67. A New Derivation of the Electric Field Dependence of Optical Absorptions of Isotropic Samples

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(16.XI.77)

Summary

A calculation of the modification of the optical absorptions of an isotropic sample by a uniform external electric field is presented. The induced orientational anisotropy, the *Stark* shift and the field dependence of the transition moment are taken into account up to the second order in the field. The final expressions differ in the contributions from the transition polarizabilities from previous results.

Introduction. - The optical absorptions of isotropic samples due to electronic transitions are modified by an externally applied electric field. *Labhart* [1] examined the dependence of the oscillator strength of the transition on the field. Using second order *Rayleigh-Schrödinger* perturbation theory *Liptay* [2] incorporated the influence of the field on the transition moment in a calculation of the field dependent absorption.

Our derivation differs from the one just mentioned in three respects:

1) The field dependence of the transition moment is introduced in a general way by defining transition polarizabilities. This has the advantage that physical quantities enter in a manner, which does not involve the numerical methods required to approximate their magnitude;

2) Average values of molecular quantities are directly expanded in a *Taylor* series in the field **F**, instead of calculating the ratio of two separate series expansions [3];

3) The explicit description of molecular orientations in terms of Eulerian angles [3] is avoided by working algebraically with rotational invariants.

Classical statistical mechanics is used to describe the orientational distribution of molecules in the field. As a consequence the result holds only if the temperature of the sample is high enough for kT to be much larger than the energy separation between molecular rotational levels.

The derivation is further restricted to the case of an electronic transition in a frequency range, where there are no contributions from other transitions to the absorption.

The field dependence of the molar extinction coefficient. - In the absence of the perturbing electric field **F**, the molar extinction coefficient $\varepsilon_0(\nu)$ observed in an experiment with polarized monochromatic light of frequency ν is given by (1):

$$\varepsilon_0(\nu) = K\nu\langle(\mathbf{e}\cdot\mathbf{P}_0)^2 S_0(\nu)\rangle \quad (1)$$

where

$$K \equiv 8\pi^3 N_A/2.303\,(1000\,hc) \quad (2)$$

and **e** is a unit vector along the electric field of the lightwave, $\mathbf{P}_0$ is the electronic transition moment, $S_0(\nu)$ is a shape function describing the contour of the absorption band, $\langle\rangle$ stands for averaging in general, N_A is *Avogadro*'s number and h is *Planck*'s constant.

Averaging the R.H.S. of (1) over an isotropic distribution of transition moments, we find

$$\varepsilon_0(\nu) = 1/3\,K\nu\,\mathbf{P}_0^2 S_0(\nu) \quad (3)$$

The introduction of a uniform static electric field **F** affects the absorption of a non-rigid sample, consisting of non-interacting absorbing molecules, in four ways:

1) The energies of initial- and final molecular state are changed;
2) The shape function $S(\nu)$ is altered;
3) The transition moment **P** is modified;
4) The distribution of molecular orientations becomes anisotropic.

The first effect causes a Stark shift given by (4):

$$h\Delta\nu = -\Delta\boldsymbol{\mu}\cdot\mathbf{F} - \frac{1}{2}\mathbf{F}\cdot\Delta\boldsymbol{\alpha}\cdot\mathbf{F} \quad (4)$$

with

$$\Delta\boldsymbol{\mu} \equiv \boldsymbol{\mu}(f) - \boldsymbol{\mu}(i) \qquad \Delta\boldsymbol{\alpha} \equiv \boldsymbol{\alpha}(f) - \boldsymbol{\alpha}(i)$$

and where $\boldsymbol{\mu}(k)$ is the dipole moment and $\boldsymbol{\alpha}(k)$ the polarizability in the k^{th} state and i and f labels the initial and final state respectively.

The alteration in the shape function is considered to consist merely of a uniform shift $\Delta\nu$ of the band, without changing the contour [4] *i.e.*

$$S(\mathbf{F},\nu) = S_0(\nu - \Delta\nu) \quad (5)$$

With the aid of (5), realizing $\Delta\nu$ given by (4), to be sufficiently small, $S(\mathbf{F},\nu)$ may be approximated by the first three terms of its *Taylor* expansion in $\Delta\nu$, *i.e.*:

$$S(\mathbf{F},\nu) = S_0(\nu) - \Delta\nu\left(\frac{dS_0}{d\nu}\right)_\nu + \frac{1}{2}(\Delta\nu)^2\left(\frac{d^2S_0}{d\nu^2}\right)_\nu + \quad (6)$$

The perturbation of the molecular hamiltonian by the field **F** causes a change in the wavefunctions of initial and final state and hence gives rise to a field induced part in the transition moment. Just like an ordinary dipole moment we describe **P** (**F**) by a power series in **F**:

$$\mathbf{P}(\mathbf{F}) = \mathbf{P}_0 + \mathbf{A} \cdot \mathbf{F} + \mathbf{B} : \mathbf{F}\,\mathbf{F} + \cdots \tag{7}$$

which defines the transition polarizability **A** and the transition hyperpolarizability **B**. The tensors **A** and **B** are of second and third rank respectively.

Unlike the polarizability $\boldsymbol{\alpha}$, the transition polarizability needs not to be a symmetrical tensor.

