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ON DIELECTRIC CONSTANTS AND MAGNETIC SUSCEPTIBILITIES IN THE NEW QUANTUM MECHANICS.

PART II—APPLICATION TO DIELECTRIC CONSTANTS

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Abstract

1,2. The proof of the Langevin-Debye formula given in part I with the new quantum mechanics is rather abstract because of its very generality, and so the results are made more concrete and non-mathematical by discussing some of the models that are included as special cases. This general derivation shows that the Debye formula applies to asymmetrical models with three unequal moments of inertia quite as well as to the symmetrical molecules previously studied by various writers with the aid of special models. Unlike the old quntum theory, there is no abrupt change of dielectric constant with pressure or field strength due to the passage from "weak" to "strong" spacial quantization.

3. Influence of a magnetic field. The mathematical theory of part I shows that very generally a magnetic field H should be without effect on the dielectric constant (or, 4, on the refractive index, except for the Faraday and Cotton-Mouton effects) unless we consider very small terms in H^2. Recent spectroscopic data show that apparently the only feasible explanation of the absence of a "*magneto-electric directive effect*" in NO is Piccard's and de Haas' suggestion of equal numbers of "left" and "right-handed" molecules having mutually opposite senses of electronic rotation relative to the molecular axis.

4. Refractive index—effect of vibration bands. A general formula is given for the refractive index which shows that the refractivity per molecule should not vary with temperature despite "temperature rotation" of the nuclei about the center of gravity. The experimental confirmation of this fact may be regarded as verifying the "sum-rules" characteristic of the new quantum mechanics. The suggestion of Debye and Ebert that the experimental discrepancy between n_0^2-1 and $4\pi N\alpha$ is due to infra-red nuclear vibration bands is shown to be untenable in molecules such as HCl. Here n_0 denotes the extrapolation of the index of refraction to zero frequency from visible dispersion curves, and $N\alpha$ is the part of the static dielectric susceptibility due to "induced polarization." Measurements by Bourgin and others of the intensity of infra-red absorption bands furnish values of the "effective charge" associated with the nuclear oscillations and so enable one to calculate the contribution of the vibration bands to the polarization. In HCl this contribution proves to be about 1/100 of that necessary to account for the discrepancy mentioned above.

5. Limit of accuracy of the Debye formula. Because a fraction, usually small, of the molecules have sufficiently large rotational quantum numbers to make their frequencies of rotation comparable with kT/h, the Debye formula holds only asymptotically at high temperatures in the new quantum mechanics, and at ordinary temperatures the correction for departures from the asymptotic value consists approximately in adding a very small term $-NC/T^2$ to the ordinary Debye expression $N\alpha+N\mu^2/3kT$ for $(\epsilon-1)/4\pi$. The value of C is calculated for the most general rigid asymmetrical molecule, and reduces for symmetrical molecules to the value previously obtained for them by Kronig and Manneback by an entirely different method.

6. General classical derivation of the Langevin-Debye formula. It is shown that according to classical mechanics in any multiply periodic dynamical system amenable to statistical theory the susceptibility equals $N\overline{\mathbf{M}^2}/3kT$, where $\overline{\mathbf{M}}^2$ is the statistical mean square of the vector moment of the molecule; i. e., the average over the phase space weighted according to Boltzmann factor, which is not to be confused with the time average for an individual molecule. This formula for the susceptibility is a generalization of the Langevin-Debye formula, and reduces to the ordinary Debye expression $A+B/T$ if the dynamical system consists of a rotating elastic polar molecule executing small vibrations about an equilibrium configuration.

IN PART I[1] a very general derivation was given of the Debye formula[2]

$$\frac{3}{4\pi}\frac{\epsilon-1}{\epsilon+2}=N\left(\alpha+\frac{\mu^2}{3kT}\right) \tag{1}$$

for the dielectric constant ϵ. This proof was based on the new quantum mechanics, and assumed only that the molecule has a "permanent" dipole moment of constant magnitude μ and that the precession frequencies of the moment vector are small compared to kT/h. For a more detailed explanation of these assumptions, discussion of the conditions under which they are likely to be fulfilled, etc., the reader is referred to part I. Sections 1–4 of the present paper are, however, mainly descriptive and do not require any extensive familiarity with the mathematical analysis in part I. The term $N\alpha$ in (1) arises from the "induced polarization" and was shown in part I to be associated with "high frequency" matrix elements representing transitions from normal states to "excited states" whose energies are large compared to kT.

1. Atoms and Non-Polar Molecules

Atoms and non-polar molecules have, of course, as a rule[3] no permanent dipole moment, so that the right-hand side of (1) reduces to $N\alpha$, an expression which does not vary with temperature except through the number N of molecules/cc. This is in accord with the fact that the quotient of the left-hand side of (1) by density is ordinarily found experimentally[4] to be independent of the temperature in monatomic and non-polar gases. The value of α can be calculated exactly for monatomic hydrogen from the quantum theory of the second order Stark effect,[5] and yields a dielectric

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[1] J. H. Van Vleck, Phys. Rev. **29**, 727 (1927). Referred to as part I throughout the present paper.

[2] Eq. (1) of this paper differs from Eq. (1) of part I and from the Eqs. of section 6 in having the well-known Clausius-Mosotti correction for the fact that the "local field" is not the same as the large-scale field F. See p. 729 of part I. Without this correction the left side of (1) would be simply the susceptibility $\chi=(\epsilon-1)/4\pi$.

[3] An exception to the statement that the temperature coefficient of the dielectric constant of a monatomic gas is zero at constant density occurs in case the states occupied by the atom at the temperature under consideration consist of a multiple level whose components have a separation comparable with or less than kT. This is a situation not commonly encountered in monatomic gases, but a hypothetical example, calculated by the writer (see notes 6 and 31), is monatomic hydrogen gas at temperatures so high than the electrons are in excited "fine structure" levels rather than the normal singlet level.

[4] Occasionally, however, due to molecular association or other causes, anomalous temperature variations are observed in the dielectric constants of non-polar gases. Cf., for instance, Bramley's observations on bromine, Journ. Frank. Inst., Feb. 1927.

[5] G. Wentzel, Zeits. f. Physik, **38**, 527 (1926); I. Waller, *ibid.* **38**, 635 (1926); P. S. Epstein, Phys. Rev. **28**, 695 (1926).

constant[6] 1.000229 at 0°C and atmospheric pressure. This value is, of course, very hard to check experimentally because of the difficulty of dissociating hydrogen into the monatomic form, but approximate calculations can be made of the dielectric constants of other atoms, and even of some non-polar molecules, by supposing their electronic motions to be nearly hydrogenic. The effective nucear charge for the equivalent hydrogenic atom can then be deduced from observed dielectric constants, and compared with estimates obtained by other methods. This has been done by the writer[6] for molecular hydrogen and helium, and by Pauling[7] for numerous other atoms. Especially in He and H_2 the agreement between various estimates of the nuclear charge is much better with the new than with the old quantum theory.

2. Polar Molecules

Polar molecules, of course, have in general a permanent electrical moment different from zero, and hence a dielectric constant which varies with temperature even at constant density. This is just what is found experimentally, and from observed temperature coefficients of dielectric constants it is possible to determine the electrical moment μ. The results often throw very interesting light on molecular structure. It is found, for instance, that CH_4 and CCl_4 are non-polar, whereas permanent electrical moments are observed[8] for the intermediate molecules CH_3Cl, CH_2Cl_2, $CHCl_3$ in which the carbon atom is united to two kinds of atoms instead of to four alike. In the present paper, however, no attempt will be made to discuss the numerical application of the Debye formula to the vast amount of experimental material on dielectric constants, and to thus form quantitative estimates of the dipole moments for different molecules. The requisite calculations are already available in the literature[9] for a large number of different substances, and are, of course, simply trial and error determinations of the values of the constants α and μ in Eq. (1) which yield closest agreement with the experimental temperature curves. Eq. (1) is identical with the classical formula, and so, unlike the old quantum theory (cf. p. 728, part I), the new quantum mechanics gives the same numerical dipole moments as the classical theory. It is to be clearly understood that Eq. (1) applies primarily to gases. Efforts, to be sure, have been made to apply the Debye formula to liquids, but, as emphasized by Debye[9] himself, Eq. (1) is in general valid in the liquid state only in the case of dilute solutions of polar molecules in non-polar solvents.

Our discussion of Eq. (1) will thus usually center around its general theoretical basis rather than its numerical application. In order to correlate the different theoretical derivations of (1) which have previously been given

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[6] J. H. Van Vleck, Proc. Nat. Acad. **12,** 662 (1926).

[7] L. Pauling, Proc. Roy. Soc., **114A,** 181.

[8] Cf. R. Sanger, Phys. Zeits. **27,** 563 (1926).

[9] An excellent summary of the experimental work until 1924 has been given by Debye in vol. VI of the Handbuch der Radiologie. A comprehensive survey of the more recent experimental data, together with copious references to the literature, is given by O. Blüh, Phys. Zeits. **27,** 226 (1926).

for special models, we may distinguish between the four following types of molecules:

(*a*) non-gyroscopic diatomic molecules,

(*b*) diatomic molecules which are gyroscopic due to an electronic angular momentum about the axis of figure,

(*c*) symmetrical polyatomic molecules; i.e., molecules which are composed of more than two atoms but in which two of the three principal moments of inertia are equal,[10]

(*d*) asymmetrical polyatomic molecules, characterized by three unequal moments of inertia.

