Nonlinear Optical Coefficients

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We consider, from a number of different viewpoints, the tensor coefficients which describe second harmonic generation, optical rectification, and the Pockels or linear electro-optic effect in acentric crystals. Stationary perturbation theory is used to calculate the low-frequency limit of the intrinsic electronic nonlinearity neglecting all effects due to local fields or lattice polarization. Solid methane is used as an example and the result used to estimate the coefficient in hexamethylene tetramine. The calculated result is within a factor of 2 of the experimental figure. The method is susceptible to further refinement and, since it requires only a knowledge of ground state wave functions, and is essentially very simple, it appears to offer a useful approach to the calculation of the coefficients.

The classical anharmonic oscillator model is briefly covered and the model is related to a quantal treatment. We find that the anharmonic potential used in the model is directly related to the actual crystalline potential. It can also be related to the charge distribution in the electronic ground state.

Local field corrections and the effects of lattice polarization are presented. These alter the nonlinear properties in a simple and obvious way, but one which has been misunderstood in some of the literature.

Our results form a theoretical background to Miller's empirical rule relating the nonlinear coefficients to the linear susceptibilities. An extensive table of Miller-reduced tensor coefficients collated from the published literature is presented.

Finally, we draw together some of the threads of the previous sections. An appendix deals with the vexing question of definitions.

I. INTRODUCTION

Second harmonic generation, optical rectification, and the linear electro-optic effect are particular aspects of a process in which two fields, $E_j^\beta e^{i\beta t}$ and $E_k^\gamma e^{i\gamma t}$, generate a polarization

$$P_i^\alpha e^{i\alpha t} = d_{ijk}^{\alpha\beta\gamma} E_j^\beta e^{i\beta t} E_k^\gamma e^{i\gamma t}. \tag{1}$$

Our concern is with the tensor coefficients $d_{ijk}^{\alpha\beta\gamma}$ which (Nye[1]) necessarily vanish in centric (centrosymmetric) crystals and which, in acentric crystals, are subject to symmetry restrictions, (Kleinman[2]) which often leave only one or two independent components.

Experimentally, the values of the allowed components of d in different materials and at different frequencies range from about 2.10^{-10} esu (cm/stat volt) to about 6.10^{-5} esu. This range may be contrasted with the linear optical susceptibility χ which is between 0.1 and 0.3 for the vast majority of materials and only quite exceptionally exceeds unity. There is, however, a connection between the tensor d and χ which is expressed by an important empirical rule due to Miller.[3] If we write $d_{ijk}^{\alpha\beta\gamma}$ as

$$d_{ijk}^{\alpha\beta\gamma} = \chi_{ii}^{\alpha}\chi_{jj}^{\beta}\chi_{kk}^{\gamma}\Delta_{ijk} , \tag{2}$$

where χ_{ii}^{α} is the ii component of χ at a frequency α, and if we have chosen a principal axis system for χ, then the allowed components of Δ_{ijk} for all effects and all materials are similar in magnitude. We shall see in a later section that for very many materials in both the visible and 10 μ region of the spectrum (Patel[4]), Δ_{ijk} is near 3×10^{-6} esu. No materials with Δ above 20×10^{-6} esu have yet been found and very few are known to have a value below 0.2×10^{-6} esu. In the case of $NH_4H_2PO_4$ where the best measurements of s.h.g., optical rectification and the electro-optic effect are available (Francois,[5] Ward,[6] Carpenter[7]) the value of Δ_{123} from all three effects is 3×10^{-6} esu within the experimental error of 15 percent. The fact that s.h.g., a purely optical effect, leads to the same value of Δ as rectification and the electro-optic effect indicates quite clearly that the basic mechanism of the nonlinearities is common to all three effects and must therefore reside in the electronic motion of the system. In the next section, we shall concentrate on this aspect of the problem and neglect the effects of local fields and lattice polarization.

A number of authors (see Section IV for references) have given quantal treatments of the optical nonlinearities whose end result is an expression for the coefficients $d_{ijk}^{\alpha\beta\gamma}$ in terms of sums of rather inaccessible matrix elements. Useful as these expressions are, in establishing some of the general properties of the coefficients, they are not a practical step on the road to calculating the coefficients from other empirical quantities. At the other extreme, the classical anharmonic oscillator model has been used to demonstrate some of the qualitative features of nonlinear behavior (see Section III). This treatment, though simple and appealing, suffers from the defect that the relation between the parameters of the model and those of the real system is obscure. In Section IV, we shall remedy this defect and show that the two approaches are closely related.

First, however, we give an approximate method of calculating the low-frequency limit of the coefficients from stationary perturbation theory in a form in which it has been successfully applied to the linear properties of n electron atoms (see, e.g., Dalgarno[8]).

II. MAGNITUDE OF THE COEFFICIENTS

At low frequencies, i.e., well below any electronic resonance we can use stationary perturbation theory to calculate, to arbitrary order in the applied field $\underline{E}$ the energy W of the ground state. The polarization is then given by

$$P_i = -\frac{\partial W}{\partial E_i}. \tag{3}$$

We shall assume that we are dealing with a crystal containing N identical atoms or molecules in unit volume whose individual ground state energies are w, so that $W = Nw$.

If H_o is the Hamiltonian of an unperturbed molecule, its Hamiltonian in the field $\underline{E}$ is

$$H = H_o + h = H_o - e\underline{E}\cdot\underline{R}, \tag{4}$$

where

$$e\underline{R} = e\sum_{m=1}^{n} \underline{r}^m \tag{5}$$

is the dipole moment operator of the molecule, and the sum extends over all n valence electrons. We can neglect the core electrons because of their high binding energies. If we expand w in increasing order in $\underline{E}$ as

$$w = w_0 + w_1 + w_2 + w_3\ , \quad \text{etc.}, \tag{6}$$

the term w_1 gives the permanent dipole moment of the molecule, w_2 gives the linear susceptibility and w_3 gives a polarization quadratic in $\underline{E}$ which leads to the desired nonlinear coefficients. The electric field will perturb the state function ψ and we shall write the perturbed function as either

$$\psi = \psi_0 + \psi_1 + \psi_2 + \cdots \quad \text{or} \quad |\ \rangle = |0\rangle + |1\rangle + |2\rangle + \cdots. \tag{7}$$

Knowledge of ψ or $|\ \rangle$ to first order in $\underline{E}$ is sufficient to determine w_1 , w_2 , and w_3 for

$$\begin{aligned} w_1 &= \langle 0|\, h\, |0\rangle \\ w_2 &= \langle 0|\, \hat{h}\, |1\rangle \\ w_3 &= \langle 1|\, \hat{h}\, |1\rangle. \end{aligned} \tag{8}$$

Moreover, the correct value of ψ_1 or $|\, 1\rangle$ is determined by the requirement that it minimize w. Thus, we can obtain $|\, 1\rangle$ by a variational procedure and the only element of choice left to us is that of the trial wave function.

Minimizing w is equivalent (see Dalgarno and Lewis[9]) to the simpler problem of minimizing

$$\langle 1|\, \hat{H}_o\, |1\rangle + 2\langle 0|\, \hat{h}\, |1\rangle, \tag{9}$$

where the notation $\hat{H}_o$ or $\hat{h}$ means $H_o - \langle 0\mid H_o \mid 0\rangle$ or $h - \langle 0 \mid h \mid 0\rangle$.

As a trial function, we take

$$|1\rangle = \lambda \hat{h}\, |0\rangle \tag{10}$$

so that (9) becomes

$$\lambda^2 \langle 0|\, \hat{h}\hat{H}_o\hat{h}\, |0\rangle + 2\lambda \langle 0|\, \hat{h}^2\, |0\rangle. \tag{11}$$

The minimization with respect to λ gives

$$\lambda = -\frac{\langle 0|\, \hat{h}^2\, |0\rangle}{\langle 0|\, \hat{h}\hat{H}_o\hat{h}\, |0\rangle} \equiv -\frac{\langle 0|\, \hat{h}^2\, |0\rangle}{\langle 0|\, h\hat{H}h\, |0\rangle}. \tag{12}$$

The unperturbed Hamiltonian of the system is of the form

$$H_o = -\frac{\hbar^2}{2m} \sum_{m=1}^{n} \nabla_m^2 + V_o \tag{13}$$

and so, in the denominator of (12),

$$\hat{H}_o h = h\hat{H}_o + \frac{\hbar^2}{m} e\underline{E} \cdot \sum_m \nabla_m \;. \tag{14}$$

Thus,

$$\langle 0|\, h\hat{H}_o h\, |0\rangle = -\frac{e^2\hbar^2}{m} \int \psi_o \sum_{m'} \underline{E} \cdot \underline{r}_{m'} \underline{E} \cdot \sum_m \nabla_m \psi_o \, d\tau, \tag{15}$$

where $d\tau$ is an element of configuration space and we have used $\hat{H} \mid 0\rangle = 0$. Equation (15) can be written as

$$\langle 0|\, h\hat{H}_o h\, |0\rangle = -\frac{e^2\hbar^2}{2m} \underline{E} \cdot \int \sum_m \nabla_m \psi_o^2 \sum_{m'} \underline{E} \cdot \underline{r}_{m'} \, d\tau, \tag{16}$$

and integrated by parts, to give

$$\langle 0|\, h\hat{H}_o h \,|0\rangle = +\frac{e^2\hbar^2}{2m}\, \underline{E}\cdot\underline{E} \sum_m \int \psi_o^2 \, d\tau, \tag{17}$$

where the discarded first integration part vanishes at the limits, if these are infinite, or if they are the boundary of a cell in periodic lattice, provided only that $\underline{E}$ does not vary appreciably within a cell (dipole approximation).