In the static field **F** the molecules acquire a potential energy $-\mathrm{V}(\Omega,\mathbf{F})$ depending on their orientation Ω relative to the field **F**.

$$\mathrm{V}(\Omega,\mathbf{F}) = \boldsymbol{\mu}(\mathrm{i}) \cdot \mathbf{F} + \frac{1}{2} \mathbf{F} \cdot \boldsymbol{\alpha}(\mathrm{i}) \cdot \mathbf{F} \tag{8}$$

The normalized distribution function for molecular orientations $\mathrm{f}(\Omega,\mathbf{F})$ is given by

$$\mathrm{f}(\Omega,\mathbf{F}) = \int_0 \exp[\beta\,\mathrm{V}(\Omega,\mathbf{F})] / \int_0 \exp[\beta\,\mathrm{V}(\Omega,\mathbf{F})]\,\mathrm{d}\Omega \tag{9}$$

where $\beta \equiv 1/\mathrm{kT}$ and where 0 indicates that the integration is over all orientations. In view of the development which follows, we emphasize that at zero field (9) represents an isotropic distribution of orientations.

The extinction coefficient $\varepsilon(\nu,\mathbf{F})$ in the presence of **F** can be calculated from the following expression.

$$\varepsilon(\nu,\mathbf{F}) = K\nu \langle \{\mathbf{e} \cdot \mathbf{P}(\mathrm{F})\}^2 \, \mathrm{S}(\mathbf{F},\nu) \rangle \tag{10}$$

where the distribution function from (9) has to be used in the averaging.

Using (6) and (3) the R.H.S of (10) may be transformed into an expression depending on $\varepsilon_0(\nu)$ and its derivatives.

$$\varepsilon(\nu,\mathbf{F}) = \frac{3\,\varepsilon_0(\nu)}{\mathrm{P}_0^2} \left\langle \{\mathbf{e} \cdot \mathbf{P}(\mathbf{F})\}^2 \left\{ 1 - \Delta\nu \frac{\mathrm{d}\ln(\varepsilon_0/\nu)}{\mathrm{d}\nu} + \frac{1}{2}(\Delta\nu)^2 \left[\left(\frac{\mathrm{d}\ln(\varepsilon_0/\nu)}{\mathrm{d}\nu} \right)^2 + \frac{\mathrm{d}^2 \ln(\varepsilon_0/\nu)}{\mathrm{d}\nu^2} \right] \right\} \right\rangle \tag{11}$$

The averaging indicated on the R.H.S. of (11) will be performed term by term. For a general term Q (**F**) we shall show the route for the calculation. We define:

$$\mathrm{T}(\mathbf{F}) \equiv \int_0 \phi(\Omega,\mathbf{F}) \exp\beta\,\mathrm{V}(\Omega,\mathbf{F})\,\mathrm{d}\Omega \tag{12}$$

$$\mathrm{N}(\mathbf{F}) \equiv \int_0 \exp\beta\,\mathrm{V}(\Omega,\mathbf{F})\,\mathrm{d}\Omega \tag{13}$$

$$\mathrm{Q}(\mathbf{F}) \equiv \langle \phi(\Omega,\mathbf{F}) \rangle \tag{14}$$

Hence: $Q(\mathbf{F}) = T(\mathbf{F})/N(\mathbf{F})$.

Expanding Q(F) into a *Taylor* series in the field components F_i, retaining terms up to the second order in **F**, we obtain:

$$Q(\mathbf{F}) = Q(0) + \sum_i F_i \left(\frac{\partial Q}{\partial F_i}\right)_{\mathbf{F}=0} + \frac{1}{2} \sum_{ij} F_i F_j \left(\frac{\partial^2 Q}{\partial F_i \partial F_j}\right)_{\mathbf{F}=0} \tag{15}$$

The derivatives are given by:

$$\frac{\partial Q}{\partial F_i} = N^{-1} \frac{\partial T}{\partial F_i} - N^{-2} T \frac{\partial N}{dF_i} \tag{16}$$

$$\begin{aligned}\frac{\partial^2 Q}{\partial F_i \partial F_j} = {} & N^{-1} \frac{\partial^2 T}{\partial F_i \partial F_j} - N^{-2} \frac{\partial T}{\partial F_i} \frac{\partial N}{\partial F_j} - N^{-2} T \frac{\partial^2 N}{\partial F_i \partial F_j} - N^{-2} \frac{\partial N}{\partial F_i} \frac{\partial T}{\partial F_j} \\ & + 2 N^{-3} T \frac{\partial N}{\partial F_i} \frac{\partial N}{\partial F_j}\end{aligned} \tag{17}$$

$$\frac{\partial T}{\partial F_i} = \int_0 \frac{\partial \phi}{\partial F_i} \exp \beta V \, d\Omega + \beta \int_0 \phi \frac{\partial V}{\partial F_i} \exp \beta V \, d\Omega \tag{18}$$

$$\begin{aligned}\frac{\partial^2 T}{\partial F_i \partial F_j} = {} & \int_0 \frac{\partial^2 \phi}{\partial F_i \partial F_j} \exp \beta V \, d\Omega + \beta \int_0 \frac{\partial \phi}{\partial F_i} \frac{\partial V}{\partial F_j} \exp \beta V \, d\Omega \\ & + \beta \int_0 \frac{\partial \phi}{\partial F_j} \frac{\partial V}{\partial F_i} \exp \beta V \, d\Omega + \beta \int_0 \phi \frac{\partial^2 V}{\partial F_i \partial F_j} \exp \beta V \, d\Omega \\ & + \beta^2 \int_0 \phi \frac{\partial V}{\partial F_i} \frac{\partial V}{\partial F_j} \exp \beta V \, d\Omega\end{aligned} \tag{19}$$

$$\frac{\partial N}{\partial F_i} = \beta \int_0 \frac{\partial V}{\partial F_i} \exp \beta V \, d\Omega \tag{20}$$

$$\frac{\partial^2 N}{\partial F_i \partial F_j} = \beta^2 \int_0 \frac{\partial V}{\partial F_i} \frac{\partial V}{\partial F_j} \exp \beta V \, d\Omega + \beta \int_0 \frac{\partial^2 V}{\partial F_i \partial F_j} \exp \beta V \, d\Omega . \tag{21}$$

