

The Calculation of Statistical Averages for Perturbed Systems

ROBERT SERBER, *University of Wisconsin*

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A general expression is derived for the statistical mean value of any function of dynamical variables, averaged over all the molecules of a gas in the presence of external fields. This expression is in the form of a multiple Taylor's series in powers of $1/kT$ and of the field strengths. Explicit formulas, valid for diatomic and polyatomic molecules, are given for the coefficients in this series, up to and

including the cubic terms. The general formula is then applied in the solution of two specific problems: (1) Effect of a magnetic field on the electric susceptibility of a molecule. (2) Theory of the Kerr effect in diatomic and polyatomic molecules. The concluding sections give applications of the formulas developed in §1 to the perturbation theory of conservative and non-conservative systems.

IN many problems in quantum mechanics we are concerned with finding the value of a function of dynamical variables, $u(p, q)$, averaged over a large number of molecules, when the molecules are subject to an external field λ . This statistical mean value is given by

$$\bar{u} = \frac{N \text{Sp}(ue^{-H/kT})}{\text{Sp}(e^{-H/kT})} \quad (1)$$

where $H = H(p, q, \lambda)$ is the Hamiltonian function, and N is the number of molecules per cubic centimeter. Letters such as H, H_0, u, v, w, W , with no indices attached, are to be understood as denoting matrices. The exponential function is, of course, defined by a power series. In writing (1) it is not necessary to specify the system of representation used, as the spur of a matrix is invariant of a canonical transformation.¹

The usual procedure is to employ a system of representation in which H is diagonal, then to express the diagonal elements of H in terms of the matrix elements of H in an unperturbed system of representation, i.e., one in which the external field is zero, by means of perturbation theory. Except in the simplest cases this procedure has serious disadvantages. For one thing, the quantities which we are forced to evaluate are not invariant of a rotation of coordinate axes; thus sum rules and symmetry properties cannot be employed. This condition can be remedied by Van Vleck's method of "pairing" terms,² provided all frequencies of the unperturbed molecule can be classified as "high" or "low," that is, as large or small compared to kT/h . After "pairing" only rotational invariants appear in our equations. However, although this method works beautifully for the term linear in the field strength, it becomes very difficult to apply to higher order terms. The calculation is not straightforward, but demands considerable ingenuity on the part of the calculator. A second difficulty lies in the increasing complexity in the perturbation formulas as we go to higher order terms. The equations become very cumbersome, and of course the "pairing" is thereby made more difficult.

In the following section a new method of handling such problems is given, which involves exactly the same approximations as the perturbation method, but which has great practical advantages. Both the above-mentioned difficulties disappear; complicated perturbation formulas are not needed, and the terms always automatically appear properly "paired."

¹This fact has been utilized by F. Bloch, *Zeits. f. Physik* **74**, 295 (1932), and by E. Wigner, *Phys. Rev.* **40**, 749 (1932). Their use of it differs from ours in that they employ representations in which coordinates or momenta

are diagonal, while we diagonalize the energy.

²J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, p. 191.

§1. GENERAL METHOD OF SOLUTION

Let us suppose, for simplicity, that the Hamiltonian function in the presence of the external field, λ , is of the form

$$H = H_0(p, q) + \lambda v(p, q).$$

Hamiltonian functions in which higher order terms in λ appear can readily be handled by an obvious extension of the method which we use for this most simple, and most important, case. We will employ a system of representation in which H_0 is diagonal³; this will be indicated by writing $H_0 = W$. The first step is to expand the matrix $e^{-(W+\lambda v)/kT}$, appearing in (1), as a power series in λ . The elements of this matrix are

$$(e^{-(W+\lambda v)/kT})_{n'n} = \delta_{n'n} + \sum_{r=1}^{\infty} \frac{(-1)^r [(W+\lambda v)^r]_{n'n}}{(kT)^r}. \tag{2}$$

Multiplying out the factor $(W+\lambda v)^r$ we find

$$\begin{aligned} [(W+\lambda v)^r]_{n'n} &= W_n^r \delta_{n'n} + \lambda v_{n'n} \sum_{s=0}^{r-1} W_n^{r-s-1} W_n^s + \lambda^2 \sum_{n''} v_{n'n''} v_{n''n} \sum_{s=0}^{r-2} \sum_{t=0}^{r-2-s} W_n^{r-2-s-t} W_n^{s,t} + \dots \\ &= W_n^r \delta_{n'n} + \lambda v_{n'n} \left[\frac{W_n^r}{h\nu_{n'n}} + \frac{W_n^r}{h\nu_{nn'}} \right] \\ &\quad + \lambda^2 \sum_{n''} v_{n'n''} v_{n''n} \left[\frac{W_n^r}{h^2 \nu_{n'n''} \nu_{n''n}} + \frac{W_{n'',r}}{h^2 \nu_{n''n'} \nu_{n'n''}} + \frac{W_n^r}{h^2 \nu_{nn'} \nu_{n'n''}} \right] + \dots \end{aligned} \tag{3}$$

The latter form is obtained on summing the geometric series involved in the former. Substitution of this in (2) gives⁴

$$\begin{aligned} (e^{-(W+\lambda v)/kT})_{n'n} &= e^{-W_n/kT} \delta_{n'n} + \lambda v_{n'n} \left[\frac{e^{-W_n/kT}}{h\nu_{n'n}} + \frac{e^{-W_n/kT}}{h\nu_{nn'}} \right] \\ &\quad + \lambda^2 \sum_{n''} v_{n'n''} v_{n''n} \left[\frac{e^{-W_{n''}/kT}}{h^2 \nu_{n'n''} \nu_{n''n}} + \frac{e^{-W_{n'',r}/kT}}{h^2 \nu_{n''n'} \nu_{n'n''}} + \frac{e^{-W_n/kT}}{h^2 \nu_{nn'} \nu_{n'n''}} \right] + \dots \end{aligned} \tag{4}$$

The general term in this expansion is

$$\lambda^\mu \sum_{n'' \dots n^{(\mu)}} v_{n'n''} \dots v_{n^{(\mu)}n} \left[\frac{e^{-W_{n''}/kT}}{h^\mu \nu_{n'n''} \dots \nu_{n''n}} + \dots + \frac{e^{-W_n/kT}}{h^\mu \nu_{nn'} \dots \nu_{n^{(\mu)}n}} \right], \tag{5}$$

as is shown in the appendix. If two or more of the indices in (5) are the same, say $n'' = n''' = \dots = n^{(s)}$ the bracketed factor is an indeterminate form. In this case the bracketed factor is to be understood as meaning its limit as $\nu_{n''n''}, \dots, \nu_{n^{(s)}n^{(s)}} \rightarrow 0$. This limit always exists.⁵ The advantage of writing these “degenerate” terms as indeterminate forms is that (5), so written, is symmetric in “degenerate” and “low frequency” elements, that is, in elements for which the ν 's in the denominator actually vanish, and those in which the ν 's are small. The whole aim of Van Vleck's method of “pairing” is to achieve this symmetry.