Probable examples of the four cases $(a)-(d)$ are respectively HCl, NO, NH_3, and CH_2Cl_2. The order of the list $(a)-(d)$ is that of increasing difficulty for calculation with special models. The general derivation of the Debye formula given in part I, however, is applicable to all four cases, for the condition imposed in part I that the molecule have a permanent moment vector whose precession frequencies are small compared to kT/h is satisfied in most of the normal states. This is true since in the first place molecules are usually rigid enough to fulfill fairly closely the demand of permanency of moment (see especially in this connection the paragraph at the end of section 6), and in the second place practically all molecules have large enough moments of inertia so that the frequencies of rotation of the nuclei about the center of gravity are small compared to kT/h except in states with abnormally large rotational quantum numbers for the given temperature. These "nuclear" or "temperature" rotation frequencies[11] can, to be sure, be made as large as we please relative to kT/h by assigning sufficiently large values to the rotational quantum numbers, but states with such large quantum numbers have a large energy W, and hence a small Boltzmann probability factor $e^{-W/kT}$, so that it is fairly apparent that their contribution may be neglected without sensible error (cf. note 26, part I). This is also demonstrated mathematically in section 5, where the error due to neglecting higher powers of $h\nu/kT$ is calculated explicitly.

(*a*) Instead of thus establishing the applicability of the general proof given in part I, one can also derive the Debye formula for the case (*a*) of

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[10] It is often stated in the literature than the essential criterion for case (*c*) is an axis of symmetry, but this is incorrect if the term axis of symmetry is construed in the usual crystallographic sense of meaning that a rotation of 180° about this axis brings the system back to a configuration indistinguishable from the initial one, for this condition by no means implies two equal moments of inertia. Instead (*c*) seems usually to result from a grouping of identical atoms about the axis at corners of a regular polygon (e. g. in NH_3 the N atom is probably at the apex of a pyramid whose base is an equilateral triangle with H atoms at the corners).

[11] In dealing with dielectric constants we do not ordinarily need to consider the precessions due to internal spins of the electrons, for with very few exceptions (notably NO) the normal states of most molecules are non-magnetic. Diatomic molecules with spin moments are considered in case (*b*) below, while even polyatomic molecules with spin moments (e. g. ClO_2) are included in the general proof of the Debye formula given in part I, certainly provided the frequencies with which the spin axis precesses are small compared to kT/h, and as a matter of fact even if this condition is not met the proof may still apply, for the precessions of the spin moment probably often do not carry with them the heavy nuclear framework containing the permanent dipole moment, except for small nutations (cf. note 20).

non-gyroscopic diatomic molecules, by making the calculation directly with the amplitude matrices for the rotating dipole given by Mensing,[12] Oppenheimer,[13] Fues,[13] or Dennison.[14] Such calculations were made independently and practically simultaneously by Mensing and Pauli,[15] Kronig,[16] and the writer.[17] A variant of the computations using the wave rather than matrix method has been given by Manneback.[18] We shall give only a brief summary of case (*a*) because details are already in the literature.[15,16,17,18] An interesting result found in (*a*) but not in (*b–c–d*) nor in the old quantum theory, is that the contribution of the permanent moment to the dielectric constant; i.e., the second right-hand term of Eq. (1) or of Eq. (2) below, arises entirely from molecules in the lowest rotational state $j=0$. This is a beautiful quantum analog of the fact that classically in models of type (*a*) the corresponding "temperature" term ensues entirely[19] from the sluggish molecules having energies less than μF. The quantum mechanics show that in case (*a*) the dielectric constant is given by the simple expression

$$\frac{3}{4\pi}\,\frac{\epsilon-1}{\epsilon+2}=N\left(\alpha+\frac{8\pi^2 I\mu^2 N_0}{3h^2 N}\right) \tag{2}$$

where N_0 is the number of molecules in the lowest rotational state. By evaluation of the ratio N_0/N, formula (2) is readily shown to merge into (1) at high temperatures. Eq. (2), however, has the added advantage of holding even at temperatures so low that $h\nu/kT$ is comparable with unity. Eq. (1), nevertheless, is an adequate approximation at ordinary temperatures. From (2) it is seen that the susceptibility remains finite even at $T=0$, where $N_0/N=1$. In the classical theory, on the other hand, there is complete saturation at the absolute zero, and the susceptibility increases without limit for given F when T approaches zero.

(*b*) In models of type (*b*) a component of electronic angular momentum along the axis of figure makes the diatomic molecule behave like a gyroscope, and hence an approximate model[20] is furnished by the "symmetrical top"

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[12] L. Mensing, Zeits. f. Physik, **36,** 814 (1926).

[13] J. R. Oppenheimer, Proc. Cambr. Phil. Soc. **23,** 327 (1926); E. Fues, Ann. der Phys. **81,** 281, (1926).

[14] D. M. Dennison, Phys. Rev. **28,** 318 (1926).

[15] L. Mensing and W. Pauli, Jr., Phys. Zeits. **27,** 509 (1926).

[16] R. d. L. Kronig, Proc. Nat. Acad. **12,** 488 (1926).

[17] J. H. Van Vleck, Nature, **118,** 226 (1926).

[18] C. Manneback, Phys. Zeits. **27,** 563 (1926).

[19] W. Alexandrow Phys. Zeits. **22,** 258 (1921); W. Pauli, Jr., Zeits. f. Physik, **6,** 319 (1921).

[20] The symmetrical top model for molecules of type (*b*) has frequently been used in band spectra (cf., for instance E. C. Kemble, "Molecular Spectra in Gases," Bull. Nat. Research Council No. 57, p. 313). We disregard the component of electronic angular momentum normal to the axis of figure, whose presence would make the top asymmetrical. We can do this because at least in NO (see part III), the normal component of electronic angular momentum (unlike the stationary normal component in the well-known Kratzer-Kramers-Pauli model for gyroscopic molecules) precesses so rapidly compared to the temperature rotation that its main effect is only to superpose a small nutation on the temperature rotation, and hence the symmetrical top is a fair approximation to the motion. A mathematical basis for regarding molecules of type (*b*) as symmetrical tops has recently been given by Landau, Zeits. f. Physik, **40,** 621 (1926), who is led essentially to the Dennison amplitude matrices by treating the interaction of nuclear rotation and electronic motions as a problem in perturbation theory.

which has been analysed in the matrix dynamics by Dennison[14] and Landau,[20] and in the wave mechanics by Reiche and Rademacher,[21] Kronig and Rabi,[22] and Debye and Manneback.[23]

(*c*) Case (*c*) is much more frequent than (*b*), as NO is about the only common example of a molecule normally of type (*b*). The polyatomic molecules characteristic of type (*c*) have two equal moments of inertia, and consequently are likewise represented by the symmetrical top model, but the angular momentum about the axis of figure is now due to nuclear rotations rather than to purely electronic motions as in (*b*). There is also the important distinction that in (*c*) there may be a large number of different possible values for the quantum number σ specifying the angular momentum about the axis of figure, whereas in (*b*) the axial component of electronic angular momentum has only one or at most a few possible values in the normal states. The Debye formula has been deduced for case (*c*) by Kronig[24] and by Manneback.[23] These writers appear to overlook the close resemblance of their calculations for (*c*) to the computations for case (*b*) which the writer previously reported, though rather sketchily, at the close of his note to Nature.[17,25] In (*b*), to be sure, we do not sum over all values of the quantum number σ mentioned above, but, as noted to the writer by Dr. Pauling, since the Debye expression is obtained in (*b*) and does not involve σ, it must hold for a gas such as that of type (*c*) which can be regarded as a mixture of molecules with different values of σ.[26]

(*d*) The general polyatomic molecule is so unsymmetrical that it would be very laborious to work out the numerical values of amplitude matrices with a concrete model,[27] and so in this case (*d*) the general proof given in

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[21] F. Reiche, Zeits. f. Physik, **39,** 444 (1926); H. Rademacher and F. Reiche, *ibid.* **41,** 453 (1927).

[22] R. d. L. Kronig and I. I. Rabi, Phys. Rev. **29,** 262 (1927).

[23] P. Debye and C. Manneback, Nature, **119,** 83 (1927); also especially C. Manneback, Phys. Zets. **28,** 72 (1927).

[24] R. d. L. Kronig, Proc. Nat. Acad. **12,** 608 (1926)

[25] In his preliminary letter[17] to Nature the writer promised to publish later the details of his calculations of the dielectric constant in cases (*a*) and (*b*), which he made originally by the Dennison[14] amplitude matrices. However, the simultaneous publication by Mensing and Pauli of their computations for case (*a*) and by Kronig for (*a*) and later (*c*) makes this unnecessary as their calculations are identical in character with those reported by the writer, except for Kronig's addition of summing over σ and calculating the small correction terms in T^{-2}. Also all four cases (*a*)–(*d*) are covered by the general proof in part I, which the writer developed subsequently to his work with the Dennison model.

[26] As a corollary to calculating the dielectric constant with special models for cases (*a*), (*b*), and (*c*) a formula for the Stark effect to terms in F^2 is obtained which is the analog in the new mechanics of formulas obtained in the old quantum theory by Hettner for case (*a*) (Zeits. f. Physik, **2,** 349, 1920) and by Lessheim for case (*c*) or (*b*) (*ibid.* **35,** 831, 1926). The new formula for case (*c*) has been given by Debye and Manneback.[23] This formula was also obtained by the writer in connection with his unpublished calculations for case (*b*) (as well as qualitatively by Landau[20]). Unlike (*a*), cases (*b*–*c*) involve linear Stark effects. Manneback[23] computes the Stark effect to terms in F^2 in the old quantum theory for case (*c*) (or equally well *b*) not knowing that the calculation had already been made by Lessheim.

[27] Even in the absence of external fields the energy (not to mention amplitude matrices) can be obtained for asymmetrical molecules apparently only as a laborious series development. See E. E. Witmer, Proc. Nat. Acad. **13,** 60 (1927).

part I furnishes much the easiest derivation of the Debye formula with quantum mechanics, in fact the only derivation yet given. In the classical theory the Debye formula can be obtained fairly directly for rigid molecules even of type (*d*) by proper choice of the variables of integration, and the writer is informed that such classical derivations for the general asymmetrical molecule are contained in unpublished work of Debye[79] and of Born. An alternative classical proof is also furnished by the methods given in section 6 of the present paper. Gaseous molecules of this complex type (*d*) are fairly common. Any non-colinear triatomic molecule, for instance, ordinarily belongs to this catagory, as in general it will have three unequal moments of inertia. A common example is H_2O. It is to be clearly understood that in asymmetrical molecules the expression μ in Eq. (1) is the scalar magnitude $(\mu_u^2+\mu_v^2+\mu_w^2)^{1/2}$ of the permanent vector electrical moment, which is in general obliquely inclined relative to the three principal axes of inertia u, v, w.

