^\pi \Theta_{gh} \Theta_{g'h} \sin \vartheta \, d\vartheta = \delta_{gg'} , \tag{1.5}$$

where $\delta_{gg'} = 1$ for $g = g'$ and 0 otherwise. Similarly, $\Omega_h(\varphi)$ is seen to be a normalized trigonometric function. The range of

variation of the index g is from zero to infinity; that of h from zero to g. The term with g = 0, however, represents the trivial case of a constant potential, for which G_{oo} may be arbitrarily set equal to zero. The sum in equation (1.3) is to be interpreted to include both sine and cosine terms in Ω, each with a coefficient $G_{g,h}$, except that when h = 0 only the cosine term is to be considered. The coefficient $2\sqrt{\frac{\pi}{3}}$ is inserted in order that G_{gh} reduce to the familiar strength of field for the case g = 1.

2. The Schrödinger Equation. The wave equation for the perturbed hydrogenic atom is

$$-\frac{h^2}{8\pi^2\mu} \nabla^2 \psi(r,\vartheta,\varphi) - \frac{Ze^2}{r}\psi(r,\vartheta,\varphi) + V(r,\vartheta,\varphi)e\,\psi(r,\vartheta,\varphi)$$

$$= W\psi(r,\vartheta,\varphi) \qquad (2.1)$$

where ψ is the wave function for the system, h is Planck's constant, μ the "reduced mass" of the electron and nucleus $\left(\frac{1}{m_1}+\frac{1}{m_2}=\frac{1}{\mu}\right)$, Ze the nuclear charge, e the electronic charge, and W the energy constant of the system. For convenience a change of variable will be made, letting

$$\xi = \frac{2Zr}{n'a_0}, \qquad a_0 = \frac{h^2}{4\pi^2\mu e^2} \qquad (2.2)$$

The transformed wave equation is

$$\nabla^2\psi(\xi,\vartheta,\varphi) + \left(\frac{n'}{\xi}-\frac{1}{4}\right)\psi(\xi,\vartheta,\varphi) + A\psi(\xi,\vartheta,\varphi) = \beta\psi(\xi,\vartheta,\varphi) \qquad (2.3)$$

where
$$A = \sum_{g,h} E_{g,h}\, \xi^g \Theta_{g,h}(\vartheta)\,\Omega_h(\varphi),$$

$$E_{g,h} = -2\sqrt{\frac{\pi}{3}}\frac{n'}{Ze}\left(\frac{n'a_0}{2Z}\right)^{g+1} G_{g,h}$$

$$\beta = -\frac{n'^2 a_0}{2Z^2 e^2}\,W - \frac{1}{4} \qquad (2.4)$$

The transformed equation will be represented symbolically by

$$\underline{H}^{\circ}\psi + \underline{H}'\psi = \beta\,\psi \tag{2.5}$$

where $\underline{H}^{\circ} = \nabla^2 + \frac{n'}{\xi} - \frac{1}{4}$ and $\underline{H}' = A$, the "perturbation operator."

When $V = 0$ (that is, all the $G_{g,h} = 0$) equation (2.1) reduces to the familiar equation for the unperturbed hydrogenic atom, with characteristic solutions

$$\psi^{\circ}_{n\ell m} = R_{n\ell}(r)\,\Theta_{\ell|m|}(\vartheta)\,\Phi_m(\varphi) \tag{2.6}$$

and allowed values of the energy constant

$$W^{\circ}_n = \frac{Z^2 e^2}{2n^2 a_0} \tag{2.7}$$

Here $R_{n\ell}(r) = -\left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!^3}\right]^{1/2} e^{-\frac{2Z}{na_0}r}\left(\frac{2Z}{na_0}r\right)^{\ell} L^{2\ell+1}_{n+\ell}\left(\frac{2Z}{na_0}r\right)$

and $\Phi_m(\varphi) = \frac{1}{\sqrt{\pi}}\,e^{im\varphi}$, $\tag{2.8}$

$\Theta_{\ell|m|}$ being functions already defined (equation (1.4)). The functions $L^{2\ell+1}_{n+\ell}(\rho)$ are associated Laguerre polynomials, expressed explicitly by

$$L^{2\ell+1}_{n+\ell}(\rho) = \sum_{k=0}^{n-\ell-1} (-1)^{k+1} \frac{(n+\ell)!^2}{(n-\ell-1-k)!\,(2\ell+1+k)!\,k!}\,\rho^k. \tag{2.9}$$

n, l, and m are the usual quantum numbers defining the quantum state of the system.

3. The Variation Functions. In the method of treatment employed, the true wave function ψ is expanded in terms of a suitable set of functions $F_{\nu,\lambda,\mu}(\xi,\vartheta,\varphi)$, so that

$$\psi(\xi,\vartheta,\varphi) = \sum_{\nu,\lambda,\mu} B_{\nu,\lambda,\mu}\,F_{\nu,\lambda,\mu}(\xi,\vartheta,\varphi). \tag{3.1}$$

ψ must satisfy the wave equation in the form of equation (2.5), namely

$$\left(\underline{H}^{\circ} + \underline{H}'\right)\sum_{\nu,\lambda,\mu} B_{\nu,\lambda,\mu}\,F_{\nu,\lambda,\mu}(\xi,\vartheta,\varphi) = \beta \sum_{\nu,\lambda,\mu} B_{\nu,\lambda,\mu}\,F_{\nu,\lambda,\mu}(\xi,\vartheta,\varphi$$

Multiplying both sides of the equation by $F^{*}_{\nu'\lambda'\mu'}(\xi,\vartheta,\varphi)\,\xi^2 d\xi\,\sin\vartheta\,d\vartheta\,d\varphi$

and integrating over the entire range of variability of the coordinates, one obtains

$$\sum_{\nu,\lambda,\mu} \left(H^{\circ}_{\substack{\nu'\lambda'\mu' \\ \nu\lambda\mu}} + H'_{\substack{\nu'\lambda'\mu' \\ \nu\lambda\mu}} - \Delta_{\substack{\nu'\lambda'\mu' \\ \nu\lambda\mu}} \beta \right) B_{\nu\lambda\mu} = 0 \tag{3.2}$$

where

$$H^{\circ}_{\substack{\nu'\lambda'\mu' \\ \nu\lambda\mu}} = \int_0^\infty d\xi \int_0^\pi d\vartheta \int_0^{2\pi} d\varphi \, F^*_{\nu'\lambda'\mu'} \underline{H}^{\circ} F_{\nu\lambda\mu} \, \xi^2 \sin\vartheta$$

$$H'_{\substack{\nu'\lambda'\mu' \\ \nu\lambda\mu}} = \int_0^\infty d\xi \int_0^\pi d\vartheta \int_0^{2\pi} d\varphi \, F^*_{\nu'\lambda'\mu'} \underline{H}' F_{\nu\lambda\mu} \, \xi^2 \sin\vartheta \tag{3.3}$$

$$\Delta_{\substack{\nu'\lambda'\mu' \\ \nu\lambda\mu}} = \int_0^\infty d\xi \int_0^\pi d\vartheta \int_0^{2\pi} d\varphi \, F^*_{\nu'\lambda'\mu'} F_{\nu\lambda\mu} \, \xi^2 \sin\vartheta$$

and F^* signifies the complex conjugate of F.

Equation (3.2) represents a set of simultaneous, homogeneous, linear equations in the constants $B_{\nu\lambda\mu}$. A necessary and sufficient condition that it have a solution other than all the $B_{\nu\lambda\mu}$'s zero is that the determinant of the coefficients of the $B_{\nu\lambda\mu}$'s vanish.

$$\left| \left(H^{\circ}_{\substack{\nu'\lambda'\mu' \\ \nu\lambda\mu}} + H'_{\substack{\nu'\lambda'\mu' \\ \nu\lambda\mu}} - \Delta_{\substack{\nu'\lambda'\mu' \\ \nu\lambda\mu}} \right) \right| = 0 \tag{3.4}$$

This will be true for certain values of β , which in turn will give characteristic values of the energy constant W.

The set of functions $F_{\nu\lambda\mu}(\xi,\vartheta,\varphi)$ used in the present treatment was introduced into quantum mechanics by P. S. Epstein[2]. It is

$$F_{\nu\lambda\mu}(\xi,\vartheta,\varphi) = \Lambda_{\nu\lambda}(\xi) \Theta_{\lambda|\mu|}(\vartheta) \Phi_{\mu}(\varphi) \tag{3.5}$$

where

$$\Lambda_{\nu\lambda}(\xi) = -\left[\frac{(\nu-\lambda-1)!}{(\nu+\lambda)!^3} \right]^{1/2} L^{2\lambda+1}_{\nu+\lambda}(\xi) e^{-\xi/2} \tag{3.6}$$

The functions $L_n^\ell(\xi)$, $\Theta_{\lambda\mu}(\vartheta)$ and $\bar{\Phi}_\mu(\varphi)$ have already been defined.

Some properties of these functions are important. They satisfy the differential equation

$$\underline{H}^{\circ} F_{\nu\lambda\mu} = \nabla^2 F_{\nu\lambda\mu} + \left(\frac{n'}{\xi} - \frac{1}{4} \right) F_{\nu\lambda\mu} = -\left(\frac{\nu-n'}{\xi} \right) F_{\nu\lambda\mu} \tag{3.7}$$

and the orthogonality-normalization conditions

$$\int_0^\infty d\xi \int_0^\pi d\vartheta \int_0^{2\pi} d\varphi \, F^*_{\nu'\lambda'\mu'} F_{\nu\lambda\mu} \, \xi \, \sin \vartheta = \delta_{\nu'\nu} \, \delta_{\lambda'\lambda} \, \delta_{\mu'\mu} \, . \tag{3.8}$$

The functions $\Lambda_{\nu\lambda}$ are themselves orthogonal and normalized:

$$\int_0^\infty \Lambda_{\nu'\lambda} \, \Lambda_{\nu\lambda} \, \xi \, d\xi = \delta_{\nu'\nu} \tag{3.9}$$

A recursion formula for $F_{\nu\lambda\mu}$ which may be derived easily will prove useful.

$$\xi \, F_{\nu\lambda\mu} = -\{(\nu-\lambda)(\nu+\lambda+1)\}^{1/2} F_{\nu+1,\lambda,\mu} + 2\nu F_{\nu\lambda\mu} - \{(\nu+\lambda)(\nu-\lambda-1)\}^{1/2} F_{\nu-1,\lambda,\mu} \tag{3.10}$$

If the variable ξ in these functions is that defined by equation (2.2) and if n' is identified with the principal quantum number n of the unperturbed wave functions, the functions $F_{\nu\lambda\mu}$ and $\psi^\circ_{\nu\lambda\mu}$ become identical (except for a constant factor) for $\nu =$ n, but not for other values of ν . In this treatment n' will be set equal to n, the total quantum number of the particular unperturbed state which is of interest; that is, the state whose energy W_n is to be found. Hence

$$\xi = \frac{2Zr}{n a_o} \qquad and \qquad \beta_n = -\frac{n^2 a_o}{2Z^2 e^2} W_n - \frac{1}{4} = \frac{n^2}{4W_H}(W_n - W_n^\circ) \tag{3.11}$$

where W_H is a constant equal to the lowest unperturbed energy, namely $\frac{Z^2 e^2}{2 a_o}$. β_n is seen to be proportional to the perturbation energy of the system. Similarly the operator $\underline{H}^\circ$ is seen to be proportional to the true Hamiltonian operator diminished by W_n° , so that the integral $H^\circ_{\nu'\lambda'\mu'\,\nu\lambda\mu}$ is proportional to the difference between the corresponding integral involving the true Hamiltonian operator and the quantity $\Delta^{\nu'\lambda'\mu'}_{\nu\lambda\mu} W_n^\circ$.

4. Simplification of the Secular Equation. Since the value of β is desired only to second order terms in $E_{\zeta,h}$ and for a certain state of the unperturbed system, namely the

state (n, 1, m), some important simplifications can be made
in the determinantal equation (3.4). If the first order in-
tegral $H'^{\nu'\lambda'\mu'}_{\nu\lambda\mu}$ is neglected in all non-diagonal elements except
in the row and column with ν', λ', and μ' or ν, λ, and μ equal to
n, 1, and m respectively, no errors of second order or larger
will be introduced into $\beta_{n\ell m}$. Similarly, if β is replaced by
a first order approximation in the diagonal elements and in this
row and column (except in the element $\begin{pmatrix} n\ 1\ m \\ n\ 1\ m \end{pmatrix}$ where it must be
left explicitly) and by a zeroth order approximation (which is
zero) elsewhere, the value of $\beta_{n\ell m}$ to a second approximation
is unaffected. Furthermore $H^{o\,\nu'\lambda'\mu'}_{\nu\lambda\mu}$ is easily evaluated by use
of equations (3.7) and (3.8).

$$H^{o\,\nu'\lambda'\mu'}_{\nu\lambda\mu} = -(\nu-n)\,\delta_{\nu'\nu}\,\delta_{\lambda'\lambda}\,\delta_{\mu'\mu} \tag{4.1}$$

With these simplifications, equation (3.4) reduces to

$$\begin{vmatrix} (H'^{n\ell m}_{n\ell m} - \Delta^{n\ell m}_{n\ell m}\beta_{n\ell m}) & (H'_{n\ell m\,\nu\lambda\mu} - \Delta_{n\ell m\,\nu\lambda\mu}\beta'_{n\ell m}) & \cdots \\ (H'_{\nu\lambda\mu\,n\ell m} - \Delta_{\nu\lambda\mu\,n\ell m}\beta'_{n\ell m}) & -(\nu-n) & 0 \\ \cdots & 0 & \cdots \end{vmatrix} = 0 \tag{4.2}$$

Here $\beta'_{n\ell m}$ represents a first approximation to $\beta_{n\ell m}$. In the
diagonal elements the first order terms have been neglected
in comparison to those of zeroth order.

It is now necessary to specify more closely the nature
of the state (n, 1, m) of the unperturbed system which is
under consideration. If it is desired to treat atoms with in-
completely filled electronic shells, the correct zeroth order
wave functions will have to be found and the secular equation
(4.2) rearranged in order that the element $\begin{pmatrix} n\ 1\ m \\ n\ 1\ m \end{pmatrix}$ where $\beta_{n\ell m}$
appears shall correspond to the system described by this correct

zeroth order wave function. The present treatment, however, is primarily concerned with ions with completely filled shells. In this case hybridization of the zeroth order wave functions for the individual electrons has no effect on the result, as will be shown in section 10 of this paper. Hence for convenience the simple s and p orbital wave functions will be treated, the latter in the complex form.

5. The s State $(n00)$. Since the s state corresponds to a spherically symmetrical electron distribution, there can be no first order perturbation, provided that the possibility of hybridization with another orbital is precluded. β'_{n00} may therefore be set equal to zero. The integrals $H'_{\nu\lambda\mu}$ which do not vanish are finite in number and are shown in the Appendix to have the following values.

$$H'_{r,g,\pm h} = E_{gh} (-1)^{n-r+g} \left[\frac{(r+g)!\, np}{2n(r-g-1)!}\right]^{1/2} \frac{(2g+2)!}{2(n-r+g+1)(g+1-n+r)!} , \quad (5.1)$$

for $g+1 \leq r \leq g+1+n$, with $H'_{\substack{r,g,\pm h \\ n,0,0}} = H'^{*}_{\substack{n,0,0 \\ r,g,\pm h}}$.

The sum over g and h which enters into the definition of $H'_{\substack{\nu\lambda\mu \\ n00}}$ is seen to have reduced to a single term depending on g and h for any given set of indices ν,λ,μ. This makes it possible to express β_{n00} as a sum:

$$\beta_{n00} = \sum_{g,h} \beta_{n00} (g,h) \qquad (5.2)$$

in which $\beta_{n00} (g, h)$ is the perturbation energy produced by the g h term of the potential, acting alone. For simplicity, the subsequent calculations will concern the g h term alone.

The diagonal elements whose row and column still contain some non-vanishing integrals are seen to be $-(r-n)$, and $\Delta_{\substack{n\ell m \\ n\ell m}}$ is easily seen from equations (3.10) and (3.8) to be 2n.