³ This representation, in general, is not unique, but any representation which makes H_0 diagonal will do.

⁴ The term linear in λ has recently been given by I. Waller, Zeits. f. Physik 79, 370 (1932).

⁵ Eq. (8) serves as a simple example. It will be observed that a confluence of two W 's always leads to an indeterminate form because of the reversal of indices of the ν 's in passing from one term to another.

Using (4), we find

$$\begin{aligned} \text{Sp}(ue^{-(W+\lambda v)/kT}) = \sum_n \left\{ u_{nn} e^{-W_n/kT} + \lambda \sum_{n'} u_{nn'} v_{n'n} \left[\frac{e^{-W_{n'}/kT}}{h\nu_{n'n}} + \frac{e^{-W_n/kT}}{h\nu_{nn'}} \right] \right. \\ \left. + \lambda^2 \sum_{n'n''} u_{nn'} v_{n'n''} v_{n''n} \left[\frac{e^{-W_{n'}/kT}}{h^2\nu_{n'n''}\nu_{n''n}} + \frac{e^{-W_{n''}/kT}}{h^2\nu_{n''n'}\nu_{n'n}} + \frac{e^{-W_n/kT}}{h^2\nu_{nn'}\nu_{nn''}} \right] + \dots \right\}. \quad (6) \end{aligned}$$

Our considerations thus far have been perfectly general. In the remainder of this section two assumptions will be made⁶:

(a) It will be supposed that intermolecular forces are negligible, so that we have complete spatial degeneracy.

(b) It will be supposed that all frequencies of the unperturbed molecule which appear in (6) are large or small compared to kT/h .

Each state will be designated by (n, j, m) , where n represents the high frequency quantum numbers, j and m the rotational and axial quantum numbers respectively, which can be considered constants of the motion in consequence of (a).

The term of (6) linear in λ can now be written

$$\lambda \sum_{\substack{njm \\ n'm'j'}} u_{njm; n'j'm'} v_{n'j'm'; njm} \left[\frac{e^{-W_{n'j'}/kT}}{h\nu_{n'j'; nj}} + \frac{e^{-W_{nj}/kT}}{h\nu_{nj; n'j'}} \right] + \lambda \sum_{\substack{njm \\ j'm'}} u_{njm; n'j'm'} v_{n'j'm'; njm} \left[\frac{e^{-W_{n'j'}/kT}}{h\nu_{n'j'; nj}} + \frac{e^{-W_{nj}/kT}}{h\nu_{nj; n'j'}} \right]. \quad (7)$$

The prime on the first summation sign indicates that $n' = n$ is to be omitted from the summation. On expanding $e^{-W_{n'j'}/kT} = e^{-(W_{nj} + h\nu_{n'j'; nj})/kT}$ in powers of $h\nu_{n'j'; nj}/kT$ we find that

$$\left[\frac{e^{-W_{n'j'}/kT}}{h\nu_{n'j'; nj}} + \frac{e^{-W_{nj}/kT}}{h\nu_{nj; n'j'}} \right] = -\frac{1}{2kT} [e^{-W_{n'j'}/kT} + e^{-W_{nj}/kT}] \quad (8)$$

plus terms of order $(h\nu_{n'j'; nj}/kT)^3$ and higher. Since $h\nu_{n'j'; nj}$ is small compared to kT , these high-order terms will be neglected. It will be observed that the above relation holds exactly for the degenerate terms, i.e., for $\nu_{n'j'; nj} \rightarrow 0$. Substituting (8) in (7), we obtain, after a simple relabeling of indices,

$$\begin{aligned} -\lambda \text{Sp} \left\{ \sum_{n'j'm'} \frac{[u_{njm; n'j'm'} v_{n'j'm'; njm} + v_{njm; n'j'm'} u_{n'j'm'; njm}]}{h\nu_{n'j'; nj}} e^{-W_{nj}/kT} \right. \\ \left. + (1/2kT) \sum_{j'm'} [u_{njm; n'j'm'} v_{n'j'm'; njm} + v_{njm; n'j'm'} u_{n'j'm'; njm}] e^{-W_{nj}/kT} \right\}. \quad (9) \end{aligned}$$

The frequencies $\nu_{n'j'; nj}$ can, with good approximation, be replaced by centroid frequencies $\nu_{n'n}$. As the number of molecules in excited states will be negligible, we can replace Sp by Sp_{jm} .⁷ If we introduce the übermatrix notation,⁷ we can now rewrite (9) as

$$-\lambda \left\{ \sum_{n'} \frac{\text{Sp}_{jm} \{ [u^{(nn')} v^{(n'n)} + v^{(nn')} u^{(n'n)}] e^{-W^{(n)}/kT} \}}{h\nu_{n'n}} + (1/2kT) \text{Sp}_{jm} \{ [u^{(nn)} v^{(nn)} + v^{(nn)} u^{(nn)}] e^{-W^{(n)}/kT} \} \right\}.$$

Higher order terms in (6) can be handled in the same way. In writing the results it is convenient to introduce the abbreviation

$$\begin{aligned} 2 \Re \text{Sp}_{jm} [a^{(nn')} b^{(n'n'')} \dots c^{(n''n'IV)} d^{(nIV)} e^{-W^{(n)}/kT}] \\ = \text{Sp}_{jm} \{ [a^{(nn')} b^{(n'n'')} \dots c^{(n''n'IV)} d^{(nIVn)} + d^{(nIVn')} c^{(nIVn'')} \dots b^{(n'n'')} a^{(n'n)}] e^{-W^{(n)}/kT} \}. \quad (10) \end{aligned}$$

⁶ If these assumptions are not made, we obtain a result which, formally, is only trivially different from (12) (see §5).

