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

PART I.

A GENERAL PROOF OF THE LANGEVIN-DEBYE FORMULA

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Abstract

In contradistinction to the old quantum theory, the new quantum mechanics yields very generally the Langevin and Debye formulas $\chi = N\alpha + N\mu^2/3kT$ for the magnetic and dielectric susceptibilities respectively. It is believed that our proof is considerably more comprehensive than previous ones, for it assumes only that the atom or molecule has a "permanent" vector moment of constant magnitude μ whose precession frequencies are small compared to kT/h. There is no limit to the allowable number of superposed precessions. There can, for instance, be simultaneous precessions due to internal spins of the electron and to "temperature rotation" of the nuclei. The presence of other simultaneous external fields in addition to the applied electric or magnetic field introduces no difficulty. Besides the effect due to the permanent moment, there is the term $N\alpha$ which arises from "high frequency" matrix elements associated with transitions from normal to excited states. This term is proved independent of the temperature. The susceptibility formula contains the factor 1/3 in the temperature term as generally as in the classical theory because of the high spectroscopic stability characteristic of the new quantum mechanics. It is shown that the mean squares of the x, y, and z components of a vector are equal in the new quantum dynamics just as in the classical theory, the only difference being that in the new quantum theory we take the average by summing over a discrete distribution of quantum-allowed orientations instead of by integrating over a uniform continuous distribution.

1. Introduction.

THE present paper is part I of a series of articles on magnetic and dielectric susceptibilities in the new quantum mechanics, and contains the main elements of the mathematical theory. Part II will discuss the application to dielectric constants, especially in relation to previous work by other authors with particular models. Part III will deal with applications to magnetism, including the paramagnetism of O_2 and NO.

The main purpose of part I is to give a very general derivation, also some critical discussion, of the Langevin-Debye formula

$$\chi = N\left(\alpha + \frac{\mu^2}{3kT}\right). \tag{1}$$

Here χ is the susceptibility, N is the number of atoms or molecules per unit volume, k is the gas constant, and α is a constant independent of the absolute

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temperature T. We shall suppose the susceptibility χ to be either magnetic or electric, not because of any deep physical resemblance of the magnetic and electric polarizations, but simply because it is well known that they can both be calculated by quite similar mathematical procedures, so that we shall treat them together wherever possible. Thus $1+4\pi\chi$ will denote the dielectric constant or magnetic permeability, and μ the permanent electric or permanent magnetic moment of the molecule, depending on whether we are dealing with electric or magnetic polarization. The interpretation of the constant α is somewhat different in the two cases; in the electric one α is the "induced moment" due to elastic polarization of the atom or molecule by the impressed field, while in the magnetic case α is usually negative and represents the induced diamagnetic moment, although we shall see in part III that the magnetic α is occasionally positive due to the quadratic Zeeman effect associated with multiplet structures. Thus in magnetism α is usually small, and so ordinarily omitted. Historically, Eq. (1) was first applied to magnetism, as in 1905 Langevin[1] published his famous paper, and it was not until 1912 that Debye[2] extended the formula to dielectric constants by assuming that there could be a "permanent" as well as "induced" electric moment in polar molecules.

Our derivation of (1) will be based on the new quantum mechanics. There is, however, an interesting analogy with the classical theory, as it will be shown in part II that the same result could be obtained classically if we averaged continuously over all possible orientations of the moment and precession vectors relative to each other and to the field instead of summing over the discrete quantum states. It must be regarded as one of the triumphs of the new quantum mechanics that it will give the Langevin or Debye formulas very generally, whereas the old quantum theory replaced the factor $\frac{1}{3}$ in (1) by a constant C whose numerical value depended rather chaotically on the type of model employed, whether whole or half quanta were used, whether there was "weak" or "strong" spacial quantization, etc.[3] This replacement of $\frac{1}{3}$ by C caused an unreasonable discrepancy with the classical theory at high temperatures, and in some instances the constant C even had the wrong sign.[4] All these vicissitudes in C are avoided in the new mechanics, which gives the factor $\frac{1}{3}$ quite as generally as the classical theory. This

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[1] P. Langevin, Journal de Physique, (4), **4,** 678 (1905); Annales de Chim. et Phys. (8), **5,** 70 (1905).

[2] P. Debye, Phys. Zeits. **13,** 97 (1912). See also his excellent compendium on electric and magnetic polarizations in vol. VI of the Handbuch der Radiologie. The temperature effect due to permanent dipoles was also suggested later independently by J. J. Thomson, Phil. Mag. **27,** 757 (1914).

[3] Cf. W. Pauli, Jr., Zeits. f. Physik, **6,** 319 (1921); L. Pauling, Phys. Rev. **27,** 568 (1926).

[4] Pauling[3] shows that C would be negative in molecules of the HCl type if we use the a-priori probability $2m$ indicated by the recent band spectrum intensity measurements of Bourgin and Kemble. He therefore uses a probability $2m+1$ and finds C to be about 14 times the classical value 1/3, but in a later paper[5] shows that C would even then become negative in the formula for the dielectric constant on applying a magnetic field at right angles to the electric field. Needless to say, such a behavior is not found experimentally.

has already been shown by several writers[5] for special models, and the present paper may be regarded as extending the result to the general case. In our opinion the general proof is usually quite as simple as the specialized ones with particular models, since the algebra of writing out and summing the various matrix elements is avoided, and there is the great advantage that it is unnecessary to know the precise form or values of these elements.

At this point it may be remarked that most of the classical derivations of (1) appear rather inadequate. The literature, to be sure, is full of purported "generalized Langevin theories,"[6] but these for the most part are based on rather unsatisfactory physical premises, such as rigid magnetons, steady molecular currents, etc. The usual elementary derivation of the Langevin formula omits even the kinetic energy of rotation. Fortunately the calculations of Alexandrow[7] and van Leeuwen[8] show that the inclusion of this energy occasions no particular difficulty in symmetrical diatomic molecules. Miss van Leeuwen replaces an electron orbit by a current, but unlike most writers, she does not overlook the gyroscopic effect arising from the angular momentum concomitant to magnetic moment. No computations, however, appear to have previously been published which allow for the high degree of dissymmetry characteristic of the general polyatomic molecule, or for the precessions caused by internal spins[9] of the electrons which are an important factor in magnetism. Thus the following treatment not only substitutes the new quantum for the classical viewpoint, but also gives increased generality. Yet it must be understood that we shall calculate only the terms in the susceptibility which are independent of the field strength. These are the only terms ordinarily of consequence in dielectric or in para- (or dia-) magnetic media, but the present paper does not pretend to treat ferromagnetism or saturation phenomena in which higher powers of the field F must be considered. Hence we have written Langevin's formula in its asymptotic form (1) valid for small (i.e. ordinary) values of the field rather than giving his more complete expression which contains the effect of all powers of $\mu F/kT$. We suppose throughout for simplicity that the effective average field on the atom is F rather than the more rigourous expression $F+4\pi P/3$. This amounts to assuming the polarization so small that the Clausius-Mosotti constant $(\epsilon-1)/(\epsilon+2)N$ reduces to $(\epsilon-1)/3N$; if this condition is not met there is no trouble, as we would simply have to replace χ in (1) by $3\chi/(3+4\pi\chi)$.

