

# THE QUANTUM THEORY OF THE DIELECTRIC CONSTANT OF HYDROGEN CHLORIDE AND SIMILAR GASES

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## ABSTRACT

**The quantum theory of diatomic dipoles.**—Using the treatment of Pauli, an expression for the dielectric constant of a diatomic dipole gas is obtained, in which half-quantum numbers are used. It is shown that for cases of practical interest the approximation suggested by Pauli is not valid; hence numerical values of the temperature-function  $C$  have been calculated and tabulated.

**Application to experimental measurements.**—The theory has been applied in the interpretation of Zahn's measurements of the dielectric constants of the hydrogen halides. The electric moments of molecules of hydrogen chloride, bromide, and iodide were found to be 0.3316, 0.252, and  $0.146 \times 10^{-18}$  cgsu respectively; i.e., only about one-third of the values given on the basis of the classical theory. Moreover, the values 0.00077 and 0.00102 for  $4\pi N_0\alpha$  for hydrogen chloride and bromide, in which  $\alpha$  is the coefficient of induced polarization, are shown to be in better agreement with measurements of indices of refraction than are the classical theory values. A discussion is given of possible inaccuracies in the theory, of the choice of quantum numbers, and of the possibility of weak quantization.

## INTRODUCTION

UNDER the influence of an electric field a gas whose molecules have a permanent electric moment and in addition can have a further moment induced in them by deformation becomes polarized in the direction of the field, the amount of polarization per unit volume being<sup>1</sup>

$$P = \frac{3}{4\pi} \frac{\epsilon - 1}{\epsilon + 2} F = N\mu \overline{\cos \theta} + N\alpha F, \quad (1)$$

in which  $\epsilon$  is the dielectric constant of the gas,  $F$  the strength of the applied field,  $N$  the number of molecules in unit volume,  $\mu$  the permanent electric moment of a molecule, and  $\alpha$  the coefficient of induced polarization of a molecule.  $\overline{\cos \theta}$  is the average value of  $\cos \theta$  for all molecules in the gas, and  $\overline{\cos \theta}$  is the time-average of  $\cos \theta$  for one molecule in a given state of motion,  $\theta$  being the angle between the axis of the electric dipole and the lines of force of the applied field.

An expression for  $\overline{\cos \theta}$  applicable to polyatomic molecules in general was obtained by Debye<sup>2</sup> with the use of classical statistical mechanics.

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<sup>1</sup> See, for example, Debye in Marx "Handbuch der Radiologie," Leipzig Akademische Verlagsgesellschaft, 6, 619 (1925).

<sup>2</sup> P. Debye, Phys. Zeits. 13, 97 (1912).

From the Maxwell-Boltzmann distribution law the probability that the axis of the electric dipole in the molecule will lie between the angles  $\theta$  and  $\theta + d\theta$  with the lines of force is

$$\frac{e^{\mu F \cos \theta / kT} \sin \theta d\theta}{\int_0^\pi e^{\mu F \cos \theta / kT} \sin \theta d\theta},$$

and the average value of  $\cos \theta$  is

$$\overline{\cos \theta} = \frac{\int_0^\pi e^{\mu F \cos \theta / kT} \cos \theta \sin \theta d\theta}{\int_0^\pi e^{\mu F \cos \theta / kT} \sin \theta d\theta}. \quad (2)$$

This expression becomes on integration the Langevin function,

$$L\left(\frac{\mu F}{kT}\right) = \coth \frac{\mu F}{kT} - \frac{kT}{\mu F},$$

which reduces for values of  $\mu F$  small in comparison with  $kT$  to

$$\overline{\cos \theta} = \frac{1}{3} \frac{\mu F}{kT}. \quad (3)$$

This result must now, however, be replaced by one based upon the quantum theory. In this case a generally applicable expression cannot be obtained, and it is necessary to consider particular molecular models. The simplest of these, the diatomic molecule for which the axis of the electric dipole coincides with the line joining the nuclei of the two atoms, is believed to represent the hydrogen halides, for which data are available to make possible the evaluation of their electric moments.

#### THE QUANTUM THEORY OF THE DIATOMIC DIPOLE

The dielectric constant of diatomic dipole gases has been treated on the basis of the quantum theory by W. Pauli, Jr.,<sup>3</sup> whose treatment forms the basis of the following discussion.