If we are dealing with isolated atoms $\int \psi_o^2 \, d\tau = 1$ and we have

$$\langle 0|\, h\hat{H}_o h \,|0\rangle = +n \frac{e^2\hbar^2}{2m}\, \underline{E}\cdot\underline{E}, \tag{18}$$

a somewhat unfamiliar form of the sum rule. If, on the other hand, we are dealing with overlapping molecules in a periodic lattice, the variational problem is to minimize the contribution to w from a single cell of the lattice. Thus, in (11) and all succeeding equations, the integrals implied by the expectation values are to be taken only over the interior of a cell. This will also apply to all integrals involved in evaluating $w_2 = \langle 1 \mid \hat{h} \mid 0\rangle$ and $w_3 = \langle 1 \mid \hat{h} \mid 1\rangle$. In this case (18) remains unchanged. This can be shown to be a general consequence of time reversal invariance and the commutation rule

$$(p,\, q) = i\hbar. \tag{19}$$

We now have

$$|1\rangle = \lambda\hat{h}\; |0\rangle = +\frac{2m\langle 0|\; \hat{h}^2 \;|0\rangle}{ne^2\hbar^2E^2}\, \hat{h}\; |0\rangle \tag{20}$$

or

$$|1\rangle = +\frac{2me\langle 0|\; (\underline{E}\cdot\hat{\underline{R}})^2 \;|0\rangle}{n\hbar^2E^2}\, \underline{E}\cdot\hat{\underline{R}}\; |0\rangle. \tag{21}$$

From this we obtain the second-order energy

$$w_2 = -\frac{2}{na_o}\, \frac{\langle (E\cdot\hat{R})^2\rangle^2}{E^2}\,, \tag{22}$$

where $a_o = \hbar^2/me^2 = 0.53$ Å. If we let $E = E_x, 0, 0$, and $\underline{R} = X, Y, Z$ this gives

$$w_2 = -\frac{2}{na_o}\, \langle \hat{X}^2\rangle^2 E_x^2 \tag{23}$$

and the atomic polarizability is

$$\alpha = \frac{4}{na_o} \langle \hat{X}^2 \rangle^2. \tag{24}$$

For the H atom, this gives $\alpha = 4a_0^3$ instead of the correct value $4.5a_0^3$, while for the helium atom, taking an effective nuclear charge $Z = 27/16$ gives 1.8×10^{-25} ccs. The experimental value is 2.1×10^{-25} ccs. In general, (24) is a lower limit to α, if we evaluate $\langle \hat{X}^2 \rangle$ correctly as the expectation value of the mean square moment of all the electrons. If the electrons are uncorrelated

$$\langle \hat{X}^2 \rangle = n \langle \hat{x}^2 \rangle, \tag{25}$$

where $\langle \hat{x}^2 \rangle$ refers to one electron. We used this procedure in helium since the two electrons are in orthogonal spin states and are automatically uncorrelated. In more complicated atoms correlation exists and almost always results in

$$\langle \hat{X}^2 \rangle < n \langle \hat{x}^2 \rangle \tag{26}$$

since electrons repel each other. Thus, while (24) is a lower limit we cannot say anything about the sign of the error in

$$\alpha = \frac{4n}{a_o} \langle \hat{x}^2 \rangle^2. \tag{27}$$

We note, in passing, that, in a solid with overlapping molecules, α the polarizability is large. This leads to an element of instability in the situation for as α increases the screening of the coulomb potential becomes more effective and the electrons less localized leading to a further increase in α and eventually metallic behavior. For this reason, most materials, which are not regular insulators, are metals. Those rare materials which have values of $N\alpha$ appreciably greater than 0.3 ($n > 2.2$) owe their existence to a rather delicate balance of forces.

The third-order energy is

$$w_3 = \langle 1 | \, \hat{h} \, | 1 \rangle = -\left(\frac{2m}{n\hbar^2 E^2}\right)^2 \langle (E \cdot \hat{R})^2 \rangle^2 e^3 \langle (E \cdot \hat{R})^3 \ . \tag{28}$$

In most cases α is very nearly isotropic and we have

$$\tfrac{1}{2}\alpha E^2 = -w_2 = \left(\frac{2me^2}{n\hbar^2 E^2}\right) \langle (E \cdot \hat{R})^2 \rangle^2 \tag{29}$$

so that

$$w_3 = -\frac{\alpha}{na_o e} \langle (E \cdot \hat{R})^3 \rangle. \tag{30}$$

With N molecules in unit volume this gives a nonlinear coefficient

$$d_{ijk} = \frac{3N\alpha}{a_o e}\frac{T_{ijk}}{n} = \frac{3\chi}{a_o e}\frac{T_{ijk}}{n}, \tag{31}$$

where

$$T_{ijk} = \langle \hat{R}_i\hat{R}_j\hat{R}_k\rangle = \langle R_iR_jR_k\rangle - \langle R_i\rangle\langle R_jR_k\rangle - \langle R_j\rangle\langle R_kR_i\rangle - \langle R_k\rangle\langle R_iR_j\rangle + 2\langle R_i\rangle\langle R_j\rangle\langle R_k\rangle. \tag{32}$$

Equation (31) is the central result of this section. It expresses d_{ijk} in terms of the linear (corrected for local fields) susceptibility χ and a cubic moment (third-order semi-invariant) of the electronic distribution in the ground state.

If we neglect overlap and, for simplicity, also assume that the electrons are uncorrelated so that $T_{ijk} = nt_{ijk}$ where t_{ijk} refers to a single electron we have

$$d_{ijk} = \frac{3\chi}{a_o e}t_{ijk} \tag{33}$$

and T_{ijk} is now apart from numerical factors the octupole moment of the charge distribution. If the electron density in the molecule is $\rho(\underline{r})$

$$T_{ijk} = \iiint \hat{r}_i\hat{r}_j\hat{r}_k\rho(\underline{r})\, d^3r. \tag{34}$$

If we account for local fields through a Lorentz correction the correct value of χ to insert in (33) is obtained from

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3}\chi \tag{35}$$

and the observed value of d_{ijk} (see Section V) is

$$d_{ijk}^{\mathrm{obs}} = \left(\frac{n^2 + 2}{3}\right)^3 d_{ijk}. \tag{36}$$

At first sight (33) seems to imply that d is proportional to χ in conflict with Miller's rule. However, χ depends on $N/n\langle\hat{R}^2\rangle^2 \approx nN\langle\hat{r}^2\rangle^2$ and N is inversely proportional to $\langle r^2\rangle^{\frac{3}{2}}$ so that $\chi \approx nr$, while $d \approx r^4$. Thus, d is in fact more nearly proportional to χ^4 than χ.

We now consider as an example, the tetrahedral molecule methane CH_4, which crystallizes in the tetrahedral space group $F\bar{4}3m$ with a lattice parameter ≈6 Å and a molar volume of 32 ccs. If we take Cartesian axes along the sides of the cubic cell, the bonds point in the 111, and tetrahedrally related, $1\bar{1}\bar{1}$, $\bar{1}1\bar{1}$, $\bar{1}\bar{1}1$, directions. From symmetry, there is only one independent component of d_{ijk}, in which all the subscripts are unequal.

The shortest c-c distance is 4.2 Å and from the size of the free molecule we conclude that overlap is unimportant.

Turner, Saturno, Hauk and Parr[10] have used one center wave functions to calculate the electronic density ρ in the molecule. From this we can obtain t_{123} using (34).

The result is

$$t_{ijk} = 0.5 \times 10^{-24} \text{ cm}^3 \tag{37}$$

and this is not very sensitive to the limits of integration. The experimental molar susceptibility of CH_4 is 1.6 ccs and so $\chi = 0.05$. Thus, if we neglect correlations between the eight valence electrons we have from (33)

$$d_{123} = 3 \times 10^{-9} \text{ esu.} \tag{38}$$

In a similar way, neglecting correlations, we can calculate the molar susceptibility from (27). Turner *et al*'s charge density leads to

$$\langle x^2 \rangle = 3.3 \times 10^{-17} \text{ cm}^2$$

and so, with eight valence electrons, we obtain $\alpha = 6.5 \times 10^{-24}$ and χ = a molar susceptibility of 3.9 ccs, rather over twice the experimental value.

This is a clear indication that the electrons are correlated. However, the correlation enters twice in χ but only once in d (since we have expressed d in terms of the experimental χ). Thus, d problaby lies between 2×10^{-9} and 3×10^{-9} esu.

To see whether 3×10^{-9} esu is a reasonable value for d_{123} we compute the Miller reduced tensor $d/\chi^3 = \Delta_{123} = 24 \times 10^{-6}$ esu.

This is quite exceptionally high. Most materials have allowed components of Δ near 3×10^{-6} esu and only one coefficient in $LiNbO_3$ (9×10^{-6}) and Δ_{123} in hexamethylene tetramine (15×10^{-6}) approach this value.

However, we believe it is in fact not far wrong. In most materials geometric factors conspire to reduce d by various factors of $\cos \theta$ and the atomic groups are in the first instance less aspherical than CH_4. In CH_4 the effects of every electron are directly additive.

Hexamethylene tetramine (HMT), the other exception to Miller's rule, is, like methane, a tetrahedral molecule $N_4(CH_2)_6$ in a tetrahedral $I\bar{4}3m$ crystal. The 4 nitrogen atoms form the 111 $1\bar{1}\bar{1}$, $\bar{1}1\bar{1}$, $\bar{1}\bar{1}1$, corners of a regular tetrahedron and the CH_2 groups occupy the edges but the N–C–N bonds are bent outwards in such a way that all the angles are very nearly tetrahedral. The carbon atoms occupy the six sites 2, 0, 0 etc. (see Kitaigorodskii[11]).

The refractivity of the molecule as a whole can be very satisfactorily accounted for by a system of additive bond refractions. (See LeFevre[12] for a review of bond refractions.) The three basic units are 12 C–H bonds pointing in the $\bar{1}$, $\bar{1}$, $\bar{1}$, and related directions, 4 nonbonding orbitals on the nitrogen atoms pointing in the 111 and related directions, and 12 N–C bonds in the 111 directions.

Since the refractivities are additive, these units appear to act independently in determining the molar refractivity. Le Fevre (*loc. cit.*) gives values of $R = (4\pi/3)L\alpha$ (where L is Avagadro's number) of 2.8 ccs for each unbonded nitrogen pair, 1.65 ccs for each C–H bond and 0.62 ccs for each N–C bond. Thus, the N–C bonds make a rather small contribution to χ, and probably even less to d since they have an approximate inversion centre at the centre of the bond (C and N are similar atoms as compared with C and H). We therefore neglect them.