Inserting eqs (18) to (21) into (16) and (17) and introducing the symbol $\langle\langle\rangle\rangle$ for averaging over an isotropic distribution, we arrive at:

$$\begin{aligned}\left(\frac{\partial Q}{\partial F_i}\right)_{\mathbf{F}=0} = {} & \left\langle\left\langle \left(\frac{\partial \phi}{\partial F_i}\right)_{\mathbf{F}=0} \right\rangle\right\rangle + \beta \left\langle\left\langle \phi(0) \left(\frac{\partial V}{\partial F_i}\right)_{\mathbf{F}=0} \right\rangle\right\rangle \\ & - \beta \langle\langle \phi(0) \rangle\rangle \left\langle\left\langle \left(\frac{\partial V}{\partial F_i}\right)_{\mathbf{F}=0} \right\rangle\right\rangle\end{aligned} \tag{22}$$

$$\begin{aligned}\left(\frac{\partial^2 Q}{\partial F_i \partial F_j}\right)_{F=0} = & \left\langle\!\left\langle \left(\frac{\partial^2 \phi}{\partial F_i \partial F_j}\right)_{F=0} \right\rangle\!\right\rangle + \beta \left\langle\!\left\langle \left(\frac{\partial \phi}{\partial F_i}\right)_{F=0} \left(\frac{\partial V}{\partial F_j}\right)_{F=0} \right\rangle\!\right\rangle \\ & + \beta \left\langle\!\left\langle \left(\frac{\partial \phi}{\partial F_j}\right)_{F=0} \left(\frac{\partial V}{\partial F_i}\right)_{F=0} \right\rangle\!\right\rangle + \beta \left\langle\!\left\langle \phi(0) \left(\frac{\partial^2 V}{\partial F_i \partial F_j}\right)_{F=0} \right\rangle\!\right\rangle \\ & + \beta^2 \left\langle\!\left\langle \phi(0) \left(\frac{\partial V}{\partial F_i}\right)_{F=0} \left(\frac{\partial V}{\partial F_j}\right)_{F=0} \right\rangle\!\right\rangle \\ & - \beta \left\langle\!\left\langle \left(\frac{\partial V}{\partial F_i}\right)_{F=0} \right\rangle\!\right\rangle \left\{ \left\langle\!\left\langle \left(\frac{\partial \phi}{\partial F_j}\right)_{F=0} \right\rangle\!\right\rangle \right. \\ & \left. + \beta \left\langle\!\left\langle \phi(0) \left(\frac{\partial V}{\partial F_j}\right)_{F=0} \right\rangle\!\right\rangle \right\} \\ & - \beta \left\langle\!\left\langle \left(\frac{\partial V}{\partial F_j}\right)_{F=0} \right\rangle\!\right\rangle \left\{ \left\langle\!\left\langle \left(\frac{\partial \phi}{\partial F_i}\right)_{F=0} \right\rangle\!\right\rangle \right. \\ & \left. + \beta \left\langle\!\left\langle \phi(0) \left(\frac{\partial \phi}{\partial F_i}\right)_{F=0} \right\rangle\!\right\rangle \right\} \\ & - \beta \langle\!\langle \phi(0) \rangle\!\rangle \left\{ \left\langle\!\left\langle \left(\frac{\partial^2 V}{\partial F_i \partial F_j}\right)_{F=0} \right\rangle\!\right\rangle \right. \\ & \left. + \beta \left\langle\!\left\langle \left(\frac{\partial V}{\partial F_i}\right)_{F=0} \left(\frac{\partial V}{\partial F_j}\right)_{F=0} \right\rangle\!\right\rangle \right\} \\ & + 2\beta^2 \langle\!\langle \phi(0) \rangle\!\rangle \left\langle\!\left\langle \left(\frac{\partial V}{\partial F_i}\right)_{F=0} \right\rangle\!\right\rangle \left\langle\!\left\langle \left(\frac{\partial V}{\partial F_j}\right)_{F=0} \right\rangle\!\right\rangle \end{aligned} \tag{23}$$