With these substitutions the secular equation becomes

$$\begin{vmatrix} -2n\,\beta_{noo}\,(g,h) & H'_{\substack{noo\\r,g,\pm h}} \\[2mm] H'^{*}_{\substack{noo\\r,g,\pm h}} & -(r-n) \end{vmatrix} = 0 \qquad (5.3)$$

Two elements are to be included for each value of r, one corresponding to the index + h and one to - h; however when h = 0 only one element should be included for a given r. The solution of (5.3) is

$$\beta_{noo}(g,h) = \frac{1}{pn}\sum_{r=g+1}^{g+1+n} \frac{\left| H'_{\substack{noo\\r,g,\pm h}} \right|^{2}}{(r-n)} \qquad (5.4)$$

6. The P_z State (210). The non-vanishing integrals are (see Appendix)

$$H'_{\substack{r,g-1,\pm h\\n,1,0}} = E_{g,h}\,(-1)^{g+n-r}\,\frac{1}{4}\left[\frac{(g-h)(g+h)(n+1)!\,(g+r-1)!\,6p}{(2g-1)(2g+1)(n-2)!\,(r-g)!\,\pi}\right]^{\frac{1}{2}}\frac{(2g+2)!}{(g+1-n+r)!\,(g+1+n-r)!}$$

with $g \le r \le g+n+1$

and

$$H'_{\substack{r,g+1,\pm h\\n,1,0}} = E_{g,h}\,(-1)^{g+n-r}\,\frac{1}{2}\left[\frac{(g-h+1)(g+h+1)(n-2)!\,(g+r+1)!\,6p}{(2g+1)(2g+3)(n+1)!\,(r-g-2)!\,\pi}\right]^{\frac{1}{2}}\frac{(2g+1)!\,[n(g+2)-r]}{(g+1+n-r)!\,(g+1-n+r)!} \qquad (6.1)$$

with $g+2 \le r \le g+n+1$

With no hybridization, a first order perturbation can appear only if one of these integrals reduces to $H'_{\substack{210}}$. This can occur only for g = 2; the case should be given special consideration. In general then $\beta'_{n10}(g,\ h) = 0$. The secular equation reduces to

$$\begin{vmatrix} -2n\,\beta_{n10}\,(g,h) & H'_{\substack{n10\\r,g-1,\pm h}} & H'_{\substack{n10\\r,g+1,\pm h}} \\[2mm] H'^{*}_{\substack{n10\\r,g,\pm h}} & -(r-n) & 0 \\[2mm] H'^{*}_{\substack{n10\\r,g,\pm h}} & 0 & -(r-n) \end{vmatrix} = 0 \qquad (6.2)$$

whence

$$(6.3)$$

$$\beta_{n10}(g,h) = \frac{1}{pn}\sum_{r=g}^{g+n+1} \frac{\left| H'_{\substack{r,g-1,\pm h\\n,1,0}} \right|^{2}}{(r-n)} + \frac{1}{pn}\sum_{r=g+2}^{g+n+1} \frac{\left| H'_{\substack{r,g+1,\pm h\\n,1,0}} \right|^{2}}{(r-n)}$$

7. The States $(2,1,1)$ and $(2,1,-1)$. The non-vanishing integrals are (see Appendix)

$$H'_{\substack{r,g-1,1-h \\ n,1,1}} = H'_{\substack{r,g-1,-1+h \\ n,1,-1}} = \sum_{g,h} (-1)^{g+n-r} \frac{1}{4} \left[\frac{3p(n+1)!(g+r-1)!(g+h-1)(g+h)}{(n-2)!(r-g)!(2g-1)(2g+1)\pi} \right]^{\frac{1}{2}} \frac{(2g+2)!}{(g+1-n+r)!(g+1+n-r)!}$$

$$g \leq r \leq g+n+1$$

$$H'_{\substack{r,g-1,1+h \\ n,1,1}} = H'_{\substack{r,g-1,-1-h \\ n,1,-1}} = E_{g,h} (-1)^{g+n-r+1} \frac{1}{4} \left[\frac{3p(n+1)!(g+r-1)(g-h-1)(g-h)}{\pi(2g+1)(2g+3)(n+1)!(r-g-1)!} \right]^{\frac{1}{2}} \frac{(2g+2)!}{(g+1-n+r)!(g+1+n-r)!}$$

$$g \leq r \leq g+n+1$$

$$H'_{\substack{r,g+1,1-h \\ n,1,1}} = H'_{\substack{r,g+1,-1+h \\ n,1,-1}} = E_{g,h} (-1)^{g+n-r+1} \frac{1}{2} \left[\frac{3p(g-h+1)(g-h+2)(n-2)!(g+1+r)!}{\pi(2g+1)(2g+3)(n+1)!(r-g-2)!} \right]^{\frac{1}{2}} \frac{(2g+1)![n(g+2)-r]}{(g+1-n+r)!(g+1+n-r)!}$$

$$g+2 \leq r \leq g+n+1$$

$$H'_{\substack{r,g+1,1+h \\ n,1,1}} = H'_{\substack{r,g+1,-1-h \\ n,1,-1}} = E_{g,h} (-1)^{g+n-r} \frac{1}{2} \left[\frac{3p(g+h+1)(g+h+2)(n-2)!(g+1+r)!}{\pi(2g+1)(2g+3)(n+1)!(r-g-2)!} \right]^{\frac{1}{2}} \frac{(2g+1)![n(g+2)-r]}{(g+1-n+r)!(g+1+n-r)!}$$

$$g+2 \leq r \leq g+n+1 \tag{7.1}$$

Again with no hybridization, a first order perturbation can occur only if $g = 2$, $h = 0$, and again this case needs special consideration. In general again $\beta'_{n11}(g,h) = \beta'_{n1-1}(g,h) = 0$, and the secular equation becomes, for $(m11)$

$$\begin{vmatrix} -2n\beta_{n11}(g,h) & H'_{\substack{n11 \\ r,g-1,1-h}} & H'_{\substack{n11 \\ r,g-1,1+h}} & H'_{\substack{n11 \\ r,g+1,1-h}} & H'_{\substack{n11 \\ r,g+1,1+h}} \\ H'^{*}_{\substack{n11 \\ r,g-1,1-h}} & -(r-n) & 0 & 0 & 0 \\ H'^{*}_{\substack{n11 \\ r,g-1,1+h}} & 0 & -(r-n) & 0 & 0 \\ H'^{*}_{\substack{n11 \\ r,g+1,1-h}} & 0 & 0 & -(r-n) & 0 \\ H'^{*}_{\substack{n11 \\ r,g+1,1+h}} & 0 & 0 & 0 & -(r-n) \end{vmatrix} = 0 \tag{7.2}$$

The result for $(n,1,-1)$, as can easily be seen, is identical.

8. Hybrid p Orbitals. It will be useful to consider the states of the unperturbed system obtainable by hybridization of the three p states just treated. Take, for example

$$\psi^{\circ}_{p} = \frac{1}{\sqrt{3}} \left(F_{n10} + F_{n11} + F_{n1,-1} \right) \tag{8.1}$$

The perturbation integrals for this state are

$$H'_{\underset{p}{\nu\lambda\mu}} = \frac{1}{\sqrt{3}}\left(H'_{\underset{n10}{\nu\lambda\mu}} + H'_{\underset{n11}{\nu\lambda\mu}} + H'_{\underset{n,1,-1}{\nu\lambda\mu}}\right) \tag{8.2}$$

However, for particular values of g and h only one term of this sum will be different from zero, as will be seen upon examination of the non-vanishing integrals. Furthermore, this wave function represents a spherically-symmetrical electron distribution, and as such cannot give rise to a first order perturbation energy for any perturbing potential, g = 2, h = 0 included. It is, also, as good a basis for treating filled-shell ions as the simple p functions treated above. It can easily be seen that the secular equation for this hybrid state will have the solution

$$\beta_p (g,h) = \frac{1}{3}\left[\beta_{n10}(g,h) + \beta_{n11}(g,h) + \beta_{n,1,-1}(g,h)\right] \tag{8.3}$$

and is good for all values of g and h, including g = 2, h = 0.

Two other linearly independent hybrid orbitals may be constructed, such as $F_{n10} + F_{n11} - F_{n,1,-1}$ and $F_{n10} - F_{n11} - F_{n,1,-1}$; these will give results identical to that indicated in equation (8.3).

9. Final Expressions. On introduction of the explicit values of the integrals calculated in the Appendix into the expressions for β (gh) calculated in the preceding paragraphs, the following expressions are obtained for β (gh) and for W'' (gh).

For the unperturbed state (n00):

$$\beta_{n00}(g,h) = E^2_{g,h}\frac{(2g+2)!^2}{8\pi}\sum_{r=g+1}^{g+1+n}\frac{(r+g)!}{(r-g-1)!\,(g+1+n-r)!^2\,(g+1-n+r)!^2\,(r-n)}$$

$$\tag{9.1}$$

$$W''_{n00}(g,h) = -G^2_{g,h}\frac{1}{3a_o}\left(\frac{na_o}{2Z}\right)^{2g+2}(2g+2)!^2\sum_{r=g+1}^{g+1+n}\frac{(r+g)!}{(r-g-1)!\,(g+1+n-r)!^2\,(g+1-n+r)!^2\,(r-n)}$$

For the hybrid state $\rho = \frac{1}{\sqrt{3}}(n_{10} + n_{11} + n_{1,-1})$:

$$\beta_{np}(g_h) = E_{g,h}^2 \cdot \frac{1}{8\pi n} \left\{ \frac{g(n+1)!(2g+2)!^2}{(2g+1)(n-2)!} \sum_{r=g}^{g+1+n} \frac{(r+g-1)!}{(r-g)!(g+1+n-r)!^2(g+1-n+r)!^2(r-n)} \right.$$

$$\left. + \frac{4(g+1)(n-2)!(2g+1)!^2}{(2g+1)(n+1)!} \sum_{r=g+2}^{g+1+n} \frac{(r+g+1)![n(g+2)-r]^2}{(r-g-2)!(g+1+n-r)!^2(g+1-n+r)!(r-n)} \right\}$$

$$\tag{9.2}$$

$$W_{np}''(g,h) = -G_{g,h}^2 \cdot \frac{1}{3a_0}\left(\frac{na_0}{2Z}\right)^{2g+2} \left\{ \frac{g(n+1)!(2g+2)!^2}{n(2g+1)(n-2)!} \sum_{r=g}^{g+1+n} \frac{(r+g-1)!}{(r-g)!(g+1+n-r)!^2(g+1-n+r)!^2(r-n)} \right.$$

$$\left. + \frac{4(g+1)(n-2)!(2g+1)!^2}{n(2g+1)(n+1)!} \sum_{r=g+2}^{g+1+n} \frac{(r+g+1)![n(g+2)-r]^2}{(r-g-2)!(g+1+n-r)!^2(g+1-n+r)!^2(r-n)} \right\}$$

It will be noticed that the energy expression for the hybrid p orbital is independent of h; this result is necessary on account of the spherical symmetry of the wave function.

C. The Generalization to Filled Shell Ions

10. The Splitting of Degenerate Energy Levels. It will be noticed that in case n is greater than or equal to g there will be a term for r = n in one or both of the energy expressions in equations (9.1) and (9.2), and that then the factor (r-n) in the denominators of the expressions will vanish. This factor is $-H^{\circ}{}_{n\lambda\mu}^{n\lambda\mu}$, proportional to the energy difference between the state $(n\lambda\mu)$ and the state $(n\ell m)$ whose perturbation energy is being calculated. Since the wave functions being used are hydrogen-like, these states are treated as degenerate. If it is desired to treat a hydrogen-like atom, this degeneracy makes the calculation of perturbation for non-hybridized orbitals unsuitable; the correct procedure is to solve a first-order secular equation for the correct zeroth order wave functions and to use these in the subsequent calculations. The subject of the present treatment, however, is not the hydrogen-like atom, but the filled shell ion with more complex structure. In this case the degeneracy of these states is removed by the non-coulomb field of the other electrons and the integral $-H^{\circ}{}_{n\lambda\mu}^{n\lambda\mu}$ should have a finite value. As the present method fails to give this result, an empirical estimate of the splitting for the atom in question must be made and a suitable value inserted in place of the factor (r-n).

The integral $H^{\circ}{}_{\nu\lambda\mu}^{\nu\lambda\mu}$ may be shown by equations (2.5), (2.8), (3.6) and (3.11) to be equal to

$$H^{\circ}{}_{\nu\lambda\mu}^{\nu\lambda\mu} = -\frac{\nu^{4}}{2W_{h}\,n}\left\{\int \psi_{\nu\lambda\mu}^{\circ *}\left(-\frac{h^{2}}{8\pi^{2}\mu}\nabla^{2} - \frac{Ze^{2}}{r}\right)\psi_{\nu\lambda\mu}^{\circ}\,d\tau + W_{n\ell m}^{\circ}\right\} \quad (10.1)$$

For the case $\nu = n$ in which we are interested

$$H^\circ_{\substack{n\lambda\mu \\ n\lambda\mu}} = -\frac{n^3}{2W_H}\left(W^\circ_{n\lambda\mu} - W^\circ_{n\ell m}\right) \tag{10.2}$$

By use of the energy screening constants of Pauling and Sherman[8], the latter factor may be estimated. If S'_E is the required screening constant for the atom being treated for the state $(n\lambda\mu)$ and S_E that for the state $(n\ 1\ m)$

$$-H^\circ_{\substack{n\lambda\mu \\ n\lambda\mu}} = +\frac{n^3}{2W_H}\left[\frac{(Z-S'_E)^2 e^2}{2a_0 n^2} - \frac{(Z-S_E)^2 e^2}{2a_0 n^2}\right] \tag{10.3}$$

$$= +\frac{n}{2Z^2}(S_E - S'_E)(2Z - S_E + S'_E)$$

This quantity should replace the factor $(r-n)$ in the term of equations (9.1) and (9.2) for which $r = n$.

11. Effect of Hybridizing Unperturbed Wave Functions. The next step in generalizing the expressions in equations (9.1) and (9.2) to apply to filled shell ions will be justification of the statement made in paragraph 4 that the perturbation energies for filled shell ions are independent of the type of hybridization assumed for the individual electrons. If ψ_n° is the wave function for the nth state of the unperturbed system, the first order perturbation energy is given in general by

$$W' = \int \psi_n^{\circ*} H' \psi_n^\circ \, d\tau \tag{11.1}$$

and the second order perturbation energy by

$$W'' = \sum_{j\neq n} \frac{\int \psi_j^{\circ*} H' \psi_n^\circ \, d\tau \int \psi_n^{\circ*} H' \psi_j^\circ \, d\tau}{W_j^\circ - W_n^\circ} \tag{11.2}$$

For a system with several electrons these ψ's are the complete zeroth order wave functions and $d\tau$ is the product of the volume elements of all the electrons. In case the perturbation

operator $\underset{\sim}{H}{}'$ is a sum of terms each depending on the coordinates of a single electron, as it is in our case, the wave equation remains separable into several single electron equations, if interelectronic interactions are neglected. The complete unperturbed wave function can therefore be expressed as a completely antisymmetric product of single electron wave functions

$$\Psi^{\circ}(q_1, \ldots q_N) = \frac{1}{\sqrt{N}} \begin{vmatrix} \psi_1(q_1) & \cdots & \psi_1(q_N) \\ \vdots & & \vdots \\ \vdots & & \vdots \\ \psi_N(q_1) & \cdots & \psi_N(q_N) \end{vmatrix} \qquad (11.3)$$

where q_α represents all the coordinates of the α-th electron and N is the number of electrons. Electron spin is neglected here; however its consideration makes no essential change in the argument. Since we are considering a filled shell, the number of orbitals in the shell is the same. We wish now to investigate the effect of replacing each $\psi_\alpha(q_\beta)$ in equation (11.3) by a hybrid function of the form

$$\varphi_\alpha(q_\beta) = \sum_{i=1}^{N} a_{\alpha i} \, \psi_i(q_\beta) \qquad (11.4)$$

The equation now assumes the form

$$\Phi^{\circ}(q_1 \cdots q_N) = \frac{1}{\sqrt{N}} \begin{vmatrix} \sum\limits_{i=1}^{N} a_{1i} \psi_i(q_1) & \cdots & \sum\limits_{i=1}^{N} a_{1i} \psi_i(q_N) \\ \vdots & & \vdots \\ \sum\limits_{i=1}^{N} a_{Ni} \psi_i(q_1) & \cdots & \sum\limits_{i=1}^{N} a_{Ni} \psi_i(q_N) \end{vmatrix} \qquad (11.5)$$

This determinant is immediately recognized to be a product of determinants, so that

$$\Phi^{\circ}(q_1, \ldots q_N) = \frac{1}{\sqrt{N}} \begin{vmatrix} a_{11} & \cdots & a_{1N} \\ \vdots & & \\ \vdots & & \\ a_{N1} & \cdots & a_{NN} \end{vmatrix} \times \begin{vmatrix} \psi_1(q_1) & \cdots & \psi_1(q_N) \\ \vdots & & \vdots \\ \psi_N(q_1) & \cdots & \psi_N(q_N) \end{vmatrix} \quad (11.6)$$

According to equation (11.6) $\bar{\phi}^0$ and ψ^0 differ only by a constant factor. If however the individual ψ_i's and the hybrid φ_α's are all normalized, both ψ^0 and ϕ^0 are also, and the first determinant in equation (11.6) must be equal to unity. Hence ψ^0 and $\bar{\phi}^0$ are identical. It follows from this and equations (11.1) and (11.2) that the first and second perturbation energies in filled shell ions are independent of the type of hybridization chosen for the individual electrons. This being the case, the simple s functions and the hybrid p functions of the type of equation (8.1) have been chosen for the present treatment.