The 12 CH bonds in the $\bar{1}\bar{1}\bar{1}$ direction are roughly equivalent to 3 methane molecules in the molecular volume 105 ccs, and further the electrons will be less correlated than in methane. Thus, their contribution to d_{123} is

$$d_{123}^{\mathrm{Me}} = -\tfrac{3}{105}\cdot\tfrac{32}{1}\cdot 3 \times 10^{-9} = -2.7 \times 10^{-9}\ \text{esu}. \tag{39}$$

To calculate the effect of the nonbonding nitrogen electrons we assume that they occupy SP^3 hybrid orbitals directed along 111 etc. with Slater radial wave functions $Ar \exp(-2.5r/2a_o)$. It is then straightforward to show that for *one* electron

$$t_{xyz} = -0.055 \times 10^{-24}\ \text{cm}^3. \tag{40}$$

The contribution of the 4 nitrogen atoms to χ is

$$\chi^N = \frac{3}{4\pi}\cdot\frac{4 \times 2.8}{105} = 0.0255$$

and so

$$d_{123}^{N} = -1.7 \times 10^{-9}\ \text{esu}. \tag{41}$$

Thus, the total value of d_{123} is -4.5×10^{-9} esu. This could be slightly increased by the effects of atomic overlap, and possibly by contributions from the N–C bonds. It could be either increased or decreased by electron correlations on individual CH_2 groups. The experimental values for the electro-optic effect Heilmeyer[13] and second harmonic generation, Heilmeyer, Ockman, Braunstein, and Kramer,[14] when corrected for local field effects using a Lorentz factor, both give $d = \pm 8.2 \times 10^{-9}$ esu. Thus, our calculation is within a factor 2 of the observed value.

This method is therefore capable, in simple cases, of predicting the magnitude of d rather successfully. Moreover, the experimental value of d for HMT suggests that we were correct in assuming that CH_4 will have an anomalously large reduced tensor Δ_{123} .

The fact that the division of a complex molecule such as HMT into simple components leads to a reasonable value for d leads us to hope that a similar procedure will be possible in other cases. It might then be possible to assign empirical values of d to basic components such as the C–H bond or the N: nonbonding pair, and to combine these additively (with a proper attention to geometry) to predict the values of d for even more complex molecules. This would not be surprising since a similar procedure (see LeFevre *loc. cit.*) works very satisfactorily for the linear susceptibilities.

It is then obvious that large nonlinear effects will only result, if the molecule contains polarizable groups disposed in an arrangement which results in a ground state of, far from inversion, symmetry. The large value of Δ in HMT results from the fortunate coincidence that the most polarizable components are themselves strongly asymmetric and so oriented that their effects are additive. The much smaller values of Δ commonly observed can then be explained as partly due to no group in the crystal being quite so asymmetric as N: or CH_2 in HMT and partly due to unfavorable geometric relations between the groups. For example, if our approach is correct we should expect the analogous compound adamantane $(CH)_4(CH_2)_6$ in which the nitrogens are replaced by CH groups with the CH bond along 111, etc. to have a d_{123} appropriate to 2 (=3 − 1) CH_4 molecules in 105 ccs, i.e., $d_{123} \approx 2 \times 10^{-9}$ esu or about half the value for HMT.

Exceptionally small values of Δ will occur in materials where most of the molecule possesses local inversion symmetry, so that only a fraction of the molecule contributes to d, while the whole molecule contributes to χ. We shall consider an example of this in a later section.

Overlap between adjacent molecules is neccessarily bound to lend further uncertainty to the calculation in materials with a pronounced band structure, but it seems possible that rough approximations should be obtainable from, for example, the relation between bandgap and the corresponding separation in the isolated atoms. In fact, since what we actually require is T_{ijk}/n, which, if the electrons are uncorrelated, is simply

$$\frac{T_{ijk}}{n} = \frac{\int^{\text{Cell}} \hat{r}_i\hat{r}_j\hat{r}_k\rho(\underset{\sim}{r})\, d^3r}{\int^{\text{Cell}} \rho(\underset{\sim}{r})\, d^3r} \tag{42}$$

we may expect that this factor will, to some extent, be self-cancelling.

Finally, we may remark that very much better approximations to d_{ijk} can obviously be made if we know the ground state wave function explicitly and also use more sophisticated trial wave functions in the variational calculation. It is at first sight surprising that a knowledge of the ground state wave function alone is sufficient to determine χ and d which, in the more usual treatments involve the properties of excited states. However, we should remember that a knowledge of the exact ground state wave function is, except in pathological circumstances, sufficient to determine the unperturbed Hamiltonian; thus, the whole spectrum of states.

III. THE CLASSICAL ANHARMONIC OSCILLATOR MODEL

Although the considerations of the preceding section are sufficient to determine the magnitude of d at low frequencies, they offer little guide to the variation of d with frequency and, if recast in terms of time dependent perturbation theory they tend to lose their attractive simplicity. In the next section we shall show that a more familiar form of time dependent theory leads to results which can be represented in terms of a classical anharmonic oscillator model. Here, we discuss the properties of the model itself.

We assume that unit volume of the material contains N optical electrons which move in a potential

$$V = \tfrac{1}{2}m\Omega_i^2x_i^2 + V_{ijk}x_ix_jx_k\ , \tag{43}$$

where a sum over repeated subscripts is implied. The potential V_{ijk} obviously satisfies $V_{ijk} = V_{ikj}$, etc.

In a field $E_i^\beta e^{i\beta t}$ the equation of motion is

$$\ddot{x}_i + \Omega_i^2x_i + 3\,\frac{V_{ijk}}{m}\,x_jx_k = \frac{e}{m}\,E_i^\beta e^{i\beta t} \tag{44}$$

and the linear response obtained by neglecting V_{ijk} is

$$x_i^{(1)} = \frac{\frac{e}{m}\,E_i^\beta e^{i\beta t}}{\Omega_i^2 - \beta^2}. \tag{45}$$

There will be a similar response to a field $E_i^\gamma e^{i\gamma t}$ and, if we introduce these responses back into the nonlinear term in (44) we obtain a response at the sum frequency $\alpha = \beta + \gamma$ given by

$$x_i^{(2)} = -\frac{3V_{ijk}e^2}{m^3}\frac{1}{\Omega_i^2 - \alpha^2}\frac{1}{\Omega_j^2 - \beta^2}\frac{1}{\Omega_k^2 - \gamma^2}(E_j^\beta E_k^\gamma + E_k^\gamma E_j^\beta)e^{i\alpha t}. \quad (46)$$

The resulting polarization is $Nex_i^{(2)}$ and so the nonlinear coefficient is

$$d_{ijk}^{\alpha\beta\gamma} = -\frac{3V_{ijk}Ne^3}{m^3}\frac{1}{\Omega_i^2 - \alpha^2}\frac{1}{\Omega_j^2 - \beta^2}\frac{1}{\Omega_k^2 - \gamma^2}. \quad (47)$$

Thus, the symmetry of d_{ijk} mimics that of V_{ijk} if we neglect the resonance denominators.

The linear susceptibility obtained from (45) is the familiar expression

$$\chi_{ii}^\omega = \frac{Ne^2}{m}\frac{1}{\Omega_i^2 - \omega^2} \quad (48)$$

and so if we express $d_{ijk}^{\alpha\beta\gamma}$ as

$$d_{ijk}^{\alpha\beta\gamma} = \chi_{ii}^\alpha \chi_{jj}^\beta \chi_{kk}^\gamma \Delta_{ijk} \quad (49)$$

the reduced Miller tensor is

$$\Delta_{ijk} = -\frac{3V_{ijk}}{N^2e^3}, \quad (50)$$

which is frequency independent and has the same symmetry as V_{ijk}.

If we assume that V_{ijk} is electrostatic in origin its order of magnitude will be e^2/d^4 where d is an atomic spacing and we shall also have $Nd^3 \approx 1$. Thus,

$$|\Delta_{ijk}| \approx 3\frac{d^2}{e}. \quad (51)$$

With d equal to 2 Å this is 2.5×10^{-6} esu, about the mean value of Δ for most materials. In a later section, we shall give another estimate of Δ.

The potential $V_{ijk}x_ix_jx_k$ distorts the shape of the ground state of the harmonic oscillator and as a result the system acquires a cubic moment t_{ijk} [defined in (32)] which we now calculate.

Let $|\,0\rangle$ represent the unperturbed ground state wave function in the absence of the anharmonic term and $|\,p\rangle$ be an excited state, then the perturbed wave function is

$$|\ \rangle = |0\rangle - \sum_p{}' \frac{\langle p|\ V\ |0\rangle}{\hbar\omega_p}|p\rangle. \quad (52)$$

The expectation values of even operators such as $\langle x_i^2\rangle$, $\langle x_i x_j\rangle$ are unaltered by V, while the expectation value of an odd operator such as x_i or $x_i x_j x_k$ is given by

$$\langle x_i x_j x_k\rangle = -2 \sum_p{}' \frac{\langle 0|\, x_i x_j x_k \,|p\rangle\langle p|\, V \,|0\rangle}{\hbar\omega_p}. \tag{53}$$

It will suffice if we calculate t_{ijk} with $i \neq j \neq k$. Since $\langle x_i x_j\rangle = 0$ if $i \neq j$ we only require $\langle x_i x_j x_k\rangle$ and contributions to this come only from the $6 = 3!$ terms in V with $i \neq j \neq k$. The only state which contributes to the sum is $|\, p\rangle = |\, 1, 1, 1\rangle$ with an energy $\hbar(\Omega_1 + \Omega_2 + \Omega_3)$. The matrix element is

$$\langle 0|\, x_1 x_2 x_3 \,|111\rangle = \left(\frac{\hbar}{2m}\right)^{\frac{3}{2}}\left(\frac{1}{\Omega_1\Omega_2\Omega_3}\right)^{\frac{1}{2}}$$

and so

$$t_{123} = \langle x_1 x_2 x_3\rangle = -12\left(\frac{\hbar}{2m}\right)^3 \frac{V_{123}}{\hbar\Omega_1\Omega_2\Omega_3(\Omega_1 + \Omega_2 + \Omega_3)}.$$

It is straightforward to show that a similar result

$$t_{ijk} = -\frac{3}{2}\left(\frac{\hbar}{m}\right)^3 \frac{V_{ijk}}{\hbar\Omega_i\Omega_j\Omega_k(\Omega_i + \Omega_j + \Omega_k)} \tag{54}$$

holds for all the components of t_{ijk}.

If we substitute this relation in (47) and take the limit as $\alpha\beta\gamma \to 0$ we obtain

$$d_{ijk} = 2\,\frac{3\chi}{a_o e}\, t_{ijk}\,. \tag{55}$$

This is twice the value obtained in (33) because there we treated t_{ijk} as a fixed property of the ground state which was then perturbed by E; whereas here we have considered an even ground state perturbed by E and a fixed potential.

Thus, if the real system has a cubic moment t_{ijk} in the ground state, the equivalent anharmonic oscillator model requires an anharmonic potential

$$V'_{ijk} = -\frac{m^3\Omega^4}{\hbar^2}\, t_{ijk} \tag{56}$$

and this will result in a cubic moment $t'_{ijk} = \frac{1}{2}t_{ijk}$ in the oscillator ground state.