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[5] L. Mensing and W. Pauli, Jr., Phys. Zeits. **27**, 509 (1926); J. H. Van Vleck, Nature, **118**, 226 (1926); R. d. L. Kronig, Proc. Nat. Acad. **12**, 488, 608 (1926); C. Manneback, Phys. Zeits. **27**, 563 (1926); P. Debye and C. Manneback, Nature, **119**, 83 (1927); L. Pauling, Phys. Rev. **29**, 145 (1927).

[6] For references see "Theories of Magnetism," Bull. Nat. Research Coun. no. 18; also van Leeuwen.[8]

[7] W. Alexandrow, Phys. Zeits. **22**, 258 (1921).

[8] van Leeuwen, Leyden Thesis; summary in J. de Physique, (6), **2**, 361 (1921).

[9] We assume the reader to be familiar with the Uhlenbeck-Goudsmit spinning electron, die Naturwissenschaften **13**, 953 (1925); Nature **117**, p. 264 (1926).

2. The Fundamental Assumptions

In order to derive the second term of (1) *we find it necessary to assume only that the atom or molecule has a "permanent" moment vector whose precession frequencies are small compared to kT.* Another way of saying the same thing is that the various component normal states have a vector moment of common magnitude μ, and have an energy spacing small compared to the equipartition allowance kT. A more precise explanation of these conditions is given in the following paragraphs.

The stationary states of many atoms and molecules are so spaced that at ordinary temperatures there is a fairly sharp delineation between normal and excited states. The excited states we define as having energies of excitation which are large in comparison with kT, and so they may be considered as virtually unoccupied in making the calculations. The normal states generally are a family of "component" energy levels whose separation is usually smaller than or comparable with kT. This splitting into components ordinarily results from the mutual precessions of the various constituent angular momentum vectors of the atom or molecule and from the precession of their resultant about some direction fixed in spaced. Thus the excited states are usually characterized by different electronic or possibly vibrational quantum numbers from the normal, whereas the component normal levels result from giving the molecules different amounts of "temperature rotation," different orientations relative to the external fields, or from allowing the spin axis of the electron to assume different orientations relative to the rest of the system.

It is clear that the magnetic or electric moment of the atom or molecule is a vector matrix **M**. We follow Born's procedure of writing matrices in bold-face type. Certain elements of the matrix **M** will be identified with transitions between normal and excited states, and will be shown in section 3 to contribute only to the constant term $N\alpha$ in (1) which is independent of the temperature; even without proof this seems fairly obvious from the fact that excited states have by definition energies large compared with kT. Hence to calculate the second or "temperature" term of (1) we replace **M** by a matrix $\boldsymbol{\mu}$ formed from **M** by dropping the high frequency elements of **M** associated with transitions to excited states. This replacement of **M** by $\boldsymbol{\mu}$ corresponds to the well-known separation of the "secular" from the high frequency variations in perturbation theory, and means that in computing the temperature effect the moment matrix may be considered to involve just the family of normal states rather than the more complicated aggregate of both normal and excited states. We suppose, moreover, that the atom (or molecule) has a moment of "definite" or "permanent" magnitude μ. This is not at all a drastic assumption, as it is involved in all permanent dipole theories, and without it the expression μ in (1) would have no meaning. This means that the magnitude $\mu=(\boldsymbol{\mu}_x^2+\boldsymbol{\mu}_y^2+\boldsymbol{\mu}_z^2)^{1/2}$ of the vector matrix $\boldsymbol{\mu}$ is constant with respect to the time and the same for the various normal states. Hence $|\boldsymbol{\mu}|$ is a diagonal matrix whose elements are all equal and in the terminology of Dirac it may be called a "*c*-number," which is the moment μ entering in Eq. (1). The vector $\boldsymbol{\mu}$ will be constant in magnitude but usually not in direction. The components $\mathbf{\mu}_x$, $\mathbf{\mu}_y$, $\mathbf{\mu}_z$ will, to be sure, involve no high frequency elements, as the latter have been eliminated in forming $\mathbf{\mu}$ from **M**, but these components will in general vary with the time due to the existence of "low frequency elements" which correspond to transitions between the different levels constituting the normal states and which arise usually from precessions of the various types cited in the preceding paragraph. In order to obtain the Langevin formula (1) it is essential simply that these "low frequencies" be small in comparison with kT/h, which is equivalent to saying that transitions between the various normal states involve energy changes of magnitude much less than kT.

In the above and elsewhere we use the terms, "direction of a vector," "precession," etc., rather freely, as a vector matrix clearly cannot be assigned the same simple geometrical interpretation as an ordinary directed segment. We mean, of course, simply the quantities in the Born-Heisenberg matrix theory which "correspond" to the precessions, directions, etc., of classical mechanics. In particular the precession frequencies mean the spectroscopic frequencies emitted or absorbed in transitions between various component levels whose separation is caused by the quantum analog of a classical precession effect. Throughout the present paper, and also in parts II and III, we use the language of the matrix rather than wave form of the new quantum mechanics, but the same results follow equally well with the wave viewpoint, in virtue of the general formal identity[10] of the wave and matrix formulations for closed ("abgeschlossen") atomic systems. In fact we could even obtain the Langevin formula by going to the opposite extreme from the matrix aspect, and employing the "field" theory of Schroedinger, Madelung, and Gordon,[11] in which the electric charges are spread through space with a continuous density proportional to $|\psi|^2$, where ψ is the well-known Schroedinger wave-function. The identity of the results regarding susceptibilities ensues since Schroedinger[10] has shown that the field theory gives the same electrical moment as the matrix viewpoint (neglecting relativity corrections), while Fermi[12] has proved it gives the same magnetic moment,[13] utilizing the definition of the velocity of flow given by Schroedinger and others.[14]

[10] E. Schroedinger, Ann. der Physik, **79**, 734 (1926); C. Eckhart, Phys. Rev. **28**, 711 (1926).

[11] E. Schroedinger, Ann. der Physik, **81**, 109 (1926) **82**, 257, 265 (1927); E. Madelung, Naturwissenschaften, **14**, 1004 (1926); Zeits. f. Physik, **40**, 322 (1926); W. Gordon, *ibid.*, **40**, 117 (1926).

[12] Fermi, Nature, **118**, 876 (1926).