⁷ This notation is explained immediately above (10) in the preceding paper.

If a, b, \dots, c, d are Hermitian, \Re means simply "the real part of". Rather than write in all the indices, we shall use the symbol $*$ to indicate an excursion of the indices from the normal state to excited states and back to the normal state again. Thus

$$abcd = a^{(nn')}b^{(n'n'')}c^{(n''n''')}d^{(n''''n)}, \quad ab*cd = a^{(nn')}b^{(n'n)}c^{(nn'')}d^{(n''n)}, \quad ab*c*d = a^{(nn')}b^{(n'n)}c^{(nn)}d^{(nn)}, \quad (11)$$

and so forth. Carrying out the calculation, we find

$$\begin{aligned} \bar{u} = B \Re \left[\text{Sp}_{jm} \{ u* e^{-W/kT} \} - \lambda \left\{ \frac{1}{kT} \text{Sp}_{jm} \{ u*v* e^{-W/kT} \} + 2 \sum' \frac{\text{Sp}_{jm} \{ uv* e^{-W/kT} \}}{h\nu_{n'n}} \right\} \right. \\ \left. + \lambda^2 \left\{ (1/6k^2T^2) \text{Sp}_{jm} \{ (2u*v*v + v*u*v)* e^{-W/kT} \} \right. \right. \\ \left. + \sum' \left[\frac{1}{kTh\nu_{n'n}} - \frac{1}{h^2\nu_{n'n}^2} \right] \left[\text{Sp}_{jm} \{ (u*v*v + uv*v + v*u*v)* e^{-W/kT} \} \right] + \sum' \frac{\text{Sp}_{jm} \{ (2uvv + vuv)* e^{-W/kT} \}}{h^2\nu_{n'n}\nu_{n''n}} \right\} \\ - \lambda^3 \left\{ (1/12k^3T^3) \text{Sp}_{jm} \{ (u*v*v*v + v*u*v*v)* e^{-W/kT} \} + \frac{2}{3} \sum' \left[\frac{1}{2k^2T^2h\nu_{n'n}} - \frac{1}{kTh^2\nu_{n'n}^2} + \frac{1}{h^3\nu_{n'n}^3} \right] \right. \\ \left. \times \left[\text{Sp}_{jm} \{ (uv*v*v + vu*v*v + v*uv*v + u*v*v*v + u*v*v*v + v*u*v*v)* e^{-W/kT} \} \right] \right. \\ \left. + \sum' \left[\frac{1}{kTh^2\nu_{n'n}\nu_{n''n}} - \frac{\nu_{n'n} + \nu_{n''n}}{h^3\nu_{n'n}^2\nu_{n''n}^2} \right] \left[\text{Sp}_{jm} \{ (uvv*v + u*v*v + uv*v + v*uvv + vu*v + vu*v)* e^{-W/kT} \} \right] \right. \\ \left. + 2 \sum' \frac{\text{Sp}_{jm} \{ (uvv + vuv)* e^{-W/kT} \}}{h^3\nu_{n'n}\nu_{n''n}\nu_{n''''n}} \right\} + \dots \Big], \quad (12) \end{aligned}$$

where

$$\begin{aligned} B = N \left[\text{Sp} \{ e^{-(W+\lambda v)/kT} \} \right]^{-1} = N \left[Z - (\lambda/kT) \text{Sp}_{jm} \{ v* e^{-W/kT} \} \right. \\ \left. + \frac{\lambda^2}{2kT} \left\{ \frac{1}{kT} \text{Sp}_{jm} \{ v*v* e^{-W/kT} \} + 2 \sum' \frac{\text{Sp}_{jm} \{ vv* e^{-W/kT} \}}{h\nu_{n'n}} \right\} + \dots \right]^{-1} \\ = NZ \left[1 + (\lambda/kT) Z \text{Sp}_{jm} \{ v* e^{-W/kT} \} + (\lambda^2/k^2T^2) Z^2 (\text{Sp}_{jm} \{ v* e^{-W/kT} \})^2 \right. \\ \left. - \frac{\lambda^2}{2kT} Z \left\{ \frac{1}{kT} \text{Sp}_{jm} \{ v*v* e^{-W/kT} \} + 2 \sum' \frac{\text{Sp}_{jm} \{ vv* e^{-W/kT} \}}{h\nu_{n'n}} \right\} + \dots \right], \quad (13) \end{aligned}$$

with $Z = [\text{Sp}_{jm} \{ e^{-W/kT} \}]^{-1}$.

§2. SUM RULES FOR SPURS FOR DIATOMIC AND POLYATOMIC MOLECULES

Calculations using (12) and (13) are greatly aided by the fact that the spurs appearing in these equations are rotational invariants. For example, symmetry properties can frequently be used to show that certain terms are zero. Moreover, sum rules are often available for evaluating such spurs. When we deal with diatomic and polyatomic molecules Niessen's sum rules⁸ are very useful. These rules hold only with neglect of the high frequency terms in the Hamiltonian function which lead to rotational

⁸ K. F. Niessen, Phys. Rev. **34**, 253 (1929).

distortion, A type doubling in diatomic molecules, and such small effects, but the influence of these effects on a statistical mean value is generally of negligible importance.