12. Selection of Screening Constants. Finally it is necessary to allow for the perturbing effect of interelectronic interactions on the energy expressions. This will be done in an approximate way by use of well-known screening constant wave functions. The quantity Z, the nuclear charge of the atom, is replaced by an "effective nuclear charge" Z - S; S, the screening constant, represents the average effect of the additional electrons in shielding the electron under consideration from the nucleus.

S will depend both upon the atom under consideration and upon the property whose calculation is to be attempted. According to a calculation by Pauling[9], a proper value of S for calculation of a property proportional (for a hydrogen-like electron) to $n^r Z^{-t}$ is given by

$$S = \sum_i z_i - \frac{r}{t} \sum_i z_i D_i \qquad (12.1)$$

Here z_i is the number of electrons in the ith shell and D_i is known as the screening defect for an electron in the ith shell. D may be calculated theoretically; it is better how-

ever to obtain it from the semi-empirical screening constants of Pauling and Sherman[8].

Approximate values of r are obtained by calculating values of W'' for various values of g and n and plotting their logarithms against log n. Fig. 1 shows this plot for g = 4 and 6, two cases which are of interest in the subsequent application. The result shows r for both the s and p states to be approximately 16 for g = 4 and 22 for g = 6. The value of t is seen from equations (9.2) to be 2g + 2, hence

$$\frac{r}{t} \approx 1.6 \qquad \text{for } g = 4 \text{ and } g = 6 \; .$$

In the following table, Pauling's and Sherman's semi-empirical "size" screening constants S_s were used to calculate $\sum_i z_i D_i$; this in turn gave S for $\frac{r}{t} = 1.6$, by equation (12.1)

Table 1. Screening Constants

Structure Type	S_s	Orbital	$\sum_i z_i$	$\sum_i z_i D_i$	S
He	0.19	1s	1	0.40	0.35
Ne	{3.10 / 4.57}	2s} 2p}	9	{2.95 / 2.22}	{4.28 / 5.46}
Ar	{9.1 / 10.9}	3s} 3p}	17	{3.95 / 3.05}	{10.7 / 12.1}
Kr	{24.2 / 26.6}	4s} 4p}	35	{5.4 / 4.2}	{26.4 / 28.3}
Xe	{38.8 / 41.8}	5s} 5p}	53	{7.1 / 5.6}	{41.6 / 44.0}

13. Final Expressions. The final expressions for the second order polarization in an ion with two s and six p electrons is the following

$$W_n''(g,h) = -G_{gh}^2 \frac{2}{3a_0}\left(\frac{na_0}{Z}\right)^{2g+2}\left\{\frac{J_{ns}(g,h)}{[Z-S_{ns}(g,h)]^{2g+2}} + \frac{3J_{np}}{[Z-S_{np}(g,h)]^{2g+2}}\right\}$$

(13.1)

Figure 1.

The y-axis is labeled: $Log_{10}\left\{-W''(g,h) \cdot a_o \left(\frac{2Z}{na_o}\right)^{2g+2} \cdot \frac{1}{G_{gh}}\right\}$

The x-axis is labeled: $Log_{10}\ n$

Curves labeled: p, s for g = 6 and p, s for g = 4
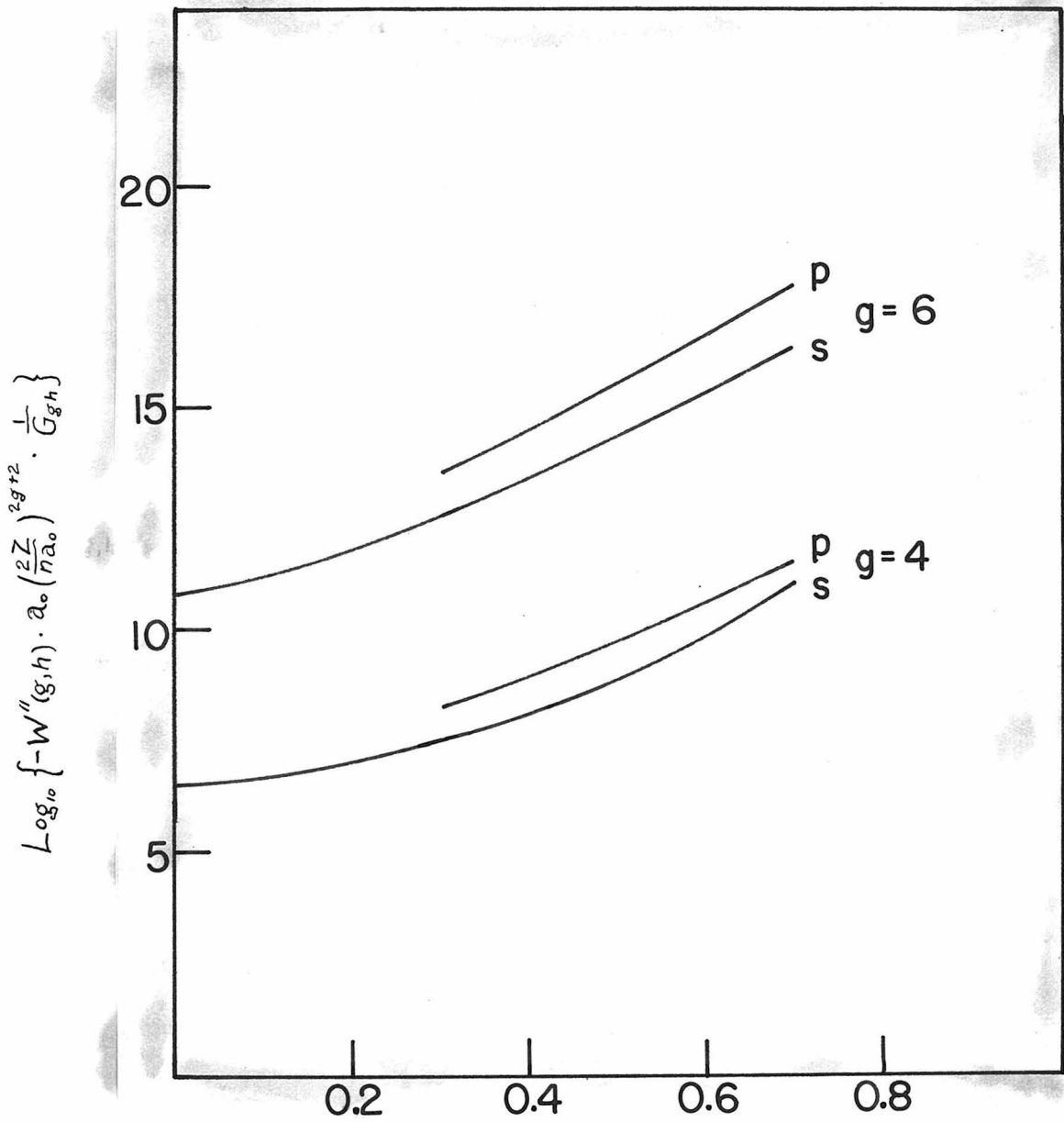
where
$$J_{ns}(g,h) = (2g+2)!^2 \sum_{r=g+1}^{g+1+n} \frac{(r+g)!}{(r-g-1)!\,(g+1+n-r)!^2\,(g+1-n+r)!^2\,q_{ns}(r,g)} \tag{13.2}$$

$$J_{np}(g,h) = \frac{g(n+1)!\,(2g+2)!^2}{n(2g+1)(n-2)!} \sum_{r=g}^{g+1+n} \frac{(r+g-1)!}{(r-g)!\,(g+1+n-r)!^2\,(g+1-n+r)!^2\,q_{np}(r,g-1)}$$

$$+ \frac{4(g+1)(n-2)!\,(2g+1)!^2}{n(2g+1)(n+1)!} \sum_{r=g+2}^{2g+1+n} \frac{(r+g+1)!\,[n(g+2)-r]^2}{(r-g-2)!\,(g+1+n-r)!^2\,(g+1-n+r)!^2\,q_{np}(r,g+1)} \tag{13.3}$$

$$q_{ns} = q_{np} = r-n \quad \text{for } r \neq n \tag{13.4}$$

$$q_{ns}(n,g) = \frac{n}{2(Z-S_{ns})^2}\left[S_E(n00) - S_E(n,g,h)\right]\left[2Z - S_E(n00) + S_E(ngh)\right] \tag{13.5}$$

$$q_{np}(n,\lambda) = \frac{n}{2(Z-S_{np})^2}\left[S_E(n10) - S_E(n\lambda\mu)\right]\left[2Z - S_E(n10) + S_E(n\lambda\mu)\right] \tag{13.6}$$

$S_{ns}(g,h)$ and $S_{np}(g,h)$ are appropriate screening constants for the potential V_{gh}, and $S_E(n\lambda\mu)$ are energy screening constants for the states $(n\lambda\mu)$.

D. Application to the Lattice Energy of a Sodium Chloride
   Type Crystal.

14. Introduction.   In an ionic crystal, the electron
clouds of the individual ions are polarized in the field of
the surrounding ions. This polarization gives rise to a
stabilizing term in the lattice energy, the magnitude of which
may be calculated by use of the theory developed in the
preceeding sections. The present application will be limited
to crystals with the halite structure.

15. Potentials with Cubic Symmetry.   Since the environment
of every ion in the halite structure is cubically symmetric,
the potential function due to the ion environment must also be
cubically symmetric. The conditions for cubic symmetry may
be derived by expressing a general potential in cartesian
coordinates and equating coefficients of equal powers of x,
y, z, -x, -y, and -z.

The general potential function is

$$V(x,y,z) = 2\sqrt{\frac{\pi}{3}} \sum_{g,h} G_{g,h} \, K_{gh}(x,y,z) \tag{15.1}$$

where K_{gh} is a spherical harmonic. K_{gh} is homogeneous in
$\sqrt{x^2+y^2+z^2}$ of degree g. Because of this, any symmetry proper-
ties possessed by the complete function V (x, y, z) must also
be possessed by the sums of terms with the same value of g.

Since V (x, y, z) must be symmetric in positive and
negative values of the variables, all odd powers of the
variables must vanish. That is, $\sum_{h} G_{gh} K_{gh}$ = 0 for all sine terms, all
terms with h odd, and all cosine terms with g - h odd. Since
the functions K_{gh} are linearly independent, this condition
requires that G_{gh} vanish for all of these cases. In addition,

in the spherical harmonics with g even and h equal to twice an odd integer the coefficients of x^n and y^n are equal and opposite, n being an even integer, while in those with the remaining even values of h the coefficients of x^n and y^n are equal. Under these circumstances the former are incompatible with cubic symmetry. Hence $\sum_h G_{gh} K_{gh} = 0$ for g even, h = 2 (2n + 1). Again this condition requires that all these G_{gh}'s be zero.

There remains the cosine functions with g even and h = 4 n. By expressing these explicitly and equating coefficients of x^n, y^n and z^n , the following conditions are obtained

$$G_{20} = 0$$

$$G_{40} = \frac{1}{5} \sqrt{35}\ G_{44} \tag{15.2}$$

$$G_{60} = -\frac{1}{\sqrt{7}}\ G_{64}$$

Other relations exist for higher order terms.

16. Evaluation of Coefficients for the Halite Structure. The potential due to a distribution of point charges is given by Coulomb's law as

$$V(r) = \sum_i \frac{q_i}{|\underline{a}_i - \underline{r}|} \tag{16.1}$$

where g is the magnitude of the ith charge, $\underline{a}_i$ is the vector from the origin to the ith charge, and $\underline{r}$ is the vector from the origin to the point of interest. By use of an expansion theorem[10], equation (16.1) can be expressed as

$$V(r) = \sum_i q_i \sum_{g,h} \frac{2p\pi}{2g+1} K_{gh}(r,\vartheta,\varphi) \cdot \frac{1}{a_i^{2g+1}} K_{gh}(a_i,\vartheta_i,\varphi_i) \tag{16.2}$$

where $r, \vartheta,$ and φ give the length and direction of $\underline{r}$ and $\underline{a}_i$, ϑ_i , φ_i those of $\underline{a}_i$. In order that V(r) should be in the form of equation (15.1) we must have

$$G_{gh} = \sum_i \frac{\sqrt{3\pi}}{2g+3} \cdot \frac{q_i}{a_i^{2g+1}} K_{gh}(x_i, y_i, z_i) \tag{16.3}$$

where x_i, y_i, z_i are the cartesian components of the vector $\underline{a}_i$.

The halite structure is based on a face-centered cubic lattice. There are positive ions at (000), $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2}0\frac{1}{2})$, and $(0\frac{1}{2}\frac{1}{2})$, and negative ions at $(\frac{1}{2}00)$, $(0\frac{1}{2}0)$, $(00\frac{1}{2})$, and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$: It is convenient to classify the ions surrounding a given ion into groups of similar ions at the same distance.

The following table enumerates the first six such groups of ions about the origin and gives values of $\frac{a_i}{a}$, the common distance from the origin of the ions of group j, expressed in terms of the unit translation of the lattice a, and values of the group coefficient $G_{g,h}^{(j)}$, defined as the sum over the group of *the part of G_{gh} referring to a single ion.*

$$G_{gh}^{(j)} = \sum_i \frac{\sqrt{3\pi}}{2g+1} \frac{q_j}{a_j^{2g+1}} K_{gh}(x_i y_i z_i) \qquad (16.4)$$

Table 2.

Group No.	No. of Ions	Ion Charge	Ion Coordinates	$\frac{a_j}{a}$	$G_{40}^{(j)} \frac{a^5}{e}$	$G_{60}^{(j)} \frac{a^7}{e}$
1.	6	$6-e$	$(\frac{1}{2}00)\circlearrowright$ $(\frac{1}{2}00)\circlearrowright$	$\frac{1}{2}$	-32.31	-23.03
2.	12	$+e$	$(\frac{1}{2}\frac{1}{2}0)\circlearrowright$ $(\bar{1}\frac{1}{2}0)\circlearrowright$ $(\frac{1}{2}\bar{1}0)\circlearrowright$ $(\bar{1}\frac{1}{2}0)\circlearrowright$	$\frac{1}{\sqrt{2}}$	-2.86	-14.26
3.	8	$-e$	$(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ $(\frac{1}{2}\frac{1}{2}\bar{1})\circlearrowright$ $(\frac{1}{2}\bar{1}\frac{1}{2})\circlearrowright$ $(\frac{1}{2}\bar{1}\bar{1})$	$\frac{\sqrt{3}}{2}$	$+1.84$	-1.17
4.	24	$-e$	$(1\frac{1}{2}0)\circlearrowright$ $(1\bar{1}0)\circlearrowright$ $(\bar{1}\frac{1}{2}0)\circlearrowright$ $(\bar{1}\frac{1}{2}0)\circlearrowright$ $(\frac{1}{2}10)\circlearrowright$ $(\bar{1}10)\circlearrowright$ $(\frac{1}{2}\bar{1}0)\circlearrowright$ $(\frac{1}{2}\bar{1}0)\circlearrowright$	$\frac{\sqrt{5}}{2}$	-0.46	$+0.22$

Table 2 (continued)

Group No.	No. of Ions	Ion Charge	Ion Coordinates	$\dfrac{d_j}{a}$	$G_{4b}^{(j)}$	$G_{6b}^{(j)}$
5.	24	+ 2	$(1\,\tfrac{1}{2}\,\tfrac{1}{2})S$ $(1\,\bar{\tfrac{1}{2}}\,\tfrac{1}{2})S$ $(1\,\tfrac{1}{2}\,\bar{\tfrac{1}{2}})S$ $(1\,\bar{\tfrac{1}{2}}\,\bar{\tfrac{1}{2}})S$ $(\bar{1}\,\bar{\tfrac{1}{2}}\,\bar{\tfrac{1}{2}})S$ $(\bar{1}\,\bar{\tfrac{1}{2}}\,\tfrac{1}{2})S$ $(\bar{1}\,\tfrac{1}{2}\,\bar{\tfrac{1}{2}})S$ $(\bar{1}\,\tfrac{1}{2}\,\tfrac{1}{2})S$	$\sqrt{\tfrac{3}{2}}$	−0.37	+0.06
6.	24	− e	$(\bar{1}\,1\,\tfrac{1}{2})S$ $(1\,\bar{1}\,\tfrac{1}{2})S$ $(1\,1\,\bar{\tfrac{1}{2}})S$ $(\bar{1}\,\bar{1}\,\tfrac{1}{2})S$ $(\bar{1}\,1\,\bar{\tfrac{1}{2}})S$ $(1\,\bar{1}\,\bar{\tfrac{1}{2}})S$ $(\bar{1}\,\bar{1}\,\bar{\tfrac{1}{2}})S$ $(1\,1\,\tfrac{1}{2})S$	$\tfrac{3}{2}$	+0.03	−0.02

Each positive ion in this table is the first of an infinite, equally-spaced row of similar ions. Each negative ion is the first of a similar row of alternately negative and positive ions. The effect of the other ions in the row can conveniently be taken into account by multiplying $G_{gh}^{(j)}$ for a group of positive ions by $\sum_{\alpha=1}^{\infty} \left(\tfrac{1}{\alpha}\right)^{g+1}$ and $G_{gh}^{(j)}$ for a group of negative ions by $\sum_{\alpha=1}^{\infty} (-1)^{\alpha+1} \left(\tfrac{1}{\alpha}\right)^{g+1}$. Values of these sums are

$$\sum_{\alpha=1}^{\infty} \left(\tfrac{1}{\alpha}\right)^{5} = 1.037 \qquad\qquad \sum_{\alpha=1}^{\infty} \left(\tfrac{1}{\alpha}\right)^{7} = 1.008$$

$$\sum_{\alpha=1}^{\infty} (-1)^{\alpha+1}\left(\tfrac{1}{\alpha}\right)^{5} = 0.972 \qquad\qquad \sum_{\alpha=1}^{\infty} (-1)^{\alpha+1}\left(\tfrac{1}{\alpha}\right)^{7} = 0.993$$

$$\tag{16.5}$$

Carrying out this calculation, summing over the groups,

and using equations (15.2), we obtain the following results

$$G_{40} = -33.35 \ e/a^5$$

$$G_{44} = -28.22 \ e/a^5$$

$$G_{60} = -38.15 \ e/a^7$$

$$G_{64} = +100.92 \ e/a^7$$

(16.6)

For NaCl, the unit translation is a = 5.628 A . This gives the following numerical values, expressed for convenience in terms of $a_0 = \dfrac{h^2}{4\pi^2 \mu e^2} = 0.5282$ A for infinite nuclear mass.

$$G_{40} = -2.430 \times 10^{-9} \ e/a_0^5$$

$$G_{44} = -2.057 \times 10^{-9} \ e/a_0^5$$

$$G_{60} = -2.451 \times 10^{-6} \ e/a_0^7$$

$$G_{64} = +6.483 \times 10^{-6} \ e/a_0^7$$

(16.7)

17. Polarization Energy for Na Cl Crystal. From these coefficients and the energy expression (48) a value may be obtained for the polarization energy in the Na Cl crystal. The effective nuclear charges used are the following.