The Hamiltonian function for the motion of a diatomic dipole in an electric field, using polar coordinates with the polar axis in the direction of the lines of force, is

$$H = \frac{1}{2I} \left( p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) - \mu F \cos \theta, \quad (4)$$

<sup>3</sup> W. Pauli, Jr., *Zeits. f. Physik* **6**, 319 (1921).

in which  $p_\theta$  and  $p_\phi$  are the momenta corresponding to the coordinates  $\theta$  and  $\phi$ , and  $I$  is the moment of inertia of the rotator about an axis through its center of mass and normal to the lines joining the atomic nuclei. The coordinate  $\phi$  is cyclic, and  $p_\phi$  is accordingly constant. Applying the Wilson-Sommerfeld quantum conditions we write

$$\oint p_\theta d\theta + \left| \oint p_\phi d\phi \right| = mh \quad (5)$$

and

$$\oint p_\phi d\phi = 2\pi p_\phi = nh^2, \quad (6)$$

in which  $m$  and  $n$  are the two quantum numbers describing the condition of motion of the rotator. Introducing (6) and the relation  $p_\theta = I\dot{\theta}$  in (4), there is obtained the differential equation

$$dt = \frac{2\pi I d\theta}{\sqrt{8\pi^2 IW - \frac{n^2 h^2}{\sin^2 \theta} + 8\pi^2 I \mu F \cos \theta}}, \quad (7)$$

in which  $W$  is the energy-constant. The time-average value of  $\cos \theta$  for a rotator in a given state of motion is, then,

$$\overline{\cos \theta} = \frac{\oint (8\pi^2 IW - \frac{n^2 h^2}{\sin^2 \theta} + 8\pi^2 I \mu F \cos \theta)^{-\frac{1}{2}} \cos \theta d\theta}{\oint (8\pi^2 IW - \frac{n^2 h^2}{\sin^2 \theta} + 8\pi^2 I \mu F \cos \theta)^{-\frac{1}{2}} d\theta}. \quad (8)$$

If  $\mu F$  is very small in comparison with the total energy  $W$  these expressions may be expanded in powers of  $\mu F$  and terms higher than linear neglected; it is, moreover, permissible to substitute for  $W$  the value  $W_0 = m^2 h^2 / 8\pi^2 I$  corresponding to zero field. Upon evaluating the resultant integrals by contour integration there is obtained the expression

$$\overline{\cos \theta} = \frac{4\pi^2 \mu F I}{m^2 h^2} \left( \frac{3}{2} \frac{n^2}{m^2} - \frac{1}{2} \right). \quad (9)$$

Pauli assigned to  $m$  values  $1, 2, 3, \dots, \infty$ , and to  $n$   $\pm 1, \pm 2, \pm 3, \dots, \pm m$ . We shall give  $m$  the values  $1/2, 3/2, 5/2, \dots, \infty$ , and  $n$   $\pm 1/2, \pm 3/2, \pm 5/2, \dots, \pm m$ ; for these half-quantum numbers for  $m$  are indicated by the infra-red oscillation-rotation absorption spectrum<sup>4</sup>

<sup>4</sup> Colby, *Astrophys. J.* **58**, 303 (1923).

of hydrogen chloride and definitely required by the recently observed<sup>5</sup> pure rotation absorption spectrum. The choice of values for  $n$  will be discussed later. Assigning equal *a priori* probabilities to all of the possible quantum states characterized by half-integral values of  $m$  and  $n$  we have for the probability of a given state

$$\omega(m, n) = \frac{e^{-W/kT}}{\sum_{m=1/2}^{\infty} \sum_{n=-m}^{+m} e^{-W/kT}}. \quad (10)$$

Introducing the variable  $\sigma = \Theta/T = h^2/8\pi^2 I k T$  we obtain the following expression for  $\overline{\cos \theta}$ :

$$\overline{\cos \theta} = \frac{\mu F}{kT} \frac{1}{2\sigma} \frac{\sum_{m=1/2}^{\infty} \sum_{n=-m}^{+m} \frac{1}{m^2} \left( \frac{3}{2} \frac{n^2}{m^2} - \frac{1}{2} \right) e^{-\sigma m}}{\sum_{m=1/2}^{\infty} \sum_{n=-m}^m e^{-\sigma m}}. \quad (11)$$