The sum rules for products of two vectors are well known, and need not be repeated. We shall be particularly interested in the sum rules for products of four vectors. If x', y', z' be a system of axes fixed in space, and x, y, z a system fixed in the molecule, and if $\mathbf{R}, \mathbf{S}, \mathbf{T}, \mathbf{U}$ are any four vectors with components R_x, R_y, R_z , etc., then Niessen's rules show that

$$15\text{Sp}_m(R_{\alpha'}^{(nn')}S_{\beta'}^{(n'n'')}T_{\gamma'}^{(n''n''')}U_{\delta'}^{(n''''n)})_{(ij)} = (2j+1)g[[R_{\alpha}^{(nn')}S_{\beta}^{(n'n'')}T_{\gamma}^{(n''n''')}U_{\delta}^{(n''''n)}]], \quad (14)$$

where g is the statistical weight of the normal state of the stationary molecule, and the double bracket symbol is defined by

$$[[R_{\alpha}S_{\beta}T_{\gamma}U_{\delta}]] = (1/g) \sum_{xyz} \text{Sp}\{aR_xS_xT_xU_x + b[R_xS_xT_yU_y + R_yS_yT_xU_x] + c[R_xS_yT_xU_y + R_yS_xT_yU_x] + d[R_xS_yT_yU_x + R_yS_xT_xU_y]\}, \quad (15)$$

where

$$\begin{aligned} a=1, \quad b=-\frac{1}{2}, \quad c=2, \quad d=-\frac{1}{2} & \text{ when } \alpha=\gamma=x, \quad \beta=\delta=z; \\ a=1, \quad b=-\frac{1}{2}, \quad c=-\frac{1}{2}, \quad d=2 & \quad \text{ " } \quad \alpha=\delta=x, \quad \beta=\gamma=z; \\ a=1, \quad b=2, \quad c=-\frac{1}{2}, \quad d=-\frac{1}{2} & \quad \text{ " } \quad \alpha=\beta=x, \quad \gamma=\delta=z; \\ a=3, \quad b=1, \quad c=1, \quad d=1 & \quad \text{ " } \quad \alpha=\beta=\gamma=\delta=z. \end{aligned}$$

In accordance with the convention (11), we have omitted all the indices in writing (15). The symbol \sum_{xyz} indicates a sum of the three terms obtained by cyclic interchange of x, y, z . Quantities like $R_x^{(nn')}$ are the matrix elements (or teilmatrices, if the states of the stationary molecule are degenerate) of \mathbf{R} referred to axes fixed in the molecule. The spur is to be taken only over the normal state.⁹

The relation

$$[[R_zS_zT_zU_z]] - [[R_xS_xT_xU_x]] = [[R_xS_zT_xU_z]] + [[R_xS_zT_zU_x]] \quad (16)$$

follows immediately from (15). This can also be proved directly from the symmetry properties of the spurs by an argument similar to that used in obtaining (8) in the preceding paper.

The utility of sum rules such as (14) is that they enable us to eliminate the Boltzmann factors in (12) and (13). For example

$$\frac{\text{Sp}_{jm}\{R_{\alpha'}S_{\beta'}T_{\gamma'}U_{\delta'}e^{-W/kT}\}}{\text{Sp}_{jm}\{e^{-W/kT}\}} = \frac{\sum_j \text{Sp}_m(R_{\alpha'}^{(nn')}S_{\beta'}^{(n'n'')}T_{\gamma'}^{(n''n''')}U_{\delta'}^{(n''''n)})_{(ij)} e^{-W_j/kT}}{g \sum_j (2j+1) e^{-W_j/kT}} = (1/15)[[R_{\alpha}S_{\beta}T_{\gamma}U_{\delta}]]. \quad (17)$$

All terms in (12) and (13) can be handled in this way.

§3. INFLUENCE OF A MAGNETIC FIELD ON THE ELECTRIC SUSCEPTIBILITY

The analysis of §1 can readily be extended to the case in which two or more external fields are applied simultaneously. If the Hamiltonian function is

$$H = H_0(p, q) + \lambda v(p, q) + \gamma w(p, q),$$

(4) must be modified by replacing

$$\lambda v_{n'n} \text{ by } [\lambda v_{n'n} + \gamma w_{n'n}],$$

$$\lambda^2 v_{n'n'} v_{n''n} \text{ by } [\lambda^2 v_{n'n'} v_{n''n} + \lambda \gamma (v_{n'n'} w_{n''n} + w_{n'n'} v_{n''n}) + \gamma^2 w_{n'n'} w_{n''n}],$$

⁹ The normal states of unsymmetrical polyatomic molecules will of course be nondegenerate, so the spur reduces to a single term. The states of diatomic and linear polyatomic molecules will be doubly degenerate, here $g=2$, and Sp means a sum over $+\Lambda$ and $-\Lambda$, or $+\Omega$ and $-\Omega$.

and so forth. The formula corresponding to (12) can be immediately written down if we note that in the reordering of products such as $u_{nn'}v_{n'n''}w_{n''n}$ in passing from (6) to (12) the cyclic order of the factors u, v, w is preserved.

This method will now be applied in calculating the effect of a magnetic field on the electric susceptibility. First let us suppose that the electric and magnetic fields are both directed along the z' axis. Denoting the components of electric and magnetic moment by $X', Y', Z', M_{x'}, M_{y'}, M_{z'}$ respectively, we have $u = Z', \lambda v = -EZ', \gamma w = -HM_{z'}$. Many terms of (12) and (13) (generalized, of course, as explained above) are immediately seen to vanish. The term independent of E and H in (12) and the terms linear in E and H in (13) are zero, since obviously $\text{Sp}_m\{Z'^{(nj; n'j)}\} = 0; \text{Sp}_m\{M_{z'}^{(nj; n'j)}\} = 0$. The term in (12) linear in H is zero because $Z'_{njm; n'j'm'}M_{z'n'j'm'; njm}$ is invariant of a reflection of coordinates in the origin, and under such a reflection this term goes into its own negative. The terms in (12) proportional to H^3 and E^2H , and the term in (13) proportional to EH vanish for the same reason. The terms in (12) proportional to $E^2, EH,$ and H^2 are zero because spurs like $\text{Sp}_m(Z'^{(nn')}M_{z'}^{(n'n'')}Z'^{(n''n)})^{(ij)}$ are rotational invariants, and go into their negatives under a rotation in which $z' \rightarrow -z'$. There remains an expression of the form

$$\chi_E E = \bar{Z}' = N[\chi^0_E E + bEH^2 + cE^3 + \dots]. \tag{18}$$

The quantity χ^0_E is given by the well-known Langevin-Debye equation,¹⁰

$$\chi^0_E = \frac{\mu^2_E}{3kT} + \frac{2}{3} \sum_{n'} \frac{P(n'n)^2}{h\nu_{n'n}}. \tag{19}$$

To find b , we have only to replace, in the coefficient of λ^3 in (12), each term, $\{uvv\}$ for example, by three terms:

$$\{uvv\} \rightarrow \{uvvw + uvv\bar{w} + uv\bar{v}w\}. \tag{20}$$

There is also, in b , one term contributed by B , which is easily seen to be $-(1/2kT)\chi^0_E\chi^0_M$, with χ^0_M representing the magnetic analogue of (19).