Table 3. Values of S and Z for Na Cl.

Ion	Orbital	S	Z
Na	2s	4.28	6.72
	2p	5.46	5.54
Cl	3s	10.7	6.3
	3p	12.1	4.9

The results are summarized below, in units e/a_0 .

Table 4. Values of W″ for Na Cl

(see next page)

Table 4. Values of W'' for Na Cl

g	Na	Cl
4	0.12×10^{-5}	455×10^{-5}
6	0.02×10^{-5}	224×10^{-5}
Total	0.14×10^{-5}	679×10^{-5}

Total $W'' = 679 \times 10^{-5} = 4.24$ kcal / mol.

The sodium chloride lattice is stabilized to the extent of about 4 kilocalories per mol by high order polarization of the ions. The accuracy of this value will be discussed in the next section.

18. Errors. The one great error which overshadows all others arises from uncertainties in the effective nuclear charge $Z - S$. Pauling and Sherman[8] estimate their error in the screening constants to be 10% in the screening defect.. Accepting this value, the uncertainty in $Z - S$ is about 6%; and in $Z - S$ to the tenth power, about 60%. Taking a generous estimate, we may place the uncertainty in the result at about a factor of two or three.

The expansion (16.2) used to evaluate the potential V (r) is convergent only for $r < a$. In applying it to this problem, the assumption has been tacitly made that the electron distribution of one ion does not extend to the position of the next ion. A more serious assumption is made in applying the formula (16.1) for the potential due to a distribution of point charges. Both of these assumptions, however, introduce negligible errors if the overlapping of the electron distributions of adjacent ions in negligibly small, a condition which is probably fulfilled. At any rate, the error intro-

duced is negligible in comparison to the uncertainty discussed in the preceeding paragraph.

E. Discussion

19. Precision of the Calculation. The fundamental condition underlying the applicability of the perturbation method, namely that the perturbation energy may be small in comparison to the energy separations of the unperturbed state of the system from the adjoining excited states, is fulfilled in the case under discussion. The calculation of the energy expression for the hydrogen-like electron is straight-forward and devoid of approximations affecting the result to second order terms.

The generalized expression applying to filled shell ions is in error chiefly because the use of a central coulomb field to describe the potential on one electron due to the others is not valid. The error due to this is perhaps reasonably small because the quantity calculated, the perturbation energy, is the difference between two quantities which might be expected to be in error by about the same amount in the same direction. A larger error is introduced by the practical difficulty of obtaining the best value of the parameter describing this coulomb field, namely the effective nuclear charge. The magnitude of this error was discussed in connection with the application of this theory to the sodium chloride crystal.

The non-coulomb character of the atomic field made it necessary to introduce into the derived expressions an empirical quantity corresponding to the splitting of degenerate energy levels of the unperturbed state. The error due to this cause depends upon the accuracy with which this splitting can be estimated in the individual cases in which it enters.

Whether or not there is any appreciable error in other integrals due to displacement of excited energy levels away from their values with a central coulomb field is difficult to say, since the functions used to calculate these integrals are not wave functions of the system. It seems likely that any error of this type would be small compared to the other errors discussed.

The spin of the electrons and the small splitting of energy levels introduced by it has been ignored throughout; its effect is undoubtedly negligible.

20. Value of the Treatment. Although this treatment gives a value for the high order polarization energy of an ionic crystal which is uncertain to a degree approaching an order of magnitude there are nevertheless situations in which it should prove to be of value. It should be possible, for example, to compare with reasonable confidence the polarization energy of a substance in two different crystal modifications, such as sodium chloride in its normal structure and in the cesium chloride structure.

If it were possible to obtain experimental values for some of the energy quantities predicted by this treatment, very accurate screening constants could be obtained for use in treating other atoms. Such experimental values, however, are not available, and would be excessively difficult to obtain because of the difficulty in producing accurately known electric fields of the type needed.

21. Acknowledgment. Before closing, I wish to thank Professor Linus Pauling, who proposed this problem, for the

benefit of excellent instruction in the theory of quantum mechanics and for a large number of helpful discussions during the course of this investigation.

Appendix

The evaluation of the integrals was carried out as follows:

$$H'^{*}_{\substack{\nu'\lambda'\mu' \\ \nu\lambda\mu}} = \int F^{*}_{\nu'\lambda'\mu'} A F_{\nu\lambda\mu} d\tau = \int F_{\nu\lambda\mu} A^{*} F^{*}_{\nu'\lambda'\mu'} d\tau = H'^{*}_{\substack{\nu\lambda\mu \\ \nu'\lambda'\mu'}} \tag{100}$$

$$H'_{\substack{\nu\lambda\mu \\ noo}} = \sum_{g,h} E_{gh} \int \Lambda_{\nu\lambda}\, \xi^{g+2} \Lambda_{lo}\, d\xi \int_{0}^{\pi} \Theta_{\lambda|\mu|}\, \Theta_{gh}\, \Theta_{oo}\, \sin\vartheta\, d\vartheta \int_{0}^{2\pi} \overset{*}{\Phi}_{\mu}\, \Omega_{h}\, \Phi_{o}\, d\varphi$$

$$\int_{0}^{2\pi} \overset{*}{\Phi}_{\mu}\, \Omega_{h}\, \Phi_{o}\, d\varphi = \frac{1}{2\pi\sqrt{p\pi}} \int_{0}^{2\pi} e^{-i\mu\varphi} \frac{\cos}{\sin} h\varphi\, d\varphi = \begin{cases} \frac{1}{2}\sqrt{\frac{p}{\pi}}\, \delta_{\mu,\pm h} \\ \mp\frac{i}{2}\sqrt{\frac{p}{\pi}}\, \delta_{\mu,\pm h} \end{cases}$$

$$\int_{0}^{\pi} \Theta_{\lambda h}\, \Theta_{gh}\, \Theta_{oo}\, \sin\vartheta\, d\vartheta = \int_{0}^{\pi} \Theta_{\lambda h}\, \Theta_{gh}\, \frac{1}{\sqrt{2}}\, \sin\vartheta\, d\vartheta$$

$$= \frac{1}{\sqrt{2}}\, \delta_{\lambda g}$$

by equation (7)

To evaluate the remaining integral let

$$\xi^{g+1} \Lambda_{no} = \sum_{r} a_{r} \Lambda_{rg} \tag{101}$$

Then by equation (3.9)

$$\int_{0}^{\infty} \Lambda_{rg}\, \xi^{g+1} \Lambda_{no}\, \xi\, d\xi = a_{r}\, \delta_{\nu r} \tag{102}$$

The values of Λ_{no} and Λ_{rg} are taken from equations (3.6) and (2.9); equation (101) becomes

$$\xi \sum_{i=0}^{n-1} (-1)^{i+1} \frac{n!^{2}}{(n-1-i)!\,(1+i)!\,i!}\, \xi^{i} = \sum_{j=0}^{n} b_{j} \sum_{i=0}^{j} (-1)^{i+1} \frac{(2g+1+j)!^{2}}{(j-i)!\,(2g+1+i)!\,i!}\, \xi^{i} \tag{103}$$

where $j = r-g-1$ and $b_{j} = \left[\frac{(r-g-1)!}{(r+g)!^{3}}\right]^{\frac{1}{2}} n!\sqrt{\pi}\, a_{r}$. The upper limit of the summation over r is found by recognizing that the polynomial of highest degree which can enter is of degree n. By changing the order of summation, with an appropriate change in limits, making the substitution

$$C_{k} = \frac{(2g+1+j)!^{2}}{n!^{2}}\, b_{j} \qquad \text{with } k = n-j,$$

and equating coefficients of equal powers of ξ, we obtain a set of simultaneous linear equations for the coefficients c_{k}.

$$\sum_{k=0}^{n-i} \frac{c_{k}}{(n-i-k)!} = -\frac{(2g+1+i)!}{(n-i)!\,(i-1)!} , \quad 0 \le i \le n \tag{104}$$

Solving the equations for i = n, n-1, n-2, n-3 successively,

$$c_o = - \frac{(2g+n+1)!}{(n-1)!}$$

$$c_1 = - \frac{(2g+n)!}{(n-1)!} \left\{ (n-1) - (2g+n+1) \right\}$$

$$c_2 = - \frac{(2g+n-1)!}{(n-1)!} \left\{ \frac{1}{2}(n-2)(n-1) - (2g+n)(n-1) + \frac{1}{2}(2g+n)(2g+n+1) \right\}$$

$$c_3 = - \frac{(2g+n-2)!}{(n-1)!} \left\{ \frac{1}{6}(n-3)(n-2)(n-1) - \frac{1}{2}(n-2)(n-1)(2g+n-1) + \frac{1}{2}(n-1)(2g+n-1)(2g+n) \right.$$

$$\left. - \frac{1}{6}(2g+n-1)(2g+n)(2g+n+1) \right\}$$

Apparently the general coefficient c_σ is

$$c_\sigma = - \frac{(2g+n+1-\sigma)!}{(n-1)!} \sum_{s=0}^{\sigma} \frac{(n-1)!(2g+n+2-\sigma)_s (-1)^s}{(\sigma-s)!(n-\sigma)! s!(n-\sigma-1)!} \, ,$$

$$= - \frac{(2g+n+1-\sigma)!}{(n-\sigma-1)!\,\sigma!} \sum_{s=0}^{\sigma} \frac{(2g+n+2-\sigma)_s(-\sigma)_s}{(n-\sigma)_s \, s!} \tag{105}$$

where the notation $(a)s = a \cdot (a+1) \cdot (a+2) \ldots (a + s-1)$ has

been introduced. This sum, however, is an hypergeometric series[11]

with unit argument F (a,b;c; 1) where, in this case

$$a = 2g+n+2-\sigma \, , \quad b = -\sigma \, , \quad c = n-\sigma$$

The value of the function is[12]

$$F(a,b;c;1) = \frac{\Gamma(c)\,\Gamma(c-a-b)}{\Gamma(c-a)\,\Gamma(c-b)} \tag{106}$$

Applying this formula

$$c_\sigma = (-1)^\sigma \frac{(2g+n+1)!\,(-2g-2)_\sigma}{(n-1)!\,\sigma!\,(-2g-h-1)_\sigma} \tag{107}$$

To prove this value is correct, it is substituted into equations (104) to give

$$\sum_{k=0}^{n-i} \frac{c_k}{(n-i-k)!} = \sum_{k=0}^{n-i} \frac{(-1)^k(-n+i)_k}{(n-i)!} c_k = - \frac{(2g+n+1)!}{(n-1)!(n-i)!} \sum_{k=0}^{n-i} \frac{(-n+i)_k(-2g-2)_k}{(-2g-n-1)_k}$$

$$= - \frac{(2g+n+1)!\,\Gamma(-2g-n-1)\,\Gamma(1-i)}{(n-1)!(n-i)!\,\Gamma(-2g-i-1)\,\Gamma(-n+1)}$$

$$= - \frac{(2g+i+1)!}{(n-i)!(n-1)!} \tag{108}$$

where the first transformation results from the introduction
of the notation of equation (105), and the third from the
recognition that the sum in the second line is an hypergeometric
function with unit argument. The final form is seen to be
identical with that in equation (104), thus proving the
correctness of equation (106). A series of simple substitu-
tions now gives

$$a_r = (-1)^{n-r+g} \left[\frac{(r+g)! n}{(r-g-1)!} \right]^{1/2} \frac{(2g+2)!}{(g+1+n-r)!(g+1-n+r)!} \quad ,$$

and

$$H'_{r,g,\pm h} \Big|_{n \, 0 \, 0} = (-1)^{n-r+g} \left[\frac{(r+g)! n p}{2(r-g-1)! \pi} \right]^{1/2} \frac{(2g+2)!}{2(g+1+n-r)!(g+1-n+r)!} \quad (109)$$

for a cosine term in V_{gh}; the corresponding sine term in ob-
tained by multiplication of $\mp i$.

The method of evaluating the other integrals is identical
with this; their evaluation will be outlined more briefly.

$$H'_{\nu\lambda\mu} \Big|_{n \, 1 \, 0} = E_{gh} \int_0^\infty \Lambda_{\nu\lambda} \, \xi^{g+2} \Lambda_{n} \, d\xi \int_0^\pi \Theta_{\lambda|\mu} \, \Theta_{gh} \, \Theta_{10} \sin\theta \, d\theta \int_0^{2\pi} \Phi_\mu^* \Omega_h \, \Phi_0 \, d\varphi$$

$$\int_0^{2\pi} \Phi_\mu^* \Omega_h \, \Phi_0 \, d\varphi = \frac{1}{2\pi\sqrt{p\pi}} \int_0^{2\pi} e^{-i\mu\varphi} \frac{\cos}{\sin} h\varphi \, d\varphi \begin{cases} = \frac{1}{2} \sqrt{\frac{p}{\pi}} \, \delta_{\mu,\pm h} \\ = \mp \frac{i}{2} \sqrt{\frac{p}{\pi}} \, \delta_{\mu,\pm h} \end{cases}$$

$$\int_0^\pi \Theta_{\lambda h} \, \Theta_{gh} \, \Theta_{10} \sin\theta \, d\theta = \frac{\sqrt{6}}{2} \int_0^\pi \Theta_{\lambda h} \, \Theta_{gh} \cos\theta \sin\theta \, d\theta \quad (110)$$

$$= \frac{\sqrt{6}}{2} \left[\frac{(g-h)(g+h)}{(2g-1)(2g+1)} \right]^{1/2} \delta_{\lambda, g-1} + \frac{\sqrt{6}}{2} \left[\frac{(g-h+1)(g+h+1)}{(2g+1)(2g+3)} \right]^{1/2} \delta_{\lambda, g+1}$$

this last step resulting from the application of the formula[13]

$$\cos\theta \, \Theta_{gh} = \left[\frac{(g-h)(g+h)}{(2g-1)(2g+1)} \right]^{1/2} \Theta_{g-1,h} + \left[\frac{(g-h+1)(g+h+1)}{(2g+1)(2g+3)} \right]^{1/2} \Theta_{g+1,h} \quad (111)$$

and the orthogonality conditions (1.5).