Pauli, who obtained a similar expression with whole quantum numbers, evaluated the sums by assuming  $\sigma$  to be very small. This is not justifiable, however, for it leads to results in error by 30 percent or more in cases of practical interest, for which  $\sigma$  has values near 0.05. Replacing  $m$  by  $r - \frac{1}{2}$  and  $n$  by  $s - \frac{1}{2}$  and summing for  $s$  one obtains

$$\overline{\cos \theta} = \frac{\mu F}{kT} C, \quad (12)$$

where

$$C = \frac{1}{4\sigma} \frac{\sum_{r=1}^{\infty} \frac{r}{(r-\frac{1}{2})^3} e^{-\sigma(r-\frac{1}{2})^2}}{\sum_{r=1}^{\infty} r e^{-\sigma(r-\frac{1}{2})^2}}. \quad (13)$$

For very large values of  $\sigma$ ; i. e., for very low temperatures,  $C$  is equal to  $2/\sigma$ . As  $\sigma$  tends to zero  $C$  approaches asymptotically the value 4.570, for  $\sum_{r=1}^{\infty} \frac{r}{(r-\frac{1}{2})^3} e^{-(r-\frac{1}{2})^2}$  approaches  $\sum_{r=1}^{\infty} \frac{r}{(r-\frac{1}{2})^3}$ , which has the value 9.140, and  $\sum_{r=1}^{\infty} r e^{-(r-\frac{1}{2})^2}$  can be replaced by the integral  $\int_0^{\infty} r e^{-\sigma(r-\frac{1}{2})^2} dr$ , which is equal to  $1/2\sigma$ .  $C$  has been determined for intermediate values of  $\sigma$  by numerical substitution, from five to twenty-

<sup>5</sup> Czerny, *Zeits. f. Physik* 34, 227 (1925).

five terms being used in order that the final figure might be accurate to 0.05 percent. The results of the calculations are given in Table I.

TABLE I

$\sigma$	$C$	$\sigma$	$C$
Very large	$2/\sigma$	0.05	3.599
1.00	1.578	.04	3.690
0.20	2.848	.03	3.796
.10	3.264	.02	3.929
.07	3.445	0.00	4.570

## CONSIDERATION OF EXPERIMENTAL RESULTS

Substituting (12) in (1), we obtain

$$\frac{3}{4\pi} \frac{\epsilon - 1}{\epsilon + 2} = N \frac{\mu^2}{kT} C + N\alpha, \quad (14)$$

in which  $C$  is a function of the temperature. This property differentiates this result from those of Debye and Pauli, who obtained for  $C$  the constant values  $1/3$  and  $1.5367$  respectively. Since for gases  $\epsilon + 2$  is approximately 3, we may write

$$(\epsilon - 1)T = 4\pi N \frac{\mu^2}{k} C + 4\pi N\alpha T. \quad (15)$$

The equations of Debye and Pauli require that a plot of  $(\epsilon - 1)_0 T$ , in which the subscript 0 indicates that the dielectric constant is that of the gas at constant density (that at standard conditions), against  $T$  be a straight line; the calculations given in this paper, on the other hand, require the curve to deviate from a straight line, since  $C$  is found not to be a linear function of the temperature. Moreover,  $\alpha$  and  $4\pi N\alpha$  will have one value when obtained from measurements of  $\epsilon$  with the use of the equation of Debye or of Pauli, and a different value if our calculations are used.

The only extensive measurements of the dielectric constants of diatomic dipole gases are those of Zahn<sup>6</sup> on hydrogen chloride, bromide, and iodide. Values of  $\Theta$  for these gases are obtained in the interpretation of their infra-red spectra. Czerny<sup>5</sup> gives for hydrogen chloride the value  $10.397$  for  $hc/8\pi^2 I$ , which leads to  $\Theta = 14.9^\circ$  for this gas. An equally accurate value for hydrogen bromide is not at hand, for its pure rotation spectrum has not been observed. Kratzer<sup>7</sup> gives for  $I$  the value  $3.258 \times 10^{-40}$  g. cm<sup>2</sup>, from oscillation-rotation spectra, corresponding to  $\Theta 12.15^\circ$ . Since Kratzer's value  $I = 2.594 \times 10^{-40}$  g. cm<sup>2</sup> for hydrogen chloride corresponds to  $\Theta = 15.09^\circ$ , which is slightly high,

<sup>6</sup> Zahn, Phys. Rev. **24**, 400 (1924).