In the real crystal t_{ijk} may be an accessible quantity. It obviously is in molecular crystals of strongly covalent compounds such as CH_4. But, in ionic crystals it may be more sensible to consider the ions as spheres perturbed by a crystal potential V^c_{ijk}. In a later section we shall see that there is a simple relation between the model potential and V^c_{ijk}.

The classical anharmonic oscillator model has previously been used by Bloembergen,[15] Garrett and Robinson[16] and Kurtz[17] to give a qualitative account of nonlinear phenomena. The latter authors also discuss in some detail its relation to Miller's rule.

Obviously, the model is the nonlinear analogue of the classical harmonic oscillator model used with such success for the last 60 years in the discussion of linear behavior such as dispersion, and, just as the harmonic model is directly related to the results of a quantum mechanical treatment, we may expect the anharmonic oscillator to have a similar basis. In the next section we explore this relation.

IV. TIME DEPENDENT QUANTAL TREATMENT

A number of authors Bloembergen,[15] Armstrong, Bloembergen, Ducuing and Pershan,[18] Butcher and McLean,[19] Kelley,[20] Cheng and Miller[21] and Ward[22] have given rigorous quantal treatments of optical nonlinearities in solids. We select an expression due to Armstrong, et al (*loc. cit.*) which expresses the nonlinear coefficients in terms of the energies $\hbar\omega_p$ of excited states and the matrix elements $\langle 0 \mid x_i \mid p\rangle$, $\langle p \mid x_i \mid q\rangle$, etc. of the dipole operator between states. The ground state is $\langle 0 \mid$.

This expression is valid, either for an assembly of N isolated atoms in unit volume or, in the dipole approximation, for a real solid where the wave functions overlap. In the latter case, the solid must be divided into cells of the periodic lattice, and N is then the density of cells, while the matrix elements are to be evaluated only over the interior of a cell. The periodicity of the lattice ensures that contributions from parts of the wave function outside a cell cancel in the crystal as a whole.

To avoid a plethora of subscripts we let each of x, y, and z serve to represent any one of the components and we can then write the expression for d as

$$d^{\alpha\beta\gamma}_{xyz} = \frac{Ne^3}{\hbar^2} \sum_p \sum_q \left\{ x_{op} y_{pq} z_{qo} \frac{\omega_p \omega_q + \alpha\gamma}{(\omega_p^2 - \alpha^2)(\omega_q^2 - \gamma^2)} \right.$$

$$\left. + \, y_{op} z_{pq} x_{qo} \frac{\omega_p \omega_q + \beta\alpha}{(\omega_p^2 - \beta^2)(\omega_q^2 - \alpha^2)} + z_{op} x_{pq} y_{qo} \frac{\omega_p \omega_q - \gamma\beta}{(\omega_p^2 - \gamma^2)(\omega_q^2 - \beta^2)} \right\}. \tag{57}$$

This expression vanishes if the states $| 0\rangle$, $| p\rangle$, etc. have a definite parity, its value therefore depends on the existence of matrix elements whose presence is contingent on the absence of inversion symmetry. For this reason, it is almost impossible to make an informed guess about its magnitude or behavior.

An analogous expression for the linear susceptibility is

$$\chi^{\omega}_{xy} = \frac{2Ne^2}{\hbar} \sum_p \frac{\omega_p x_{op} y_{po}}{\omega_p^2 - \omega^2} \tag{58}$$

and in both expressions an operator x is to be understood as the total operator for the contents of a cell, i.e., the sum of the individual electron operators. Of course, we can neglect the core (nonvalence) electrons on the grounds that they are too tightly bound to contribute to the optical properties.

A familiar approximation to χ is obtained if we note that in (58) the variation of the summand with $| p\rangle$ is almost exclusively due to the matrix elements. These not only obey selection rules, but also decrease rapidly in magnitude as the state $| p\rangle$ increases in energy, and therefore overlaps the ground state less and less. For example, in the H atom with a $1S$ ground state the matrix element x_{op} vanishes unless p is one of the states $2P$, $3P$, etc. Moreover, as we go from the $2P$ state to the $8P$ state $x_{op}x_{po}$ decreases by over a hundredfold. At the same time, ω_p changes by less than 30 percent. Thus, except near a resonance, we can treat ω_p as a constant Ω, somewhere near the first allowed transition and write (3.2) as

$$X^{\omega}_{xy} = \frac{2Ne^2\Omega}{\hbar(\Omega^2 - \omega^2)} \sum_p{}' x_{op} y_{po} \tag{59}$$

where the primed sum excludes $p = 0$. Now

$$\begin{aligned} \sum{}' x_{op} y_{po} &\equiv \sum x_{op} y_{po} - x_{oo} y_{oo} \equiv (xy)_{oo} - x_{oo} y_{oo} \\ &\equiv \langle (x - \langle x\rangle)(y - \langle y\rangle)\rangle \end{aligned} \tag{60}$$

where a $\langle\ \rangle$ denotes a ground state expectation value. Thus,

$$\chi^{\omega}_{xy} = \frac{2Ne^2\Omega}{\hbar(\Omega^2 - \omega^2)} \langle (x - \langle x\rangle)(y - \langle y\rangle)\rangle. \tag{61}$$

We shall not pursue the further manipulations of (61) using the sum rule which lead back to (27) but we remark that in many cases a form such as (61) for χ, involving a single Sellmeier or classical oscillator term, gives an excellent account of optical dispersion, and that when applied to the hydrogen atom, with $\hbar\Omega$ set equal to $\frac{3}{8}e^2/a_o$ the $1S - 2P$ energy, it leads to a value of χ at low frequencies

$$\chi = \tfrac{16}{3}a_o^3$$

which exceeds the correct value 4.5 a_0^3 by 32/27 or 18 percent.

Before we can adopt a similar procedure with the nonlinear coefficient we must first satisfy ourselves that there is no essential difference between a sum with three matrix elements and one with two. In χ all matrix elements terminate on $|\,0\rangle$ but in d it is quite possible in a term such as $x_{op}y_{pq}z_{qo}$, with $p \approx q$ corresponding to highly excited states, of great spatial extent, that the term y_{pq} may be large enough to compensate for the smallness of $x_{op}z_{qo}$. If this were the case it would be possible for the exact value of the sum to depend critically on cancellations between large terms involving highly excited states. The removal of the frequencies ω_p, etc. as a single average would then have disastrous results on the sum.

We will advance three arguments why this is unlikely. Consider first an even higher-order calculation, that of the fourth-order Stark shift of the ground state of atomic hydrogen due to a field F. In atomic units this is given by an exact calculation (Dalgarno[23]) as

$$W^{(4)} = -\tfrac{3555}{64}F^4 \approx -56F^4. \tag{62}$$

We can also express $W^{(4)}$ (Dalgarno, *loc. cit.*) as

$$W^{(4)} = -\sum_p{}' \sum_q{}' \sum_r{}' \frac{x_{op}\hat{x}_{pq}\hat{x}_{qr}x_{ro}}{\omega_p\omega_q\omega_r} + \sum_p{}' \frac{x_{op}x_{po}}{\omega_p} \sum{}' \frac{x_{op}x_{po}}{\omega_p^2}.$$

Our procedure treats $\omega_p\omega_q$ and ω_r as a single constant Ω and leads to

$$W^{(4)} = -\frac{F^4}{\Omega^3}\{\langle(x - \langle x\rangle)^4\rangle - 2\langle(x - \langle x\rangle)^2\rangle^2\}. \tag{63}$$

For the H atom $\langle x\rangle = 0$, $\langle x^2\rangle = 1$ a.u. and $\langle x^4\rangle = 9/2$ a.u. so that, if we set $\Omega = 3/8$ a.u., the $1S - 2P$ energy difference

$$W^{(4)} = -\tfrac{1280}{27}F^4 \approx -48F^4. \tag{64}$$

This is close to the correct result (36), but despite the fact that we have taken the lowest possible value of Ω it is too small. This is a clear indication that some cancellation of higher terms, which we have aggravated by our cavalier treatment of ω_p, etc., is occurring. This is not surprising for, if in the triple sum we consider the lowest possible sequence of levels $1S$ $2P$ $2S$ $2P$ $1S$ for which $\omega_p = \omega_q = \omega_r = \Omega$ the product of the matrix elements is 5 a.u. while for the sequence $1S$ $8P$ $8S$ $8P$ $1S$ the product is 10 a.u. made up of a contribution of 0.0033 from the two $1S$ $8P$ elements and 3000 from the $8S$ $8P$ elements.

However, this is not quite so serious as it appears, for in a real solid no matrix element can exceed the linear dimensions of a cell say 5 a.u. so that the product in the low transition would remain at 5 a.u. while the product for the upper transition would be reduced to 0.08.

Our final argument is empirical. If cancellations between large terms are critically important, the relevant feature of our procedure is the change in the ratio ω_p/ω_q it causes for highly excited neighboring states. In hydrogen the ratio of the $1S - 8P$ energy to the $1S - 7P$ energy is 1.005 and we replace this by unity. In a time dependent theory resonance denominators appear, and if the sum is really so critically balanced, we expect the observed quantity, in this case the hyperpolarizability, to vary rapidly with frequency when $\omega^2 \approx 0.005\ \Omega^2$, i.e., at a frequency 10 times lower than the first absorption edge. In nonlinear optics, no such variation is observed until one of the frequencies approaches much more closely (about 70 percent) to the absorption edge (Chang, Ducuing, and Bloembergen[24]).

Taken together these arguments give us reasonable grounds for hoping that the sums will not bite us if we remove ω_p, etc. from under the summation sign.

In the sum in (57) there is no restriction on p or q, in particular terms with either $p = 0$ or $q = 0$ occur. These will lead to trouble if we attempt to approximate the sums as they stand. We therefore first segregate all such terms. Let $\{\ \}$ denote the entire summand in (57), then

$$\begin{aligned}\sum_p \sum_q \{\ \} = \sum_p{}' \sum_q{}' \{\ \} &- x_{oo}\frac{\gamma}{\alpha}\sum_r \frac{y_{or}z_{ro}}{\omega_r^2-\gamma^2} - z_{oo}\frac{\alpha}{\gamma}\sum_r{}' \frac{x_{or}y_{ro}}{\omega_r^2-\alpha^2} \\ &- y_{oo}\frac{\alpha}{\beta}\sum_r \frac{z_{or}x_{ro}}{\omega_r^2-\alpha^2} - x_{oo}\frac{\beta}{\alpha}\sum_r{}' \frac{y_{or}z_{ro}}{\omega_r^2-\beta^2} \\ &+ z_{oo}\frac{\beta}{\gamma}\sum_r \frac{x_{or}y_{ro}}{\omega_r^2-\beta^2} + y_{oo}\frac{\gamma}{\beta}\sum_r{}' \frac{z_{or}x_{ro}}{\omega_r^2-\gamma^2}. \qquad (65)\end{aligned}$$

Three single sums remain unprimed, but because $\alpha = \beta + \gamma$ the terms with $r = 0$ cancel and so we may regard all the sums as primed.