The derivatives of V with respect to the field components are found by differentiating the form (8). If the fact that $\langle\!\langle \mu_i \rangle\!\rangle = 0$ is used, the following expressions result:

$$\left(\frac{\partial Q}{\partial F_i}\right)_{F=0} = \left\langle\!\left\langle \left(\frac{\partial \phi}{\partial F_i}\right)_{F=0} \right\rangle\!\right\rangle + \beta \langle\!\langle \mu_i \phi(0) \rangle\!\rangle \tag{24}$$

$$\begin{aligned}\left(\frac{\partial^2 Q}{\partial F_i \partial F_j}\right)_{F=0} = & \left\langle\!\left\langle \left(\frac{\partial^2 \phi}{\partial F_i \partial F_j}\right)_{F=0} \right\rangle\!\right\rangle + \beta \left\langle\!\left\langle \mu_i \left(\frac{\partial \phi}{\partial F_j}\right)_{F=0} \right\rangle\!\right\rangle + \beta \left\langle\!\left\langle \mu_j \left(\frac{\partial \phi}{\partial F_i}\right)_{F=0} \right\rangle\!\right\rangle \\ & + \beta^2 \langle\!\langle \mu_i \mu_j \phi(0) \rangle\!\rangle - \beta^2 \langle\!\langle \phi(0) \rangle\!\rangle \langle\!\langle \mu_i \mu_j \rangle\!\rangle \\ & + \frac{1}{2} \beta \langle\!\langle a_{ij} \phi(0) \rangle\!\rangle - \frac{1}{2} \beta \langle\!\langle \phi(0) \rangle\!\rangle \langle\!\langle a_{ij} \rangle\!\rangle \end{aligned} \tag{25}$$

After the expressions (7) for $\mathbf{P}(\mathbf{F})$ and (4) for $\Delta\nu$ are inserted and distributed over all terms in (11) we retain terms up to the second order in $\mathbf{F}$ and write:

$$\varepsilon(\nu, F) = \frac{3\varepsilon_0(\nu)}{P_0^2} \left\langle \left\{ \sum_{k=1}^{4} \phi_k + \frac{1}{h} \frac{d \ln \varepsilon_0/\nu}{d\nu} \sum_{k=1}^{3} \phi'_k + \frac{1}{2h^2} \left[\left(\frac{d \ln \varepsilon_0/\nu}{d\nu} \right)^2 + \frac{d^2 \ln \varepsilon_0/\nu}{d\nu^2} \right] \phi'' \right\} \right\rangle \tag{26}$$

where

$$\phi_1=(\mathbf{e}\cdot\mathbf{P}_0)^2 \qquad \phi_1'=(\mathbf{e}\cdot\mathbf{P}_0)^2(\Delta\boldsymbol{\mu}\cdot\mathbf{F})$$
$$\phi_2=(\mathbf{e}\cdot\mathbf{A}\cdot\mathbf{F})^2 \qquad \phi_2'=2(\mathbf{e}\cdot\mathbf{P}_0)(\mathbf{e}\cdot\mathbf{A}\cdot\mathbf{F})(\Delta\boldsymbol{\mu}\cdot\mathbf{F})$$
$$\phi_3=2(\mathbf{e}\cdot\mathbf{P}_0)(\mathbf{e}\cdot\mathbf{A}\cdot\mathbf{F}) \qquad \phi_3'=\frac{1}{2}(\mathbf{e}\cdot\mathbf{P}_0)^2(\mathbf{F}\cdot\Delta\boldsymbol{\alpha}\cdot\mathbf{F}) \tag{27}$$
$$\phi_4=2(\mathbf{e}\cdot\mathbf{P}_0)(\mathbf{e}\cdot\mathbf{B}:\mathbf{FF}) \qquad \phi''=(\mathbf{e}\cdot\mathbf{P}_0)^2(\Delta\boldsymbol{\mu}\cdot\mathbf{F})^2$$

Now relation (15) together with (24) and (25) enable us to calculate any such term as $Q_k\equiv\langle\Phi_k\rangle$. The problem of averaging has been reduced to that of finding average values in an isotropic system.

Average values in an isotropic system. - Let us agree to choose in a molecule a cartesian coordinate system defined by three orthonormal vectors $\{\mathbf{i}\}$. The components of a tensor **T** of rank n with respect to this basis are denoted by $T_{ij\ldots}$.

We select a space-fixed coordinate system defined by the three orthonormal vectors $\{\xi\}$. The two coordinate systems are related to each other by the orthogonal transformation R:

$$\{\xi\}=R\{\mathbf{i}\} \quad \text{or} \quad \xi=\sum_i R_{\xi i}\mathbf{i} \quad \text{with} \quad R_{\xi i}=\boldsymbol{\xi}\cdot\mathbf{i} \tag{28}$$

The components of the tensor **T** in the two coordinate systems are coupled by the following transformation:

$$\begin{aligned} T_{\xi\eta}\cdots &= \sum_{ij\cdots} R_{\xi i}R_{\eta j}\cdots T_{ij\ldots} \\ &= \sum_{ij\cdots} (\boldsymbol{\xi}\cdot\mathbf{i})(\boldsymbol{\eta}\cdot\mathbf{j})\cdots T_{ij\ldots} \end{aligned} \tag{29}$$

If the system $\{\mathbf{i}\}$ can take all possible orientations in space, the average value of the component $\langle\langle T_{\xi\eta\ldots}\rangle\rangle$ is determined by the averages values of quantities of the form $\langle\langle(\boldsymbol{\xi}\cdot\mathbf{i})(\boldsymbol{\eta}\cdot\mathbf{j})\cdots\rangle\rangle$. We shall refer to these as a n-factor product depending on the number n of scalar products involved. In our problem we shall not exceed n=4. The average value of an n factor product is completely determined by the rotational invariants it contains. At the end of this paper we shall present in an appendix a method to find these invariants. Here we give the rules which follow from the discussion in the appendix.