[13] It must be remarked, however, that calculations similar to Fermi's establish the similarity of results for the part of the paramagnetism arising from orbital angular momentum, and do not indicate just how to treat the "spin" phenomenon, as Fermi assumes the normal ratio of magnetic moment to angular momentum holds throughout. A further complication is that diamagnetism involves the velocity of light to the power $1/c^2$ rather than $1/c$, and the ordinary technique does not furnish a correlation to $1/c^2$, as the magnetic modifications in the definition of momenta, etc., would have to be considered; so that there is a bare possibility of a discrepancy. It seems, however, highly improbable that any successful theory will give different susceptibilities than those calculated by the matrix method.

[14] For references see note 11.

The basic assumptions may be summarized in the words "permanence of moment" and "slowness of precession." The great generality arises from the fact that it is not necessary to specify the exact form of the precession, or the numerical formulas for the frequencies and amplitudes. The phrase "slowness of precession" must not be construed too literally, for the low frequency elements could result equally well from slow oscillations or other types of motion than precessions. We use the term "precession" for the sake of concreteness and because precessions are much the most common cause of low frequency components; "temperature rotation" of the nuclei about the center of gravity, for instance, can be considered as simply a precession about the invariable axis. It is also to be understood that besides the "low frequency elements" there are generally high frequency terms which are responsible for the constant term $N\alpha$ in (1). The essential requirement, of course, is that the "high" and "low" frequencies be always respectively large and small compared to kT/h. An important feature is that there is no limit to the number of precessions which can be superposed. Nevertheless, even our hypotheses are not sufficiently general in some instances. In the first place, in the case of dielectric constants, the centrifugal expansion of the molecule will violate the assumption of a "permanent electric moment," as the stretching will slightly increase the dipole moment in the higher quantum states, so that the diagonal elements of the matrix $|\mathfrak{u}|$ are no longer equal. Fortunately this expansion effect is small, as band spectra show that the variation of moment of inertia with rotation rarely exceeds six per cent even in the more elastic excited states.[15] A more important restriction is imposed by the requirement that the elements in the moment matrix $\mathbf{M}$ are all of the "high" or "low" frequency type. Actually Laporte and Sommerfeld[16] find that in atoms of the first long period of the Mendeleeff table the internal spins of the electron lead to precessions in the magnetic moment of what we may term the "medium" frequency type; i.e., precessions whose frequencies are of the same order of magnitude as kT/h. We shall find it necessary to treat the magnetism of NO by a special calculation in part III because the spacing of its spin doublet is about $.6kT/h$. Also the variable vibrational specific heats of certain molecules indicate that the energies of excitation of their nuclear vibrations are comparable with kT. Undoubtedly because of its secular character the magnetic moment does not have any terms of appreciable amplitude involving the vibrational frequencies. The electric moment will contain such terms, but fortunately their temperature effect will be very subordinate since the amplitude of nuclear vibration is usually small compared to the equilibrium nuclear spacing, and also since the polarization of a linear oscillator, which represents the nuclear vibrations to a first approximation, is independent of the temperature.[17]

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[15] Cf. R. T. Birge, Nature, **116,** 783 (1925).

[16] Laporte and Sommerfeld, Zeits. f. Physik, **40,** 333 (1926).

[17] This independence of the temperature for the polarization due to a linear oscillator is proved with the classical theory by P. Debye, Handbuch der Radiologie, Vol. VI, p. 613, and a simple calculation shows that it also holds in the new quantum mechanics.

3. Proof

Let us suppose for simplicity that we are dealing with electric rather than magnetic polarization. The slight adaptations in the proof necessary to the magnetic case will be given in part III. Before application of the field F the electrical moment **M** will be a matrix whose typical element may be denoted by

$$M_z(njm\ ;\ n'j'm')e^{2\pi i\nu(njm;n'j'm')t}$$

We have here taken the z-component, but there are, of course, similar formulas for the x and y components. For brevity we throughout omit commas from the arguments, and write $(njm;\ n'j'm')$ for $(n,\ j,\ m;\ n',\ j',\ m')$, etc. Following the conventional notation, such an element is associated with a transition from a state specified by indices n, j, m to one by n', j', m'. We shall let the first of the three indices be identified with quantum numbers (e.g. "electronic" and "vibrational") which have an effect on the energy large compared to kT, so that one particular value of this index gives states of especially low energy. This value will be denoted by n and yields the normal levels of the atom or molecule. The second index j or j' corresponds to quantum numbers (e.g. "inner," "rotational," "spin") whose effect on the energy is comparable with or smaller than kT. We do not, however, include in the second index the "axial" (also called "equatorial" or "magnetic") quantum number which specifies the spacial orientation by quantizing angular momentum about some fixed direction in space. Instead the third index m or m' is to be considered as representing the axial quantum number. Thus the various component levels of the normal state correspond to fixed n but different values of j and m, whereas the excited states have an index n' different from n. It is clearly to be understood that *each index, except the third, in general symbolizes more than one quantum number*; i. e., represents a multiple rather than single array. Hence we designate n, j, m as "indices" rather than quantum numbers. Our proof is thus by no means confined to systems with three quantum numbers or degrees of freedom.

Let us suppose an electric field F is applied in the z-direction. The susceptibility is the quotient of polarization by field strength, or $N\overline{M}_z^{(F)}/F$, where N is the number of molecules (or atoms) per unit volume, and $\overline{M}_z^{(F)}$ is the average value of the z-component of the electrical moment per molecule. This average, of course, differs from the time mean[18] $M_z^{(F)}\ (njm;\ njm)$ for individual molecules, as the latter will be distributed among the different components of the normal levels. To get $\overline{M}_z^{(F)}$ we must average over these components with each assigned the probability required by the Boltzmann distribution formula. Hence it is apparent that

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[18] The time mean value in a non-degenerate system is a diagonal term of a matrix, and hence specified by an element in which the second trio of indices is the same as the first. In defining this time mean it is, of course, supposed that the molecule always remains in the same state. Thus the time mean is over a period long compared to the periods of the spectral lines but short compared to the duration of a stationary state. Heisenberg's statistics of fluctuations (Zeits. f. Physik, **40**, 501, 1926) shows that (2) is still applicable even if we allow for a molecule changing states.

$$\chi=\frac{N}{F}\,\frac{\sum_{j,m} M_z^{(F)}(njm\,;\,njm)e^{-W(\;\_\;)(njm)/kT}}{\sum_{j,m} e^{-W(F)(njm)/kT}}, \tag{2}$$

where W as usual denotes the energy. We suppose the system non-degenerate,[19] so that all states have the same statistical weight; i.e. the same factor g in the Boltzmann expression $ge^{-W/kT}$.