After using (14) and (17) we find

$$\begin{aligned} b_i = & (1/2k^3T^3) \{ [Z^*Z^*M_i^*M_i] \\ & + 2 \sum_{n'} \left\{ \frac{1}{2k^2T^2h\nu_{n'n}} - \frac{1}{kTh^2\nu_{n'n}^2} + \frac{1}{h^3\nu_{n'n}^3} \right\} \{ [[ZZ^*M_i^*M_i]] + 4[[Z^*ZM_i^*M_i]] + [[Z^*Z^*M_iM_i]] \} \\ & + 2 \sum_{n'n''} \left\{ \frac{1}{kTh^2\nu_{n'n}\nu_{n''n}} - \frac{\nu_{n'n} + \nu_{n''n}}{h^3\nu_{n'n}^2\nu_{n''n}^2} \right\} \{ 2[[ZZM_i^*M_i]] + 2[[Z^*ZM_iM_i]] + [[ZM_iZ^*M_i]] \\ & \quad + [[Z^*M_iZM_i]] + [[ZZ^*M_iM_i]] + [[ZM_i^*M_iZ]] + [[ZM_i^*ZM_i]] \} \\ & + 2 \sum_{n'n''n'''} \frac{1}{h^3\nu_{n'n}\nu_{n''n}\nu_{n''n''n}} \{ 2[[ZZM_iM_i]] + 2[[ZM_iZM_i]] + [[ZM_iM_iZ]] + [[M_iZZM_i]] \} \\ & \quad - (1/2kT)\chi^0_E\chi^0_M, \tag{21} \end{aligned}$$

where $i = z$. In order to indicate that the electric and magnetic fields are in the same direction we have written $b = b_z$. In the same way it can be shown that when the electric and magnetic fields are applied perpendicular to each other b is given by (21) with $i = x$.

If the magnetic field is applied at an angle θ with the electric field, we have

$$w = -(M_{z'} \cos \theta + M_{x'} \sin \theta).$$

¹⁰ J. H. Van Vleck,² p. 186. The quantity $P(n'n)^2$ is defined on p. 1007 of the preceding paper.

Then in (20)

$$ww = \{M_{z'}M_{z'} \cos^2 \theta + M_{x'}M_{x'} \sin^2 \theta + (M_{z'}M_{x'} + M_{x'}M_{z'}) \sin \theta \cos \theta\}.$$

The last term contributes no nonvanishing terms to b , in consequence of the rotational invariance of the spurs, so the general expression for b is simply

$$b = b_z \cos^2 \theta + b_x \sin^2 \theta.$$

If we neglect all matrix elements of the magnetic moment involving excited states (i.e., all elements except $M^{(nn)}$) it is readily shown that this expression for b is exactly the same as that derived classically by Van Vleck.¹¹ For a further discussion of the magnitude of the effect and the dependence upon the angle between the fields the reader is referred to the work of Professor Van Vleck.¹¹

The quantity c , the saturation term in (18), can be obtained by replacing M_i by Z throughout (21), and χ^0_M by χ^0_E , and dividing all except the term $-(1/2kT)\chi^0_E^2$ by three. This factor three arises because in c only the one term on the left in (20) appears, rather than the three terms on the right. The expression for c obtained in this way agrees with that previously given by Niessen.⁸

The formula for the magnetic moment in the presence of an electric field,

$$\chi_M H = \overline{M_{z'}} = N[\chi^0_M H + b'E^2 H + c'H^3 + \dots],$$

is found by simply interchanging the rôles of Z and M_i , E and H , in the proceeding calculation.¹² Since (21) is symmetric in the electric and magnetic moments, we obviously have $b' = b$.

§4. THEORY OF THE KERR EFFECT

A further modification of the method of §1 must be made when u is an explicit function of λ , $u = u(p, q, \lambda)$. Then u must be expanded in a power series in λ by methods analogous to those used in expanding $e^{-H/kT}$. Eq. (12) now holds with this power series substituted for u .

This situation is encountered when we seek to calculate the Kerr constant. If the static electric field is directed along the z' axis, the Kerr constant is given by¹³

$$K = (2\pi/hE^2)(\overline{u^{(z)}} - \overline{u^{(x)}}),$$

where, in a system of representation in which $H = H_0 - EZ'$ is diagonal,

$$u^{(z)}_{nn} = \sum_{n'} \frac{\nu_{n'n}}{\nu^2_{n'n} - \nu^2} Z'_{nn'} Z'_{n'n}, \quad u^{(x)}_{nn} = \sum_{n'} \frac{\nu_{n'n}}{\nu^2_{n'n} - \nu^2} X'_{nn'} X'_{n'n}, \quad (22)$$

ν being the frequency of the incident light. The $\nu_{n'n}$ are explicit functions of E . The method of §1 cannot be applied directly, as $u^{(i)}(p, q, E)$, ($i = Z, X$), is not given, but only its diagonal elements in a particular representation. Our object is thus to determine two functions $u^{(i)}(p, q, E)$ such that, in a representation in which H is diagonal, their diagonal elements are the same as (22). The theorem of spur invariance then assures us that if $u^{(i)}(p, q, E)$ is any such function, the expression (1), with $u = u^{(i)}(p, q, E)$, has the correct value whatever the representation.

Let us suppose, for the moment, that ν is larger than any of the $\nu_{n'n}$. Then $u^{(i)}_{nn}$ can be written

$$u^{(i)}_{nn} = - \sum_{r=0}^{\infty} \sum_{n'} P^{(i)}_{nn'} P^{(i)}_{n'n} \frac{\nu_{n'n}^{2r+1}}{\nu^{2r+2}} = - \sum_{r=0}^{\infty} \sum_{t=0}^{2r+1} (-1)^t \binom{2r+1}{t} \frac{\{\sum_{n'} P^{(i)}_{nn'} P^{(i)}_{n'n} H_n^{2r+1-t} H_n^t\}}{h^{2r+1} \nu^{2r+2}}, \quad (23)$$

¹¹ J. H. Van Vleck,³ p. 113.