We can now remove ω_p, ω_q and ω_r as a single average Ω, and this leads to an expression containing terms such as

$$\begin{aligned}\sum_p{}' \sum_q{}' x_{op}y_{pq}z_{qo} = \sum_p \sum_q x_{op}y_{pq}z_{qo} &- x_{oo}\sum_r y_{or}z_{ro} \\ &- z_{oo}\sum_r x_{or}y_{ro} + 2x_{oo}y_{oo}z_{oo}\ .\end{aligned}$$

Each of the sums on the right is now a ground state expectation value. When all the terms are collected together we obtain

$$d_{xyz}^{\alpha\beta\gamma} = \frac{Ne^3}{\hbar^2} \frac{\Omega^2(3\Omega^2 + \beta\gamma - \alpha^2)}{(\Omega^2 - \alpha^2)(\Omega^2 - \beta^2)(\Omega^2 - \gamma^2)} \{\langle xyz\rangle - \langle x\rangle\langle yz\rangle - \langle y\rangle\langle zx\rangle - \langle z\rangle\langle xy\rangle + 2\langle x\rangle\langle y\rangle\langle z\rangle\} \qquad (66)$$

which we can also write as

$$d_{xyz}^{\alpha\beta\gamma} = \frac{Ne^3}{\hbar^2} D(\Omega, \alpha, \beta, \gamma) T_{xyz} \qquad (67)$$

in terms of the, by now, familiar cubic moment T_{xyz}. This expression bears an obvious resemblance to (61) for χ.

Our expression (66) or (67) would be very nearly exact if all the optical levels had very nearly the same energy. It would then correspond to the fictitious two level system (see Refs. 15, 16, 18) often used to obliterate some of the intractable features of (57). Unlike this model, however, our expression retains the geometry of the system implicit in the selection and sum rules.

Equation (66) is possibly valid up to a frequency where one of α, β, or γ approaches the first allowed transition frequency. At somewhat lower frequencies, it is legitimate to drop the term $\beta\gamma - \alpha^2$ in the numerator. This then allows us to make a further generalization at no increase in complexity.

By removing ω_p and ω_q from (57) as a single average we have tacitly neglected the possibility that the system might be birefringent. We can remedy this by noting that in (57) each frequency ω_p or ω_q is uniquely associated with a matrix element such as x_{op} or z_{qo} which terminates on the ground state $|\ 0\rangle$ and therefore also appears in χ. Thus, we can consistently introduce three averages Ω_x, Ω_y, and Ω_z associated with correspondingly polarized transitions. If we follow this process through all its tedious ramifications, we find that, except in the term $\beta\gamma - \alpha^2$ which we are omitting, it leads to the surprisingly simple result that $D(\Omega,\alpha,\beta,\gamma)$ is replaced by

$$D(\underline{\Omega}, \alpha, \beta, \gamma) = \frac{\Omega_x\Omega_y\Omega_z(\Omega_x + \Omega_y + \Omega_z)}{(\Omega_x^2 - \alpha^2)(\Omega_y^2 - \beta^2)(\Omega_z^2 - \gamma^2)}. \qquad (68)$$

Thus,

$$d_{xyz}^{\alpha\beta\gamma} = \frac{Ne^3}{\hbar^2} \frac{\Omega_x\Omega_y\Omega_z(\Omega_x + \Omega_y + \Omega_z)}{(\Omega_x^2 - \alpha^2)(\Omega_y^2 - \beta^2)(\Omega_z^2 - \gamma^2)} T_{xyz}\ . \qquad (69)$$

If we compare this with the result for the classical anharmonic oscillator obtained by combining (54) with (47) we see that they are identical except for a factor 2 which once again arises because in one case we assumed that T_{xyz} was a fixed parameter while in the other it was V_{xyz}.

We now see that the classical model is equivalent to the quantal treatment, except near a resonance, in the following sense.

If we construct the model, by choosing Ω_x, Ω_y, and Ω_z to give the correct linear properties then we must choose the anharmonic term in the potential to produce a cubic moment in the ground state of the model equal to $\frac{1}{2}$ the corresponding moment in the real system. The dynamical properties of the two systems are then equivalent and the model can be used to treat more complicated systems where the quantal treatment is too difficult.

We now consider the relation of V'_{xyz} to the actual potential responsible for the existence of T_{xyz}. Obviously, the relation is obtained by requiring that both potentials yield the same cubic moment, one in the model, the other in the real system. In this case, there will be no factor of 2.

For simplicity, we consider only a system which is isotropic before the application of the anharmonic potential. Further, we restrict ourselves to atoms in which there is only one valence electron. Our results will, however, be directly applicable to atoms with more electrons if we can neglect electron correlations.

We already have an expression for the oscillator (54) which we can write as

$$T_{ijk} = -4a^6 \frac{V'_{ijk}}{\hbar\omega_o}, \tag{70}$$

where ω_o, the classical frequency, also corresponds to the first allowed transition, and

$$a = \left(\frac{\hbar}{2m\omega_o}\right)^{\frac{1}{2}} \tag{71}$$

is a measure of the extent of the system in one dimension. The direct proportionality between T_{ijk} and the corresponding component of V_{ijk} occurs because the oscillator Schrödinger equation separates in Cartesian coordinates. In general, as we shall show, it will only hold if $V = V_{ijk}x_ix_jx_k$, the crystal potential, satisfies Laplace's equation.

We will consider a more general potential of the form

$$V = \sum_{nlm} V_{nl}^{m} r^n P_l^m(\theta, \varphi), \tag{72}$$

where P_l^m is an associated Legendre polynomial normalized to unity. This potential satisfies Laplace's equation only if $n \equiv l$.

If the unperturbed ground state wave function is ψ_0 the first-order correction ψ_1 due to V satisfies

$$(H_o - E_o)\psi_1 + (V - E_1)\psi_0 = 0.$$

Since T is an odd moment we need only consider odd terms in V (in fact only $l = 1$ and $l = 3$) and for these E_1 vanishes since ψ_0 has definite parity.

We let

$$\psi_1 = f\psi_0 \tag{73}$$

and then

$$(H_0 - E_0)f\psi_0 = -V\psi_0$$

but, since

$$H_o = -\frac{\hbar^2}{2m}\nabla^2 + V_o ,$$

this leads to

$$\nabla^2 f + 2\nabla f \cdot \nabla \log \psi_0 = \frac{2m}{\hbar^2} V. \tag{74}$$

Now ψ_0 is a function of r alone and so we can write

$$f = \sum_{nlm} V_{nl}^m \alpha_{nl}(r) P_l^m(\theta, \varphi), \tag{75}$$

where $\alpha_{nl}(r)$, which does not depend on m, satisfies

$$\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial \alpha}{\partial r} - \frac{l(l+1)}{r^2}\alpha + 2\frac{\partial \alpha}{\partial r}\frac{\partial \log \psi_0}{\partial r} = \frac{2m}{\hbar^2} r^n. \tag{76}$$

The perturbed ground state is therefore,

$$\psi = \{1 + \sum_{nlm} V_{nl}^m \alpha_{nl}(r) P_l^m(\theta, \varphi)\} \psi_0(r) \tag{77}$$

and in this new ground state we can easily evaluate expectation values such as

$$\langle r^\nu P_\lambda^{-\mu} \rangle = \sum_n V_{n\lambda}^\mu \beta_{\nu n\lambda} , \tag{78}$$

where

$$\beta_{\nu n\lambda} = \int_0^\infty r^\nu \alpha_{n\lambda}(r) \psi_0^2(r) r^2 \, dr. \tag{79}$$

In evaluating T_{ijk} we shall need $\langle x_i \rangle$, $\langle x_i^2 \rangle$, and $\langle x_i x_j x_k \rangle$. The even moments are unchanged by V and we obtain the odd moments by expanding x_i and $x_i x_j x_k$ in terms of Legendre polynomials and powers of r.

We omit most of the gruesome details of the calculation, and further restrict V to contain only terms of the type

$$V = V_{ijk} x_i x_j x_k + X_i x_i = \sum_m V_{33}^m r^3 P_3^m + V_{31}^m r^3 P_1^m + V_{11}^m r P_1^m . \tag{80}$$

The term in V_{31}^m which does not satisfy Laplace's equation is necessary to obtain the most general form of the cubic part of the potential $V_{ijk} x_i x_j x_k$. This contains 10 independent parameters while P_3^m has only 7. The missing 3 are supplied by P_1^m.

If this term is absent, we have

$$\nabla^2 V = 0 \tag{81}$$

and then

$$S_i \equiv V_{iii} + V_{ijj} + V_{ikk} = 0. \tag{82}$$

With all the terms present we obtain

$$\langle x_i \rangle = \tfrac{2}{5} \beta_{131} S_i + \tfrac{2}{3} \beta_{111} X_i \tag{83}$$

$$\langle x_i^3 \rangle = \tfrac{4}{35} \beta_{333} V_{iii} + 3 \{ \tfrac{2}{25} \beta_{331} - \tfrac{4}{175} \beta_{333} \} S_i + \tfrac{2}{5} \beta_{311} X_i \tag{84}$$

$$\langle x_i x_j^2 \rangle = \tfrac{4}{35} \beta_{333} V_{ijj} + \{ \tfrac{2}{25} \beta_{331} - \tfrac{4}{175} \beta_{333} \} S_i + \tfrac{2}{15} \beta_{311} X_i \tag{85}$$

$$\langle x_i x_j x_k \rangle = \tfrac{4}{35} \beta_{ijk} V_{ijk} , \tag{86}$$

where it is to be understood that $i \neq j \neq k$.