1.
$$\langle\langle\boldsymbol{\xi}\cdot\mathbf{i}\rangle\rangle=0 \tag{30}$$

2. The contribution from a 2-factor product is given by

$$\langle\langle(\boldsymbol{\xi}\cdot\mathbf{i})(\boldsymbol{\eta}\cdot\mathbf{j})\rangle\rangle=\frac{1}{3}\delta_{\xi\eta}\delta_{ij} \tag{31}$$

3. A 3-factor product averages to zero unless the vectors $\boldsymbol{\xi},\boldsymbol{\eta},\boldsymbol{\zeta}$ and **i,j,k** appear only once.

$$\langle\langle(\boldsymbol{\xi}\cdot\mathbf{i})(\boldsymbol{\eta}\cdot\mathbf{j})(\boldsymbol{\xi}\cdot\mathbf{k})\rangle\rangle=\frac{1}{6} \tag{32}$$

4. A 4-factor product yields a non-vanishing contribution in two cases.
   a) One of the vectors ξ appears in all the factors

$$\langle\langle(\xi\cdot\mathbf{i})(\xi\cdot\mathbf{j})(\xi\cdot\mathbf{k})(\xi\cdot\mathbf{l})\rangle\rangle=\frac{1}{15}\{\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{kj}\} \tag{33}$$

   b) The two vectors ξ and η each appear twice.

$$\langle\langle(\xi\cdot\mathbf{i})(\xi\cdot\mathbf{j})(\eta\cdot\mathbf{k})(\eta\cdot\mathbf{l})\rangle\rangle=\frac{2}{15}\delta_{ij}\delta_{kl}-\frac{1}{30}\delta_{ik}\delta_{jl}-\frac{1}{30}\delta_{il}\delta_{kj} \tag{34}$$

A most convenient choice of the space-fixed coordinate system is to have ξ in the direction of the external field **F**.

The result of the averaging of the quantities listed in (27) will depend on the direction of **e**, *i.e.* on the polarization of the lightwave. The job has to be done for two situations, namely **e** // **F** *i.e.* $\mathbf{e}=\xi$ and $\mathbf{e}\perp\mathbf{F}$, say $\mathbf{e}=\eta$. From these we shall synthesize the general result for an angle χ between **e** and **F**. All quantities in (27) are quadratic in **e** and hence for any Φ we have a relation:

$$\phi(\chi)=\phi(0°)\cos^2\chi+\phi(90°)\sin^2\chi \tag{35}$$

For a particular Φ, say Φ'', we shall present the steps leading to $\langle\langle\Phi(\chi)\rangle\rangle$ as an example. From (27) it follows, using the alternative notation $\mathbf{P}^0\equiv\mathbf{P}_0$:

$$\phi''(0°)=P^0_\xi P^0_\xi\Delta\mu_\xi F_\xi\Delta\mu_\xi F_\xi \qquad \phi(90°)=P^0_\eta P^0_\eta\Delta\mu_\xi F_\xi\Delta\mu_\xi F_\xi \tag{36}$$

$$\left(\frac{\partial\phi''(0°)}{\partial F_\xi}\right)_{F=0}=0 \qquad \left(\frac{\partial\phi''(90°)}{\partial F_\xi}\right)_{F=0}=0 \tag{37}$$

$$\left(\frac{\partial^2\phi''(0°)}{\partial F_\xi^2}\right)_{F=0}=2P^0_\xi P^0_\xi\Delta\mu_\xi\Delta\mu_\xi \qquad \left(\frac{\partial^2\phi''(90°)}{\partial F_\xi^2}\right)_{F=0}=2P^0_\eta P^0_\eta\Delta\mu_\xi\Delta\mu_\xi \tag{38}$$

$$\begin{aligned}\langle\langle\phi''(0°)\rangle\rangle&=F_\xi^2\langle\langle P^0_\xi P^0_\xi\Delta\mu_\xi\Delta\mu_\xi\rangle\rangle=F_\xi^2\sum_{ijkl}\langle\langle(\xi\cdot\mathbf{i})(\xi\cdot\mathbf{j})(\xi\cdot\mathbf{k})(\xi\cdot\mathbf{l})P^0_iP^0_j\Delta\mu_k\Delta\mu_l\rangle\rangle\\&=F_\xi^2\left\{\frac{1}{15}\sum_{ik}P^0_iP^0_i\Delta\mu_k\Delta\mu_k+\frac{1}{15}\sum_{ik}P^0_iP^0_k\Delta\mu_i\Delta\mu_k+\frac{1}{15}\sum_{ik}P^0_iP^0_k\Delta\mu_k\Delta\mu_i\right\}\end{aligned} \tag{39}$$

$$\begin{aligned}\langle\langle\phi''(90°)\rangle\rangle&=F_\xi^2\langle\langle P^0_\eta P^0_\eta\Delta\mu_\xi\Delta\mu_\xi\rangle\rangle=F_\xi^2\sum_{ijkl}\langle\langle(\eta\cdot\mathbf{i})(\eta\cdot\mathbf{j})(\xi\cdot\mathbf{k})(\xi\cdot\mathbf{l})P^0_iP^0_j\Delta\mu_k\Delta\mu_l\rangle\rangle\\&=F_\xi^2\left\{\frac{2}{15}\sum_{ik}P^0_iP^0_i\Delta\mu_k\Delta\mu_k-\frac{1}{30}\sum_{ik}P^0_iP^0_k\Delta\mu_i\Delta\mu_k-\frac{1}{30}\sum_{ik}P^0_iP^0_k\Delta\mu_k\Delta\mu_i\right\}\end{aligned} \tag{40}$$