There are now two cases to consider: $\lambda = g-1$ and $\lambda = g+1$.

$$\int_0^\infty \Lambda_{\nu,g-1} \, \xi^{g+2} \Lambda_{n_1} \, d\xi = \int_0^\infty \Lambda_{\nu,g-1} \sum_r (a_r \Lambda_{r,g-1}) \xi \, d\xi = a_r \delta_{\nu,r} \tag{112}$$

with $\xi^{g+1} \Lambda_{n_1} = \sum_r a_r \Lambda_{r,g-1}$. This leads as before to a set of simultaneous linear equations in the coefficient a_r,

$$\sum_{k=0}^{n+1-i} \frac{c_k}{(n+1-i-k)!} = -\frac{(2g-1+i)!}{(n+1-i)!(i-3)} \; ; \quad 0 \leqslant i \leqslant n+1 \tag{113}$$

after the substitutions

$$c_k = \left[\frac{(g+r-1)!\,(r-g)!}{(n+1)!\,(n-2)!} \right]^{\frac{1}{2}} a_r \; ; \qquad k = g+1+n-r.$$

The solution to these equations may be found by generalizing the solutions of the first few, it is

$$c_\sigma = (-1)^{\sigma+1} \frac{(2g+n)!\,(-2g-2)_\sigma}{(n-2)!\,\sigma!\,(-2g-n)_\sigma} \, , \tag{114}$$

which may be proved correct by substitution in equation (113). Hence

$$a_r = (-1)^{g+n+r} \left[\frac{(n+1)!\,(g+r-1)!}{(n-2)!\,(r-g)!} \right]^{1/2} \frac{(2g+2)!}{(g+1-n+r)!\,(g+1+n-r)!} \tag{115}$$

and

$$H'_{r,g-1,\pm h \atop n,1,0} = E_{gh} (-1)^{g+n-r} \frac{1}{4} \left[\frac{(n+1)!\,(g+r-1)!\,(g-h)(g+h)6P}{(2g-1)(2g+1)(n-2)!\,(r-g)!\,\pi} \right]^{\frac{1}{2}} \frac{(2g+2)!}{(g+1-n+r)!\,(g+1+n-r)!} \tag{116}$$

for cosine potentials; the integral for sine potentials is obtained by multiplication by $\mp i$.

$$\int_0^\infty \Lambda_{\nu,g+1} \, \xi^{g+2} \Lambda_{n_1} \, d\xi = \int_0^\infty \Lambda_{\nu,g+1} (\sum_r a_r \Lambda_{r,g+1}) \xi \, d\xi = a_r \delta_{\nu,r} \tag{117}$$

where $\xi^{g+1} \Lambda_{n_1} = \sum_r a_r \Lambda_{r,g+1}$. Again this leads to a set of simultaneous linear equations in the coefficients a_r, if

$$c_k = \left[\frac{(g+1+r)!\,(r-g-2)}{(n+1)!\,(n-2)!} \right]^{1/2} a_r \; ; \quad k = g+1+n-r \, . \tag{118}$$

After the substitutions we obtain

$$\sum_{k=0}^{n-i-1} \frac{c_k}{(n-i-1-k)!} = -\frac{(2g+3+i)!\,i}{(n-i-1)!\,(i+2)!} \, , \quad 0 \leqslant i \leqslant n-1 \, .$$

Again the general solution is inferred from the form of the

first few expressions:

$$C_\sigma = - \frac{(2g+n+2-\sigma)!}{(n+1-\sigma)!\,\sigma!} \sum_{s=0}^{\sigma} \frac{(n-\sigma-1+s)(-\sigma)_s\,(2g+n+3-\sigma)_s}{s!\,(n+2-\sigma)_s}$$

(119)

$$= - \frac{(2g+n+2-\sigma)!}{(n+1-\sigma)!\,\sigma!} \left\{ (n-\sigma-1) \sum_{s=0}^{\sigma} \frac{(-\sigma)_s\,(2g+n+3-\sigma)_s}{s!\,(n+2-\sigma)_s} \right.$$

$$\left. - \frac{\sigma(2g+n+3-\sigma)}{(n+2-\sigma)} \sum_{s=0}^{\sigma-1} \frac{(-\sigma+1)_s\,(2g+n+4-\sigma)_s}{s!\,(n+3-\sigma)_s} \right\}$$

$$= - \frac{(2g+n+2-\sigma)!}{(n+1-\sigma)!\,\sigma!} \left\{ (n-\sigma-1) \frac{\Gamma(n-2-\sigma)\,\Gamma(\sigma-2g-1)}{\Gamma(n+2)\,\Gamma(-2g-1)} \right.$$

$$\left. - \frac{\sigma(2g+n+3-\sigma)}{(n+2-\sigma)} \frac{\Gamma(n+3-\sigma)\,\Gamma(-2g-2+\sigma)}{\Gamma(n+2)\,\Gamma(-2g-1)} \right\}$$

$$= (-1)^{\sigma+1} \frac{(2g+n+2)!\,(-2g-2)_\sigma}{(n+1)!\,(g+1)\,(\sigma)!\,(-2g-n-2)_\sigma} \left[(n-1)(g+1)+\sigma\right],$$

(120)

where the essential transformation again depends upon recognizing the hypergeometric sum and applying equation (106). That this is correct may be proved by substituting it in equation (118). Hence

$$a_r = (-1)^{g+n-r} \left[\frac{(n-2)!\,(g+1+r)!}{(n+1)!\,(r-g-2)!}\right]^{1/2} \frac{2(2g+1)!\,[n(g+2)-r]}{(g+1+n-r)!\,(g+1-n+r)!}$$

(121)

and

$$H'_{r,g+1,\pm h \atop h,\,1,\,0} = E_{gh}\,(-1)^{g+n-r}\,\frac{1}{2}\left[\frac{(g-h+1)(g+h+1)(n-2)!\,(g+r+1)!\,6p}{(2g+1)(2g+3)(n+1)!\,(r-g-2)!\,\pi}\right]^{1/2} \frac{(2g+1)!\,[n(g+2)-r]}{(g+1+n-r)!\,(g+1-n+r)!}$$

for cosine potentials; the value for sine is this expression multiplied by $\mp i$.

(122)

$$H'_{\nu\lambda\mu} = \sum_{g h \atop n\,l\,l} E_{gh} \int \Lambda_{r\lambda}\, \mathfrak{z}^{g+2} \Lambda_{nl}\, d\mathfrak{z} \int_0^\pi \Theta_{\lambda|\mu|}\,\Theta_{gh}\,\Theta_{ll}\,\sin\vartheta\,d\vartheta \int_0^{2\pi} \overset{*}{\Phi}_\mu \Omega_h \Phi_l\, d\varphi$$

$$\int_0^{2\pi} \overset{*}{\Phi}_\mu \Omega_h \Phi_l\, d\varphi = \frac{1}{2\pi\sqrt{p\pi}} \int^{2\pi} e^{-i\mu\varphi}\,{\cos \atop \sin}\,h\varphi\,e^{i\varphi}\,d\varphi = \int^{2\pi} e^{i(l-\mu)\varphi}\,{\cos \atop \sin}\,h\varphi\,d\varphi$$

(123)

$$= \begin{cases} \frac{1}{2}\sqrt{\frac{p}{\pi}}\,\delta_{\mu\,(l\pm h)} \\[2ex] \mp\frac{i}{2}\sqrt{\frac{p}{\pi}}\,\delta_{\mu\,(l\pm h)} \end{cases}$$

$$H'^{\nu\lambda\mu}_{n,l,-1} = \sum_{g,h} E_{g,h} \int_0^\infty \Lambda_{\nu\lambda}\, \xi^{g+2} \Lambda_{nl}\, d\xi \int_0^\pi \Theta_{\lambda|\mu|} \Theta_{gh} \Theta_{ll}\, \sin\vartheta\, d\vartheta \int_0^\pi \Phi_\mu^* \Omega_h \Phi_{-l}\, d\varphi$$

$$\int_0^{2\pi} \Phi_\mu^* \Omega_h \Phi_{-l}\, d\varphi = \frac{1}{2\pi\sqrt{p\pi}} \int_0^{2\pi} e^{i\mu\varphi} \frac{\cos}{\sin} h\varphi\, e^{-i\mu\varphi}\, d\varphi = \frac{1}{2\pi\sqrt{p\pi}} \int_0^{2\pi} e^{i(-l-\mu)\varphi} \frac{\cos}{\sin} h\varphi\, d\varphi$$

$$= \begin{cases} \frac{1}{2}\sqrt{\frac{p}{\pi}}\, \delta_{\mu,(-l\pm h)} \\[2mm] \mp \frac{i}{2}\sqrt{\frac{p}{\pi}}\, \delta_{\mu,(-l\pm h)} \end{cases} \tag{124}$$

There are two cases to consider: $|\mu| = |(l+h)|$ and $|\mu| = |(l-h)|$

$$\int_0^\pi \Theta_{\lambda,l+h}\, \Theta_{gh}\, \Theta_{ll}\, \sin\vartheta\, d\vartheta = \frac{\sqrt{3}}{2}\int_0^\pi \Theta_{\lambda,l+h}\cdot \Theta_{gh}\, \sin^2\vartheta\, d\vartheta$$

$$= \frac{\sqrt{3}}{2}\left[\frac{(g+h+1)(g+h+2)}{(2g+1)(2g+2)}\right]^{\frac{1}{2}} \delta_{\lambda,g+1} - \frac{\sqrt{3}}{2}\left[\frac{(g-h-1)(g-h)}{(2g+1)(2g-1)}\right]^{\frac{1}{2}} \delta_{\lambda,g-1} \tag{125}$$

$$\int_0^\pi \Theta_{\lambda,|h-l|}\, \Theta_{gh}\, \Theta_{ll}\, \sin\vartheta\, d\vartheta = \frac{\sqrt{3}}{2}\int_0^\pi \Theta_{\lambda,l+h}\, \Theta_{gh}\, \sin^2\vartheta\, d\vartheta$$

$$= \frac{\sqrt{3}}{2}\left[\frac{(g+h-1)(g+h)}{(2g-1)(2g+1)}\right]^{\frac{1}{2}} \delta_{\lambda,g-1} - \frac{\sqrt{3}}{2}\left[\frac{(g-h+1)(g-h+2)}{(2g+1)(2g+3)}\right]^{\frac{1}{2}} \delta_{\lambda,g+1} \tag{126}$$

These results were obtained by use of the formulas[13].

$$\sin\vartheta\, \Theta_{gh} = \left[\frac{(g+h+1)(g+h+2)}{(2g+1)(2g+3)}\right]^{\frac{1}{2}} \Theta_{g+1,h+1} - \left[\frac{(g-h-1)(g-h)}{(2g-1)(2g+1)}\right] \Theta_{g-1,h+1} \tag{127}$$

$$\sin\vartheta\, \Theta_{gh} = \left[\frac{(g+h-1)(g+h)}{(2g-1)(2g+1)}\right]^{\frac{1}{2}} \Theta_{g-1,|h-1|} - \left[\frac{(g-h+1)(g-h+2)}{(2g+1)(2g+3)}\right]^{\frac{1}{2}} \Theta_{g+1,|h-1|}$$

The ξ part of integrals (123) and (124) is identical with the integrals (112) and (117) which have already been evaluated. Hence

$$H'^{r,g-1,l-h}_{n,l,l} = H'^{r,g-1,-l+h}_{n,l,-1} = E_{gh}(-1)^{g+n-r}\frac{1}{4}\left[\frac{3p(n+1)!\,(g+r-1)!(g+h-1)(g+h)}{\pi\,(2g-1)(2g+1)(n-2)!\,(r-g)!}\right]^{\frac{1}{2}} \frac{(2g+2)!}{(g+1-n+r)!\,(g+1+n-r)!}$$

$$H'^{r,g-1,l+h}_{n,l,l} = H'^{r,g-1,-l-h}_{n,l,-1} = E_{gh}(-1)^{g+n-r+1}\frac{1}{4}\left[\frac{3p(n+1)!\,(g+r-1)!(g-h-1)(g-h)}{\pi\,(2g-1)(2g+1)(n-2)!\,(r-g)!}\right]^{\frac{1}{2}} \frac{(2g+2)!}{(g+1-n+r)!\,(g+1+n-r)!}$$

$$H'^{r,g+1,l-h}_{n,l,l} = H'^{r,g+1,-l+h}_{n,l,-1} = E_{gh}(-1)^{g+n-r+1}\frac{1}{2}\left[\frac{3p(g-h+1)(g-h+2)(n-2)!\,(g+l+r)!}{\pi\,(2g+1)(2g+3)(n+1)!\,(r-g-2)!}\right]^{\frac{1}{2}} \frac{(2g+1)!\,[n(g+2)-r]}{(g+1-n+r)!\,(g+1+n-r)!}$$

$$H'^{r,g+1,1+h}_{n,1,1} = H'^{r,g+1,-1-h}_{n,1,-1} = E_{gh}\,(-1)^{g+n-r}\,\frac{1}{2}\left[\frac{3p(g+h+1)(g+h+2)(n-2)!\,(g+1+r)!}{\pi\,(2g+1)(2g+3)(n+1)!\,(r-g-2)!}\right]^{1/2}\frac{(2g+1)!\,[h(g+2)-r]}{(g+1+n-r)!\,(g+1-n+r)!}$$

$$(128)$$

Each of these is for a cosine term in V_{gh}; the value for the corresponding sine term is obtained by multiplying $H'^{r,g\pm1,(1\pm h)}_{n,1,1}$ or $H'^{r,g\pm1,(-1\pm h)}_{n,1,-1}$ by $\mp i$, the $\mp$ signs being correlated with the $\pm$ sign on h. When h = 0 only two of these four integrals exist.

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11. The author is indebted to Mr. Simon Pasternack for recognizing this fact.

12. See for example E. T. Copson, "Functions of a Complex Variable," 1st ed., p. 249, Clarendon Press, Oxford, 1935.

13. The derivation of these formulas may be found in a treatise on the theory of surface harmonics.

The Molecular Structures of the Bromomethanes,

Boron Trimethyl, and Three Boron Trihalides

Introduction.   The determination of molecular structures of
gas molecules by electron diffraction was first carried out
in 1931 by R, Wierl[1]. During the relatively short time which
has elapsed since this date the method has been applied to
several hundred substances, with several investigat*ors* active
in the field. One of these, L. O. Brockway, has given a com-
prehensive review[2] of the method,its history and its applica-
tions.

During the investigations presented in the following
pages, the author had the pleasure of working with Dr. Brockway
and the use of his apparatus.

1. R. Wierl, Ann. d.Physik 8, 521 (1931)

2. L. O. Brockway, Rev. Mod. Phys. 8, 231 (1936)

The Molecular Structures of the Bromomethanes

By Henri A. Lévy and L. O. Brockway

The investigation of the molecular structures of the halogen substituted methanes has been undertaken in these Laboratories as a means of testing the constancy of chemical bond lengths and of determining the bond radii and the variations in bond angles in unsymmetrical molecules. The results of the investigations on the fluoro-, chloro- and fluorochloromethanes already have been reported.[1] Using the experimental procedure which has been described in detail elsewhere,[2] we have applied the electron diffraction method of studying molecular structures to the bromomethanes, obtaining the results which are reported in this paper.
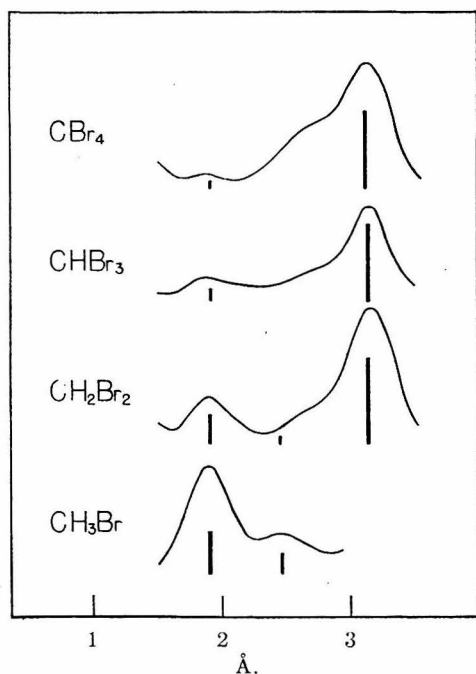

Fig. 1.—Radial distribution curves for the bromomethanes. The tall peaks near 3 Å. represent the Br–Br distances; those near 2 Å. the C–Br distances.

The electron wave length was 0.0611 Å. and the camera distance was near 10.5 cm. The diameters of the maxima and minima appearing in the photographs were measured visually, and

(1) L. E. Sutton and L. O. Brockway, This Journal, **57**, 473 (1935); L. O. Brockway, J. Phys. Chem., **41**, 185, 747 (1937).

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the corresponding S_0 values (equal to $4\pi(\sin \theta/2)/\lambda$), where θ is the angle of scattering and λ is the electron wave length, are tabulated below for each substance. These were combined with the visually estimated intensities (shown under the column heading I) to give the observed radial distribution of scattering matter shown by the curves in Fig. 1. The "calculated S" values are taken from the theoretical scattering curves in Figs. 2 and 3.