Because of "induced polarization," the time mean $M_z^{(F)}\,(njm;\,njm)$ of the electrical moment in the field F is not the same as this mean $M_z(njm;\,njm)$ before application of F. We shall throughout use the superscript $^{(F)}$ to distinguish values in the field from those in its absence. It is clearly to be understood that all amplitudes, frequencies, and energies without this superscript relate to the case $F=0$. Now $M^{(F)}$ is easily calculated in terms of M by the perturbation methods of Born, Heisenberg, and Jordan,[20] or of Schroedinger.[21] These writers show that [22]

$$M_z^{(F)}(njm\,;\,njm)=M_z(njm\,;\,njm)-\frac{2F}{h}{\sum}'_{n'\,j'\,m'}\frac{|\,M_z(njm\,;\,n'j'm')\,|^2}{\nu(njm\,;\,n'j'm')}\,. \tag{3}$$

This is, of course, the same result as given by extrapolation of the Kramers dispersion formula to infinitely long impressed wave-lengths. The sum over n', j', m' includes all excited and normal states except the given state n, j, m. This exclusion of the one term $n', j', m'=n, j, m$ is indicated by the prime inside the summation sign, and this interpretation of the prime is to be understood throughout the article. As usual ν denotes the frequency emitted (or absorbed) in the transition between two states when $F=0$. Eq. (3) is utilized by all the various writers[5] who have calculated dielectric constants for particular models. It gives the polarization to terms of the first order in F, as this degree of approximation is necessary to get the ordinary susceptibility effects (cf. section 1).

Now the energy in the field is to first powers in F

$$W^{(F)}\,(njm)=W(njm)-FM_z(njm;\,njm). \tag{4}$$

This follows by well-known perturbation formulas of the new quantum mechanics,[20] which show that here just as in the old quantum theory the perturbed energy is to a first approximation the energy $W(njm)$ in the absence of F augmented by the perturbative potential (here $-FM_z$) averaged over the unperturbed motion.

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[19] In case the system is degenerate, we may imagine the degeneracy removed by introducing a sufficient number of hypothetical supplementary infinitesmal internal forces. This is legitimate, as Eq. (25) of section 4 shows that the result is invariant of the manner in which the degeneracy is removed. There can be no spacial degeneracy, for the field F provides an axis for quantization if not already present when $F=0$.

[20] Born, Heisenberg, and Jordan, Zeits. f. Physik, **35**, 567 (1927).

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

[22] Expressions of the type form $|M_z(njm;n'j'm')|^2$ occurring in Eq. (3) etc. may also be written as the product $M_z(njm;n'j'm')\;M_z(n'j'm';njm)$; for as the moment matrix is Hermitian, $M_z(n'j'm';njm)$ is the conjugate of $M_z(njm;n'j'm')$, and the product of any complex number and its conjugate is the square of its absolute value. This other method of writing is that used by Born, Heisenberg, and Jordan.[20]

We now expand the exponentials in (2) as power series in F by means of (4). When we do this and substitute (3) in (2) we find

$$\begin{aligned}\chi=\frac{N}{F}\,&\frac{\sum_{j,m} M_z(njm\,;\,njm)e^{-W(njm)/kT}}{\sum_{j,m} e^{-W^{(F)}(njm)/kT}}\\&+(B/kT)\sum_{j,m}\left| M_z(njm\,;\,njm)\right|^2 e^{-W(njm)/kT}\\&-\frac{2B}{h}{\sum}'_{j,m,n',j',m'}\frac{\left| M_z(njm\,;\,n'j'm')\right|^2 e^{-W(njm)/kT}}{\nu(njm\,;\,n'j'm')}.\end{aligned}\tag{5}$$

Here we have discarded terms in F, F^2, $\cdots$, as we are interested in calculating only the constant part of the susceptibility. We have written $|M_z(njm;\, njm)|^2$ for $M_z(njm;\, njm)^2$ which is legitimate since diagonal elements are real. Also we have introduced the abbreviation

$$B=\frac{N}{\sum_{j,m} e^{-W(njm)/kT}}.\tag{6}$$

We must now suppose that the first line of (5) vanishes. (For this reason we have not bothered to expand the exponentials in the denominator of this line.) This involves no essential loss of generality,[23] for if it did not we would have a "permanent" or "residual" polarization even in the absence of the field.[24] Clearly the numerator of the first line of (5) vanishes by symmetry if the only external field is the applied electric field F, for in the absence of all fields there can be no preference between directions parallel and antiparallel to F, and hence no moment along F; another way of saying the same thing is that in the absence of all fields states with positive and negative values of the axial quantum number are equally probable. In solids there is, of course, the possibility of directed[25] inter-molecular fields, which might give the body a residual polarization when $F=0$, but such effects are not ordinarily found experimentally except in ferromagnetic media or in crystalline dielectrics, both of which are beyond the scope of the present article.

Separation of high and low frequency terms. Eq. (5) is a perfectly general expression for the susceptibility which does not require the hypotheses of "slowness of precession" or "permanent dipole moment" presented in section 2. For further simplification, however, these postulates must be introduced, and so we now proceed to make the separation into "low" and "high" frequency terms. In order to make connection with the notation employed in section 2, we write $\mu(jm;\, j'm')$ for the low frequency elements $M_z(njm;\, nj'm')$. Eq. (5), with first line omitted, then becomes

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[23] Debye also notes (Phys. Zeits. **27**, 67, 1926) in a calculation with the old quantum theory that the vanishing of an expression similar to the first line of (5) involves no essential loss of generality.

[24] The first line of (5) will not vanish if there is a "magneto-electric directive effect", to be explained in part II, but this effect is apparently never found experimentally.

[25] Random inter-molecular fields give no trouble, as with them the first line of (5) vanishes on the average by symmetry.

$$
\begin{aligned}
\chi = {} & (B/kT) \sum\nolimits_{j,m} | \mu_z(jm\,;jm) |^2 e^{-W(njm)/kT} \\
& -\frac{2B}{h} \sum\nolimits'_{j,m,j',m'} \frac{| \mu_z(jm\,;j'm') |^2 e^{-W(njm)/kT}}{\nu(njm\,;nj'm')} \\
& -\frac{2B}{h} \sum\nolimits_{j,m,n',j',m',\,(n'\neq n)} \frac{| M_z(njm\,;n'j'm') |^2}{\nu(njm\,;n'j'm')} e^{-W(njm)/kT}.
\end{aligned} \tag{7}
$$

Here the first two and the third lines represent respectively the "low" and "high" frequency terms, as the third line involves only terms associated with transitions to the excited states $n' \neq n$.