$$\begin{aligned}\langle\langle\phi''(\chi)\rangle\rangle&=\langle\langle\phi''(0°)\rangle\rangle\cos^2\chi+\langle\langle\phi''(90°)\rangle\rangle(1-\cos^2\chi)\\&=F^2\frac{2}{90}\{5\tilde{\mathscr{H}}+\tilde{\mathscr{I}}(3\cos^2\chi-1)\}\end{aligned} \tag{41}$$

where

$$\tilde{\mathscr{H}} = P_0^2 (\Delta\mu)^2 \tag{42}$$

$$\tilde{\mathscr{I}} = 3(\mathbf{P}_0 \cdot \Delta\boldsymbol{\mu})^2 - P_0^2 (\Delta\mu)^2 \tag{43}$$

Working along this line an expression is finally obtained for $\varepsilon_\chi(\nu,F)/\varepsilon(\nu)$.

$$\frac{\varepsilon_\chi(\nu,F)}{\varepsilon_0(\nu)} = 1 + F^2 \left\{\mathscr{A}_\chi + \frac{1}{15\,h}\mathscr{B}_\chi \frac{d\ln\varepsilon_0/\nu}{d\nu} + \frac{1}{30\,h^2}\mathscr{C}_\chi\left[\left(\frac{d\ln\varepsilon_0/\nu}{d\nu}\right)^2 + \frac{d^2\ln\varepsilon_0/\nu}{d\nu^2}\right)\right\} \tag{44}$$

The quantities $\mathscr{A}_\chi, \mathscr{B}_\chi$ and $\mathscr{C}_\chi$ all depend linearly on $\cos^2\chi$. These linear relations are written in the form:

$$\mathscr{A}_\chi = \frac{1}{3}\mathscr{D} + \frac{1}{30}\mathscr{E}(3\cos^2\chi - 1) \tag{45}$$

$$\mathscr{B}_\chi = 5\mathscr{F} + \mathscr{G}(3\cos^2\chi - 1) \tag{46}$$

$$\mathscr{C}_\chi = 5\mathscr{H} + \mathscr{I}(3\cos^2\chi - 1) \tag{47}$$

The coefficients $\mathscr{D}, \mathscr{E}, \mathscr{F}, \mathscr{G}, \mathscr{H}$ and $\mathscr{I}$ are given in terms of molecular quantities by the following relations.

$$\mathscr{D} = 2\beta\frac{\mathbf{P}_0 \cdot \mathbf{A} \cdot \boldsymbol{\mu}}{P_0^2} + \frac{1}{P_0^2}\sum_{ij} A_{ij}^2 + \frac{2}{P_0^2}\sum_{ij} P_{0i} B_{ijj} \tag{48}$$

$$\begin{aligned}\mathscr{E} = {} & \beta^2[3(\boldsymbol{\mu}\cdot\mathbf{p})^2 - \mu^2] + \frac{3}{2}\beta\,\mathbf{p}\cdot\boldsymbol{\alpha}\cdot\mathbf{p} - \frac{1}{2}\beta\,\mathrm{Tr}\,\boldsymbol{\alpha} \\ & + 6\beta\frac{(\boldsymbol{\mu}\cdot\mathbf{P}_0)\,\mathrm{Tr}\,\mathbf{A}}{P_0^2} + 6\beta\frac{\boldsymbol{\mu}\cdot\mathbf{A}\cdot\mathbf{P}_0}{P_0^2} - 4\beta\frac{\mathbf{P}_0\cdot\mathbf{A}\cdot\boldsymbol{\mu}}{P_0^2} + \frac{3}{P_0^2}(\mathrm{Tr}\,\mathbf{A})^2 \\ & + \frac{3}{P_0^2}\sum_{ij} A_{ij}A_{ji} - \frac{2}{P_0^2}\sum_{ij} A_{ij}^2 + \frac{6}{P_0^2}\sum_{ij} P_{0i}B_{jij} + \frac{6}{P_0^2}\sum_{ij} P_{0i}B_{jji} - \frac{4}{P_0^2}\sum_{ij} P_{0i}B_{ijj}\end{aligned} \tag{49}$$

$$\mathscr{F} = \beta\,\boldsymbol{\mu}\cdot\Delta\boldsymbol{\mu} + 2\frac{\mathbf{P}_0\cdot\mathbf{A}\cdot\Delta\boldsymbol{\mu}}{P_0^2} + \frac{1}{2}\mathrm{Tr}\,\Delta\boldsymbol{\alpha} \tag{50}$$

$$\begin{aligned}= {} & \beta[3(\boldsymbol{\mu}\cdot\mathbf{p})(\Delta\boldsymbol{\mu}\cdot\mathbf{p}) - \boldsymbol{\mu}\cdot\Delta\boldsymbol{\mu}] \\ & + \frac{3}{2}\mathbf{p}\cdot\Delta\boldsymbol{\alpha}\cdot\mathbf{p} - \frac{1}{2}\mathrm{Tr}\,\Delta\boldsymbol{\alpha} + 3\frac{(\Delta\boldsymbol{\mu}\cdot\mathbf{P}_0)\,\mathrm{Tr}\,\mathbf{A}}{P_0^2} + 3\frac{\Delta\boldsymbol{\mu}\cdot\mathbf{A}\cdot\mathbf{P}_0}{P_0^2} - 2\frac{\mathbf{P}_0\cdot\mathbf{A}\cdot\Delta\boldsymbol{\mu}}{P_0^2}\end{aligned} \tag{51}$$

$$\mathscr{H} = (\Delta\mu)^2 \tag{52}$$

$$\mathscr{I} = 3(\Delta\boldsymbol{\mu} \cdot \mathbf{p})^2 - (\Delta\mu)^2 \tag{53}$$

In the relations above $\mathbf{p}$ represents a unit vector along $\mathbf{P}_0$.