Invariance of field strength, pressure, etc. It was shown in part I that the dielectric susceptibility $(\epsilon-1)/4\pi$ is invariant of the direction of the axis of quantization. Hence the dielectric constant has the same value with random orientation, in which all directions for the atom or molecule are supposed equally probable, as with spacial quantization. Hence there is no possibility of the dielectric constant varying with the field strength due to the passage from "weak" to "strong"[28] spacial quantization, one of the bugbears of the old quantum theory. Also the spectroscopic stability relations given in section 4, part I, show that in a degenerate dynamical system the susceptibility is invariant of the manner in which the degeneracy is removed,[29] and so there is no change in dielectric constant with field due to a different type of quantization in weak and strong fields.[30] Thus the dielectric constant has the same value in weak fields, where spherical coordinates are used to handle the relativity and spin corrections, as in fields strong enough to produce a linear Stark effect, where parabolic coordinates must be employed.[31]

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[28] For explanation of the terms "weak" and "strong" spacial quantization, and references to the original literature on this subject, see the writer's "Quantum Principles and Line Spectra," p. 165 (Bull. Nat. Research Council, No. 54.).

[29] The discussion in part I emphasized primarily the invariance of the spacial quantization, but the mathematics in part I, especially Eq. (25), establish equally well the invariance of the sums entering in the susceptibility formula under any transformation used in treating a perturbed degenerate system.

[30] The possibility of a change with field strength due to this cause has been suggested in the old quantum theory b yP. Debye, Phys. Zeits. **27,** 70 (1926).

[31] We may here correct an error in the writer's calculation of the dielectric constant of excited hydrogen atoms (Proc. Nat. Acad. **12,** 665, 1926). This error is not found in his computation for normal hydrogen atoms, given in the same paper, which is the case of greatest interest, but it was incorrectly stated that in excited states that the "temperature term" resulting from the Boltzmann distribution factor is important only if the field is strong enough to produce a linear Stark effect. This statement is false as the writer overlooked the contribution from terms of the form given on the 2nd line of Eq. (7), part I. Instead the spectroscopic stability relations mentioned above show that, even for excited states, the dielectric constant has the same value for weak and strong fields. This means that in the formula for $\epsilon-1$ given on p. 665 of the writer's Nat. Acad. paper, the factor $f(F)$ is unity regardless of the field strength. This is gratifying, as we can now use under all conditions this numerical formula for the dielectric constant of excited states which we previously supposed valid only for strong fields.

There, of course, still remains the change in susceptibility with field strength when the field F is strong enough to produce an appreciable tendency towards saturation. This saturation effect first enters[32] when we consider terms in the susceptibility of the order F^2, and so is detectable only in very large fields.[33] The susceptibility per molecule should not change with pressure except in so far as molecular association, inter-molecular fields, etc. are involved, as they often are to a great extent in liquids. As noted by Ebert,[34] molecular susceptibilities should be approximately the same in dilute solutions, at least with non-polar solvents, as in the gaseous state. This accords with experiment, whereas in the old quantum theory we might expect strong spacial quantization in gases at low pressures and weak in gases at high pressures and in solutions.

3. Influence of a Magnetic Field on the Dielectric Constant

There has been, first and last, a great deal of speculation as to whether a magnetic field should influence the dielectric constant. The calculation given in part I shows that, unless the fields are so exceedingly large as to necessitate a study of higher order terms[35] than those ordinarily considered, a magnetic field should according to the new quantum mechanics be without effect on the dielectric constant. This follows since in the derivation of the Langevin-Debye formula given in part I we admitted the possibility of the molecule being in external fields even when the electric field F is zero. Thus Eq. (1) is unaltered when there are other fields, in particular a magnetic field, present in addition to F.

This result is not at all surprising. Using the amplitude matrices for the simple rotating dipole Kronig[16] and especially Pauling[36] have already shown that a magnetic field should not influence the dielectric constant of a non-gyroscopic diatomic molecule (type *a*, section 2). By analogy we might expect that a magnetic field would have no effect in the more complicated cases (*b–c–d*) and part I establishes mathematically that this is indeed so. The reason why the new quantum mechanics gives a null effect as generally as does the classical theory is, of course, the high degree of spectroscopic stability

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[32] For greater detail on this saturation effect (especially from the classical viewpoint) see Debye, Handbuch der Radiologie, vol. VI, p. 777 ff. Debye shows that there are two terms in the susceptibility of the order F^2, one of which is the ordinary effect due to alignment of permanent dipoles and the other of which is due to the torque on the atom or molecule arising from the induced polarization. This second term has the opposite sign from the first (i. e. is positive) and is closely related to the Kerr effect.

[33] S. Ratnowsky, Verhandl. d. D. phys. Ges. **15**, 497 (1913): J. Herweg, Zeits. f. Physik, **3**, 36 (1920); J. Herweg and W. Pötzsch, *ibid.* **8**, 1 (1922). Very interesting indirect evidence for saturation is furnished by the decrease of the dielectric constants of liquids on dissolving strong electrolytes. The ions of the dissolved electrolyte saturate the surrounding molecules of the liquid and hence lower the susceptibility. See, for instance, H. Sack, Phys. Zeits. **28**, 199 (1927).

[34] L. Ebert, die Naturwissenschaften, **14**, 919 (1926).

[35] As noted to the writer by Prof. Debye, a magnetic field H might influence the dielectric constant if H were so large as to necessitate the consideration of terms in the susceptibility of the order H^2. Such an effect would be analogous to a saturation effect, and so only observable in enormously large fields.

[36] L. Pauling, Phys. Rev. **29**, 145 (1927).

characteristic of the new dynamics (section 4, part I). This is in marked contrast to the old quantum theory, in which Pauling[36] shows a magnetic field would cataclysmically change the sign of the temperature coefficient of the dielectric constant, at least in case (*a*). Also the magnitude of the induced polarization, i.e., the first right-hand term of (1) would probably depend on the type of spacial quantization in the old quantum theory, whereas part I shows it is invariant in the new mechanics.

The predicted null effect of magnetic fields of ordinary magnitude on the dielectric constants of gases is well confirmed experimentally. Weatherby and Wolf[37] show that a field of 8000 gauss does not change the dielectric susceptibility of He, O_2, or air within the limits of experimental error[38] (10% in He and .4% in O_2 and air), while Mott-Smith and Daily[39] show with about equal accuracy[38] (8% in NO and 1% in HCl) that the dielectric susceptibilities of the polar gases NO and HCl are unaffected by a field of 4800 gauss. It must not, however, be inferred that the dielectric constants of all substances are not influenced by magnetic fields. For instance, the experiments of Friedel, Jezewski, and especially Kast[40] show that the dielectric constants of certain "mesomorphic" substances (anisotropic liquids) are somewhat altered by magnetic fields, as recently emphasized by Bauer.[41] This, nevertheless, must not be regarded as disproving the theory for, as noted by Ornstein,[42] liquid crystals are likely built out of large complexes ("elementary crystals") rather than out of ordinary free molecules such as were assumed in part I.

The magneto-electric directive effect ("Richteffekt"). There is one exception to the statement made above that according to the theory given in part I a magnetic field should be without effect upon the dielectric constant. That

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[37] B. B. Weatherby and A. Wolf, Phys. Rev. **27,** 769 (1926). Their experiments were undertaken partly to see whether it was possible to determine whether or not the helium atom has a magnetic moment, for Breit and Ruark suggested that in the old quantum theory the dielectric constants of atoms with a magnetic moment would because of spacial quantization be influenced by a magnetic field to an appreciable degree (Phil. Mag. **49,** 504, 1925). In the new mechanics, however, we have seen that the dielectric constant is, as suspected by Heisenberg (Zeits. f. Physik, **31,** 617, 1925), invariant of a magnetic field regardless of whether or not the atom possesses a magnetic moment.

[38] We give the percentage error in the dielectric susceptibility rather than in the dielectric constant. The error in the susceptibility is the more significant because the dielectric constants of gases are nearly unity. Consequently a high precision in measuring the dielectric constant (1 part in 500,000 for He, O_2; 1 in 100,000 for NO, HCl) is necessary to determine the susceptibilities as accurately as mentioned above.

[39] L. M. Mott-Smith and C. R. Daily, Phys. Rev. **28,** 976 (1926). The HCl molecules molecules studied by Mott-Smith and Daily would have no magnetic moment if their nuclei were at rest, but the "temperature rotation" gives the molecules a magnetic polarity, leading to spacial quantization, etc. (cf. Pauling[36]). This magnetic moment due to nuclear rotation has been directly verified experimentally for H_2O in the molecular ray experiments of Knauer and Stern, Zeits. f. Physik, **39,** 780 (1926).

[40] E. Friedel, Comptes Rendus, **180,** 269 (1925); Jezewski, Journ. de Phys. **5,** 59 (1924); W. Kast, Ann. der Physik, **73,** 145 (1924).

[41] E. Bauer, Comptes Rendus, **182,** 1541 (1926).