The terms in the summation in the second line of (7) may be grouped together in pairs P_{12} of the form

$$
\begin{aligned}
P_{12} = -\frac{2B}{h} \Bigg\{ & \frac{| \mu_z(j_1m_1\,;j_2m_2) |^2}{\nu(nj_1m_1\,;nj_2m_2)} e^{-W(nj_1m_1)/kT} \\
& + \frac{| \mu_z(j_2m_2\,;j_1m_1) |^2}{\nu(nj_2m_2\,;nj_1m_1)} e^{-W(nj_2m_2)/kT} \Bigg\}.
\end{aligned} \tag{8}
$$

Now $\mu_z(j_2m_2;\, j_1m_1)$ is the conjugate of $\mu_z(j_1m_1;\, j_2m_2)$ and so has the same absolute magnitude. Also $\nu(nj_2m_2;\, nj_1m_1) = -\nu(nj_1m_1;\, nj_2m_2)$, and by the Bohr frequency condition $W(nj_2m_2) = W(nj_1m_1) - h\nu(nj_1m_1;\, nj_2m_2)$. Under the hypothesis of "slowness of precession," fully explained in section 2, we may develop the second exponential in (8) as a power series in the ratio $s = h\nu(nj_1m_1;\, nj_2m_2)/kT$. Then (8) becomes

$$
P_{12} = -2(B/skT) | \mu_z(j_1m_1\,;j_2m_2) |^2 e^{-W(nj_1m_1)/kT}[1-1-s-\tfrac{1}{2}s^2-\tfrac{1}{6}s^3- \cdots] \tag{9}
$$

If we neglect terms of the order s^3 within the bracketed factor this is the same as

$$
P_{12} = (B/kT) \{ | \mu_z(j_1m_1\,;j_2m_2) |^2 e^{-W(nj_1m_1)/kT} + | \mu_z(j_2m_2;\, j_1m_1) |^2 e^{-W(nj_2m_2)/kT} \} \tag{10}
$$

Now if the influence of orientation, i.e., of the axial quantum number, on the "unperturbed" energy $W(njm)$ is small compared to kT, we may replace $W(njm)/kT$ by an expression $W(nj)/kT$ independent of the index m. This approximation is usually one which is fulfilled with a high degree of precision. In the first place the ordinary case is that in which the molecule is subject to no external field except F, and then the unperturbed energy (i.e., the energy in the absence of F) is independent of orientation, so that the index m has absolutely no effect on W. To allow for the possibility of simultaneous electric and magnetic fields, or weak inter-molecular fields in liquids and solids, we admit the more general assumption that $W(njm) - W(nj)$ is not identically zero but small compared to kT.[26] Also it is clear that the

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[26] It is to be noted that though we suppose $W(njm) - W(nj)$ and $h\nu(njm;nj'm')$ both numerically small compared to kT, we have not assumed that $W(njm) - W(nj'm')$ is negligible relative to kT. The latter assumption would be much more stringent, for usually there are selection principles which require that certain quantum numbers change only by zero or one unit, at least in the transitions of appreciable amplitude. In case the quantum numbers

"high" frequencies $\nu(njm;n'j'm')$ $(n'\neq n)$ are affected but little by the indices j, m, j', m', as the separations between components of the normal states or of the excited states are small compared to the interval between the normal and excited states. Hence in the third line or "high frequency part" of (7) we may without appreciable error replace $\nu(njm;\ n'j'm')$ by a number $\nu(n;\ n')$ independent of the indices j, m, j', m'.

If we use the simplifications given in the preceding paragraph, and substitute (10) for (8), Eq. (7) reduces to

$$\begin{aligned}\chi=(B/kT)\textstyle\sum_{j,m,j',m'}|\,\mu_z(jm\ ;j'm')\,|^2\,e^{-W(nj)/kT}&\\ -\frac{2B}{h}\textstyle\sum_{j,m,n',j',m'(n'\neq n)}\frac{|\,M_z(njm\ ;n'j'm')\,|^2}{\nu(n\ ;n')}\,e^{-W(nj)/kT},&\end{aligned}\tag{11}$$

where now the first sum includes the diagonal elements $n', j', m' = n, j, m$.

It will be proved in section 4 that in virtue of the high degree of spectroscopic stability characteristic of the new quantum mechanics, an expression of the form

$$\textstyle\sum_{m,m'}|\,A_z(njm\ ;n'j'm')\,|^2$$

is invariant of the direction of the axis of spacial quantization and equals

$$\tfrac{1}{3}\textstyle\sum_{m,m'}|\,A(njm\ ;n'j'm')^2,\,|$$

Here $A(njm;\ n'j'm')$ denotes an element of the scalar magnitude $|\mathbf{A}|=(\mathbf{A}_x^2+\mathbf{A}_y^2+\mathbf{A}_z^2)^{1/2}$ of a vector matrix $\mathbf{A}$ whose z-component has elements of the form $A_z(njm;\ n'j'm')$. This consequence of spectroscopic stability is perhaps the most interesting and vital feature of the entire proof, as it underlies the general occurrence of the factor $\frac{1}{3}$ in the temperature term of the Langevin-Debye formula. On taking $A=M$ $(n'\neq n)$ and $A=\mu$ $(n'=n)$ (this is only a difference in notation) Eq. (11) becomes by the above

$$\begin{aligned}\chi=(B/3kT)\textstyle\sum_{j,m,j',m'}|\,\mu(jm;\ j'm')\,|^2\,e^{-W(nj)/kT}&\\ -\frac{2B}{3h}\textstyle\sum_{j,m,n',j',m'(n'\neq n)}\frac{|\,M(njm\ ;n'j'm')\,|^2}{\nu(n\ ;n')}\,e^{-W(nj)/kT}&\end{aligned}\tag{12}$$

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associated with the index j can assume a wide range of values, this means that $h\nu(njm;nj'm')$ is considerably smaller in magnitude than the general expression of the form $W(njm)-W(nj'm')$ for then the selection principle requires that $h\nu(njm;nj'm')$ equal the difference of two adjacent, or nearly adjacent components of the normal levels rather than of two comparatively widely separated such levels.

This fact explains why we can apply our proof of the Langevin-Debye formula to molecules having "temperature rotation" even though by giving the molecule sufficient quanta of rotation the ratio $s=h\nu(njm;nj'm')/kT$ may be made as large as we please. For the numerical magnitude of the exponent in the Boltzmann distribution factor $e^{-W(nj)/kT}$ increases much more rapidly than s. (One varies approximately as the square, the other as the first power of the rotational quantum number.) Hence terms for which s is comparable with unity will have such a small exponential factor or probability that they can be disregarded. This will be discussed more fully in part II, where a calculation will be made of the error due to neglecting higher powers of s in (9).

Simplification of low frequency elements. From the rules for matrix multiplication it follows that

$$\sum_{j',m'} \left| \mu(jm\,;j'm') \right|^2 \tag{13}$$

is a diagonal element $\mu^2(jm;jm)$ of the matrix $\boldsymbol{\mu}^2$, which is the square of the absolute magnitude of the secular moment vector matrix $\boldsymbol{\mu}$ formed from $\mathbf{M}$ by deleting the high frequency elements (cf. p. 730). Now in consequence of the hypothesis of a "permanent dipole moment," fully explained in section 2, the magnitude of $\boldsymbol{\mu}^2$ is independent of the time and the same for all the component levels constituting the normal state. Hence $\mu^2(jm;\,jm)$ is a number μ^2 independent of j and m, so that the expression (13) reduces to μ^2 and the low frequency part (first line) of (12) now becomes

$$(B/3kT)\mu^2 \sum_{j,m} e^{-W(nj)/kT}. \tag{14}$$

Now we have already supposed on p. 736 that $W(njm)$ can be replaced by $W(nj)$ in the exponential factors, so that the denominator of (6) is identical with the sum[27] in (14). Hence by (6) Eq. (14) is simply $N\mu^2/3kT$, which is the "temperature part" of the Langevin-Debye formula.