Carbon Tetrabromide.—Photographs of carbon tetrabromide vapor were taken with a sample of the Eastman preparation heated to 115 to 130°. The pattern contains seven extraordinarily sharp, evenly-spaced rings. The radial distribution function (Fig. 1) shows a sharp peak at 3.13 Å., corresponding to the Br–Br separation, together with smaller, less reliable peaks at shorter distances. The theoretical scattering curve (Fig. 2) based on a regular tetrahedral arrangement of four bromine atoms around a central carbon atom with an assumed C–Br distance of 1.91 Å. shows excellent agreement with the photographs. The quantitative comparison in Table I and the radial distribution curve lead to final values of C–Br = 1.91 ± 0.02 Å. and Br–Br = 3.12 ± 0.03 Å.

TABLE I
CARBON TETRABROMIDE

Max.	Min.	I	S_0	$S_{calcd.}$	$S_{calcd.}/S_0$
1		12	2.662	2.49	(0.936)
	2		3.615	3.48	(.973)
2		15	4.528	4.49	.992
	3		5.597	5.51	.984
3		12	6.525	6.58	1.008
	4		7.514	7.56	1.006
4		10	8.464	8.51	1.005
	5		9.507	9.51	1.000
5		12	10.51	10.59	1.007
	6		11.56	11.62	1.005
6		5	12.49	12.58	1.007
	7		13.56	13.56	1.000
7		4	14.49	14.54	1.003

Mean 1.002

Br–Br 3.12 Å.

C–Br 1.91 Å.

In an earlier investigation, Wierl[3] obtained a

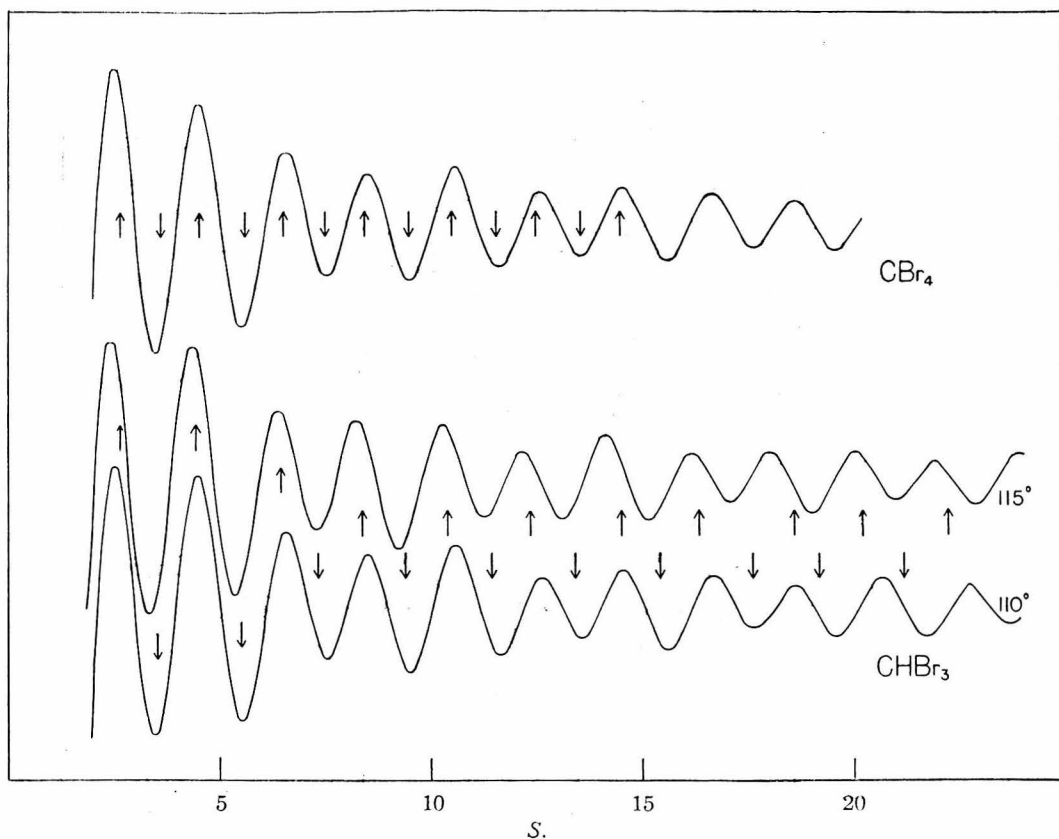(3) R. Wierl, Ann. Physik, **8**, 521 (1931).

Fig. 2.—Theoretical scattering curves for carbon tetrabromide and tribromomethane.

value of 2.05 Å. for the C–Br distance from photographs showing only three maxima. More recently de Laszlo[4] reported in a brief note a distance of 1.93 Å.

Tribromomethane.—The vapor of tribromomethane (Eastman) was photographed at a temperature of 75 to 100°. Eleven rings are observed on the photographs, whose pattern resembles that of carbon tetrabromide in general appearance. The radial distribution curve (Fig. 1) has a sharp peak due to the Br–Br interaction at 3.14 Å. and a smaller one due to the C–Br interaction at about 1.88 Å. Theoretical scattering curves were calculated for three models each having an assumed C–Br distance of 1.91 Å. and with Br–C–Br angles of 110, 112, and 115°, respectively. Because of the small scattering power of the carbon atom relative to the three bromine atoms the curves are determined chiefly by the positions of the bromine atoms; accordingly the three curves are indistinguishable except for the change in scale corresponding to the change in the assumed Br–Br separation. On

(4) H. de Laszlo, *Nature*, **135**, 474 (1935).

comparison with the observed maxima and

TABLE II
TRIBROMOMETHANE

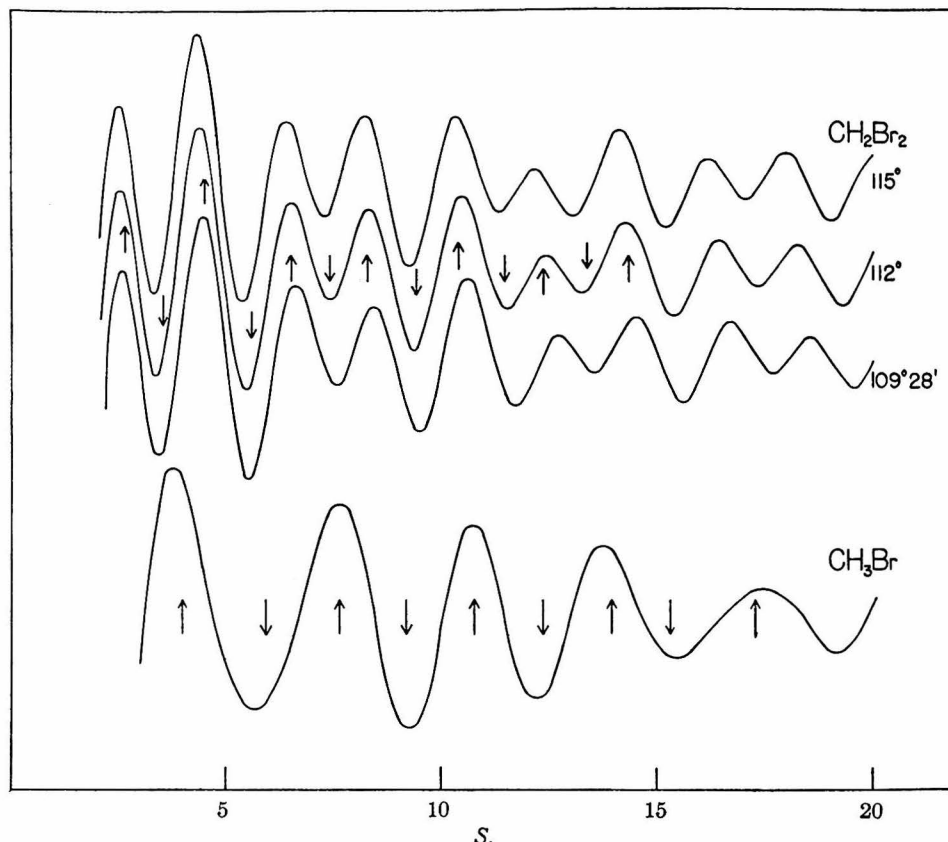| Max.	Min.	I	S_0	$S_{calcd.}$	$S_{calcd.}/S_0$
1		8	2.693	2.48	(0.921)
	2		3.563	3.39	(.952)
2		12	4.480	4.40	.983
	3		5.570	5.46	.981
3		8	6.519	6.48	.994
	4		7.419	7.41	.998
4		7	8.459	8.36	.989
	5		9.477	9.38	.990
5		9	10.48	10.43	.995
	6		11.53	11.44	.992
6		6	12.45	12.38	.994
	7		13.51	13.31	.986
7		6	14.41	14.31	.994
	8		15.53	15.37	.990
8		3	16.45	16.40	.996
	9		17.45	17.35	.995
9		3	18.32	18.28	.997
	10		19.32	19.29	.998
10		1	20.34	20.32	.998
	11		21.33	21.33	1.000
11		1	22.36	22.30	0.997

Mean 0.993

Br–Br 3.15 Å.

Fig. 3.—Theoretical scattering curves for dibromomethane and bromomethane.

minima (Table II) each of these curves leads to the value Br–Br = 3.15 Å.

Although the carbon–bromine distance cannot be determined directly in this molecule it is very probable that it has the same value as in carbon tetrabromide. This assumption is supported by the observed equality of the bond distances in trichloro- and tetrachloromethane and in trifluoro- and tetrafluoromethane. We accept as the final values: C–Br = 1.91 Å., Br–Br = 3.15 ± 0.03 Å. and ∠Br–C–Br = 111 ± 2°.

Wierl[5] found with the aid of photographs showing three maxima the values C–Br = 2.03 and ∠Br–C–Br = 111°. Dornte[6] obtained the values C–Br = 2.05 and ∠Br–C–Br = 115° from five maxima.

Dibromomethane.—Photographs of dibromomethane (Eastman) were obtained on which seven well-defined maxima are observed. Of these the second is much stronger than the first, while the fifth and the seventh are each a little stronger than the fourth and sixth maxima, respectively. The

radial distribution curve (Fig. 1) shows a strong reliable peak at 3.16 Å., the Br–Br distance.

Theoretical curves (Fig. 3) were calculated for four models. The C–Br distance was taken as 1.91 Å., the C–H distance 1.05 Å., the H–C–H angle 109°28′ and the Br–C–Br angle 109°28′, 112, 115, and 118°, respectively. As the angle is increased the model becomes unsatisfactory because the fourth maximum becomes too strong, rising above the third and fifth, and the sixth maximum becomes too weak in comparison with the fifth and seventh. For these reasons it is improbable that the angle is greater than 112°. On the other hand, the sixth and seventh maxima in the curve for the 109°28′ model are not so well set off from each other as they are in the photographs. The most probable value of the Br–C–Br angle is accordingly 112 ± 2°.

The S values for the 112° model are shown in Table III; comparison of these with the S_0 values gives a Br–Br distance of 3.17 ± 0.02 Å., in agreement with the position of the strong peak in the radial distribution curve. The C–Br distance is 1.91 ± 0.02 Å.

(5) R. Wierl, *Ann. Physik*, **13**, 453 (1932).
(6) R. W. Dornte, *J. Chem. Phys.*, **1**, 630 (1933).

TABLE III

DIBROMOMETHANE

Max.	Min.	I	S_0	$S_{calcd.}$ 112°	$S_{calcd.}/S_0$
1		5	2.641	2.50	(0.947)
	2		3.538	3.34	(.944)
2		10	4.507	4.37	(.970)
	3		5.597	5.47	(.977)
3		8	6.517	6.51	.999
	4		7.399	7.40	1.000
4		6	8.275	8.29	1.002
	5		9.407	9.34	0.993
5		7	10.40	10.47	1.007
	6		11.47	11.53	1.005
6		2	12.37	12.44	1.005
	7		13.38	13.23	0.989
7		3	14.32	14.25	.995

Mean 0.999

Br–Br 3.17 Å.

C–Br 1.91 Å.

Dornte[6] reported C–Br = 2.05 Å. and ∠ Br–C–Br = 125°. The discrepancy between this result and ours is probably due in part to the smaller number of maxima which he observed.

Bromomethane.—Bromomethane was prepared from methanol and hydrobromic acid and was fractionated at 0°. The photographs show five rather diffuse rings. The poor definition in the pattern is due to the presence in the molecule of one atom whose scattering power is much larger than that of all the other atoms.

The radial distribution curve shows one peak at 1.90 Å. The theoretical curve calculated for

TABLE IV

BROMOMETHANE

Max.	Min.	I	S_0	$S_{calcd.}$	$S_{calcd.}/S_0$
1		12	3.997	3.76	(0.942)
	2		5.942	5.67	(.954)
2		12	7.626	7.64	1.002
	3		9.186	9.20	1.000
3		10	10.77	10.74	0.998
	4		12.35	12.16	1.005
	4		13.94	13.74	0.986
4	5		15.30	15.44	1.010
5	2		17.28	17.60	1.018

Mean 0.999

C–Br 1.91 Å.

a methyl group with tetrahedral angles and C–H distances of 1.05 Å. and for a C–Br distance of 1.91 Å. gives on comparison with the photographs (Table IV) an observed distance C–Br = 1.91 ± 0.06 Å. The large estimated probable error is assigned because of the difficulty of making precise measurements on the photographs. Dornte[6] reported C–Br = 2.06 Å.

Discussion

The results for the bromomethanes are collected in Table V with assumed values given in parentheses.

TABLE V

Substance	C–Br, Å.	Br–Br, Å.	∠ Br–C–Br
CBr$_4$	1.91 ± 0.02	3.12 ± 0.03	(109°28′)
CHBr$_3$	(1.91)	3.15 ± 0.03	111 ± 2°
CH$_2$Br$_2$	1.91 ± 0.02	3.17 ± 0.03	112 ± 2°
CH$_3$Br	1.91 ± 0.06		

The observed C–Br bond distances are for all the substances equal to the sum of the single bond covalent radii[7] for carbon and bromine, 1.91 Å. The Br–C–Br bond angles show only small increases in tri- and dibromomethane above the tetrahedral angle which occurs in the symmetrical tetrabromide. This increase is of the same order as that found in the chloromethanes. The increased repulsion between the halogen atoms which might be expected in comparing the bromine and the chlorine compounds evidently is offset by the greater separation between the bromine atoms due to the larger bond distances; the bond angle is not appreciably affected when bromine is substituted for chlorine.

Summary

The molecular structures of the bromomethanes have been investigated by means of electron diffraction. The C–Br distance in each compound is 1.91 Å.; the Br–C–Br angle is 109°28′ in carbon tetrabromide, 111° in tribromomethane and 112° in dibromomethane.

(7) L. Pauling and M. L. Huggins, Z. Krist., **87**, 205 (1934).

The Molecular Structures of Boron Trimethyl, Trifluoride, Trichloride, and Tribromide. The Covalent Radius of Boron

By Henri A. Lévy and L. O. Brockway

The molecular structures of the compounds of boron are of special interest because the unusual number of electrons occurring in many of them suggests that their structures may be different from those of corresponding compounds of the other non-metallic elements of the first row of the periodic table. Because of the anomalous electronic structures of the stable hydrides due to the lack of enough electrons to form electron-pair bonds throughout the respective molecules, other compounds of boron were chosen in the hope of determining a characteristic single bond covalent radius for comparison with the radii of other elements. Although boron in its normal valence compounds (in which it is coördinated with three univalent atoms or groups) has only six electrons around it in place of the octet found in the normal valence compounds of the following first row elements, the number of electrons in the BX_3 compounds is sufficient for the formation of electron pair bonds. In particular, boron trimethyl was investigated because the methyl derivatives

of a number of non-metallic elements have previously been found to contain single covalent bonds.[1] In addition we have investigated boron trifluoride, trichloride, and tribromide.
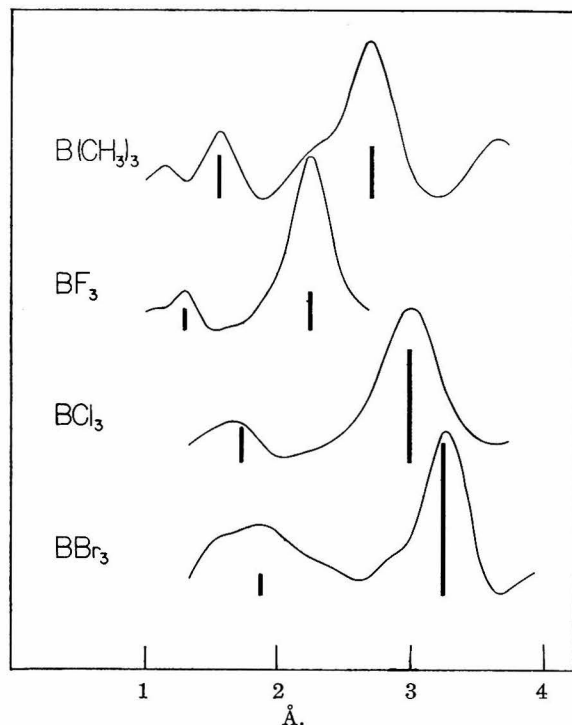

Fig. 1.—Curves showing the observed radial distributions of scattering matter. The vertical lines mark the interatomic distances as determined by comparison of the photographs with theoretical scattering curves.