[42] L. S. Ornstein, Zeits. f. Physik, **35,** 394 (1926); Ann. der Physik, **74,** 445 (1924).

exception is in case there is what may be called a "magneto-electric directive effect." By this term is meant a state of electric polarization produced by application of a magnetic field, or vica versa. The electric polarization in the magneto-electric effect is caused by alignment of molecules in the magnetic field, and if present would exist even when there is no applied electric field F. Mathematically stated, the directive effect exists if the first line of Eq. (5), part I, does not vanish when it is assumed that a magnetic field is already present in the electrically unperturbed state $F=0$. The effect is possible only if the molecule has non-vanishing and non-perpendicular magnetic and electric moments, for in the perpendicular case there is no necessary coordination between the directions of electric and magnetic polarizations. In a certain sense even the magneto-electric directive effect does not change the dielectric constant, as the mathematics in section 3, part I, shows that it does not affect the change in polarization $P-P_0$ produced by the electric field, but only introduces a residual polarization P_0 present when $F=0$. Thus the dielectric constant is unaltered if it is defined as $1+4\pi(P-P_0)/F$, but becomes infinite at $F=0$ if defined as $1+4\pi P/F$.[43]

Actually experiments endeavoring to detect a magneto-electric effect yield a null result,[44] even in liquids and solids. The only important gas in which such an effect might be expected is NO, for nitric oxide is the only common polar paramagnetic gas.[45] Hence NO has been studied experimentally with special care by Huber,[46] and has also been discussed theoretically by Debye and Huber.[47] The only way to explain the null result obtained experimentally for NO even when liquefied, is probably to assume that electronic rotations may be either clockwise or counter-clockwise with reference to the molecular axis, which we may imagine drawn from the N atom towards the O atom in order to endow this axis with sense as well as direction.

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[43] Theoretically if there is a magneto-electric effect a magnetic field might slightly alter the dielectric constant defined even as $1+4\pi(P-P_0)/F$, for the denominator of the first line of Eq. (5), part I, involves the electric field F through the exponents in the exponential factors. Hence the first line, multiplied by F to give the polarization, changes on application of F, and makes a contribution to $P-P_0$. This contribution, however, is insignificant (of the same order as the effect mentioned in note 35) since the alteration in energy caused by application of F is small compared to kT, and since even with a magneto-electric effect the numerator of the first line of Eq. (5), part I is only of the order H^2. Instead $(P-P_0)/F$ results almost entirely from the second and third lines of Eq. (5), part I, which are independent of a magnetic field.

[44] Perrier and Borel, Archives des Sciences, **7**, 289 and 375 (1925); Szivessy, Zeits. f. Physik, **34**, 474 (1925); Huber, Phys. Zeits. **27**, 619 (1926).

[45] Although NO is the only important paramagnetic polar molecule, a non-paramagnetic polar molecule (e. g., HCl) acquires some magnetic moment due to nuclear rotation (cf. note 39). One at first thought wonders whether this might not cause a magneto-electric directive effect. This effect, however, would obviously be very small, although the smallness of the magnetic moment might be partially offset by the electrical moment being large compared to that in NO. Furthermore in non-gyroscopic diatomic molecules the magnetic moment due to nuclear rotation is perpendicular to the electrical moment, making the effect vanish entirely. In polyatomic molecules there might not be this perpendicularity, but as there are both left and right-handed directions for nuclear rotation there should be on the average no necessary coordination between the directions of electric and magnetic polarizations.

[46] A. Huber, Phys. Zeits. **27**, 619 (1926).

[47] Debye and Huber, Physica, **5**, 377 (1925); Debye, Zeits. f. Physik, **36**, 300 (1926).

This suggestion was made by de Haas in a letter to Debye,[48] and also previously, though in connection with solids rather than NO, in a brief note by Piccard.[49] There should then be two kinds of NO molecules, one in which the component of magnetic moment along the axis of figure has the same sense as the electrical moment, and one in which this component has the opposite sense. These two kinds of molecules differ only in being what one might term "left-handed" and "right-handed," and, since their energies are virtually identical, statistical mechanics requires that they be present in equal amounts. There is thus on the average no correlation between the directions of electric and magnetic moments, and hence no magneto-electric effect. This idea of left and right-handed molecules does not appear unreasonable to the author, who reached independently the same conclusions as de Haas. Critical molecular ray experiments have been proposed by de Haas[48] to test directly the existence of two kinds of NO molecules. Our knowledge of the structure of the NO molecule is now too precise to permit adoption of the suggestion of Bauer[41] or Weigle[50] that the null effect is due to the magnetic and electric moments being at right angles; for band spectrum data of Jenkins, Barton, and Mulliken[51] indicate pretty definitely a component of electronic angular momentum along the axis of figure, as does also the numerical analysis of the paramagnetism of NO to be given in part III.[52]

4. Refractive Index—Effect of Vibration Bands

Hitherto we have been dealing with the dielectric constant for constant fields. It is, however, easy to develop the analogous theory for the refraction of light, as it is not difficult to carry through the mathematical analysis of part I with the modification that the impressed field is assumed periodic in the time instead of constant. The basic formula for the perturbation produced in an individual atom or molecule by an impressed periodic wave, has been given by Born, Heisenberg, and Jordan,[53] and by Schroedinger.[54] This formula is, of course, essentially the Kramers dispersion formula, and is the generalization of Eq. (3), part I, which applied only to constant fields. The mathematical work corresponding to that of part I consists in getting the total polarization from the totality of molecules distributed statistically among the component levels constituting the normal states. There is a noteworthy simplification compared to the calculation with a constant field;

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[48] Cf. Huber, Phys. Zeits. **27**, 625–626 (1926).

[49] Piccard, Archives des Sciences, **6**, 404 (1924).

[50] J. J. Weigle, Phys. Rev. **29**, 362 (1927).

[51] Jenkins, Barton, and Mulliken, Nature, **119**, 118 (1927).

[52] We may note parenthetically that a possible explanation of the absence of the magneto-electric effect in some substances is that the magnetic moment arises entirely from internal spins of the electrons. The alignment of the spin axes in a magnetic field then might not involve orientation of the molecular framework carrying the electric moment. This suggestion is feasible only when the normal states of the atoms or molecules are S-terms, but the gyromagnetic effect seems to indicate that this is quite often the case in solids. The suggestion is inapplicable to NO, as its normal levels are P-terms.

[53] Born, Heisenberg, and Jordan, Zeits. f. Physik, **35**, 572 (1926).

[54] E. Schroedinger, Ann. der Physik, **81**, 109 (1926).

viz., if the impressed frequency ν_0 is large compared to kT/h, a condition practically always met at ordinary wave-lengths, we can disregard entirely the contribution of the "low frequency elements" in the terminology of part I,[55] and so the mathematics consist only in averaging over the different spacial orientations with the aid of the spectroscopic stability formulas given in section 4, part I, and in showing by the "sum-rule" that the various component levels constituting the normal states give equal high frequency contributions. We omit details of the analysis, because they can readily be supplied by readers who understand the calculation in part I. The formula for the index of refraction n is found to be

$$\frac{3}{4\pi}\,\frac{n^2-1}{n^2+2}=\frac{2N}{3h}\sum_{n'(n'\neq n)}\frac{\nu(n\,;\,n')\,|M(n\,;\,n')|^2}{\nu_0{}^2-\nu(n\,;\,n')^2}, \tag{3}$$

as the right-hand side of this equation is readily shown to be the proper, as well as very obvious, generalization of Eq. (17), part I to a periodic rather than constant field. The notation in (3) is the same as in Eq. (17), part I, and thus the expressions $\nu(n;\,n')$, being absorption frequencies, are all negative. The important thing about Eq. (3) is that it does not contain the temperature except through N, in agreement with the well-known experimental fact[56] that the refractivity per molecule for visible light usually does not vary with temperature, unlike the dielectric susceptibility of polar gases at infinite wave-lengths. The invariance of the molecular refractivity of the temperature in non-monatomic gases appears usually to be considered as something axiomatic not requiring theoretical proof[57] despite the "temperature rotation" of the nuclei, etc., but in reality it may be regarded as an interesting experimental check on the sum-rules and spectroscopic stability.

The remarks previously made about independence of dielectric constants of magnetic fields, pressure, field strength, etc., of course apply equally well to refractive indices. A possible exception to the statement occurs when the impressed frequency is close to an absorption frequency of the atom or molecule, for then Eq. (3) fails. Also the refractive index may vary with the temperature near an absorption band, as alteration of the temperature may change the concentration of atoms in the particular component state which resonates closest to the impressed frequency. It is clearly to be understood that even in the new mechanics there is still the familiar Faraday rotation of the plane of polarization in a longitudinal magnetic field, and also an extremely intense magnetic field will produce a slight distortion in the dispersion and a double refraction such as is involved in the classical Cotton-

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[55] The reason why we can disregard the low frequency elements $(njm;\,nj'm')$ in an impressed field of high frequency ν_0 is that in such a field the low frequency elements contribute terms to the polarization of the order $(\nu(njm;\,nj'm')/\nu_0)^2$ times those in the case of a constant field.

[56] Cf. especially recent experiments by E. W. Cheney, Phys. Rev. **29**, 292 (1927).

[57] A proof that in the classical theory the optical refraction is independent of the temperature despite the nuclear rotation of the molecules will be published in the Madison lectures of Prof. Debye.

Mouton effect.[58] The latter effect, however, is analogous to the Kerr effect, and hence quadratic in H^2, or beyond the scope of the present paper (cf. note 35). In the old quantum theory, on the other hand, spacial quantization in a relatively small magnetic field would cause optical dissymmetry and a large double refraction not found experimentally.[59]

Relation of dielectric constant to index of refraction. In a non-magnetic medium the dielectric constant equals the square of the index of refraction for infinitely long wave-lengths. However, we have already seen above that the permanent dipole moment of the molecule, which is responsible for the "low frequency elements," makes an appreciable contribution to the polarization only at very long wave-lengths, and so influences the shape of the dispersion curve only in the far infra-red. Therefore we should expect the extrapolation of the dispersion curves made for visible light to infinitely long wave-lengths or zero frequency to yield a value n_0^2 for the square of the index of refraction which equals only the part of the dielectric constant due to "high frequency elements" or "induced polarization." In other words we should have $n_0^2-1=4\pi N\alpha$, as can also be seen by comparing the extrapolation of (3) with Eq. (17), part I. Here and in the remainder of the present section we for simplicity neglect the small Clausius-Mossotti correction, so that we disregard the factor $3/(n^2+2)$ in (3) and the analogous factor in (1).