Invariance of high frequency part of χ. The high frequency terms, represented by the second line of (12), are not included in the ordinary calculations of molecular susceptibilities or dielectric constants, and instead it is usually taken for granted, perhaps by analogy with a classical linear oscillator,[17] that their net effect is invariant of the temperature. The warrant for this seems to the author by no means so obvious but what it is repaying to actually demonstrate that the total contribution of the high frequency elements is independent of T. The analysis has, of course, been somewhat lengthened by their inclusion but gains considerably in completeness. The demonstration is an easy consequence of the "sum-rules" for intensities applied to absorption rather than emission, for it is the essence of these rules that an expression[28] of the form

$$\sum_{j'm'} \left| M(njm\,;n'j'm') \right|^2 \tag{15}$$

is independent of the indices j and m, provided the spacing of components is small compared to the frequency of the line itself; i.e., provided $\nu(njm;\, n'j'm')$ can be replaced by $\nu(n;\,n')$ as already assumed on p. 737. The sum-rules were first established on semi-empirical grounds, but the work of

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[27] The double sum in (14) may also be written as the single summation $\sum_j p_j e^{-W(nj)/kT}$ where p_j is the number of quantum-allowed orientations for the state j; i.e., the number of permissible values for the axial quantum number. The expression p_j would be the a-priori probability if the spacial degree of freedom were neglected and the system consequently treated as degenerate. Ordinarily $p_j - 1$ equals twice the maximum value of the axial quantum number, as positive and negative values of this number are equally probable.

[28] As usually stated, the sum-rules relate to the invariance of intensity, and intensity is proportional to the fourth power of the frequency as well as to the resultant amplitude M^2 which represents the combined effects of the x, y, and z components. However, we have seen that $\nu(njm;n'j'm')$ can without sensible error be replaced by an expression $\nu(n;n')$ independent of j,m,j',m', and so the independence of the intensity-sums of j and m also implies the independence of (15) of j and m.

Born, Heisenberg, and Jordan,[29] and of Dirac[30] shows that they are required by the new quantum mechanics.[31] The ordinary sum-rule for Zeeman components shows that $\sum_{m'}|M(njm;\, n'j'm')|^2$ is independent of m, and this taken in conjunction with the sum-rule for "multiplet" components[32] (or band spectrum components) shows that (15) is independent of both j and m, at least provided j is associated with the one type of precession ordinarily identified with the inner (or rotational) quantum number. Actually we have already stated that the index j may correspond to several quantum numbers and hence represent the effect of several superposed precessions; e.g. simultaneous precessions resulting from internal spins of the electrons and from "temperature rotation." However, Dirac notes on p. 298 of his paper[30] that there is no difficulty extending the proof of the intensity rules to systems which are composed of any number of parts and which so contain any number of precessions, provided the parts are coupled together by "secular" forces which do not distort the motion and instead give rise only to pure precession. This result is also obvious from the correspondence principle inasmuch as the sum-rule is the quantum analog of the fact that classically the intensity of radiation is not appreciably affected by slow precessions which do not sensibly alter the sizes and shapes of the orbits. It must, however, be emphasized that the validity of the sum-rule requires that the coupling responsible for the separation of the normal levels into components must result in "pure precession" without distortion. This rules out centrifugal expansion and similar effects, but we have already seen at the close of section 2 that their effect is only subordinate.

From what has been said in the preceding paragraph we may replace (15) by an expression $|M(n;\, n')|^2$ independent of j and m, and so the second line of (12) reduces to

$$-\frac{2B}{3h}\sum_{n'(n'\neq n)}\left\{\frac{|\,M(n\,;\,n')\,|^2}{\nu(n\,;\,n')}\sum_{j,m}e^{-W(nj)/kT}\right\}\tag{16}$$

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[29] Born, Heisenberg, and Jordan, Zeits. f. Physik, **35,** 605 (1926).

[30] P.A.M. Dirac, Proc. Roy. Soc. **111A,** 281 (1926).

[31] Born, Heisenberg, and Jordan deduce the formulas proposed by Goudsmit and Kronig and by Hönl for the relative intensities of Zeeman components. Dirac gives the rather more difficult derivation of the formulas advanced by Kronig, Russell, Sommerfeld and Hönl for intensities in multiplets. These various formulas are more comprehensive than but necessarily include the corresponding sum-rules for Zeeman and multiplet components.

[32] The ordinary statement of the sum-rule for the inner quantum number is essentially that the sum

$$\sum_{mj'm'}|\,M(njm\,;\,n'j'm')\,|^2\tag{A}$$

is proportional to the a-priori probability p_j (cf. [27]) of the state j, assuming momentarily that j corresponds to the inner quantum number. Eq. (A) contains sums over m and m' inasmuch as the Zeeman components are supposed unresolved in the ordinary multiplet rule. The sum-rule for the magnetic quantum number shows that all the components of the state j contribute equally in the sum over m in (A). As there are p_j such components, the factor p_j thus cancels out if we do not sum over m in (A), thus making (15) invariant of both j and m.

The double sum in this equation is the same as the denominator of (6) inasmuch as on p. 736 we made the approximation $W(njm)=W(nj)$. Thus (16) becomes an expression

$$N\alpha=-\frac{2N}{3h}\sum\nolimits_{n'(n'\neq n)}\frac{|M(n;n')|^2}{\nu(n;n')} \tag{17}$$

which is independent of T. This is the desired result, and (17) constitutes the "constant" part $N\alpha$ of the Langevin-Debye formula. The right-hand side of (17) does not involve the index m, or the direction of the axis of quantization,[33] and so the choice of this axis cannot influence $N\alpha$. It is clear that $N\alpha$ is positive since the $\nu(n;n')$ are negative or "absorption" frequencies.

Combination of the simplifications affected in the high and low frequency parts yields the complete Langevin-Debye formula $\chi=N\alpha+(N\mu^2/3kT)$.

Special case that F is the only external field. It is to be noted that the proof has nowhere assumed that the axis of spacial quantization is the same as the axis of the applied field F. Ordinarily, however, F is considered to be the only external field, and then these two axes will coincide. When this is the case there will be no external influences when $F=0$, and hence there will be no secular precessions about the axis of quantization before application of F. This means that the third index will have no influence on the energy in the absence of F and consequently that all frequencies of the form $\nu(njm;njm')$ will vanish, as the absence of the superscript ${}^{(F)}$ (cf. p. 734) means the frequencies are to be measured with $F=0$. Nevertheless there will be no trouble with zero denominators in Eqs. (3), (5), (7), (8), as the matrices $\boldsymbol{M}_z$ or $\boldsymbol{\mu}_z$ will contain no elements in which $m'\neq m$ since the z-component clearly cannot involve the frequency of precession about the z-axis, which is the direction of F. Thus in Eqs. (3), (5), (7), (11) the summation over m' may be replaced by the substitution $m'=m$.