The vapors of these substances were used in obtaining electron diffraction patterns by the known procedure[2] with an electron wave length of 0.0611 Å. and a camera distance near 10.5 cm. Photographs were obtained showing from six to ten apparent maxima which were measured visually. The corresponding s_0 values (equal to $4\pi (\sin \theta/2)/\lambda$ where θ is the angle of scattering and λ the electron wave length) are tabulated for each compound, and they were combined with the visually estimated intensities (shown under the columns headed I) to give the observed radial distributions of scattering matter shown by the curves in Fig. 1. The tables also show the comparison of the s with the "calculated s_0" values (taken from the theoretical scattering curves in Figs. 2–5) to give observed molecular dimensions.

Boron Trimethyl.—From a sample of boron trimethyl prepared by Dr. A. Burg of the Uni-

(1) L. O. Brockway and H. O. Jenkins, THIS JOURNAL, **58**, 2036 (1936).

(2) L. O. Brockway, *Rev. Modern Physics*, **8**, 231 (1936).

versity of Chicago, photographs were obtained showing a pattern of six well-defined rings which is well represented by the 120° curve in Fig. 2. The characteristic features used in distinguishing among the various molecular models are the following. The third and fourth maxima are about equal in intensity, and are resolved by a distinct minimum. The fifth maximum, slightly more intense than those preceding, is followed by a "shelf," whose intensity is about equal to that of the following (sixth) maximum. The radial distribution function (Fig. 1) shows sharp peaks at 2.69 Å., assigned to the C–C distance, and at 1.57 Å., corresponding to the B–C distance, together with other less reliable humps. Theoretical scattering curves (Fig. 2) were calculated for plane and pyramidal arrangements of tetrahedral methyl groups with C–H = 1.05 Å. about a central boron atom; approximation to free rotation of methyl groups was achieved by averaging configurations differing by methyl group rotations of 60°, a procedure which has been shown in this Laboratory to be satisfactory. A B–C distance of 1.53 Å. and C–B–C angles of 120, 118, 116, and 110° were assumed. That the 110° model is unsatisfactory is evident in that the corresponding curve shows a "shelf" following the third peak instead of the fifth. Inasmuch as the 116° curve shows the fourth peak weaker than the third and the fifth resolved from the hump following it, it is likely that the boron bond angle is larger than 116°. Furthermore, since the sixth peak appears too intense compared to the shelf in the 116 and 118° models, we feel that the photographic evidence favors the 120° model.

TABLE I
BORON TRIMETHYL

Max.	Min.	I	s_0	$s_{calcd.}$ 120°	$s_{calcd.}/s_0$
1		5	3.072	2.58	(0.840)
	2		4.178	3.79	(.907)
2		10	5.351	5.40	1.009
	3		6.470	6.60	1.020
3		7	7.577	7.70	1.016
	4		8.43	8.70	1.032
4		7	9.51	9.63	1.012
	5		10.98	11.10	1.003
5		8	12.35	12.78	1.035
5a		4	14.14	14.47	1.023
	6		15.70	15.90	1.013
6		4	16.92	17.38	1.027

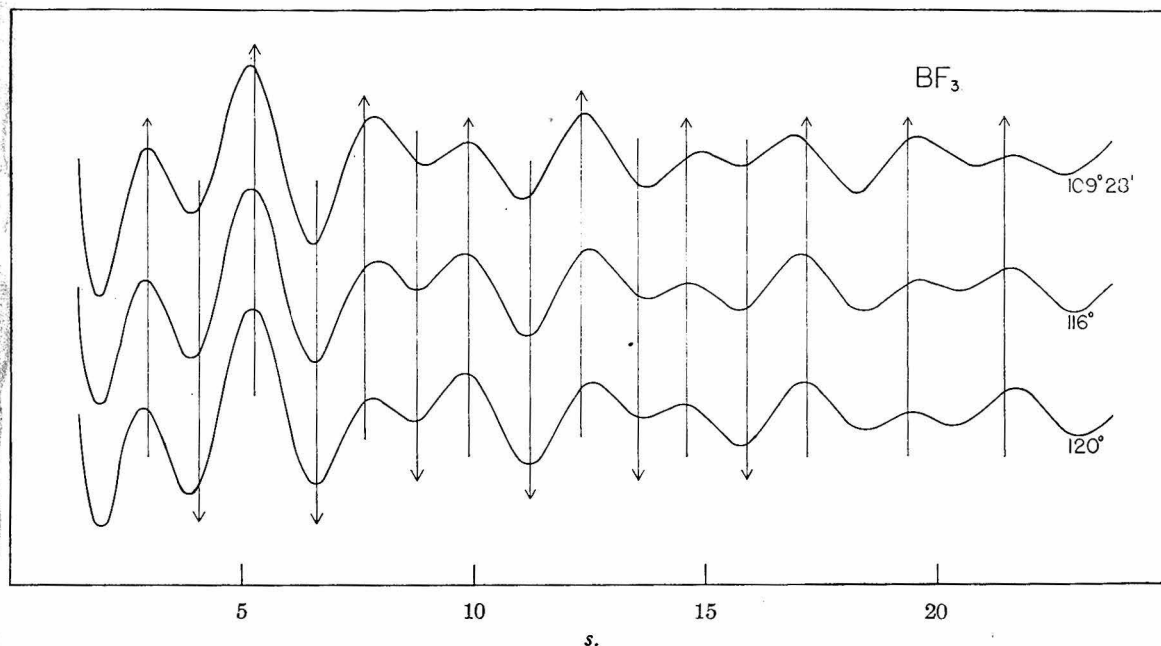Mean 1.019

C–C = 2.70 Å.

B–C = 1.56 Å.

Fig. 3.—Theoretical electron scattering curves for boron trifluoride.

tion of Badger's rule to the force constant from infrared data gives 1.33 Å., for the B–F distance.

<div align="center">

TABLE II

BORON TRIFLUORIDE

</div>

Max.	Min.	I	s_0	$s_{calcd.}$ 120°	$s_{calcd.}/s_0$
1		8	3.259	3.16	(0.969)
	2		4.446	4.21	(.946)
2		12	5.748	5.69	.990
	3		7.232	7.21	.997
3		7	8.403	8.58	1.021
	4		9.610	9.49	0.988
4		8	10.81	10.71	.991
	5		12.23	12.20	.997
5		5	13.45	13.71	1.020
	6		14.82	14.94	1.009
6		2	15.96	15.87	0.995
	7		17.37	17.21	.991
7		4	18.59	18.70	1.007
8		1	21.13	21.28	1.007
9		1	23.45	23.70	1.011

<div align="right">

Mean 1.002

F–F 2.25 Å.

B–F 1.30 Å.

</div>

Boron Trichloride.—Photographs of boron trichloride obtained with a sample of Kahlbaum's c. p. preparation showed nine well-defined uniformly spaced rings. The radial distribution curve (Fig. 1) shows a tall, sharp peak at 2.99 Å., assigned to the Cl–Cl distance, with a small, less reliable peak at a shorter distance. Theoretical scattering curves (Fig. 4) were calculated for

plane and pyramidal arrangements of chlorine atoms around a central boron, assuming a Cl–Cl distance of 3.00 Å. and a Cl–B–Cl angle of 120, 118, 116, 110, and 90°. As the angle is decreased, the fourth maximum drops below the third and fifth, contrary to the appearance of the photographs, where the third and fourth are equal, with the fifth weaker. In addition, the resolution of the sixth and seventh peaks becomes less distinct than that of the fifth and sixth in the smaller angle models, whereas in the photographs the reverse is true. These features make it improbable that the angle is less than 116°, and favor the planar configuration. The quantitative comparison shown in Table III together with the radial distribution result leads to the final values Cl–Cl = 2.99 ± 0.03 Å., B–Cl = 1.73 ± 0.02 Å., < Cl–B–Cl = 120° (within 3°). A previous electron diffraction investigation[6a] of this compound by Wierl[7] resulted in the value 3.03 ± 0.05 Å. for the Cl–Cl distance, with the configuration undetermined. The zero value obtained in the measurement of the dipole moment in benzene solution[8] supports the planar structure, as do also Raman spectral data.[5] From the latter, with the

(6a) The electron-diffraction value 1.76 ± 0.02 Å. for the B–Cl distance in BCl₃ has been reported, since our work was submitted for publication, by Gregg, Hampson, Jenkins, Jones and Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

(7) R. Wierl, *Ann. Physik*, **8**, 521 (1931).

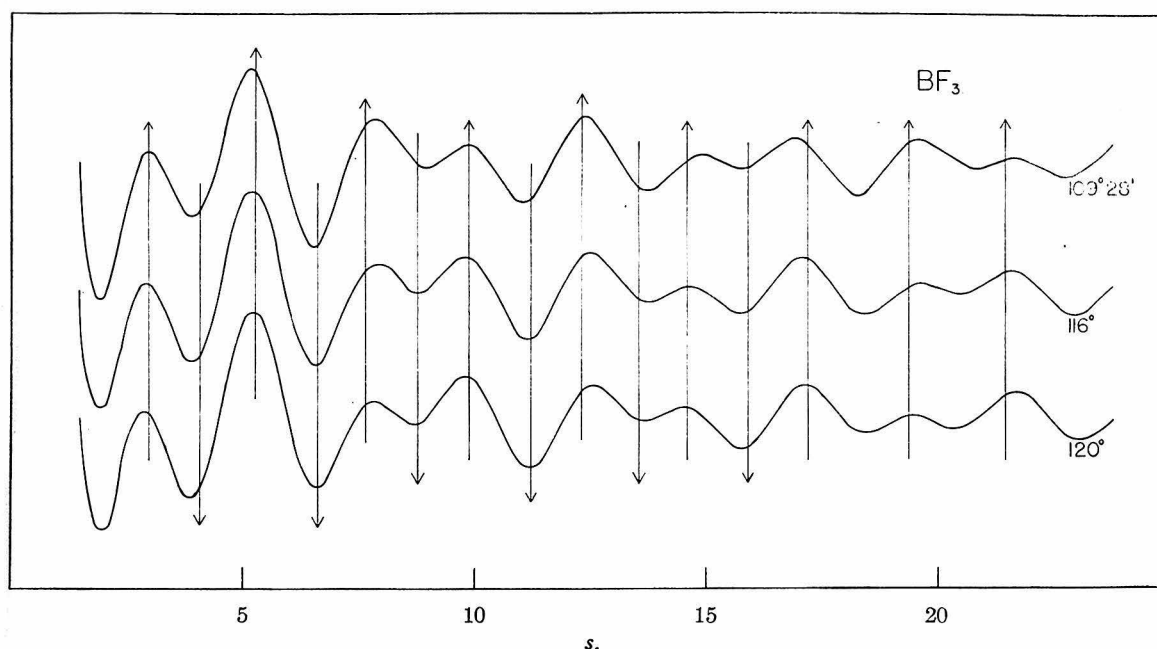(8) H. Ulich and W. Nespital, *Z. Elektrochem.*, **37**, 559 (1931).

Fig. 3.—Theoretical electron scattering curves for boron trifluoride.

tion of Badger's rule to the force constant from infrared data gives 1.33 Å., for the B–F distance.

TABLE II
BORON TRIFLUORIDE

Max.	Min.	I	s_0	$s_{calcd.}$ 120°	$s_{calcd.}/s_0$
1		8	3.259	3.16	(0.969)
	2		4.446	4.21	(.946)
2		12	5.748	5.69	.990
	3		7.232	7.21	.997
3		7	8.403	8.58	1.021
	4		9.610	9.49	0.988
4		8	10.81	10.71	.991
	5		12.23	12.20	.997
5		5	13.45	13.71	1.020
	6		14.82	14.94	1.009
6		2	15.96	15.87	0.995
	7		17.37	17.21	.991
7		4	18.59	18.70	1.007
8		1	21.13	21.28	1.007
9		1	23.45	23.70	1.011

Mean 1.002

F–F 2.25 Å.

B–F 1.30 Å.

Boron Trichloride.—Photographs of boron trichloride obtained with a sample of Kahlbaum's c. p. preparation showed nine well-defined uniformly spaced rings. The radial distribution curve (Fig. 1) shows a tall, sharp peak at 2.99 Å., assigned to the Cl–Cl distance, with a small, less reliable peak at a shorter distance. Theoretical scattering curves (Fig. 4) were calculated for plane and pyramidal arrangements of chlorine atoms around a central boron, assuming a Cl–Cl distance of 3.00 Å. and a Cl–B–Cl angle of 120, 118, 116, 110, and 90°. As the angle is decreased, the fourth maximum drops below the third and fifth, contrary to the appearance of the photographs, where the third and fourth are equal, with the fifth weaker. In addition, the resolution of the sixth and seventh peaks becomes less distinct than that of the fifth and sixth in the smaller angle models, whereas in the photographs the reverse is true. These features make it improbable that the angle is less than 116°, and favor the planar configuration. The quantitative comparison shown in Table III together with the radial distribution result leads to the final values Cl–Cl = 2.99 ± 0.03 Å., B–Cl = 1.73 ± 0.02 Å., < Cl–B–Cl = 120° (within 3°). A previous electron diffraction investigation[6a] of this compound by Wierl[7] resulted in the value 3.03 ± 0.05 Å. for the Cl–Cl distance, with the configuration undetermined. The zero value obtained in the measurement of the dipole moment in benzene solution[8] supports the planar structure, as do also Raman spectral data.[5] From the latter, with the

(6a) The electron-diffraction value 1.76 ± 0.02 Å. for the B–Cl distance in BCl₃ has been reported, since our work was submitted for publication, by Gregg, Hampson, Jenkins, Jones and Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

(7) R. Wierl, *Ann. Physik*, **8**, 521 (1931).

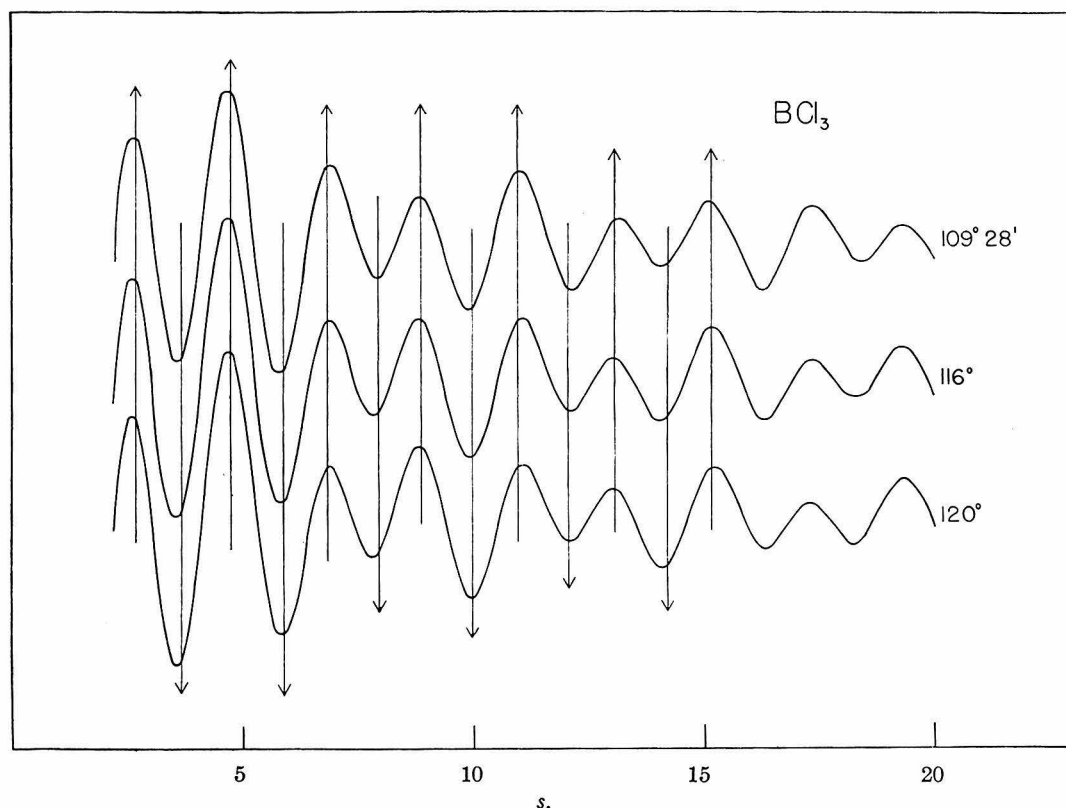(8) H. Ulich and W. Nespital, *Z. Elektrochem.*, **37**, 559 (1931).