If we let

$$\gamma = \langle x_i^2 \rangle, \tag{87}$$

then since $\langle x_i x_j \rangle = 0$, $i \neq j$, and $\langle x_i \rangle \langle x_j \rangle \langle x_k \rangle$ is third order in V, we obtain

$$T_{iii} = \tfrac{4}{35} \beta_{333} V_{iii} + 3 \{ \tfrac{3}{25} \beta_{331} - \tfrac{4}{175} \beta_{333} - \tfrac{2}{5} \gamma \beta_{131} \} S_i + 3 \{ \tfrac{2}{15} \beta_{311} - \tfrac{2}{3} \gamma \beta_{111} \} X_i \tag{88}$$

$$T_{ijj} = \tfrac{4}{35} \beta_{333} V_{ijj} + \{ \tfrac{2}{25} \beta_{331} - \tfrac{4}{175} \beta_{333} - \tfrac{2}{5} \gamma \beta_{131} \} S_i + \{ \tfrac{2}{15} \beta_{311} - \tfrac{2}{3} \gamma \beta_{111} \} X_i \tag{89}$$

$$T_{ijk} = \tfrac{4}{35} \beta_{333} V_{ijk} . \tag{90}$$

For a harmonic oscillator

$$\left.\begin{array}{lll} \beta_{333} = -35\,\dfrac{a^6}{\hbar\omega_o}, & \beta_{331} = -85\,\dfrac{a^6}{\hbar\omega_o}, & \beta_{311} = -15\,\dfrac{a^4}{\hbar\omega_o} \\ \beta_{133} = -5\,\dfrac{a^4}{\hbar\omega_o}, & \beta_{131} = -15\,\dfrac{a^4}{\hbar\omega_o}, & \beta_{111} = -3\,\dfrac{a^2}{\hbar\omega_o} \\ & \gamma = a^2 & \end{array}\right\} \tag{91}$$

and it is easy to check that the coefficients of S_i and X_i vanish, so that we recover (70).

If V satisfies Laplace's equation $S_i = 0$ and in the absence of an internal field X_i every component is given by

$$T_{ijk} = \tfrac{4}{35}\beta_{333} V_{ijk} . \tag{92}$$

Thus, in this case T_{ijk} and the reduced Miller tensor Δ_{ijk} have the same symmetry as V_{ijk}. Therefore, since $S_i = 0$ we have

$$\Delta_{iii} + \Delta_{ijj} + \Delta_{ikk} = 0. \tag{93}$$

If i is an axis of 3-fold or higher symmetry, $\Delta_{ijj} = \Delta_{ikk}$ and so, for example,

$$\Delta_{333} = -2\Delta_{311} . \tag{94}$$

This relation is rather well obeyed by the coefficients for the 6-mm crystals listed in the Table I. Signs are available only for the electro-optic

TABLE I

Material	Wavelength μ	$\Delta_{333} \times 10^6$ esu	$\Delta_{311} \times 10^6$ esu	Ratio
		Linear Electro-optic		
ZnO	optical	1.5	−0.8	−2.1
ZnS	optical	0.9	−0.45	−2.0
CdS	optical	1.2	−0.55	−2.2
		Second Harmonic		
ZnO	1.06	3.3	1.1	±3.0
ZnS	10.6	4.9	2.45	±2.0
CdS	1.06	3.2	1.6	±2.0
CdS	10.6	5.4	3.3	±1.6
CdSe	10.6	4.8	2.4	±2.0

coefficients and so the s.h.g. results represent moduli only. References to the experimental data are given in conjunction with later tables. In the case of the electro-optic data, the experimental figure is for Δ_{113} and we have assumed that Kleinman's rule (Kleinman[2]) holds and that this is equal to Δ_{311}. Except for s.h.g. in ZnO the ratio is -2 within the experimental error.

If, on the other hand, the sole perturbation in V is the field X_i, we have

$$T_{iii} = 3T_{ijj} = \tfrac{2}{5}\{\beta_{311} - 5\gamma\beta_{111}\} \tag{95}$$

and the expected ratio is $+3$. In crystals where both terms occur in V with arbitrary strength, any value of the ratio is possible. This is observed in the ferro-electric crystals $BaTiO_3$ ratio $+\frac{1}{2}$ and $LiNbO_3$ where it is $+1.7$ for the electro-optic effect and ± 11 for s.h.g. It is perhaps somewhat surprising that the ratio is so exactly -2 in the 6-mm crystals since this is a polar point group and an internal field X_3 is not forbidden by symmetry.

If V does not satisfy Laplace's equation, (it need only satisfy Poisson's equation) there is no direct relation between the components of T_{ijk} and those of V_{ijk} even in the absence of a field X_i, although, since xyz is a spherical harmonic, we still have

$$T_{123} = \tfrac{4}{35}\beta_{333} V_{123}\,. \tag{96}$$

However, since the coefficients of S_i vanish for the harmonic oscillator we may expect them to be small in other cases. We gain some support for this view by considering the hydrogen atom for which

$$\left.\begin{aligned} \beta_{333} &= -\left(\frac{105}{8}\right)^2 \frac{a_o^6}{\hbar\omega_1}\,, \quad & \beta_{331} &= -\frac{35385}{256}\frac{a_o^6}{\hbar\omega_1}\,, \quad & \beta_{311} &= -\frac{1485}{64}\frac{a_o^4}{\hbar\omega_1} \\ \beta_{133} &= -\frac{1305}{128}\frac{a_o^4}{\hbar\omega_1}\,, \quad & \beta_{131} &= -\frac{315}{16}\frac{a_o^4}{\hbar\omega_1}\,, \quad & \beta_{111} &= -\frac{81}{32}\frac{a_o^2}{\hbar\omega_1} \\ & & \gamma &= a_o^2 & & \end{aligned}\right\}, \tag{97}$$

where as usual $a_o = \hbar^2/me^2$ and $\hbar\omega_1 = 3/8(e^2/a_o)$ is the first allowed transition $(1S - 2P)$ energy.

The coefficient of V_{ijk} in each term of T_{ijk} is then $-315/16(a_o^6/\hbar\omega_1)$ while the coefficient of S_i in T_{iii} is a factor 23/200 smaller. In T_{ijj} it is 23/600 smaller. Thus, in the absence of X_i the non-Laplacean terms in V cause no more than an 11 percent departure from the relation

$$T_{ijk} = -\frac{315}{16}\frac{a_o^6}{\hbar\omega_1} V_{ijk}\,. \tag{98}$$

Since we expect the dominant terms in V to satisfy Laplace's equation it appears that T_{ijk}, Δ_{ijk} and the model potential V'_{ijk} will be very nearly proportional to the corresponding terms in V.

The potential V' required in the model is related to the crystal potential by

$$\beta_{333}^{\text{osc}} V'_{ijk} = \beta_{333} V_{ijk} . \tag{99}$$

For a hydrogen atom this gives $V'_{ijk} \approx 5V_{ijk}$ thus, insofar as real atoms behave like hydrogen atoms, a model with the same spatial extent $a \approx a_o$ and the same first allowed transition $\omega_0 \approx \omega_1$ will require a potential roughly five times as strong as the actual potential. This reflects the obvious fact that a harmonic oscillator is a stiffer system with more sharply localized ($\psi \approx e^{-r^2}$) wave functions than an atom ($\psi \approx e^{-r}$).

We have now shown that, with an appropriate choice of parameters a classical anharmonic oscillator model is a very good approximation to the intrinsic electronic nonlinearities of real systems.

In the next section, we use the model to consider the effect of lattice polarizability which we have so far neglected.

V. LOCAL FIELDS AND LATTICE POLARIZATION

We have already remarked in the introduction that the seat of the nonlinearities resides in the electronic motion. It is, however, considerably modified by local field corrections and in the case of optical rectification and the linear electro-optic effect by lattice polarization.

Miller's rule states that $d_{ijk}^{\alpha\beta\gamma}$ is proportional to the product of the observed linear susceptibilities X_{ii}^{α}, etc. at the appropriate frequencies. If one of these is dc we are to take the actual dc susceptibility and not the extrapolated long wavelength limit of the optical susceptibility.

At first sight, it seems plausible that this is simply the effect of internal fields, which cause the local field experienced by an atom to be greater than the applied field. We now examine this hypothesis and show that it is inadequate.

Microscopic calculations yield the polarization of single atoms due to local fields. In the linear case, if we have N atoms per unit volume of polarizability α

$$P = N\alpha E_l \tag{100}$$

and the local field is related to the applied field E by

$$E_l = E + \Gamma P. \tag{101}$$

In some cases the Lorentz value of $\Gamma = 4\pi/3$ is applicable and we then obtain the well-known relation between the refractive index n, or the dielectric constant $\epsilon = n^2$ and α.

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha = \frac{R}{V}, \tag{102}$$

where V is the molar volume and R is the molar refractivity.

In general,

$$P = N\alpha(E + \Gamma P) = \frac{N\alpha}{1 - \Gamma N\alpha} E \tag{103}$$

and the observed susceptibility is

$$\chi = \frac{N\alpha}{1 - \Gamma N\alpha} = \frac{E_l}{E} N\alpha \tag{104}$$

while

$$E_L = (1 + \Gamma\chi)E = \frac{E}{1 - \Gamma N\alpha}. \tag{105}$$

In nonlinear optics the two driving fields E_j^β and E_k^γ are obviously modified according to (105) but, as Armstrong, Bloembergen, Ducuing and Pershan [18] have shown, there is a further factor in P. This arises because the nonlinear polarization

$$p_i^\alpha = d_{ijk}^{\alpha\beta\gamma} (E_j^\beta)_{\text{local}} (E_k^\gamma)_{\text{local}}, \tag{106}$$

produced directly on the atoms, further polarizes the surrounding medium.

We have

$$P_i^\alpha = p_i^\alpha + \Gamma N\alpha P_i^\alpha, \tag{107}$$

so that

$$P_i^\alpha = \frac{p_i^\alpha}{1 - \Gamma N\alpha} = (1 + \Gamma\chi_{ii}^\alpha) p_i^\alpha. \tag{108}$$

Thus, if $d_{ijk}^{\alpha\beta\gamma}$ is the (calculated) intrinsic coefficient, the observed coefficient is

$$D_{ijk}^{\alpha\beta\gamma} = (1 + \Gamma\chi_{ii}^\alpha)(1 + \Gamma\chi_{jj}^\beta)(1 + \Gamma\chi_{kk}^\gamma) d_{ijk}^{\alpha\beta\gamma}. \tag{109}$$

Therefore, even if d does not vary with χ, D will do so. This is, however, not enough to explain the observed variation of D with χ. For example, in semiconductors it is very likely that Γ is small if not zero and yet the measured values of D appear to obey Miller's rule and be proportional to χ^3. Thus, the intrinsic coefficient d itself must have a similar dependence on X,

If we write

$$D^{\alpha\beta\gamma}_{ijk} = \chi^{\alpha}_{ii}\chi^{\beta}_{jj}\chi^{\gamma}_{kk}\Delta_{ijk} \tag{110}$$

in terms of the measured susceptibilities (i.e., $n^2 - 1$), which is the content of Miller's rule, and then use (104) to express D in terms of the atomic polarizabilities we obtain

$$D^{\alpha\beta\gamma}_{ijk} = (1 + \Gamma\chi^{\alpha}_{ii})(1 + \Gamma\chi^{\beta}_{jj})(1 + \Gamma\chi^{\gamma}_{kk})N^3\alpha^{\alpha}_{ii}\alpha^{\beta}_{jj}\alpha^{\gamma}_{kk}\Delta_{ijk} \tag{111}$$

so that from (109)

$$d^{\alpha\beta\gamma}_{ijk} = N\alpha^{\alpha}_{ii}N\alpha^{\beta}_{jj}N\alpha^{\gamma}_{kk}\Delta_{ijk} \, . \tag{112}$$

Thus, the reduced tensor is the same whether or not we apply local field corrections as long as we do it consistently. To obtain a more or less constant value of Δ we must have d varying as α^3.