4. THE FUNDAMENTAL SPECTROSCOPIC STABILITY RELATION.

We have already mentioned that the high spectroscopic stability characteristic of the new quantum mechanics is the cardinal principle underlying the continued validity of the Langevin-Debye formula. We shall not attempt a precise definition of the term "spectroscopic stability."[34] It means roughly that the effect of orientation or of degeneracy in general is no greater than in the classical theory, and this usually implies that summing over a discrete succession of quantum-allowed orientations gives the same result as a classical average over a continuous distribution. In calculations of susceptibilities, and also in many other problems, the principle of spectroscopic

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[33] It is obvious from the mode of definition that $M(n;n')$ cannot depend on the direction of the axis of quantization. Otherwise the total intensity of a spectral line, i.e., the x, y, and z effects combined, would depend on the direction of this axis, which is absurd.

[34] For references on spectroscopic stability and some discussion of its important application to the polarization of resonance radiation see J. H. Van Vleck, "Quantum Principles and Line Spectra," Bull. Nat. Research Council, no. 54, p. 171 ff.

stability may be regarded as embodied mathematically in the statement that the double sum

$$\sum_{l,l'} |\, f(sl\,;\,s'l')\,|^2 \tag{18}$$

is uniquely determined even in a degenerate system, and has a value invariant of the manner in which the degenerate degrees of freedom are quantized. Here $f(sl;\,s'l')$ denotes an amplitude element of any "quantentheoretische Grösse," i.e., of any matrix $\boldsymbol{f}$ which can be regarded as a function of the coordinates and momenta. We suppose the indices l and l' to correspond to a quantum number l whose value has no influence on the energy, while s and s' represent the effect of all other quantum numbers. The summation with respect to l extends over all the components of a family of states s whose energies ("Eigenwerte") coincide due to degeneracy. The interpretation of the sum over l' is similar. Thus the summation embraces all the various transitions which are possible between two "multiple" energy levels each composed of a number of equal-valued components. A simple physical illustration is summing over all the Zeeman components of a given spectral line in a vanishingly small magnetic field. The invariance of an expression similar to (18) has already been established by Born, Heisenberg, and Jordan[35] for the special case that only one of the systems of energy levels is multiple. This simplification would require that l (or else l') assume only one value in (18). The invariance of the more general expression (18) was mentioned without proof in a preceding paper by the writer,[36] and he is informed that the more general result has also been obtained independently by Born (unpublished). In the work of Born, Heisenberg, and Jordan, and of Born, it is supposed that $\boldsymbol{f}$ is a coordinate or momentum matrix, but this appears to be a needless specialization.

Proof. The demonstration is very similar to that given by Born, Heisenberg, and Jordan for the special case that one of the systems of levels s or s' is single, and we assume the reader has at least a superficial familiarity with their procedure[37] for quantizing the perturbations of a degenerate system. Let $\boldsymbol{S}$ be the "transformation matrix" associated with the passage from one mode of quantization of the degenerate system to another. The function $\boldsymbol{S}$ will generate a contact transformation from the original variables $\boldsymbol{p}_1{}^0, \cdots, \boldsymbol{p}_n{}^0, \boldsymbol{q}_1{}^0, \cdots, \boldsymbol{q}_n{}^0$ to a set of new variables $\boldsymbol{p}_1, \cdots, \boldsymbol{p}_n, \boldsymbol{q}_1, \cdots, \boldsymbol{q}_n$ by means of the connecting relations

$$\boldsymbol{p}_k = \boldsymbol{S}\boldsymbol{p}_k{}^0\boldsymbol{S}^{-1}, \qquad \boldsymbol{q}_k = \boldsymbol{S}\boldsymbol{q}_k{}^0\boldsymbol{S}^{-1}.$$

If the system is made non-degenerate by applying an external field, the secular perturbations are calculated and quantized by finding the particular contact transformation which will reduce the perturbed energy to a diagonal matrix, but this fact is of no immediate consequence. Born, Heisenberg, and Jordan show[38] that in general

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[35] Born, Heisenberg, and Jordan, Zeits. f. Physik, **35**, 590 (1926).

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

[37] Born, Heisenberg, and Jordan, Zeits. f. Physik, **35**, 577–590 (1926).

[38] Ibid., p. 574.

$$\boldsymbol{f}=\boldsymbol{S}\boldsymbol{f}^0\boldsymbol{S}^{-1} \tag{19}$$

where $\boldsymbol{f}^0$ is the same function of the $\boldsymbol{p}^0$'s and $\boldsymbol{q}^0$'s that $\boldsymbol{f}$ is of the $\boldsymbol{p}$'s and $\boldsymbol{q}$'s, so that

$$\boldsymbol{f}=\boldsymbol{f}(\boldsymbol{p}_1, \cdots, \boldsymbol{p}_n\,;\, \boldsymbol{q}_1, \cdots, \boldsymbol{q}_n) \qquad \boldsymbol{f}^0=\boldsymbol{f}(\boldsymbol{p}_1{}^0, \cdots, \boldsymbol{p}^0{}_n,\, \boldsymbol{q}_1{}^0, \cdots, \boldsymbol{q}_n{}^0).$$

Now we suppose $\boldsymbol{S}$ to be a "secular" transformation matrix associated only with the ambiguity arising from the degeneracy, and hence $S(sl;\, s'l')$ will vanish unless $s=s'$. This means simply that in the language of section 3, $\boldsymbol{S}$ possesses no "high frequency elements," and in, fact contains only elements associated with zero frequencies representing transitions between component states of coincident energy. Therefore by the rules for matrix multiplication an element of (19) may be written

$$f(sl\,;\, s'l')=\sum\nolimits_{l'',l'''}S(sl\,;\, sl'')f^0(sl''\,;\, s'l''')S^*(s'l'\,;\, s'l'''). \tag{20}$$

Here we have made use of the fact[39] that in virtue of the orthogonality properties $\boldsymbol{S}^{-1}$ equals $\tilde{\boldsymbol{S}}^*$, where $\boldsymbol{S}^*$ denotes the conjugate of $\boldsymbol{S}$, and $\tilde{\boldsymbol{S}}$ the transposed matrix formed from $\boldsymbol{S}$ by interchanging rows and columns, so that $\tilde{S}^*(s'l';\, s'l''')=S^*(s'l''';\, s'l')$.