Fig. 4.—Theoretical electron scattering curves for boron trichloride.

aid of Badger's rule, the B–Cl distance is estimated to be 1.72 Å.

TABLE III
BORON TRICHLORIDE

Max.	Min.	I	s_0	$s_{calcd.}$ 120°	$s_{calcd.}/s_0$
1		14	2.678	2.59	(0.968)
	2		3.645	3.53	(.968)
2		22	4.733	4.67	.987
	3		5.906	5.82	.985
3		11	6.837	6.88	1.006
	4		7.949	7.78	0.979
4		13	8.877	8.80	.991
	5		9.987	9.93	.994
5		6	10.99	11.09	1.009
	6		12.08	12.09	1.001
6		2	13.08	12.99	0.993
	7		14.25	14.07	1.988
7		3	15.19	15.21	1.001

Mean 0.994

Cl–Cl 2.98 Å.
B–Cl 1.72 Å.

Boron Tribromide.—A sample of boron tribromide redistilled from mercury gave photographs of fair quality with a pattern of ten rings more closely spaced but otherwise similar to that of boron trichloride. The radial distribution curve (Fig 1.) shows a tall, sharp peak at 3.27 Å., assigned to the Br–Br distance. Theoretical

TABLE IV
BORON TRIBROMIDE

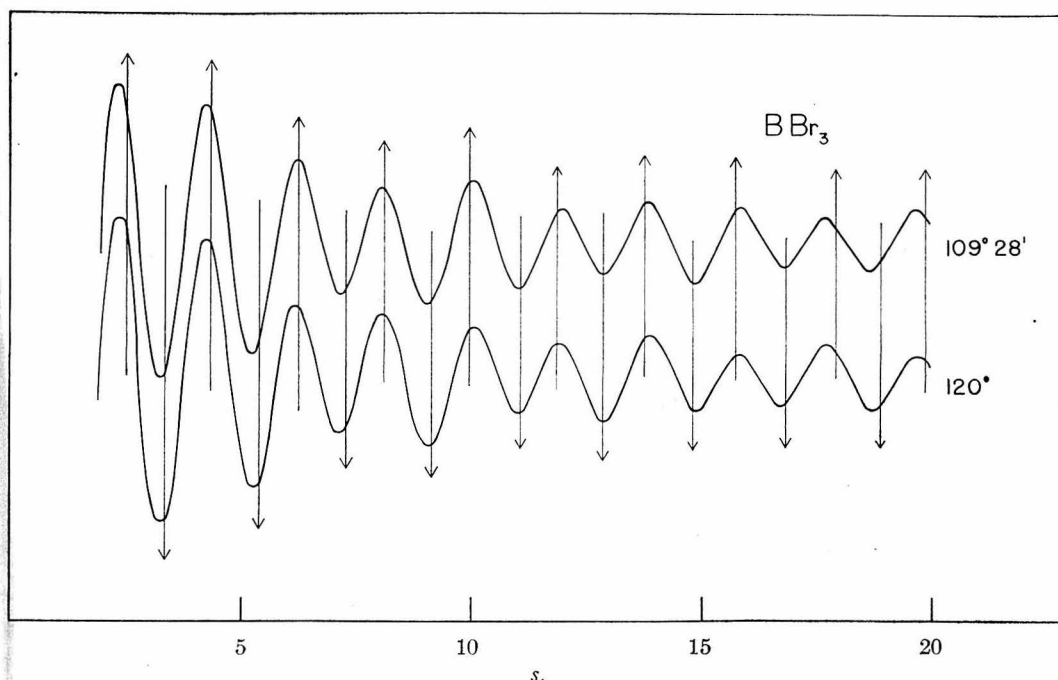| Max.	Min.	I	s_0	$s_{calcd.}$ 120°	$s_{calcd.}/s_0$
1		3	2.567	2.45	(0.954)
	2		3.400	3.29	(.968)
2		12	4.383	4.29	.979
	3		5.447	5.30	.973
3		10	6.296	6.21	.986
	4		7.335	7.18	.979
4		10	8.175	8.11	.992
	5		9.182	9.11	.992
5		8	9.999	10.11	1.011
	6		11.11	11.06	0.995
6		6	11.92	11.96	1.004
	7		12.91	12.91	1.000
7		6	13.80	13.92	1.009
	8		14.86	14.91	1.003
8		2	15.78	15.86	1.005
	9		16.89	16.74	0.991
9		1	17.97	17.75	.988
	10		18.94	18.72	.988
10		½	19.96	19.70	.987

Mean 0.993

Br–Br 3.24 Å.
B–Br 1.87 Å.

Fig. 5.—Theoretical electron scattering curves for boron tribromide.

scattering curves (Fig. 5) were calculated for models having a Br–Br distance of 3.27 Å. and a Br–B–Br angle of 120, 115, and 109°28′. Because of the large scattering power of bromine in comparison to boron, the two former curves are practically identical; in the latter, however, the fourth maximum falls below the third and fifth, whereas in the photographs the third and fourth appear equal with the fifth weaker. The angle is therefore larger than tetrahedral and is quite probably 120° as in the three compounds previously discussed. The final quantitative results are Br–Br = 3.25 ± 0.03 Å., B–Br = 1.87 ± 0.02 Å., < Br–B–Br = 120° (within 6°).

Raman spectral data[5] are consistent with the planar configuration; with the aid of Badger's rule they lead to a B–Br distance of 1.85 Å.

Discussion

The results of the electron diffraction investigation of these compounds are collected in Table V.

TABLE V

Substance	X–X distance, Å.	B–X distance, Å.
B(CH₃)₃	2.70 ± 0.03	1.56 ± 0.02
BF₃	2.25 ± .03	1.30 ± .02
BCl₃	2.99 ± .03	1.73 ± .02
BBr₃	3.25 ± .03	1.87 ± .02

The observed B–C distance of 1.56 Å. in boron trimethyl combined with the carbon single bond covalent radius,[9] 0.77 Å., leads to a value for the radius of boron of 0.79 Å. This value is to be compared with 0.89 Å., obtained by extrapolation of the radii of oxygen, nitrogen and carbon. The large discrepancy between the two, amounting to 0.10 Å., raises the question of what is represented by the extrapolated value. As has been pointed out to us by Professor Pauling, the radius values used in the extrapolation correspond to atoms having complete octets of electrons; and the value 0.89 Å. for boron presumably represents the single bond radius when the boron atom has associated with it four pairs of electrons. In boron trimethyl, on the other hand, the boron atom has only three electron pairs occupying a set of three equivalent planar orbitals probably arising from hybridization of sp^2. The larger relative contribution of the s orbital in bonds of this type as compared with the tetrahedral sp^3 bonds observed in oxygen, nitrogen and carbon would lead to a smaller bond radius. Accordingly, the discrepancy observed may well be due to a fundamental difference in bond type, the radius of 0.79 Å. being associated with boron surrounded by six electrons occupying hybridized sp^2 orbitals and that of 0.89 Å. associated with boron surrounded by a complete octet of electrons in sp^3 orbitals.

(9) L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 1223 (1937).

TABLE VI

Substance	Bond distance, Å.			Boron single bond radius, Å.	Remarks
$B(CH_3)_3$	B–C = 1.56	±	0.02	0.79	sp^2 bond type
Extrapolated from O, N, C radii				.89	sp^3 bond type
BCl_3	B–Cl = 1.73	±	.02	.89	Graphite type resonance assumed
BBr_3	B–Br = 1.87	±	.02	.89	Graphite type resonance assumed
BF_3	B–F = 1.30	±	.02	(.77)	Graphite type resonance assumed
$B_3N_3H_6$	B–N = 1.44	±	.02	.89	Benzene type resonance assumed
BN	B–N = 1.45	±	.01	.87	Graphite type resonance assumed
$BH_3N(CH_3)_3$	B–N = 1.62	±	.15	.92	
B_2H_6	B–B = 1.86	±	.04	.93	
B_5H_9	B–B = 1.76	±	.02	.88	
CaB_6	B–B = 1.716	±	.004	.86	
BH_3CO	B–C = 1.57	±	.03	.80	sp^3 state for carbon
				.88	Resonance with sp^2 state

If we accept the value 0.89 Å. for the tetrahedral radius, a satisfactory explanation of both bond distances and molecular configurations in boron trichloride and boron tribromide is possible. Resonance among the three Lewis structures of the type

$$
\begin{array}{c}
: \ddot{X}^{+} \\
: \overset{\cdots}{B}^{-} : \\
: \ddot{X} \qquad : X :
\end{array}
$$
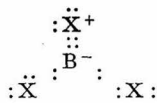
would give each B–X bond one-third double and two-thirds single bond character, sp^3 quantization being necessary to provide for the four bond orbitals. Such resonance would constrain the atoms to a coplanar configuration with 120° bond angles, as in graphite and carbonate ion. While some contribution might be made by the structure having three single bonds on boron, the loss of the energy of the extra bond would make this structure relatively less important; and a small contribution would have no effect on the bond distance because the sp^2 bonds in this structure would have a length only slightly greater than that of the bonds in the proposed resonating molecule. Applying the relation between bond distance and double bond character,[9,10] we find that the distances 1.73 and 1.87 Å. observed in the chloride and bromide, respectively, both lead to a value of 0.89 Å. for the single bond tetrahedral radius of boron.

The extremely short bond distance in boron trifluoride under the foregoing assumptions corresponds to a boron radius of 0.77 Å. It is very probable that the structure of the fluoride requires another explanation since abnormally short bond distances are observed in other fluorides as well, e. g., silicon tetrafluoride and phosphorus trifluoride.[11]

Other boron compounds which have been investigated are shown together with the above results in Table VI. In $B_3N_3H_6$[12] the molecule undoubtedly has the electronic structure of benzene and the observed B–H distance of 1.44 ± 0.02 Å. corresponds to a single bond boron radius of 0.89 Å. The boron nitride crystal has been found[12a] to have a graphite-like structure with B–N = 1.45 ± 0.01 Å., corresponding to a single bond boron radius of 0.87 Å. The single bond B–N distance in $BH_3N(CH_3)_3$[13] is combined with the nitrogen radius 0.70 Å. to give a boron radius of 0.92 Å. The boron–boron distances observed in B_2H_6[14] and B_5H_9[15] are treated as single bonds to give radii of 0.93 and 0.88 Å., respectively. It should be noted that in the latter substance one of the five boron atoms forms only three bonds while the others each form four, and the average boron radius observed is perhaps 0.03 or 0.04 Å. smaller than it would be if all of the atoms were of the tetrahedral type. In CaB_6[16] each boron forms five bonds with an observed boron–boron separation of 1.716 ± 0.004 Å.

The boron–carbon distance 1.57 ± 0.03 Å. observed in BH_3CO[13] combined with the tetrahedral radius for carbon gives a boron radius of 0.80 Å. On the other hand, the carbon–oxygen distance is observed to be near that in carbon monoxide, and accordingly the carbon–oxygen bond presumably involves resonance between double- and triple-bonded structures. In the structure having a double bond between carbon and oxygen the carbon atom is holding only three electron pairs, and in accordance with the suggestion made

(10) L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, **57**, 2705 (1935).

(11) L. O. Brockway and F. T. Wall, ibid., **56**, 2373 (1934).

(12) S. H. Bauer, paper submitted to THIS JOURNAL.

(12a) O. Hassel, Norsk Geol. Tidsskrift, **9**, 266 (1926).

(13) S. H. Bauer, THIS JOURNAL, **59**, 1804 (1937).

(14) S. H. Bauer, ibid., **59**, 1096 (1937).

(15) S. H. Bauer and L. Pauling, ibid., **58**, 2403 (1936).

(16) L. Pauling and S. Weinbaum, Z. Krist., **87**, 181 (1934).

above in the case of boron trimethyl the carbon radius in this structure would be about 0.10 Å. less than the tetrahedral radius. In resonance with the triple-bonded structure the carbon–oxygen distance would be unaffected, but the single bond distance between tetrahedral boron and carbon atoms would be decreased by about 0.08 Å. With this allowance the observed boron–carbon distance gives a boron radius of 0.88 Å.

The values for the boron radius listed in Table VI lie within 0.04 Å. of 0.89 Å. with two exceptions. In the first, boron trimethyl, the bonds are of a different type from those in the other compounds; and in the second, boron trifluoride, the anomalies observed in other fluorides make it difficult to interpret the observed distance with any assurance. The general agreement among the other data lends support to the value first obtained by extrapolation from the other first row elements. In the three compounds in which boron–boron distances have been observed there exists an insufficient number of electrons to form electron-pair bonds in every bond position. While this deficiency undoubtedly affects the character of the bonds, it is not evident that the bond distances are materially affected since the average of the three observed radii is 0.89 Å.

Summary

The electron diffraction investigation of the molecular structures of boron trimethyl, trifluoride, trichloride, and tribromide shows that these molecules are planar with the distances B–C = 1.56 ± 0.02 Å., B–F = 1.30 ± 0.02 Å., B–Cl = 1.73 ± 0.02 Å., and B–Br = 1.87 ± 0.02 Å., respectively.

These data together with those from six other boron compounds listed in Table VI support a value of 0.89 Å. for the single bond radius of boron surrounded by an octet of electrons and of 0.79 Å. for boron with only six electrons.

Summary

A quantum mechanical treatment of the perturbing effect of a general electric field on ions with completely filled electron shells is carried out with the aid of second-order perturbation theory. The perturbing field is expressed as a sum of spherical harmonic functions; the second order perturbation energies corresponding to individual terms in the sum prove to be additive. The calculation is made first for an electron in an hydrogen-like orbital, and then is generalized by means of screening constant wave functions to apply to filled shell ions. An application to the **sodium** chloride **crystal** shows that the polarization of high order of the electron clouds of the ions in the field of the surrounding ions introduces a stabilization of about four kilocalories per mol into the lattice energy of the crystal, this value being uncertain by a factor of two or three.

The molecular structures of the bromomethanes have been investigated by means of electron diffraction. The C-Br distance in each compound is 1.91A.; the Br-C-Br angle is 109°28' in carbon tetrabromide, 111° in tribromomethane and 112° in dibromomethane.

The electron diffraction investigation of the molecular structures of boron trimethyl, trifluoride, trichloride, and tribromide shows that these molecules are planar with the distances B-C = 1.56 $\pm$ 0.02 A., B-F = 1.30 $\pm$ 0.02 A., B-Cl = 1.73 $\pm$ 0.02 A., and B-Br = 1.87 $\pm$ 0.02 A., respectively.

These data together with those from six other boron compounds listed in Table VI support a value of 0.89 A. for the

single bond radius of boron surrounded by an octet of electrons
and of 0.79 A. for boron with only six electrons.

Propositions

Submitted by   Henri A. Lévy

1. An appreciable part of the lattice energy of alkali halide crystals is due to the stabilization produced by high order polarization of the electron clouds of the ions.

2. The first and second order perturbation energies in filled shell ions produced by a perturbation not involving inter-electronic interactions are equal to the sum of the perturbation energies of the individual electrons and are independent of the hybridization of one-electron orbitals which may be assumed for the individual electrons.

3. Boron atoms with three attached groups will form four bonds if the electrons needed are available.

4. The tetrahedal covalent radius of boron with a singly negative formal charge is 0.89 ± 0.02 A.

5. The experimentally observed interatomic distances in trimethyl borine support the thesis that an atom with only a sextet of electrons about it has a covalent radius shorter than its normal tetrahedral radius with a complete octet.

6. A reasonable molecular model of ethylene oxide in agreement with observed electron diffraction data cannot be found unless the thermal vibrations of the hydrogen atoms are considered. Such vibrations should not be neglected in treating electron diffraction data of molecules with relatively large numbers of hydrogen atoms.

7. In the unsymmetrically substituted bromomethanes, the large size of the bromine atoms does not cause great spreading of the carbon-bromine bonds from tetrahedral angles.

8. The correction made for formal charges in predicting interatomic distances should not be taken as constant for all elements.

9. In the linear symmetric dihalogen substituted acetylenes the structure with a carbon to halogen double bond contributes largely to the structures of the molecules -- about twenty per cent in the case of dibromoacetylene.

10. The preparation of chlorine fluoride described by Ruff can be improved by carrying out the reaction in the presence of nitrogen.

11. The silver ion catalysed reduction of peroxysulfate ion by hydrazine proceeds by the formation of an intermediate product which is probably an argenic ion.

12. The coined term "vicinence" is a satisfactory substitute for the awkward term "coordination number" and should supplant the latter in the vocabulary of the structural chemist.

13. Investigators calculating free energy changes of chemical reactions from microscopic data should not ignore the contribution to the free energy of the entropy change accompanying the reaction. A derivation of the dependence on concentration of free energy change for perfect gases or solutes can be made by a statistical consideration of this entropy term.