¹² The expression for c' obtained in this way is correct if the spin multiplets are large compared to kT/h . If the spin multiplets are small, c' gives the contribution of the orbital part of the moment correctly, but the spin moment

must be treated separately. The contribution of the spin moment is representable by a Brillouin function (see reference 2, p. 257; or reference 8).

¹³ Born and Jordan, *Elementare Quantenmechanik*, p. 262.

since

$$\nu_{n'n}^{2r+1} = \frac{1}{h^{2r+1}} [H_{n'} - H_n]^{2r+1} = \sum_{t=0}^{2r+1} (-1)^t \binom{2r+1}{t} \frac{H_{n'}^{2r+1-t} H_n^t}{h^{2r+1}}.$$

Here $P^{(Z)} = Z'$, $P^{(X)} = X'$. The factor in the curly bracket can be written in the symmetrical form

$$\frac{1}{2} (H^t P^{(i)} H^{2r+1-t} P^{(i)} + P^{(i)} H^{2r+1-t} P^{(i)} H^t)_{nn}.$$

Thus the desired functions, $u^{(i)}(p, q, E)$, are given by

$$u^{(i)} = -\frac{1}{2} \sum_{r=0}^{\infty} \sum_{t=0}^{2r+1} (-1)^t \binom{2r+1}{t} \frac{[H^t P^{(i)} H^{2r+1-t} P^{(i)} + P^{(i)} H^{2r+1-t} P^{(i)} H^t]}{h^{2r+1} \nu^{2r+2}}.$$

We can now return to a representation in which H_0 is diagonal. In this unperturbed representation $u^{(i)}$ can be expanded as a power series in E ; using (3), and reversing the steps of (23), we find

$$\begin{aligned} u^{(i)}_{nn'} &= \frac{1}{2} \sum_{n''} [\tau_{n''n} + \tau_{n'n''}] P^{(i)}_{nn''} P^{(i)}_{n''n'} - \frac{E}{2} \sum_{n''n'''} \left\{ \left[\frac{\tau_{n''n} - \tau_{n''n'''}}{h \nu_{n''n'''}} \right] Z'_{nn''} P^{(i)}_{n''n'''} P^{(i)}_{n''n'} \right. \\ &+ \left[\frac{\tau_{n''n'} - \tau_{n''n'''}}{h \nu_{n''n'''}} \right] P^{(i)}_{nn''} P^{(i)}_{n''n'''} Z'_{n''n'} + \left[\frac{\tau_{n''n'} - \tau_{n''n'''} + \tau_{n''n} - \tau_{n''n''}}{h \nu_{n''n'''}} \right] P^{(i)}_{nn''} Z'_{n''n'''} P^{(i)}_{n''n'} \left. \right\} \\ &+ \delta_{nn'} E^2 \Re \sum_{n''n'''} \left\{ \left[\frac{\tau_{n''n'''} + \tau_{n''n''}}{h^2 \nu_{n''n'''} \nu_{n''n''}} + \frac{\tau_{n''n}}{h^2 \nu_{n''n'''} \nu_{n''n''}} \right] P^{(i)}_{nn''} P^{(i)}_{n''n'''} Z'_{n''n''} Z'_{n''n'''} \right. \\ &+ \left[\frac{\tau_{n''n}}{h^2 \nu_{n''n'''} \nu_{n''n''}} + \frac{\tau_{n''n''}}{h^2 \nu_{n''n'''} \nu_{n''n''}} + \frac{\tau_{n''n''}}{h^2 \nu_{n''n'''} \nu_{n''n''}} \right] P^{(i)}_{nn''} Z'_{n''n''} Z'_{n''n''} P^{(i)}_{n''n''} \\ &\left. + \left[\frac{\tau_{n''n'''} - \tau_{n''n''} + \tau_{n''n''} - \tau_{n''n'''}}{h^2 \nu_{n''n'''} \nu_{n''n''}} \right] P^{(i)}_{nn''} Z'_{n''n'''} P^{(i)}_{n''n''} Z'_{n''n''} \right\} + \dots, \quad (24) \end{aligned}$$

where

$$\tau_{n''n} = \nu_{n''n} / (\nu_{n''n}^2 - \nu^2).$$

Eq. (24) gives the nondiagonal elements of $u^{(i)}$ to terms in E , the diagonal elements to terms in E^2 . The $\nu_{n'n}$'s appearing in this equation refer to the unperturbed molecule, whereas those in (22) refer to the molecule in the presence of the electric field. The remark made under (5) concerning degenerate terms also applies to (24). As before, we can treat degenerate and low frequency terms similarly, and remove all small ν 's from the denominators of (24) by expanding difference quotients such as

$$(\tau_{n''j''}; n_j - \tau_{n''j''}; n_j'') / \nu_{nj}; n_j''$$

as power series in $\nu_{nj}; n_j'' / (\nu_{n''j''}^2; n_j - \nu^2)$. The resulting expressions are to be substituted in (12). The calculations are rather lengthy, but we finally find

$$K = \frac{4\pi N}{15} \left\{ \sum_{n''} [\tau_{n''} A_{n''} + \omega_{n''} B_{n''} + \chi_{n''} C_{n''}] + \frac{1}{kT} \sum_{n''} [\tau_{n''} D_{n''} + \omega_{n''} E_{n''}] + \frac{1}{k^2 T^2} \sum_{n''} \tau_{n''} F_{n''} \right\}, \quad (25)$$

where

$$\tau_{n''} = \frac{\nu_{n''n}}{\nu_{n''n}^2 - \nu^2}; \quad \omega_{n''} = \frac{\nu_{n''n}^2 + \nu^2}{(\nu_{n''n}^2 - \nu^2)^2}; \quad \chi_{n''} = \frac{\nu_{n''n}(\nu_{n''n}^2 + 3\nu^2)}{(\nu_{n''n}^2 - \nu^2)^3};$$