<sup>7</sup> Kratzer, Zeits. f. Physik **3**, 289 (1920).

I have used for hydrogen bromide the value  $\Theta = 12.0^\circ$ . No spectral data for hydrogen iodide have been obtained; from a consideration of atomic sizes obtained from crystal structure data I have predicted the approximate figures  $I = 4.29 \times 10^{-40}$  g. cm<sup>2</sup> and  $\Theta = 9.2^\circ$  for this gas.

There are, then, two constants,  $\mu$  and  $\alpha$ , to be evaluated from the experimental data for each gas. These were determined in such a way as to cause the theoretical curve to pass through two experimental points, one at about  $300^\circ$  and one at about  $500^\circ$ A. The curves shown in Fig. 1 are obtained by placing  $\mu = 0.3316 \times 10^{-18}$  cgsu and  $4\pi N_0 \alpha = 0.00077$  for hydrogen chloride, and  $\mu = 0.252 \times 10^{-18}$  and  $4\pi N_0 \alpha = 0.00102$  for hydrogen bromide;  $N_0$  here represents the number of molecules per cc for the gas at standard conditions.

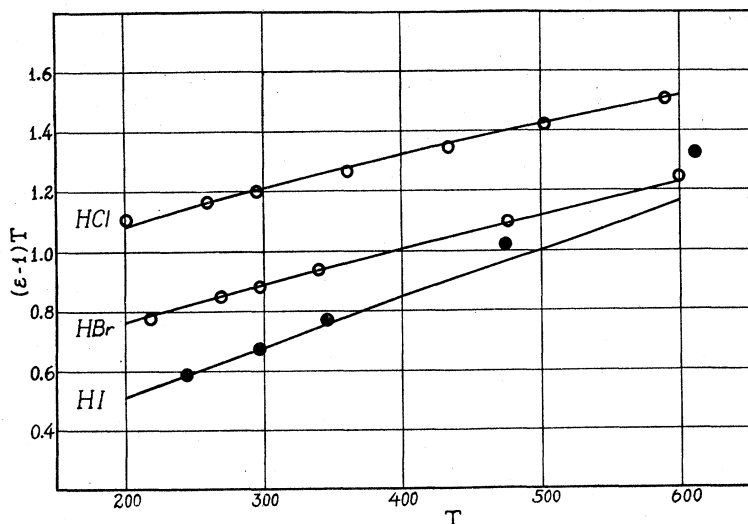


Fig. 1. Variation of  $(\epsilon-1)T$  with  $T$ .

The interpretation of the data for hydrogen iodide is made difficult by the dissociation of the gas into its elements. It is desirable to obtain some information regarding the electric moment of these molecules, however, and so a different procedure has been followed. At the lowest temperature used,  $244.5^\circ$ A, Zahn obtained the value 0.5885 for  $(\epsilon-1)_0 T$ , a value which can be accepted as correct, for the dissociation of hydrogen iodide is at that temperature only 1.3 percent. If the value 0.00160, obtained from optical data and discussed in the next section of this paper, be accepted as correct for  $4\pi N_0 \alpha$ , then the value  $0.146 \times 10^{-18}$  cgsu for  $\mu$  is required in order that the theoretical curve (shown in Fig. 1) might pass through this experimental point.

## DISCUSSION OF RESULTS

*The electric moments of the hydrogen halides.* The values found for the electric moment  $\mu$  of these gases are given in Table II, together with the classical theory values given by Zahn. It is to be noticed that the classical moments are not approximately equal to those obtained from the quantum theory, but are much larger—about three times as large. In these cases, then, considerations regarding, for example, molecular structure based on the classical values of the electric moments must be revised,<sup>8</sup> as has already been pointed out by Pauli<sup>3</sup> and by Ebert.<sup>9</sup> Indeed, it is probable that in the case of polyatomic molecules also the classical values of the electric moments may be considerably in error.