From (20) it is seen that

$$\begin{aligned}\sum\nolimits_{l,l'}f(sl\,;\, s'l')f^*(sl\,;\, s'l')=\sum\nolimits_{l,l',l'',l''',l^{\text{iv}},l^{\text{v}}}\{&f^0(sl''\,;\, s'l''')f^{0*}(sl^{\text{iv}}\,;\, s'l^{\text{v}})\\ &S(sl\,;\, sl'')S^*(sl\,;\, sl^{\text{iv}})S^*(s'l',\, s'l''')S(s'l'\,;\, s'l^{\text{v}})\}\end{aligned} \tag{21}$$

where we write l^{iv} for l'''', etc. Now the orthogonality relations[39] give

$$\sum\nolimits_{l}S(sl\,;\, sl'')S^*(sl\,;\, sl^{\text{iv}})=\delta(l'',\, l^{\text{iv}}) \tag{22}$$

where

$$\delta(l'',\, l'')=1, \qquad \delta(l'',\, l^{\text{iv}})=0, \qquad l''\neq l^{\text{iv}} \tag{23}$$

There are also, of course, equations similar to (22) and (23) in which s, l, l'', l^{iv} are replaced by $s', l', l^{\text{v}}, l'''$ respectively. Thus (21) becomes

$$\sum\nolimits_{l,l'}f(sl\,;\, s'l')f^*(sl, s'l')=\sum\nolimits_{l'',l'''}f^0(sl''\,;\, s'l''')f^{0*}(sl''\,;\, s'l'''). \tag{24}$$

Now on the right-hand side we may replace l'', l''' by l, l' for this is only a change in the notation for the variable of summation. Also the product of a complex number and its conjugate equals the square of its absolute magnitude. Therefore (24) may be written

$$\sum\nolimits_{l,l'}\left|f(sl\,;\, s'l')\right|^2=\sum\nolimits_{l,l'}\left|f^0(sl\,;\, s'l')\right|^2. \tag{25}$$

This is the desired result, for it shows that an expression of the form (18) has the same value before and after the transformation, and is thus invariant of the mode of quantization.

It is noted that the expression (18) is invariant even when $s=s'$, for there is nothing in the above demonstration which requires $s\neq s'$. With $s=s'$ the summation in (18) or (25) extends over the various transitions within a multiple level rather than over those between two multiple levels.

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[39] Ibid., p. 584, Eq. (11).

Application to spacial degeneracy. The most important application of (18) or (25) in calculating susceptibilities is to the case where the degeneracy arises from the absence of an external field, so that one direction in space is as good as another. Then the various values of the indices l and l' correspond to different values of the axial (often called "equatorial" or "magnetic") quantum number belonging to a system of "multiple" levels whose components differ from each other only in that they represent different "quantum-allowed" orientations relative to the axis of quantization. The contact transformation of the type considered above then simply involves a rotation of the coordinate axes, and means that the direction of spacial quantization is shifted from one direction in space to another. Now clearly if $\boldsymbol{A}$ is any vector, the double sum (18) has by symmetry the same value whether we take $\boldsymbol{f}$ equal to any one of the three components $\boldsymbol{A}_x$, $\boldsymbol{A}_y$, $\boldsymbol{A}_z$ provided we average (18) over all possible directions for the axis of quantization, for after the average there is no preference between the x, y, and z directions without external fields. But we have proved an expression of the form (18) invariant of the axis of quantization, and hence the average over all directions for this axis is unnecessary. Thus (18) always has the same values with $\boldsymbol{f}$ equal to $\boldsymbol{A}_x$, $\boldsymbol{A}_y$, or $\boldsymbol{A}_z$ regardless of the choice of the axis of quantization. Hence, since $\boldsymbol{A}^2=\boldsymbol{A}_x^2+\boldsymbol{A}_y^2+\boldsymbol{A}_z^2$, it follows that

$$\sum\nolimits_{l,l'} \left|A_x(sl\,;\,s'l')\right|^2=\tfrac{1}{3}\sum\nolimits_{l,l'} \left|A(sl\,;\,s'l')\right|^2 \tag{26}$$

with analogous equations involving A_y and A_z. This is the same result as was quoted on p. 737, section 3, except for a slight difference in notation. We there used the three-index notation $A(njm;\,n'j'm')$ instead of $A(sl;\,s'l')$ in order to permit further classification of the families of energy levels. The two indices n and j together correspond to s, and m to l.

The proof given above assumes complete spacial degeneracy, which means that the molecule should be subject to no external forces, and in section 3 we applied (26) to the "unperturbed motion" executed when the applied electric field F is zero. In section 3, however, we admitted the possibility of other simultaneous external fields independent of F (e.g., a "crossed" magnetic field), so that there was not necessarily spacial degeneracy and freedom from external influence when $F=0$. We can, nevertheless, still apply (26) to such cases if the result of these other external fields is only to introduce precessions or secular motions corresponding to frequencies of the form $\nu(sl;\,sl')$, without any "high frequency perturbations" of the type $(sl;\,s'l')$, $s'\neq s$. For then the effect of these external fields is given by a "secular" contact transformation of the type considered above, which will leave invariant the values of expressions similar to the left-hand side of (26). Actually an external field will in general alter to some extent the amplitudes of terms of the type $(sl;\,s'l')$ $(s'\neq s)$, but these "non-secular" perturbations will in general distort the amplitudes only to a low degree, as this is a well-known result in dynamics. Hence it is a good approximation to apply (26) even when the unperturbed motion corresponding to $F=0$ is itself a motion in some other external field. The usual case, of course, is where F is the only external field, and then (26) holds rigorously for the unperturbed motion.

Illustrations of (26). An example or two will perhaps make the results obtained above more concrete. If $\mathbf{A}$ be a unit vector matrix, then $\mathbf{A}_x$ may be regarded as the cosine of the angle between this vector and some fixed direction in space chosen as the x-axis. Eq. (26) shows that the mean value of the square of the cosine of this angle is one-third when we average over all the various allowed orientations relative to the axis of quantization (not necessarily the x-direction). This is the same value as results by symmetry in the classical theory when we average over a uniform continuous distribution of orientations. This agreement is the underlying reason why the susceptibility formula (1) contains the factor $\frac{1}{3}$ quite as generally in the new quantum mechanics as in the classical theory.

Another simple illustration of (26) is furnished by the theory of diamagnetism. It can be shown that the diamagnetic susceptibility is proportional to x^2+y^2 if the magnetic field is applied in the z-direction. Now by the rules for matrix multiplication the average value of x^2 for the state s is

$$\sum\nolimits_{l,s',l'} \left| x(sl\ ;\ s'l') \right|^2 / p_s \qquad (27)$$

where s' is to be summed over all possible states, including $s'=s$, and where p_s is the number of l-components belonging to the multiple state s. In other words p_s is the a-priori probability of the state s, or, what is essentially the same thing, the number of values assumed by its axial quantum number. Now (27) is simply an expression of the form (18) summed over s', and there are, of course, similar expressions for the y and z components. Hence by (26) the average values of x^2, y^2, and z^2 are equal, and since $r^2=x^2+y^2+z^2$, we can take $x^2+y^2=\frac{2}{3}r^2$, just as in the classical theory. This has an important experimental application, as it shows that the diamagnetic susceptibility per molecule should not vary with pressure (see ref.[36])

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