Actually n_0^2-1 often does not agree with the value of $4\pi N\alpha$ determined from measurements of dielectric constants. For instance, in HCl at 0°C and atmospheric pressure, Zahn[60] finds $4\pi N\alpha=.001040$, whereas Cuthbertson and Cuthbertson[61] find that $n^2-1=.000888$ for illumination by sodium D-light, and the extrapolation to infinite wave-lengths by their Sellmeier dispersion formula gives $n_0^2-1=.000871$.

The following explanation of discrepancies such as that mentioned in the preceding paragraph has been tentatively suggested by Debye,[62] Ebert,[34] and others. Besides the "electronic" absorption frequencies (i.e. "electron transitions" in the quantum theory), and besides the pure rotation spectrum, which is in the far infra-red and corresponds to the polarization due to permanent dipoles, we must consider the "vibrational spectrum" arising from nuclear oscillations. The latter spectrum is usually located in the infra-red, and is far enough removed from the visible so that it does not introduce any irregularity in ordinary dispersion curves for visible light. Consequently extrapolation of these curves to infinite wave lengths does not include the contribution of the vibrations to the polarization. If the dispersion curve could be carried through the infra-red, the refractive index should rise to a maximum at resonance with vibrational frequencies and should then decrease

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[58] A. Cotton and H. Mouton, Journ. de Phys. **1**, 5 (1911); Ann. de Chim. et Phys. **19**, 153, **20**, 194 (1910); cf. P. Debye, Handbuch der Radiologie, vol. VI, pp. 754 and 769.

[59] Cf. O. Stern, Zeits. f. Physik, **7**, 249 (1922); R. Fraser, Phil. Mag. **1**, 885 (1926); W. Schütz, Zeits. f. Physik, **38**, 853 (1926).

[60] C. T. Zahn, Phys. Rev. **24**, 400 (1924).

[61] C. and M. Cuthbertson, Phil. Trans. Roy. Soc. **213A**, 1 (1913).

[62] P. Debye, Handbuch der Radiologie, vol. VI, p. 620.

to a value at infinite wave-lengths which is greater than the value n_0^2 obtained by extrapolation of smooth curves taken only in the visible region.

A mathematical expression for this vibrational effect is easily obtained for diatomic molecules. Let m be the effective mass for the vibrations, which is $m_1m_2/(m_1+m_2)$, where m_1, m_2 are the masses of the two nuclei. Let q be the "effective charge," which is the factor by which we must multiply the amplitude of oscillation to get the corresponding change in moment. More precisely, q is the coefficient of the linear term in the series development $p=\mu+q(r-r_0)+\cdots$ of p in terms of $r-r_0$, where p is the electrical moment averaged over the rapid, purely electronic periods and where r is the nuclear separation, and r_0 is the equilibrium value of r. Now usually nuclear vibrations are small enough so that they may be represented quite approximately by a harmonic oscillator of frequency ν. The vibrational susceptibility, or quotient of polarization by field strength, is then

$$Nq^2/12\pi^2m(\nu^2-\nu_0^2) \tag{4}$$

Classically (4) is obtained immediately by making the well-known elementary calculation of the polarization due to a harmonic oscillator; (4) is, however, 1/3 as great as the usual Drude expression, since the nuclear vibrations are only along the molecular axis, whose orientation is random, and so represent one degree of freedom rather than three as in the usual "isotropic" oscillator. The result (4) can also be obtained with quantum mechanics by making in (3) the substitution $M(n;\, n')=qA(0,\,1)$, and also $\nu(n,\,n')=-\nu$. Here $A(0,\,1)$ denotes the amplitude associated with a transition between the two lowest states of a one-dimensional oscillator. The theoretical value[63] of $|A(0,\,1)|^2$ is $h/8\pi^2m\nu$, showing that the vibrational term of the right side of (3) gives (4). The identity of results with the classical and quantum theories is not surprising, for complete agreement between the two theories is in general characteristic of the harmonic oscillator.[64] At visible wave-lengths, the impressed frequency ν_0 is so great compared to ν that the contribution of (4) to the total polarization is negligible compared to what it is with a constant field. Since such a field corresponds to zero impressed

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[63] Cf., for instance, M. Born, "Problems of Atomic Dynamics," p. 84.

[64] We are apparently overlooking the fact that the axis of nuclear oscillation is continually rotating rather than stationary. However, we shall see classically in section 6 that the polarization of a harmonic oscillator is, at least in constant fields, unaffected by rotation of the molecule, (cf. also note 57) provided, of course, we neglect the slight distortion due to centrifugal expansion, and suppose that the nuclear rotation frequencies are negligible compared to those of vibration. A like result also holds in the quantum theory, as is to be expected since the spectroscopic stability relations given in part I show that summing over the discrete succession of quantized rotational motions gives the factor 1/3 due to spacial orientation quite as generally as the hypothesis of random orientations in the classical theory. The factor $M(n;\, n')$ in the vibrational part of the right-hand side of (3) must, in fact, have very approximately the same value as for a one-dimensional oscillator vibrating along a fixed axis, for otherwise a weak rotation would perceptibly change the total vibrational absorption, which is absurd. That a sufficiently slow rotation does not appreciably affect the validity of (4) in the quantum theory can also be seen explicitly by substituting the amplitude matrices for the rotating elastic dipole given by Mensing,[12] Oppenheimer,[13] or Fues,[13] and then adding the contributions of the "P" and "R" branches, which we have not resolved.

frequency, we see by (4) that the nuclear vibrations make a contribution $\alpha_{vib}=q^2/12\pi^2mv^2$ to the constant α in the Debye formula (1) for the static dielectric constant. According to the suggestion of Debye or Ebert, we might expect that $4\pi N\alpha_{vib}=4\pi N\alpha-(n_0{}^2-1)$.

Measurements of the absolute intensity of infra-red vibrational absorption bands, which is proportional to the square of the oscillation in moment and hence to q^2, furnish estimates of the effective charge q, and show that the vibrational polarization calculated in the above paragraph is far too small to account for the observed discrepancy between the extrapolation of n^2 and the induced polarization part of the dielectric constant in HCl. The most accurate infra-red intensity measurements are probably those of Bourgin,[65] who finds that here $q=.828\times10^{-10}$ e.s.u. Introducing this value of q, and the values $m=1.62\times10^{-24}$, $\nu=8.82\times10^{13}$ of the effective mass and vibrational frequency of HCl in the preceding formula for α_{vib}, we find that $4\pi N\alpha_{vib}$ is only 1.5×10^{-6}, whereas we have seen that the discrepancy between $n_0{}^2-1$ and $4\pi N\alpha$ is 1.7×10^{-4}. Values of q have also been calculated by Dennison[66] for HBr, CO, CO_2, NH_3, CH_4 from various intensity measurements. These values are all less than one-fifth the electronic charge 4.774×10^{-10} and correspondingly $4\pi N\alpha_{vib}$ is of the order 10^{-6} and hence negligible, as in HCl. Of course, absolute intensities are hard to measure with precision,[67] and one wonders whether the experimental values of q may not be in error. However, to account for the discrepancy 1.7×10^{-4} in HCl the effective charge would have to be about 8.7×10^{-10} e.s.u. Since the absorption coefficient varies as q^2, the measurement of this coefficient would have to be in error by a factor about 100, which seems clearly out of the question inasmuch as Bourgin claims an error of only 10 or 20 percent.

Thus the absorption measurements apparently show very definitely that in molecules such as the hydrogen halides the vibrational polarization is too small to have any bearing on the discrepancy between refractive indices and dielectric constants. The possibility of electronic bands in the infra-red as an alternative explanation does not seem at all likely, for HCl is doubtless stable enough so that its lowest normal electronic absorption frequencies

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[65] D. G. Bourgin, Phys. Rev., June, 1927. We use essentially Dennison's rather than Bourgin's definition of the effective charge, so that our q is dp/dr rather than p/r in Bourgin's notation. The reader must not confuse our q with the factor $k=\mu/r_0$ (Bourgin's q_0) by which we must multiply the nuclear separation to get the electrical moment when the molecule is at rest. It is, however, not unreasonable that q and k should be roughly of the same order of magnitude, and Bourgin's measurements seem to show that they are very nearly equal.

[66] D. M. Dennison, Phil. Mag. **1**, 195 (1926). Dennison used the old quantum theory but fortunately his amplitude for a harmonic oscillator agrees with the new mechanics, as does also Bourgin's half-quantum amplitude.

[67] As an instance of the error in absolute intensity measurements, the absorption coefficient calculated by Tolman and Badger (Phys. Rev. **27**, 383, 1926) from Czerny's intensity data on the pure rotation bands of HCl disagrees by a factor about 20 with the much more reliable theoretical value computed with the aid of the moment 1.03×10^{-18} demanded by the new quantum mechanics and Zahn's dielectric constant data (cf. Kronig[16]). The error in measuring the intensity of vibrational bands is presumably not as great, though we may note that Dennison's[66] value $.33\times10^{-10}$ of the effective charge q for HCl deduced from Bahr's and Burmeister's intensity data yields an absorption coefficient only 1/6 that of Bourgin's.

are in the ultra-violet. This, however, does not necessarily mean that in other kinds of molecules than HCl (e.g., perhaps ethyl-ether) there may not be infra-red vibrational or electronic bands of such large amplitude, high effective charge or low frequency as to have an important influence on the correlation of refractive indices and dielectric constants. It may be noted that in molecules such as HCl, the discrepancy between n_0^2-1 and $4\pi N\alpha$ is only a fraction of $4\pi N\alpha$, and that $4\pi N\alpha$ itself is often small compared to $\epsilon-1$. Therefore a small experimental error in the electrical moment, i.e., in the determination of the temperature coefficient of $(\epsilon-1)/N$ will suffice to explain away the discrepancy between n_0^2-1 and $4\pi N\alpha$. Thus in HCl, if we assume the absolute value of the total dielectric constant to be approximately correct, an increase [68] in the moment from Zahn's value 1.034×10^{-18} to 1.07×10^{-18} c.g.s.u., which corresponds to an error of 7 percent in the temperature coefficient of $(\epsilon-1)/N$, will increase the contribution of the permanent dipoles to the right-hand side of (1) enough so that the remainder $4\pi N\alpha$ is decreased to a value $.871\times 10^{-3}$ in accord with optical data. An error of 5 percent in the absolute magnitude of the polarization would also account for the discrepancy. In ammonia the contribution of permanent dipoles to the dielectric constants so overshadows the induced polarization that in increase of only .3 percent in the moment, a change clearly within the experimental error, will diminish Zahn's[69] value .000768 for $4\pi N\alpha$ to a value .000729 in accord with the Cuthbertson[61] dispersion data. In ethyl-ether, on the other hand, the contribution of permanent dipoles is relatively small,[70] and the discrepancy thus much more vital. Doubtless future experimental refinements will minimize the discrepancy between optical and dielectric constant data in many instances. Zahn's recent work,[69] for instance, greatly improved the situation in ammonia. Also we shall see in the next section that the correction for the slight departures from the Debye formula in the quantum theory helps matters a little in some cases.