TABLE II

	$\mu$		$d$	
	Quantum	Classical	Quantum	Classical
HCl	$0.3316 \times 10^{-18}$	$1.034 \times 10^{-18}$	0.0694 A.	0.217 A.
HBr	.252	0.788	.0528	.165
HI	.146	.382	.0306	.080

Under  $d$  in Table II is given the distance between an electron and a proton in order that the configuration might have the electric moment found for each of the hydrogen halides.

*Their coefficients of induced polarization.* In Table III are given the values found for  $4\pi N_0\alpha$  for hydrogen chloride and bromide, and those given by Zahn with the use of the classical theory. The quantum theory values are confirmed by independent evidence; for they agree with Maxwell's relation  $4\pi N_0\alpha = n^2 - 1$ , in which  $n_0$  is the index of refraction of the gas at standard conditions for light of frequency far from any frequency characteristic of the molecule. It is known that  $n$  determined with ordinary light is larger than  $n_0$ ; hence the observed values of  $n^2 - 1$  for the sodium  $D$  lines, given in Table III, cannot be reconciled with the considerably larger classical theory values of  $4\pi N_0\alpha$ , but support the quantum theory values.

TABLE III

	$4\pi N_0\alpha$		$n^2 - 1$ (sodium D lines)
	Quantum	Classical	
HCl	0.00077	0.001040	0.000888
HBr	.00102	.001212	.001140
HI	(.00160)	.001856	.001812

It will be seen that the values found for  $4\pi N_0\alpha$  for hydrogen chloride and bromide are in each case about 88 percent of those for  $n^2 - 1$  for

<sup>8</sup> See, for example, Smyth, Jour. Amer. Chem. Soc. **46**, 2151 (1925); Phil. Mag. **47**, 530 (1924).

<sup>9</sup> Ebert, Zeits. f. Phys. Chem. **114**, 429 (1925).

the sodium D lines. For this reason it has seemed probable that  $4\pi N_0\alpha$  for hydrogen iodide can be taken to be 0.00160, which is 88 percent of  $n^2 - 1$  for this gas.

*The discrepancies between the theoretical curve and the experimental points.* The experimentally found points for hydrogen chloride and bromide cannot be made to fall exactly on a curve of the type required by the quantum theory considerations of this paper. It is possible that experimental errors are responsible for this disagreement; further experiments are accordingly desired. On the other hand, the theoretical treatment has perhaps been over-simplified. The assumption that  $\mu F$  is much smaller than  $W$  is valid; thus for hydrogen chloride with fields of 10,000 volts/cm  $\mu F$  is less than  $1 \times 10^{-17}$  ergs, while  $W$  for the lowest quantum state ( $m = \frac{1}{2}$ ) is over  $50 \times 10^{-17}$  ergs. We have further assumed the molecule to have a definite electric moment  $\mu$ , independent of its state of rotation. That this assumption also is valid has been shown in the following way. The force tending to restore the proton to its equilibrium position when it is pulled away from the chlorine nucleus can be determined from oscillation-rotation spectra.<sup>7</sup> Equating this with the centrifugal force acting when the molecule is in rotation, it is possible to find the change in position of the nucleus on going from one state to another. The electric moment of hydrogen chloride is only about 6 percent of that which would be caused by a single negative charge located on the chlorine nucleus and a single positive charge on the proton; it seems reasonable then that an upper limit for the change in moment occurring on moving the proton in the molecule would be given by the product of the unit charge and the distance moved. On carrying out this calculation it is found that the possible changes in the electric moment are far too small to be of any influence on the dielectric constant.

The small lack of agreement between experiment and theory accordingly remains unexplained.

*The choice of quantum numbers.* The pure rotation spectrum of hydrogen chloride in the far infra-red definitely requires that  $m$  be given the values  $1/2, 3/2, 5/2, \dots \infty$ .