Since Δ for $NH_4H_2PO_4$ derived from the purely optical s.h.g. effect agrees with Δ from the quasi-static electro-optic effect to within 10 percent, although the values of d differ by a factor of 12 and in $BaTiO_3$ the two values of Δ_{311} are within a factor 2 while the d's differ by 300 it is clear that lattice polarization has a direct effect in d not described by local field terms.

We repeat that optical nonlinearities have an electronic origin. Electrons in atoms do not move in a harmonic potential. Second harmonic generation, which can only involve electronic motion, is much the same in covalent organic materials, ionic crystals and ferro-electrics. Large values of $d^{2\omega}$ are associated exclusively with large refractive indices. Thus, nonlinearities in the ionic motion play a secondary role in nonlinear optics; however important they may be in determining the ferro-electric properties.

We shall attempt to construct a model, just sufficiently general to exhibit the gross features of ferro-electric behavior, and show that it modifies the nonlinear optical behavior exactly as predicted by Miller's rule. The model is not put forward as an explanation of ferro-electricity although it has a venerable past in that connection, but as a demonstration that a simple system with singular dielectric properties behaves in a way consistent with Miller's rule.

In Fig. 1, we illustrate a moderately realistic one-dimensional model in which electrons of mass m are coupled to ions of mass M in a lattice. Forces act between like and unlike particles and of these by far the

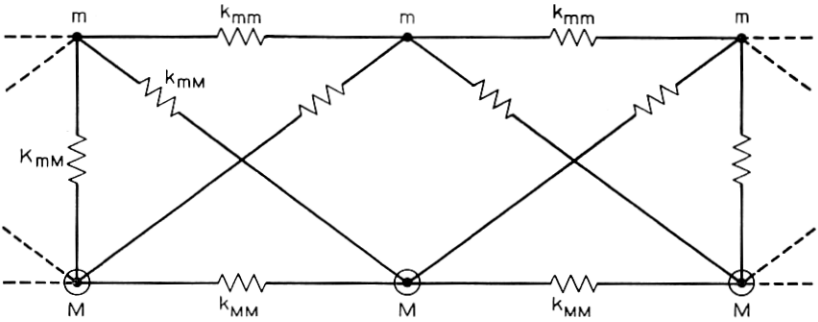

Fig. 1 — A realistic one-dimensional model.

strongest is K_{mM} which is responsible for the electronic optical spectrum. The remaining forces determine the lattice spectrum. The important nonlinearities are associated with K_{Mm}. The linear behavior of this model is formidably complicated and we therefore assume that its salient features are already evident in the much simpler model of Fig. 2.

The electron of mass $m_1 = m$ is coupled to the ion of mass $m_2 = M$ by the force constant k_{12} which replaces K_{mM}. It is anharmonic. The electron and the ion are also coupled to rigid supports representing the rest of the crystal by forces k_1 and k_2. It is as though we had gone directly from the Born-Von Karman theory of specific heats to the Einstein theory without mentioning Debye.

Let x_1 be the displacement of the electron of charge e_1 and x_2 that of the ion of charge e_2. We shall assume that the potential energy is

$$\varphi = \tfrac{1}{2}k_1x_1^2 + \tfrac{1}{2}k_2x_2^2 + \tfrac{1}{2}k_{12}(x_1 - x_2)^2 + v_{12}(x_1 - x_2)^3 \tag{113}$$

so that the anharmonic term is exclusively associated with the "atomic" binding of the electron to its parent ion. It will be convenient to define $v_{21} = -v_{12}$. The equation of motion in a field $E^\beta e^{i\beta t}$ is then

$$m_i\ddot{x}_i + k_ix_i + k_{12}(x_i - x_j) + 3v_{ij}(x_i - x_j)^2 = e_iE^\beta e^{i\beta t} \tag{114}$$

and the linear response neglecting v_{ij} is

$$x_i^{(1)} = \frac{(k_j - m_j\beta^2)e_i + k_{12}(e_1 + e_2)}{(k_1 + k_{12} - m_1\beta^2)(k_2 + k_{12} - m_2\beta^2) - k_{12}^2}\,E^\beta e^{i\beta t}. \tag{115}$$

With N units in unit volume, the polarization is

$$P^\beta = N(e_1x_1^{(1)} + e_2x_2^{(1)})$$

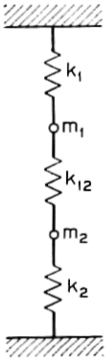

Fig. 2 — A simplified one-dimensional model.

and so

$$\chi = N\frac{e_1^2(k_2 - m_2\beta^2) + e_2^2(k_1 - m_1\beta^2) + k_{12}(e_1 + e_2)^2}{(k_1 + k_{12} - m_1\beta^2)(k_2 + k_{12} - m_2\beta^2) - k_{12}^2}. \tag{116}$$

At an optical frequency ω well above $(k_2/m_2)^{\frac{1}{2}}$ the ionic resonance

$$\chi^\omega \approx \frac{Ne_1^2}{k_1 + k_{12} - m_1\omega^2}, \tag{117}$$

while at dc

$$\chi^0 = N\frac{k_2e_1^2 + k_1e_2^2 + k_{12}(e_1 + e_2)^2}{k_1k_2 + k_{12}k_1 + k_{12}k_2}. \tag{118}$$

To obtain the sum frequency polarization due to two fields $E^\beta e^{i\beta t}$ and $E^\gamma e^{i\gamma t}$ we substitute the linear responses back into the nonlinear term in (114). The result is a nonlinear coefficient

$$d^{\alpha\beta\gamma} = -3v_{12}f(\alpha)f(\beta)f(\gamma), \tag{119}$$

where

$$f(\alpha) = \frac{e_1(k_2 - m_2\alpha^2) - e_2(k_1 - m_1\alpha^2)}{(k_1 + k_{12} - m_1\alpha^2)(k_2 + k_{12} - m_2\alpha^2) - k_{12}^2}, \quad \text{etc.} \tag{120}$$

If we express $d^{\alpha\beta\gamma}$ as $\chi^\alpha\chi^\beta\chi^\gamma\Delta$ we have

$$\Delta = -\frac{3v_{12}}{N^2e_1^3}\,g(\alpha)g(\beta)g(\gamma), \tag{121}$$

where

$$g(\alpha) = \frac{k_2 - m_2\alpha^2 - \dfrac{e_2}{e_1}(k_1 - m_1\alpha^2)}{k_2 - m_2\alpha^2 + \left(\dfrac{e_2}{e_1}\right)^2(k_1 - m_1\alpha^2) + k_{12}\left(1 + \dfrac{e_2}{e_1}\right)^2}, \quad \text{etc.} \tag{122}$$

We note first that if, as seems most reasonable, $e_2 = -e_1$ then $g(\alpha) = g(\beta) = g(\gamma) = 1$. In any case at optical frequencies $g(\omega) \approx 1$ for all reasonable values of e_2/e_1 and at dc

$$g(0) = \frac{k_2 - \dfrac{e_2}{e_1}k_1}{k_2 + \left(\dfrac{e_2}{e_1}\right)^2 k_1 + k_{12}\left(1 + \dfrac{e_2}{e_1}\right)^2} \tag{123}$$

which is also near unity if $e_2 \approx -e_1$. Thus, to all intents

$$\Delta \approx -\frac{3v_{12}}{N^2e^3} \tag{124}$$

which is exactly the result obtained by neglecting the ionic motion.

Thus, Δ is an intrinsic electronic property and the effect of ionic motion is entirely contained in its effect on χ. We note, however, that in some ferro-electrics, where the departure from inversion symmetry is both small and temperature dependent, Δ will also be temperature dependent.

If k_1, k_{12}, and k_2 are all positive, the dc susceptibility is greater than the low frequency limit of χ^ω but not dramatically so. There is, however, no reason why one of these constants should not be negative. Negative compliances are familiar in classical mechanics, a well-known example is the common automatic door stop which exhibits a positive compliance as the door is first opened but a negative compliance when the door is almost fully open. The force between atoms as a whole in a lattice exhibits a positive compliance but if we separate this force into nuclear-nuclear and electron-electron repulsion and nuclear-electron attraction, it is quite reasonable to assume that at the equilibrium distance the latter component has a negative compliance.

It is immaterial which term in (113) we take as negative although on physical grounds it seems most suitable to take k_1 and this is also a convenient choice.

Provided that

$$k_1k_2 + k_{12}k_1 + k_{12}k_2 > 0 \tag{125}$$

or

$$\eta = -k_1 \frac{k_2 + k_{12}}{k_2 k_{12}} < 1 \tag{126}$$

the system remains in stable equilibrium at $x_1 = x_2 = 0$.

The natural resonance ω_1 and ω_2 of the system satisfy

$$m_1 m_2 \omega_1^2 \omega_2^2 = k_1 k_2 + k_1 k_{12} + k_2 k_{12} \tag{127}$$

and so as $\eta \rightarrow 1$ one of these frequencies $\rightarrow 0$. At the same time the dc susceptibility (for simplicity we take $-e_2 = e_1 = e$)

$$\chi^0 = \frac{Ne^2}{k_{12}} \frac{1 - \eta \dfrac{k_{12}}{k_{12} + k_2}}{1 - \eta} \tag{128}$$

becomes infinite, while the low-frequency limit of the optical susceptibility remains finite.

If η exceeds unity there is a spontaneous polarization limited only by terms such as ωx_2^4 which we have failed to include in φ.

All this is reminiscent of ferro-electric behavior if η is temperature dependent and the Curie point corresponds to $\eta = 1$.