5. LIMIT OF ACCURACY OF THE DEBYE FORMULA IN THE QUANTUM MECHANICS

In Part I we assumed that the nuclear rotation frequencies were smal compared to kT/h, so that we could develop the polarization as a power series in the ratio $s=h\nu(njm;nj'm')/kT$. In fact we disregarded terms beyond s^2 in the bracketed part of Eq. (9), part I. We have already mentioned on p. 34 that s is not small compared to unity for states with sufficiently large

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[68] Against the possibility of an error in the moment of HCl may be mentioned the fact that Raman and Krishman (Phil. Mag. **3,** 713, 1927) deduce by an entirely different method involving combination of measurements on depolarization of light and the Kerr effect, a moment 1.04×10^{-18} in excellent accord with Zahn's value 1.03×10^{-18}. However, Raman and Krishman also similarly deduce a moment 1.66×10^{-18} for CH^3Cl, which does not agree at all with Sanger's[8] value 1.97×10^{-18} deduced from dielectric constants, of which they were not aware, and this suggests that the error in determining moments by one of the methods has been underestimated.

[69] C. T. Zahn, Phys. Rev. **27,** 455 (1926).

[70] Cf. Debye, Handbuch der Radiologie, vol. VI, p. 625.

rotational quantum numbers. We saw qualitatively in note 26 of part I, that the resulting error is not large because such states are relatively infrequent, and we shall now make a quantitative computation of this error by including two higher powers of s than previously. For explanation of the rather involved notation the reader is referred to part I. If we disregard terms beginning with s^5 instead of with s^3 in the bracketed factor of (9), part I, it is readily seen by using the same reasoning as in deducing Eq. (11), part I, that we must add to Eq. (1) the correction term

$$-(h^2B/12k^3T^3)\sum_{j,m,j',m'}\nu(njm\,;\,nj'm')^2\,|\mu_z(jm\,;\,j'm')|^2 e^{-W(nj)/kT} \qquad (5)$$

The expression (5) is readily evaluated at high temperatures by comparison with the kinetic energy function. Let us assume the most general rigid[71] polyatomic molecule, having as a rule three unequal moments of inertia. There are then three degrees of rotational freedom, and the index j represents two quantum numbers, the third being denoted by m (cf. p. 733, part I). Let $\mathbf{x}_i$, $\mathbf{y}_i$, $\mathbf{z}_i$ be the coordinates of the ith constituent nucleus referred to a set of axes fixed in space, and let u_i, v_i, w_i be its coordinates referred to the principal axes of inertia, which rotate with the molecule. The center of gravity is, of course, to be chosen as the origin of both coordinate systems, and the electric field F is assumed to be applied along the z-axis. Since the molecule is rigid the coordinates u_i, v_i, w_i are constants("c-numbers") whereas $\mathbf{x}_i$, $\mathbf{y}_i$, $\mathbf{z}_i$ are matrices, and a typical element of $\mathbf{z}_i$ may be denoted[72] by $z_i(jm\,;j'm')$. By the rules for matrix multiplication the rotational kinetic energy of the state n, j, m is

$$T(njm)=\sum_i\left\{2\pi^2m_i\sum_{j',m'}\nu(njm\,;\,nj'm')^2\,|z_i(jm\,;\,j'm')|^2\right\} + \text{similar terms in } x \text{ and } y, \qquad (6)$$

where the summation over i includes all the nuclei in the molecule, as we may neglect the contributions of the electrons to the rotational energy. Now let I^u, I^v, I^w be unit vectors coinciding with the u, v, w axes respectively, and let $l_z^u(jm\,;j'm')$ denote a matrix element of the z-components of I^u, etc. Then

$$z_i(jm\,;\,j'm')=u_il_z^u(jm\,;\,j'm')+v_il_z^v(jm\,;\,j'm')+w_il_z^w(jm\,;\,j'm') \qquad (7)$$

If we substitute (7), and the analogous formulas for x and y into (6), a considerable simplification ensues since "products of inertia" such as $\sum_i m_iu_iv_i$ vanish. Also $\sum m_iu_i^2$ is the moment of inertia U with respect to the plane vw, with corresponding definitions for V and W (this W must not be confused with an energy element $W(njm)$). The mean rotational energy is obtained by averaging over the various states j, m weighted according to the Boltzmann factor (cf. p. 733, part I). Consequently, using (7), and averaging, we find

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[71] It is to be noted that we are now assuming a rigid molecule, whereas in Part I we made the perhaps less stringent requirement of a permanent dipole moment. The difference is unimportant here, as we are calculating only a correction term.

[72] We for brevity write the arguments of an element of $\mathbf{z}_i$, etc., as $(jm;j'm')$ rather than as $(njm;nj'm')$ for the rigidity implies that there are no elements in which $n'\neq n$, making the index n unnecessary.

$$T_{\text{mean}}=6\pi^2BN^{-1}\sum\nolimits_{j,m,j',m'}U\nu(njm\ ;\ nj'm')^2\,|l_z{}^u(jm\ ;\ j'm')\,|^2e^{-W(nj)/kT} \tag{8}$$
$$+\ \text{similar terms in } v \text{ and } w,$$

where B is defined as in Eq. (6), part I, and where, as on p. 736, we neglect the difference between $W(njm)$ and $W(nj)$. Instead of adding in the contributions of the x and y components in (8), we have multiplied by the factor 3, which is legitimate in view of the spectroscopic stability relations given in section 4, part I. Now the first line of (8) is the part of the mean kinetic energy resulting from the moment of inertia U with respect to the plane vw. This energy results partly from rotation about the v axis and partly from rotation about the w axis. It is, in fact, $UT_v/B+UT_w/C$, where T_v is the mean kinetic energy of rotation about the v axis, etc., and where A, B, C are the moments of inertia about the axes u, v, w respectively. This result follows inasmuch as $C=U+V$, so that a fraction U/C of T_w is due to U, etc. Here the reader must distinguish carefully between moments of inertia about *axes* and *planes* (denoted respectively by A, B, C and U, V, W) and also between the corresponding apportionments of energy. Now at ordinary temperatures the rotational energy can be calculated fairly accurately in most gases by the classical theorem of equipartition. This is evidenced by specific heats, and is due to the asymptotic connection of classical and quantum statistics for large quantum numbers. According to classical statistics the total rotational kinetic energy is $3kT/2$, and is apportioned equally between the three principal axes[73] (though not between the three principal planes). Therefore $T_u=T_v=T_w=\frac{1}{2}kT$ and hence the first line of (8) equals

$$\tfrac{1}{2}kT(U/B+U/C) \tag{9}$$

with analogous results for the v and w parts of (8).

Now if the electrical moment vector is "permanent" and rigidly mounted on the molecules, its components μ_u, μ_v, μ_w along the u, v, w axes will be constants (c-numbers in Dirac's terminology) and $\mu_z(jm\,;j'm')$ will be given by a formula identical with the right side of (7) except that μ_u, μ_v, μ_w replace u_i, v_i, w_i. From this it follows that

$$\sum\nolimits_{m,j'm'}|\mu_z(jm\ ;\ j'm')\,|^2=\sum\nolimits_{q=u,v,w}\Big\{\sum\nolimits_{m,j',m'}\mu_q{}^2\,|l^q{}_z(jm\ ;\ j'm')\,|^2\Big\} \tag{10}$$

since sums of the form $\sum_{m,j',m'}l_z{}^u(jm\,;j'm')l_z{}^{v*}(jm\,;j'm')$ ($*=$conjugate) vanish because $\boldsymbol{l}^u$ and $\boldsymbol{l}^v$ are perpendicular vectors.[74] By (10) we see that the

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[73] The proposition that classically the mean kinetic energy associated with each principal axis is $\frac{1}{2}kT$ is easily established by a simple change of variables in the integrals associated with the distribution function. In place of the three canonical momenta conjugate to the Eulerian angles we introduce "momentoids" proportional to the instantaneous angular velocities about the three principal axes. The kinetic energy then becomes the sum of three terms which are each proportional to the square of a momentoid and which represent respectively the kinetic energy about the three principal axes. The terms are then of the squared form to which the equipartition theorem can be applied separately. Cf. Jeans, Dynamical Theory of Gases, 3rd ed., p. 97, and footnote, p. 98.