Kratzer<sup>10</sup> has advanced arguments supporting the contention that half quantum numbers are only apparent, and that in the quantization of the entire dynamical system the quantum numbers assume integral values. In the hydrogen halides he supposes to be present due to the motion of electrons an angular momentum vector perpendicular to the line joining the nuclei and of magnitude  $\frac{1}{2}h/2\pi$ . In order for

<sup>10</sup> Kratzer, Ann. d. Physik, **71**, 72 (1923).

the total angular momentum to be an integral multiple of  $h/2\pi$  the rotation of the molecule would have to contribute the amount  $mh/2\pi$ , with  $m$  having half-integral values. Kramers and Pauli<sup>11</sup> suggest that the electronic angular momentum vector has the magnitude  $h/2\pi$  and makes an angle of  $30^\circ$  with the line joining the nuclei, so that its component normal to this line is  $\frac{1}{2}h/2\pi$ . It is evident that these theories would lead to expressions for  $\overline{\cos\theta}$  differing from that used in this paper. It has not seemed worth while to evaluate these expressions; especially in view of the fact that hydrogen chloride is diamagnetic, for if the presence of electronic angular momentum requires the presence of a magnetic dipole the theories of Kratzer and Kramers and Pauli would require it to be paramagnetic.

If it be assumed, then, that in some cases quantum numbers can have half-integral values, there are two possibilities for  $n$ , for it can be placed equal to  $0, \pm 1, \pm 2, \dots \pm(m - \frac{1}{2})$ , or to  $\pm 1/2, \pm 3/2, \pm 5/2, \dots \pm m$ . It is necessary to include  $n=0$  in the first group, for with  $m = \frac{1}{2}$  this is the only integral value allowed. It can be shown unambiguously that the values  $n=0, \pm 1, \pm 2, \dots \pm(m - \frac{1}{2})$  cannot be correct. For with them the equation

$$C = \frac{1}{2\sigma} \frac{\sum_{r=1}^{\infty} \left( -\frac{1}{4(r - \frac{1}{2})^3} \right) e^{-\sigma(r - \frac{1}{2})}}{\sum_{r=1}^{\infty} (2r - 1) e^{-\sigma(r - \frac{1}{2})^2}} \quad (23)$$

is obtained in place of Eq. (13); this equation, however, leads to negative values of  $C$  for all values of  $\sigma$ . Consequently Eq. (23) requires that at all temperatures the hydrogen chloride gas possess a *negative* polarization due to permanent dipoles. *The experimental measurements of the dielectric constants of the hydrogen halides accordingly rule out the quantum-number assignment*

$m = 1/2, 3/2, 5/2, \dots \infty, n = 0, \pm 1, \pm 2, \dots, \pm(m - \frac{1}{2})$ .

The remaining assignment, with  $n = \pm 1/2, \pm 3/2, \pm 5/2, \dots, \pm m$ , has then been used in this paper. It is to be emphasized that this assignment is not compatible with the idea that true quantum numbers are integral, and that half-quantum numbers result from the presence of an angular momentum vector due to the motion of electrons.

*The possibility of weak quantization.* The sharpness of the band spectra shows that the quantization with respect to the total quantum number  $m$  is strong; this is to be expected, for the molecule goes through

<sup>11</sup> Kramers and Pauli, *Zeits. f. Physik*, **13**, 351 (1923).

many rotations between collisions. On the other hand weak spatial quantization might occur.

If all orientations were equally probable; i. e., if there were completely weak spatial quantization, the average value of  $\cos\theta$  for rotators with quantum number  $m$  would be given by Eq. (9) with  $n^2/m^2$  replaced by the average value of  $\cos^2\beta$ , which is  $\frac{1}{3}$ ;  $\beta$  is the angle between the axis of rotation of the molecule and the lines of force of the applied field.  $\overline{\cos\theta}$  would then be zero; in other words, there would be no polarization due to permanent dipoles. This is in agreement with the result of Alexander,<sup>12</sup> who showed that *on the classical theory of all of the polarization is caused by molecules whose total energy is less than  $\mu F$* . Since there are actually no such molecules present, polarization must arise from some other mechanism. This mechanism is spatial quantization.

We have assumed strong spatial quantization in determining the values of  $\mu$ ; if this assumption is incorrect, the values given are too low. But if the spatial quantization had been weak the dielectric constant would have varied with the field strengths applied. Such a variation has never been reported; Zahn and Bädeker, using different experimental methods and undoubtedly different field strengths, obtained the same values for  $\epsilon$  for hydrogen chloride. It accordingly seems highly probable that there is strong spatial quantization with respect to the applied electric field.

A brief account of this work has been published in the Proceedings of the National Academy of Sciences.<sup>13</sup>

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<sup>12</sup> Alexandrow, Phys. Zeits. **22**, 258 (1921).

<sup>13</sup> Pauling, Proc. Nat. Acad., **12**, 32 (1926).