$$\begin{aligned}
 A_{n''} &= \frac{1}{h^3} \sum' \left\{ \sum' \left[\frac{2c(n'n''n''') + a(n'n''n''')}{\nu_{n''n'}\nu_{n'n''}} + \frac{2a(n'n''n''') + a(n'n''n''')}{\nu_{n''n'}\nu_{n'n''}} + \frac{b(n'n''n''') + b(n'n''n''')}{\nu_{n''n'}\nu_{n'n''}} \right] \right. \\
 &\quad \left. \frac{2a(n'n''n''') + a(n'n''n''')}{\nu_{n''n'}^2} - \frac{2c(nn'n''') + c(n'n''n''')}{\nu_{n'n''}^2} \right\}; \\
 B_{n''} &= \frac{1}{h^3} \sum' \left\{ \frac{2b(n'n''n''') - a(nn'n''') - c(n'n''n''') - c(nn'n''')}{\nu_{n'n''}} \right. \\
 &\quad \left. + \frac{b(nn'n''') + b(nn'n''') - a(n'n''n''') - \frac{1}{2}a(n'n''n''')}{\nu_{n''n'}} \right\}; \\
 C_{n''} &= (1/h^3)[c(nnn''') + a(n'n''n''') - 2b(nn'n''')]; \\
 D_{n''} &= \frac{1}{h^2} \sum' \left\{ \frac{c(n'n''n''') + c(nn'n''')}{\nu_{n'n''}} + \frac{b(nn'n''') + b(nn'n''')}{\nu_{n''n'}} \right\}; \\
 E_{n''} &= (1/h^2)[b(nn'n''') - c(nnn''')]; \quad F_{n''} = (1/6h)[2c(nnn''') + b(nn'n''')]; \\
 a(n'n''n''') &= [[ZZZZ]] - [[ZXXZ]]; \quad b(n'n''n''') = [[ZZZZ]] - [[ZXXZ]]; \\
 c(n'n''n''') &= [[ZZZZ]] - [[ZZXX]].
 \end{aligned}$$

Although in the derivation of (25) it was formally necessary to suppose ν larger than any of the $\nu_{n'n}$, the actual restriction on ν is far less stringent. The expansion of

$$\frac{\nu_{n''n'}}{\nu_{n''n'}^2 - \nu^2} = \frac{\nu^{(0)}_{n''n'} + \nu^{(2)}_{n''n'}E^2}{(\nu^{(0)}_{n''n'} + \nu^{(2)}_{n''n'}E^2)^2 - \nu^2}$$

as a power series in E really requires only that $\nu^{(0)}_{n''n'} - \nu$ be large compared to the Stark effect. In removing the small ν 's from the denominators of (24) and replacing the $\nu_{n'j'}$; n_j by centroid frequencies, $\nu_{n'n}$, we introduce the further restriction that $\nu_{n'j'}$; $n_j - \nu$ be large compared to $\nu_{n'j'}$; n_j . Thus (25) is valid whenever ν is not too close to any absorption line of the molecule. If, among the excited states, there are overlapping band systems, we must be more cautious in defining our centroid frequencies, as factors $1/\nu_{n'n''}$ appear in (25). Here the method of dividing all states into "groups," previously used by the writer,¹⁴ must be employed. This entails no change in the equations, but merely a modification in the interpretation of the notation.

A further discussion of (25) will be found in the preceding paper.

The Faraday effect can easily be handled by the same method. The results are identical with those already found by the writer, using perturbation theory.¹⁴

§5. PERTURBATION THEORY OF CONSERVATIVE SYSTEMS

A general formula for the diagonal elements of u in a system of representation in which H is diagonal, in terms of the unperturbed matrix elements of u and v , can be obtained by using the results of §1. By "unperturbed" matrix elements we mean, of course, the elements in a representation in which H_0 is diagonal. We will suppose the unperturbed system nondegenerate; the extension to degenerate systems proceeds as in the usual perturbation theory. Consider the quantity $\text{Sp}\{ue^{-H/kT}\}$ in a representation in which H is diagonal. If we expand u and the energy as power series in λ , we have

¹⁴ R. Serber, Phys. Rev. 41, 489 (1932).

$$\begin{aligned}
\text{Sp}\{ue^{-H/kT}\} &= \sum_n [u_{nn}^{(0)} + \lambda u_{nn}^{(1)} + \lambda^2 u_{nn}^{(2)} + \dots] e^{-[W_n + \lambda W_n^{(1)} + \lambda^2 W_n^{(2)} + \dots]/kT} \\
&= \sum_n [u_{nn}^{(0)} + \lambda u_{nn}^{(1)} + \lambda^2 u_{nn}^{(2)} + \dots] \left[1 - \lambda \frac{W_n^{(1)}}{kT} + \lambda^2 \left(\frac{W_n^{(1)2}}{2k^2T^2} - \frac{W_n^{(2)}}{kT} \right) + \dots \right] e^{-W_n/kT} \\
&= \sum_n [u_{nn}^{(0)} + \lambda u_{nn}^{(1)} + \lambda^2 u_{nn}^{(2)} + \dots + \sum_{s=1}^{\infty} (kT)^{-s} (\dots)] e^{-W_n/kT}. \tag{26}
\end{aligned}$$

But in §1 we have evaluated this same quantity in terms of the matrix elements of u and v in an unperturbed system of representation. The result, in fact, is given by the series (12) if we set $B=1$, interpret quantities like $u^{(nn')}$ as matrix elements, rather than teilmatrices, and replace Sp_{jm} by a summation over n . It is readily seen that (12), with these modifications, follows rigorously from (6). Since the identity of (26) and (12) holds for all values of λ and T , and since $W_{n'} \neq W_n$ when $n' \neq n$, we see that $u_{nn}^{(r)}$ is the coefficient of $\lambda^r e^{-W_n/kT}$ in the series (12). The general term of (12) depends on λ and T through the factor $\lambda^r e^{-W_n/kT} / (kT)^s$; it must be understood that "the coefficient of $\lambda^r e^{-W_n/kT}$ " refers only to the term which has $s=0$.

This result can readily be extended to the case where two or more fields are applied simultaneously, by using the method described in §3.