Appendix. - By an n-factor product we mean a product of n factors, each of which is a scalar product of two vectors.

We shall derive for an n-factor product its average value over an isotropic distribution of orientations. Consider a space-fixed righthanded coordinate system defined by the orthonormal vectors $\boldsymbol{\xi}$, $\boldsymbol{\eta}$, $\boldsymbol{\zeta}$. We have another rigid system of independent vectors **u**,**v**,**w**. The two systems have a common origin and the tripod **u**,**v**,**w** can take all possible orientations with respect to the space-fixed one. Only rotational invariants which are independent of the mutual orientation of the two systems will survive the averaging.

1) $$\langle\langle(\boldsymbol{\xi} \cdot \mathbf{u})\rangle\rangle = 0$$

since there is no invariant linear in $\boldsymbol{\xi}$ and $\mathbf{u}$ and independent of their mutual orientation.

2a) $$\langle\langle(\boldsymbol{\xi} \cdot \mathbf{u})^2\rangle\rangle = \lambda(\boldsymbol{\xi} \cdot \boldsymbol{\xi})(\mathbf{u} \cdot \mathbf{u}) \tag{54}$$

i.e. proportional to an invariant which does not depend on the mutual orientation of $\boldsymbol{\xi}$ and $\mathbf{u}$ and which is quadratic in both $\boldsymbol{\xi}$ and $\mathbf{u}$.
We also have

$$\begin{aligned}\langle\langle(\boldsymbol{\xi} \cdot \mathbf{u})^2\rangle\rangle &= \langle\langle(\boldsymbol{\eta} \cdot \mathbf{u})^2\rangle\rangle \\ &= \langle\langle(\boldsymbol{\zeta} \cdot \mathbf{u})^2\rangle\rangle \\ &= \lambda(\mathbf{u} \cdot \mathbf{u})\end{aligned}$$

$$\begin{aligned}(\mathbf{u} \cdot \mathbf{u}) &= (\boldsymbol{\xi} \cdot \mathbf{u})^2 + (\boldsymbol{\eta} \cdot \mathbf{u})^2 + (\boldsymbol{\zeta} \cdot \mathbf{u})^2 \\ &= 3\langle\langle(\boldsymbol{\xi} \cdot \mathbf{u})^2\rangle\rangle\end{aligned}$$

thus $\lambda = \frac{1}{3}$.

2b) $$\langle\langle(\boldsymbol{\xi} \cdot \mathbf{u})(\boldsymbol{\xi} \cdot \mathbf{v})\rangle\rangle = \lambda'(\boldsymbol{\xi} \cdot \boldsymbol{\xi})(\mathbf{u} \cdot \mathbf{v}) \tag{55}$$

since this should also hold for $\mathbf{u} = \mathbf{v}$ $\quad \lambda = \lambda' = \frac{1}{3}$.

2c) $$\langle\langle(\boldsymbol{\xi} \cdot \mathbf{u})(\boldsymbol{\eta} \cdot \mathbf{v})\rangle\rangle = \lambda''(\boldsymbol{\xi} \cdot \boldsymbol{\eta})(\mathbf{u} \cdot \mathbf{v}) = 0 \tag{56}$$

since $\boldsymbol{\xi} \cdot \boldsymbol{\eta} = 0$

3) The invariant associated with three vectors ξ, η, ζ is the volume of the parallelepiped which they span. If in a 3-factor product one of the vectors occurs twice or more the average value will be zero.

$$\langle\langle(\xi \cdot \mathbf{u})(\eta \cdot \mathbf{v})(\zeta \cdot \mathbf{w})\rangle\rangle = \lambda\,[(\xi \times \eta) \cdot \zeta][(\mathbf{u} \times \mathbf{v}) \cdot \mathbf{w}] = \lambda\,(\mathbf{u} \times \mathbf{v}) \cdot \mathbf{w} \tag{57}$$

The value of λ is determined by the reasoning which follows. An interchange of $\mathbf{v}$ and $\mathbf{w}$ will introduce a change of sign on the R.H.S. of (57). Hence

$$\begin{aligned}
\langle\langle(\xi \cdot \mathbf{u})(\eta \cdot \mathbf{v})(\zeta \cdot \mathbf{w})\rangle\rangle &= \frac{1}{2}\{\langle\langle(\xi \cdot \mathbf{u})(\eta \cdot \mathbf{v})(\zeta \cdot \mathbf{w})\rangle\rangle - \langle\langle(\xi \cdot \mathbf{u})(\eta \cdot \mathbf{w})(\zeta \cdot \mathbf{v})\rangle\rangle\} \\
&= \frac{1}{2}\langle\langle(\xi \cdot \mathbf{u})\{(\eta \cdot \mathbf{v})(\zeta \cdot \mathbf{w}) - (\eta \cdot \mathbf{w})(\zeta \cdot \mathbf{v})\}\rangle\rangle \\
&= \frac{1}{2}\langle\langle(\xi \cdot \mathbf{u})\{(\eta \times \zeta) \cdot (\mathbf{v} \times \mathbf{w})\} \\
&= \frac{1}{2}\langle\langle(\xi \cdot \mathbf{u})\{\xi \cdot (\mathbf{v} \times \mathbf{w})\} \\
&= \frac{1}{6}\mathbf{u} \cdot (\mathbf{v} \times \mathbf{w})
\end{aligned}$$

In the last step the result (55) has been applied and the conclusion is $\lambda = \frac{1}{6}$.