[74] The vanishing of sums of this form is fairly obvious from the fact that it is the quantum analog of the fact that an expression of the form $\mathbf{a}_z\mathbf{b}_z$ vanishes on averaging over random orientations if $\mathbf{a}$ and $\mathbf{b}$ are perpendicular vectors. A more rigorous proof can be obtained by a slight extension of the spectroscopic stability argument given in Part I. A simple symmetry

contribution of μ_u to (5) differs from the first line of (8), and hence from (9), only by a factor $-N\mu_u^2h^2/72\pi^2Uk^3T^3$. Analogous results hold for the v and w contributions. Adding the correction term (5), thus evaluated, to the right side of (1), we obtain the revised Debye formula

$$\frac{3}{4\pi}\frac{\epsilon-1}{\epsilon+2}=N\alpha+\frac{N\mu^2}{3kT}[1-f(T)] \tag{11}$$

where the new feature in the correction term

$$f(T)=\frac{h^2}{48\pi^2kT\mu^2}\left[\mu_u^2\left(\frac{1}{B}+\frac{1}{C}\right)+\mu_v^2\left(\frac{1}{C}+\frac{1}{A}\right)+\mu_w^2\left(\frac{1}{A}+\frac{1}{B}\right)\right] \tag{12}$$

Thus in making the hypothesis of "slowness of precession" we simply disregarded higher powers of T in the denominator. If we had retained even higher powers of s, we would find $f(T)$ contained terms in T^{-2}, T^{-3}, etc. In the special case of diatomic molecules (case *a* or *b*, section 2), and of symmetrical polyatomic molecules (case *c*) we may take $\mu_w=\mu$, $\mu_v=\mu_u=0$, $A=B$, and then (12) becomes $f(T)=h^2/24\pi^2AkT$, the same value as previously obtained by Kronig[16] and Manneback[23] for cases (*a*) and (*c*) respectively by a quite different method. As noted by various writers, the correction term is usually small except at very low temperatures. In HCl, for instance, $f(T)$ is about .016 at ordinary temperatures. The main value of calculating (12) is to determine the limit of accuracy of the unmodified Debye formula in the quantum mechanics. In the classical theory, which corresponds to $h=0$, the correction of the type under consideration disappears completely.

The slight numerical correction due to $f(T)$ is, however, of some interest in correlating refractive indices and dielectric sonstants, for we have seen in section 4 that a slight change in the constants may materially alter the discrepancy between optical and electrostatic data. Experimentally the moment is approximately determined by the temperature coefficient of $(\epsilon-1)/N$ at a room temperature T_0, and hence with the correction μ^2 must be increased by a factor about $1+2f(T_0)$ to give this coefficient the same value as previously. Thus very roughly the effect of the correction is to increase the contribution of permanent dipoles to the susceptibility by a factor $1+f(T_0)$ and hence to diminish $N\alpha$ by an amount $N\mu^2f(T_0)/3kT_0$. A more careful calculation shows that Zahn's data for HCl can now be fitted as well with $\mu=1.06\times10^{-18}$, $4\pi N\alpha=.00098$ as before with his values 1.03×10^{-18} and .00104 respectively. Dispersion measurements give $n_0^2-1=.000871$, and thus the correction removes about one-third of the discrepancy between n_0^2-1 and $4\pi N\alpha$ in HCl, and decreases correspondingly the estimate made in section 4 of the experimental error necessary to explain the discrepancy.

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argument, however, shows most readily that such sums must vanish, for if they did not, the susceptibility would contain a term proportional to $\mu_u\mu_v$; alteration of the sign of μ_u would then change the susceptibility which is absurd since in our problem there is no criterion for distinguishing between the positive and negative u directions.

6. CLASSICAL DERIVATION OF THE LANGEVIN-DEBYE FORMULA

In the present section we shall derive the Langevin or Debye formula by means of classical theory. Our proof will be roughly the classical analog of the quantum calculation given in part I, and is likewise more general than the ordinary demonstrations, though very easy for those understanding the use of angle and action variables.[75] Let us suppose that we have a multiply periodic dynamical system with f degrees of freedom, specified by $2f$ canonical variables $w_1^0, \cdots, w_f^0, J_1^0, \cdots, J_f^0$. We suppose further that the w^0's and J^0's are respectively true angle and action variables for the system in the absence of the field F. When $F=0$ the w^0's are thus linear functions $w_k=\nu_k t+\epsilon_k$ of the time t, while then the J^0's are constants which incidentally in the old quantum theory would be equated to integral multiples of h. Instead of being a matrix as in part I, the z-component of electrical moment will be a multiple Fourier series

$$M_z=\sum_\tau M_\tau^{(z)}e^{2\pi i(\tau w^0)}. \tag{13}$$

We use the same notation as in Born's "Atommechanik" (p. 86, etc.) Thus (τw^0) is an abbreviation for the expression $\tau_1 w_1^0+\cdots+\tau_f w_f^0$, and the subscript $\tau_1\tau_2\cdots\tau_f$ is abbreviated to τ. The summation is f-fold, and extends over all positive and negative values of the integers $\tau_1\cdots\tau_f$. The complex amplitudes $M_\tau^{(z)}$ are, of course, functions of the J^0's as well as the τ's, and $M_{-\tau}^{(z)}$ is the conjugate of $M_\tau^{(z)}$. Classical statistics show that if a field is applied along the z-direction, the susceptibility is

$$\chi=\frac{N\displaystyle\iint M_z e^{-W(F)/kT}dJ^0dw^0}{F\displaystyle\iint e^{-W(F)/kT}dJ^0dw^0}, \tag{14}$$

where we denote by dJ^0dw^0 an element of volume $dJ_1^0\cdots dJ_f^0dw_1^0\cdots dw_f^0$ of the "phase space" and the integral sign thus denotes f integrations. The integration, of course, corresponds classically to summation over a discrete series of allowed states in quantum mechanics. It is clearly to be understood that we are keeping the *original* canonical variables $w_1^0, \cdots, w_f^0, J_1^0, \cdots, J_f^0$. Since the transformation from a Cartesian to the w^0, J^0 system is thus not modified to take account of the field F, the w^0's and J^0's will cease to be true angle and action variables; i.e., cease to be respectively linear in t and constant, after the field F is applied. The w^0's and J^0's will, however, remain canonically conjugate, and we can apply (14) because it is a fundamental theorem in statistical mechanics that the a-priori probability is proportional to the volume occupied in the phase space, regardless of what $2f$ variables we choose as constituting the coordinates of this space

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[75] For further detail on the dynamical technique underlying the use of angle and action variables, with which we assume some familiarity, see Born's "Atommechanik," or Chap. XI of the writer's "Quantum Principles and Line Spectra."

provided only they are canonical.[76] In (14) $W(F)$ denotes the energy or Hamiltonian function *in* the field F, and equals W_0-FM_z, where M_z is given by (13), and W_0 is the energy function for $F=0$. W_0 is a function only of the J^0's whereas $W(F)$ involves also the w^0's through M_z. Now approximately $e^{-W(F)/kT}=e^{-W_0/kT}(1+FM_z/kT+\cdots)$ and hence if we keep only the part of the susceptibility which is independent of F, Eq. (14) becomes

$$\chi=\frac{N\int\int M_z^2e^{-W_0/kT}dJ^0dw^0}{kT\int\int e^{-W_0/kT}dJ^0dw^0}. \tag{15}$$

Here we have assumed that the polarization vanishes when $F=0$; i.e., that the numerator of (14) vanishes when $W(F)$ is replaced by W_0. An analogous assumption was made in supposing the first line of Eq. (5), part I, equaled zero, and a more detailed justification for the assumption is given on p.735, part I. Now since the square of two multiple Fourier series is itself such a series, M_z^2 may be expressed as a multiple Fourier series in the w^0's. On integrating over the w^0-part of the phase space the contributions of all terms in this multiple Fourier development of M_z^2 vanish except the constant term $(M_z^2)_0$, for integrals of periodic terms in the w^0's taken over a period[77] are zero. By the rules for multiplying together Fourier series term by term, (M_z^2) equals $\sum_\tau M_\tau^{(z)}M_{-\tau}^{(z)}$ which is, of course, a function only of the J^0's. Eq. (15) now becomes

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[76] Another way of saying the same thing is that contact transformations have unit functional determinants, so that the "extension in phase" is invariant of the choice of canonical coordinates. Cf., for instance, Adams, "The Quantum Theory," 2nd ed., p. 26 (Bull. Nat. Research. Coun., No. 39).

[77] *Limits of integration in* (14)–(15). If we integrated over the entire phase space in the J^0,w^0 system the limits of integration for each of the w^0's in (14) or (15) would be from $-\infty$ to $+\infty$, as all of the w^0's may increase without limit. However, since the system is cyclic in each of the w^0's with unit period, it is clear that we will obtain the correct statistical average if we take the limits of integration for each of the w^0's as zero and unity. Another way of saying the same thing is that Cartesian variables are multiple valued in the w^0's, so that the entire Cartesian phase space corresponds to only one period for the w^0's.

The limits of integration for the J^0's can usually be taken as 0 and $+\infty$ by proper choice of the fundamental periods. (The limits, however, are $-\infty$ and $+\infty$ for J^0's associated with both left and right-handed rotations, as, for instance, the J^0 associated with the axial component of angular momentum.) The system must, of course, be of the type for which the J^0-integrals converge; i.e., be of a kind for which classical statistical mechanics have a meaning. This ordinarily means that the energy ranges from some finite value to $+\infty$. This condition is not met in any actual Rutherford atom based on the inverse square law, for there the energy ranges from $-\infty$ to 0, and the writer has already remarked elsewhere (cf. "Quantum Principles and Line Spectra," p. 14) that purely classical statistics are meaningless as applied to an actual atomic system, for they would give an overwhelming probability that the electrons be infinitely close to the nucleus. The only way of avoiding this difficulty would be to employ a rather illogical "semi-classical" theory in which we apply classical statistics to the degrees of freedom for which the J^0-integrals converge, but confine the remaining J^0's to certain particular (i.e., in a sense "quantized") values.

$$\chi = \frac{N\int (M_z^2)_0 e^{-W_0/kT} dJ^0}{kT\int e^{-W_0/kT} dJ^0} = \frac{N\overline{M^2}_z}{kT},$$

where $\overline{M_z^2}$ denotes the statistical mean square of M_z in the absence of the field F; i.e. the average over the J^0-space, weighted according to the Boltzmann factor, of the time average value of M_z^2 for an orbit having given values of the J^0's. Now if there are no external fields present when $F=0$, or, if as is usually the case, the other fields are weak enough so that we may neglect their effect on the spacial distribution, it is clear that all spacial orientations will be equally probable, and the mean squares of the x, y, and z components of moment will be equal. We may then replace $\overline{M_z^2}$ by one-third the statistical mean square of the vector moment $\boldsymbol{M}$ of the molecule. Thus we have

$$\chi = N\overline{\boldsymbol{M}^2}/3kT, \tag{16}$$

which is a sort of generalized Langevin or Debye formula.