The perturbed values of the energy can of course be found by setting $u=H$. However it is much simpler to consider

$$\text{Sp}\{e^{-[W_n + \lambda W_n^{(1)} + \dots]/kT}\} = \sum_n [1 - (1/kT)(\lambda W_n^{(1)} + \lambda^2 W_n^{(2)} + \dots) + \sum_{s=2}^{\infty} (kT)^{-s} (\dots)] e^{-W_n/kT},$$

and compare this with (13). The modifications in the interpretation of (12) mentioned above also apply to (13). Thus we find that $-W_n^{(r)}$ is the coefficient of $\lambda^r e^{-W_n/kT} / kT$ in the series for $\text{Sp}\{e^{-(W+\lambda v)/kT}\}$ given implicitly in (13). In this way one can readily check the formula for $W_n^{(3)}$ given by Born, Heisenberg and Jordan,¹⁵ and the formula for $W_n^{(4)}$ given by Niessen.⁸

§6. PERTURBATION THEORY OF NON-CONSERVATIVE SYSTEMS

An expansion similar to (4) is useful in the solution of problems of the following type. Consider a dynamical system, whose Hamiltonian function is $H_0(p, q)$, in a stationary state ψ_n . Suppose the system is suddenly subjected to a perturbation at time $t=0$, such that, at all subsequent times, the Hamiltonian function is $H=H_0(p, q) + \lambda v(p, q)$. We wish to find the transformation matrix which gives the state of the system, $\psi_n(t)$, at time t , in terms of the eigenfunctions of the system at time $t=0$; that is, the matrix $S(t)$ satisfying the boundary condition $S(0)=1$, and

$$\psi_n(t) = \sum_{n'} S_{n'n}(t) \psi_{n'}(0),$$

where the $\psi_{n'}(0)$ are solutions of

$$H_0 \psi_{n'} = W_{n'} \psi_{n'}.$$

The transformation matrix $S(t)$ satisfies the Schrödinger equation

$$(\hbar/2\pi i) \dot{S} + HS = 0,$$

in a system of representation in which H_0 is diagonal. It is easily verified that a solution of this equation, which obviously satisfies the boundary condition, is

$$S(t) = e^{-\chi H} = e^{-\chi(W+\lambda v)},$$

¹⁵ Born, Heisenberg, and Jordan, *Zeits. f. Physik* **35**, 557 (1926).

where

$$\chi = 2\pi it/h.$$

Replacing $1/kT$ by χ in (4), we obtain an expansion of $S(t)$ as a power series in λ .¹⁶

APPENDIX. PROOF OF (5)

To prove (5) we must evaluate the coefficient of λ^μ in $[(W+\lambda v)^r]_{n'n}$. This coefficient is

$$\lambda^\mu \sum_{n'', n''', \dots, n^{(\mu)}} v_{n'n''} v_{n''n'''} \dots v_{n^{(\mu)}n} \left\{ \sum_{s=0}^j \sum_{t=0}^{j-s} \dots \sum_{z=0}^{i-s-t-\dots-y} W_{n''^s} W_{n''^t} \dots W_{n^{(\mu)z}} W_n^{j-s-v-\dots-z} \right\}, \quad (27)$$

where $j = r - \mu$. It will be shown, by induction, that the bracketed factor is given by

$$\{ \} = \frac{W_{n''^{j+\mu}}}{h^\mu v_{n'n''} v_{n''n'''} \dots v_{n''^n}} + \frac{W_{n''^{j+\mu}}}{h^\mu v_{n''^n} v_{n''^n} v_{n''^n} \dots v_{n''^n}} + \dots + \frac{W_n^{j+\mu}}{h^\mu v_{n'n} v_{n'n} v_{n'n} \dots v_{n'n^{(\mu)}}}. \quad (28)$$

Suppose this holds when μ is replaced by $\mu - 1$. Then the left side of (28) equals

$$\sum_{s=0}^j W_{n''^s} \left[\frac{W_{n''^{j+\mu-1-s}}}{h^{\mu-1} v_{n''^n} v_{n''^n} \dots v_{n''^n}} + \dots + \frac{W_n^{j+\mu-1-s}}{h^{\mu-1} v_{n'n} v_{n'n} \dots v_{n'n^{(\mu)}}} \right] = -W_{n''^{j+1}} \left\{ \frac{W_{n''^{\mu-1}}}{h^\mu v_{n''^n} v_{n''^n} v_{n''^n} \dots v_{n''^n}} + \dots + \frac{W_n^{\mu-1}}{h^\mu v_{n'n} v_{n'n} v_{n'n} \dots v_{n'n^{(\mu)}}} \right\} + \frac{W_{n''^{j+\mu}}}{h^\mu v_{n''^n} v_{n''^n} v_{n''^n} \dots v_{n''^n}} + \dots + \frac{W_n^{j+\mu}}{h^\mu v_{n'n} v_{n'n} v_{n'n} \dots v_{n'n^{(\mu)}}}, \quad (29)$$

the latter form being found on summing the geometric series involved in the former.

The equation

$$\left\{ \frac{W_{n''^{\mu-1}}}{h^\mu v_{n''^n} v_{n''^n} \dots v_{n''^n}} + \dots + \frac{W_n^{\mu-1}}{h^\mu v_{n'n} v_{n'n} \dots v_{n'n^{(\mu)}}} \right\} = - \frac{W_{n''^{\mu-1}}}{h^\mu v_{n''^n} v_{n''^n} v_{n''^n} \dots v_{n''^n}}$$

follows from the fact that the term on the right, considered as a function of $W_{n''}$, is a rational function, and has simple poles at the points $W_{n''} = W_j$, ($j \neq n''$). Thus (29) is the same as the right side of (28). Since (28) holds for $\mu = 2$, as is shown by (3), the proof is complete. Substituting (28) in (27), and (27) in (2), and remembering that $j + \mu = r$, we obtain (5).

In this proof we have supposed $W_i \neq W_j$, ($i \neq j$), but (28) is still valid, if interpreted as indicated under (5), when $W_i = W_k = \dots = W_l = W'$, as the left side of (28) is a continuous function of the W_i .

I am indebted to Professor J. H. Van Vleck for many helpful discussions.

¹⁶ The analogy between $1/kT$ and χ has been pointed out by F. Bloch.¹ Formulae for $S^{(1)}$ and $S^{(2)}$ are given by Born and Jordan,¹³ p. 238.