4) A 4-factor product of the type $\langle\langle(\xi \cdot \mathbf{u})(\xi \cdot \mathbf{z})(\eta \cdot \mathbf{v})(\zeta \cdot \mathbf{w})\rangle\rangle$ has an average value zero, because non-vanishing would require an invariant linear in η and independent of its orientation with respect to the $\mathbf{u},\mathbf{v},\mathbf{w}$ system, which obviously does not exist. There are two cases delivering a non-vanishing average.

a) Only one of the vectors ξ, η or ζ occurs in the product.

$$\langle\langle(\xi \cdot \mathbf{u})(\xi \cdot \mathbf{v})(\xi \cdot \mathbf{w})(\xi \cdot \mathbf{z})\rangle\rangle = \lambda\,\{(\mathbf{u} \cdot \mathbf{v})(\mathbf{w} \cdot \mathbf{z}) + (\mathbf{u} \cdot \mathbf{w})(\mathbf{v} \cdot \mathbf{z}) + (\mathbf{u} \cdot \mathbf{z})(\mathbf{v} \cdot \mathbf{w})\} \tag{58}$$

from $\mathbf{u} = \mathbf{v} = \mathbf{w} = \mathbf{z}$ it follows:

$$\langle\langle(\xi \cdot \mathbf{u})^4\rangle\rangle = 3\,\lambda\,(\mathbf{u} \cdot \mathbf{u})^2 \tag{59}$$

On the other hand we have:

$$\begin{aligned}
(\mathbf{u} \cdot \mathbf{u})^2 &= \{(\xi \cdot \mathbf{u})^2 + (\eta \cdot \mathbf{u})^2 + (\zeta \cdot \mathbf{u})^2\}^2 \\
&= 3\,\langle\langle(\xi \cdot \mathbf{u})^4\rangle\rangle + 6\,\lambda\,(\mathbf{u} \cdot \mathbf{u})^2
\end{aligned} \tag{60}$$

where the last step arises from the application of (80) to $\langle\langle(\xi \cdot \mathbf{u})^2(\eta \cdot \mathbf{u})^2\rangle\rangle$. Substitution of (59) into (60) yields $\lambda = \frac{1}{15}$.

b) Two vectors from the set ξ, η, ζ appear in the product.

$$\langle\langle (\xi \cdot \mathbf{u})(\xi \cdot \mathbf{v})(\eta \cdot \mathbf{w})(\eta \cdot \mathbf{z}) \rangle\rangle = \lambda (\mathbf{u} \cdot \mathbf{v})(\mathbf{w} \cdot \mathbf{z}) + \rho \{(\mathbf{u} \cdot \mathbf{w})(\mathbf{v} \cdot \mathbf{z}) + (\mathbf{u} \cdot \mathbf{z})(\mathbf{v} \cdot \mathbf{w})\} \tag{61}$$

Consider $\mathbf{u} = \mathbf{v}$ and $\mathbf{w} = \mathbf{z}$.

$$\langle\langle (\xi \cdot \mathbf{u})^2 (\eta \cdot \mathbf{w})^2 \rangle\rangle = \lambda (\mathbf{u} \cdot \mathbf{u})(\mathbf{w} \cdot \mathbf{w}) + 2 \rho (\mathbf{u} \cdot \mathbf{w})^2 \tag{62}$$

On the other hand we have

$$\begin{aligned}(\mathbf{u} \cdot \mathbf{u})(\mathbf{w} \cdot \mathbf{w}) &= \{(\xi \cdot \mathbf{u})^2 + (\eta \cdot \mathbf{u})^2 + (\zeta \cdot \mathbf{u})^2\}\{(\xi \cdot \mathbf{w})^2 + (\eta \cdot \mathbf{w})^2 + (\zeta \cdot \mathbf{w})^2\} \\ &= 3 \langle\langle (\xi \cdot \mathbf{u})^2 (\xi \cdot \mathbf{w})^2 \rangle\rangle + 6 \langle\langle (\xi \cdot \mathbf{u})^2 (\eta \cdot \mathbf{w})^2 \rangle\rangle \end{aligned} \tag{63}$$

Application of the previous result (58) to the first term of the R.H.S. of (63) yields

$$6 \langle\langle (\xi \cdot \mathbf{u})^2 (\eta \cdot \mathbf{w})^2 \rangle\rangle = \frac{12}{15} (\mathbf{u} \cdot \mathbf{u})(\mathbf{w} \cdot \mathbf{w}) - \frac{6}{15} (\mathbf{u} \cdot \mathbf{w})^2 \tag{64}$$

Comparing (64) with (62) we see that $\lambda = \frac{2}{15}$ and $\rho = -\frac{1}{30}$.

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