Our derivation of (16) is considerably shorter than the quantum proof of the Langevin-Debye formula given in Part I. The reason for this is that we are able to apply classical statistical theory keeping the same set w^0, J^0 of canonical variables as in the absence of F, even though these variables undergo perturbations. Since $dw^0 dJ^0 = dwdJ$, Eq. (16) might also be deduced by starting with a formula identical with (14) except that the variables of integration are $w_1, \cdots, w_f, J_1, \cdots, J_f$ instead of $w_1^0, \cdots, w_f^0, J_1^0, \cdots, J_f^0$. Here the w's and J's (in distinction from the w^0's and J^0's) denote a set of true angle and action variables for the perturbed system, which are respectively linear in t and constant even when F does not vanish, and which are deduced from Cartesian variables by a transformation involving F. Then $W(F)$ is a function only of the J's, viz., $W(F) = W_0 - F(M_z^{(F)})_0$, and the effect of integrating over the w's is simply to replace the integrand M_z by the constant term $(M_z^{(F)})_0$ of its multiple Fourier development in the w's. Here $(M_z^{(F)})_0$ is not the same as the constant term $M_0^{(z)}$ of the development (13) in the w^0's and perturbation theory shows that

$$(M_z^{(F)})_0 = M_0^{(z)} - 2F\Sigma_{(\tau\nu^0)>0}\Sigma_k \tau_k \frac{\partial}{\partial J_k}\left(\frac{|M_\tau^{(z)}|^2}{(\tau\nu^0)}\right), \tag{17}$$

where the arguments of $M_0^{(z)}$ and the $M_\tau^{(z)}$ are to be taken as the J's rather than J^0's. Eq. (17) is the classical analog of Eq. (3), Part I. For proof of (17) see, for instance, Born, Zeits. f. Physik, **26**, 385 (1924); Eq. (17) is the extrapolation of Eqs. (22) and (24) of his article to infinitely long impressed wave-lengths.

The proof by the w, J method outlined in the preceding paragraph parallels in a much closer and more illuminating fashion the quantum calculation given in Part I than does the w^0, J^0 method. We have nevertheless given the w^0, J^0 method in detail because it is the simpler. If we use instead the w's and J's it is necessary to integrate by parts to get rid of the J-derivatives in (17). This partial integration corresponds in a general way to the manipulation used in simplifying Eq. (5) into (11) in Part I.

Eq. (16) does not appear to have previously been given in its full generality, and is much more comprehensive than the ordinary Eq. (1), since the statistical mean square moment appearing in (16) must not be confused with the average for an individual orbit or atom, and is in general a function of the temperature. Eq. (16) reduces to (1) only with certain simplying assumptions.

Rigid model. If we assume that the molecule has a permanent moment μ independent of the J's then we may replace $\overline{M^2}$ by μ^2 in (16). The present method thus shows that the contribution of the permanent dipoles to the susceptibility is given by the familiar Langevin expression $N\mu^2/3kT$ even in the most asymmetrical rigid molecules, despite the kinetic energy of rotation. Such a molecule has, of course, three unequal moments of inertia and three rotational degrees of freedom corresponding to three pairs of action and angle variables.

Elastic model. In general the molecule is elastic, so that the moment vector $\boldsymbol{M}$ vibrates about its mean value, and we shall show that this effect is responsible for the induced polarization, or first right-hand term of Eq. (1). Let us assume the molecule has $p=f-3$ vibrational degrees of freedom associated with oscillations about an equilibrium configuration in addition to the three rotational degrees of freedom. This model cannot be regarded as corresponding to physical reality, for in actual Rutherford atoms the electrons do not have positions of static equilibrium, although the nuclei do approximately. This objection, however, need not alarm us, for we have already mentioned in note 77 that classical statistics cannot be applied to a real atom or molecule, and it is only by picturing the electrons as linear oscillators that pure classical theory can explain dispersion, etc. Let the p vibrations have frequencies ν_i, effective charges q_i, and effective masses $m_i (i=1, \cdots, p)$. We shall suppose the vibrations small enough so that the restoring forces can be regarded as linear, and neglect the slight distortion of the vibration frequencies, etc., by centrifugal force caused by rotation of the molecule as a whole. Then the vector moment $\boldsymbol{M}$ will be the sum of a constant term $\boldsymbol{M}_0$ and p terms $\boldsymbol{M}_1, \boldsymbol{M}_2, \cdots$ which are simple harmonic functions of the time with frequencies $\nu_1, \nu_2, \cdots$ respectively, and on the average $\boldsymbol{M}^2$ equals $\boldsymbol{M}_0^2+\boldsymbol{M}_1^2+\boldsymbol{M}_2^2+\cdots$. This separation of $\boldsymbol{M}$ into $\boldsymbol{M}_0$ and periodic terms corresponds roughly to the resolution of the moment matrix into low and high frequency elements in part I. Furthermore $\boldsymbol{M}_1$ differs from the vector amplitude $\boldsymbol{A}_1$ of the corresponding oscillation only by a factor q_1, and therefore $\overline{\boldsymbol{M}_1^2}$ equals $kTq_1^2/4\pi^2 m_1\nu_1^2$, etc., since the mean of the kinetic energy $2\pi^2\nu_1^2 m_1 \boldsymbol{A}_1^2$ of a harmonic oscillator with one degree of freedom is $\frac{1}{2}kT$. Thus the mean square of the vibrational moment is proportional to T, and this cancels the T in the denominator of (16), so that the contribution of the p vibrations to the susceptibility is an expression

$$N\alpha = N\sum_{i=1,\cdots,p} q_i^2/12\pi^2 m_i \nu_i^2$$

which is independent of the temperature at constant density. In case the vibrations are due entirely to one isotropic oscillator per molecule, then as such an oscillator represents three degrees of freedom, we have $p=3$ and ν, m, q are independent of the index i, so that the formula[78] for $N\alpha$ reduces

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[78] Because all three vibrational degrees of freedom have the same frequency the time average of "cross-terms" such as $\mathbf{M}_i\mathbf{M}_j$ will not vanish for an individual molecule, and so at first thought it might appear as though we were not justified in assuming above that the statistical mean of $\mathbf{M}^2$ is the same as that of $\mathbf{M}_0^2+\mathbf{M}_1^2+\mathbf{M}_2^2+\cdots$. The "cross-terms," however, vanish when we integrate over the w^0 part of the phase space, which is tantamount to averaging over all possible phase relations between the different degrees of freedom.

to $Nq^2/4\pi^2m\nu^2$. This result could also be obtained in a well known elementary way if we assumed static equilibrium and simply equated the linear restoring force to the polarizing force Fq, and our treatment of the polarization of an isotropic oscillator as a special case of (16) is quite a contrast to the usual elementary method, but the latter has, of course, the objection that it does not consider the effect of either rotational or kinetic energy.[79]

Correction for centrifugal expansion. In the model used in the preceding paragraph the magnitude of the constant part $\boldsymbol{M}_0$ of the vector moment will be nearly the same for all molecules, and hence independent of the J^0's, so that very approximately we may take $\overline{\boldsymbol{M}_0^2}=\mu^2$, thus yielding the second right-hand term of (1). We have, however, already mentioned in part I, that there is a slight correction for centrifugal expansion. We may now compute this quantitatively for an actual diatomic molecule in which the vibrations are due to nuclear oscillations along the axis of the molecule. The model representing the nuclear motions thus has one degree of vibrational freedom and is not to be confused with the isotropic oscillator studied at the end of the preceding paragraph. Let r_0, I, and μ be respectively the nuclear separation, moment of inertia, and (scalar) moment when the molecule is at rest. Then if the molecule rotates with an angular velocity ω we find on equating the centrifugal force $mr\omega^2$ to the restoring force $4\pi^2\nu^2m(r-r_0)$ that the nuclear separation increases by an amount $r-r_0=r_0\omega^2/4\pi^2\nu^2$ if $r-r_0$ is small. The corresponding increase in electrical moment is $q(r-r_0)$. Here the effective mass m, effective charge q, and frequency ν are defined as on p. 44. Consequently we have approximately

$$\overline{\boldsymbol{M}_0^2}=\mu^2+2\mu q\overline{(r-r_0)}=\mu^2+\mu q r_0\overline{\omega^2}/2\pi^2\nu^2 \quad \text{or} \quad \overline{\boldsymbol{M}_0^2}=\mu^2+\mu q r_0 kT/I\pi^2\nu^2$$

since the mean rotational kinetic energy $\frac{1}{2}I\overline{\omega^2}$ is kT. The effect of centrifugal expansion is thus only a contribution $\mu q r_0/3\pi^2I\nu^2$ to the constant α in Eq. (1). This contribution is, however, usually quite negligible. In HCl, for instance, it accounts for less than one percent of α with Bourgin's value of q. The same formula for the correction due to centrifugal expansion can also be obtained with quantum mechanics, using the amplitude matrices for the elastic rotating dipole given by Miss Mensing,[12] Oppenheimer,[13] or Fues.[13] The agreement of quantum and classical methods in this instance is, of course, simply because rotational frequencies are usually small compared to kT/h. On the other hand, the correction for non-linearity in the polarization due to an oscillator would be entirely different calculated by (16) and by quantum mechanics, for quanta of vibratory energy are usually large compared to kT.

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[79] Prof. Debye in his Madison lectures also derives Eq. (1) for this model of harmonic oscillators mounted on a rotating molecule. His method is somewhat different, as he integrates with momentoids such as were mentioned in note 73 rather than with angle and action variables. He proves the influence of vibrational kinetic energy inconsequential also in Handbuch der Radiologie, vol. VI, p. 613.