The inclusion of a term ωx_2^4 in φ will, in fact, make η temperature dependent, for the effect of this term is to replace k_2 by an effective value for low-frequency displacements

$$k_2' \approx k_2 + 6\omega\overline{x_2^2} = k_2(1 + \lambda T), \tag{129}$$

where $\overline{x_2^2}$ is the mean square thermal displacement. As a result if η_o is the value at $T = 0$ we have

$$\eta = \eta_0\left(1 - \lambda T \frac{k_{12}}{k_2 + k_{12}}\right) \tag{130}$$

and so

$$\chi^0 = \frac{Ne^2}{k_{12}} \frac{\dfrac{k_2}{k_{12}} + \lambda\left(\dfrac{k_{12}}{k_{12} + k_2} T - T_o\right)}{\lambda(T - T_o)}, \tag{131}$$

if we define T_o as the temperature at which $\eta = 1$. This is of course a crude approximation to a Curie-Weiss Law.

By ascribing all the temperature dependence to changes in k_2, it is obvious from (117) that X^ω is temperature independent. For η to be equal to unity, it is not necessary for $-k_1$ to be of the same magnitude as k_{12}, all we require [see (126)] is that $-k_1$ be near k_2. Thus, from (117), we do not expect any very anomalous values of χ^{ω} in ferro-electrics, except in so far as materials with a high electronic polarizability are more likely to be ferro-electric.

We have now shown that it is possible to incorporate in our model features which lead to quite different behavior for the optical and dc dielectric constants without either invalidating Miller's rule or even changing the value of Δ which is essentially a purely electronic property.

We should, therefore, expect the temperature variation of $D_{ijk}^{\alpha\beta\gamma}$ to correspond to that of $\chi_{ii}^{\alpha}\chi_{jj}^{\beta}\chi_{kk}^{\gamma}$ and this is well borne out by the measurements of Zwicker and Scherrer[25] of the electro-optic coefficients and Bass, Franken, and Ward[26] of the optical rectification coefficients in the dihydrogen phosphates. Both coefficients are directly proportional to the dc dielectric constant which obeys a Curie Weiss Law.

In KDP there is almost no change of the s.h.g. coefficient (Van de Ziel and Bloembergen[27]) with temperature above or below the Curie point, in accord with our expectations, but at the Curie point there is a small discontinuous change. In an orthorhombic coordinate system $d_{311}^{2\omega}$ and $d_{322}^{2\omega}$ are equal above T_c but below T_c, $d_{311}^{2\omega}$ increases and $d_{322}^{2\omega}$ decreases while at the same time $\chi_{11} - \chi_{33}$ decreases and $\chi_{22} - \chi_{33}$ increases. With a constant Δ this is not compatible with Miller's rule.

However, at the transition there is a change in crystal class in which a_1 increases and a_2 decreases, Jona and Shirane.[28] It is not unreasonable to assume that this increases T_{311} and decreases T_{322} by more than enough to compensate for the changes in χ_{11} and χ_{22}.

VI. MILLER'S RULE

The classical anharmonic oscillator model, which we have shown to be a good approximation to the behavior of a real system, leads directly to that part of Miller's rule which refers to the geometric properties and frequency dependence of the nonlinear coefficients in a single material. We have also in (51) advanced a crude argument to show that Δ will not vary much from material to material.

When we examine the experimental data we shall see that the allowed components of Δ are between 1×10^{-6} and 6×10^{-6} esu for most materials but that there are a few materials with significantly higher values and a number with values as low as 0.1×10^{-6} esu.

In most cases, these exceptional values have a rather simple explanation and we have therefore to explain a constancy of Δ to within a factor of about 10.

Neglecting the effects of lattice polarization and local field corrections, which we have shown are irrelevant, the results for the classical anharmonic oscillator model are, from (50) and (56),

$$\Delta_{ijk} = 3\,\frac{T_{ijk}}{a_o e \chi^2}. \tag{132}$$

This is also the result from the static perturbation treatment of Section II.

If we use

$$\chi = 4N\,\frac{\langle x^2\rangle^2}{a_o} = \tfrac{4}{9}N\,\frac{\langle r^2\rangle^2}{a_o}, \tag{133}$$

we arrive at

$$\Delta_{ijk} = \frac{243}{16}\,\frac{a_o}{e}\,\frac{T_{ijk}}{N^2\langle r^2\rangle^4}. \tag{134}$$

Now the volume occupied by the oscillator is both $1/N$ and $8\,\langle r^2\rangle^{\frac{3}{2}}$ and so

$$\Delta_{ijk} \approx 10^4\langle r^3\rangle^{\frac{1}{2}}\,\frac{T_{ijk}}{\langle r^2\rangle^{\frac{3}{2}}}\ \text{esu} \tag{135}$$

where we have inserted numerical values for a_o and e. This expresses Δ_{ijk} as the product of a scale factor $\langle r^2\rangle^{\frac{1}{2}}$ and a dimensionless shape factor T/r^3. Whether we assign to each oscillator the volume per valence electron, per atom or per group of atoms, $\langle r^2\rangle^{\frac{1}{2}}$ is likely to be between 0.75 and 3 Å; so that Δ will be sensibly constant near 3×10^{-6} esu, if the shape factor is of the order of 0.01 to 0.05. We have from Turner, Saturno, Hank and Parr's[10] results for CH_4 a shape factor of 0.05, and so this range of shape factors is not unreasonable. It corresponds to a linear distortion $0.02^{\frac{1}{3}} \approx 25$ percent. It is also not unreasonable that the distortion should be of this general order, wherever it is allowed by symmetry. We may speculate that much smaller values of T/r^3 would imply very weak interatomic forces and much larger values would lead to a structure unstable relative to a more symmetric arrangement.

Thus, qualitatively, the relative constancy of Δ reflects relatively constant shape factors, although we can hardly claim that this is more than a sophisticated form of dimensional analysis. It does, however, suggest that Δ is determined primarily by the geometric properties of the molecular and crystal structure.

Large values of Δ will occur only when the molecules themselves depart considerably from inversion symmetry and are arranged in the crystal in such a way that the effects of individual parts of the molecule are additive. Small values of Δ will occur when sections of the molecule have local near inversion symmetry or when their disposition in the crystal favors the cancellation of effects from different atomic groupings. However the molecules are arranged in the lattice, Δ will be small if the molecules themselves have near inversion symmetry, or consist of uncoupled parts with the same property.

In Tables II, III, and IV, we present 50 values of Δ derived from

TABLE II—SECOND HARMONIC COEFFICIENTS

Units of d 10^{-9} esu Units of Δ 10^{-6} esu

Material	Class	λ_μ	d_{123}	Δ					Ref.
HMT = $N_4(CH_2)_6$	$\bar{4}$3m	1.06	30	17					1
ZnS	$\bar{4}$3m	1.06	153	3.5					3
ZnS	$\bar{4}$3m	10.6	146	4.5					2
ZnSe	$\bar{4}$3m	1.06	200	2.5					3
ZnSe	$\bar{4}$3m	10.6	370	6.6					2
ZnTe	$\bar{4}$3m	1.06	660	2.9					3
ZnTe	$\bar{4}$3m	10.6	440	3.6					2
CdTe	$\bar{4}$3m	10.6	800	7					2
GaP	$\bar{4}$3m	1.06	525	1.3					4
GaP	$\bar{4}$3m	1.06	255	0.6					3
GaAs	$\bar{4}$3m	1.06	1,500	1					4
GaAs	$\bar{4}$3m	10.6	1,760	3.7					2
InAs	$\bar{4}$3m	10.6	2,000	3.2					2
					d_{321}	Δ			
KH_2PO_4	$\bar{4}$2m	1.06	3	3.6	3	3.6			5
KD_2PO_4	$\bar{4}$2m	1.06	2.7	3.2	2.7	3.2			5
KH_2AsO_4	$\bar{4}$2m	1.06	3.4	2.6	3.2	2.5			4
$NH_4H_2PO_4$	$\bar{4}$2m	1.06	2.9	3.15	3.	3.15			5
			d_{333}	Δ	d_{311}	Δ	d_{113}	Δ	
ZnO	6mm	1.06	43	3.3	13	1.1	14	1.1	4
ZnS	6mm	1.06	84	1.9					3
ZnS	6mm	10.6	180	4.9	90	2.45	102	2.7	2
CdS	6mm	1.06	186	3.2	96	1.6	105	1.8	2
CdS	6mm	10.6	210	5.4	126	3.3	138	3.6	2
CdSe	6mm	1.06	500	3.4					3
CdSe	6mm	10.6	260	4.8	136	2.4	148	2.6	2
$BaTiO_3$	4mm	1.06	42	1.0	111	2.45	105	2.35	5
							d_{222}	Δ	
$LiNbO_3$	3m	1.06	250	9	36	1.1	19	0.55	6
$LiNbO_3$	3m	1.152			32	1.05	15	0.45	6
			d_{111}	Δ					
SiO_2	32	1.06	2.5	1.9					4
$AlPO_4$	32	1.06	2.5	2.2					4
Se	32	10.6	380	2.1					2
Te	32	10.6	25,400	4.3					7

TABLE III—OPTICAL RECTIFICATION COEFFICIENTS

Units of d 10^{-9} esu Units of Δ 10^{-6} esu

Material	Class	λ_μ	d_{123}	Δ				Ref.
ZnTe	$\bar{4}3m$	0.694 1.06	3650 1040	14 5				8 8
				d_{321}	Δ			
KH_2PO_4	$\bar{4}2m$	0.694			50	3.2		8
KD_2PO_4	$\bar{4}2m$	0.694			105	2.9		8
$NH_4H_2PO_4$	$\bar{4}2m$	0.694	132	3.0				9
			d_{333}	Δ	d_{311}	Δ		
CdS	6mm	0.694	700	7	900	9		8

published s.h.g. data, 7 values from optical rectification data and 50 from electro-optic data. Definitions and conventions are discussed in the appendix and a separate list of references is given for the data in the appendix. Probable errors vary from measurement to measurement. It is probably safe to say that no measurement has an accuracy better than ±10 percent and in many cases the probable error is greater. That for the s.h.g. data at 10.6 μ is 30 percent and except for ADP the rectification data is only good to a factor of 3. In addition, a few materials have discordant results reported by different groups and this suggests that, especially in the case of crystals which are difficult to grow, the data should be regarded rather critically. In the case of CuCl, Sterzer, Blattner and Miniter[29] have constructed a modulator whose behavior is consistent with the higher value of the electro-optic coefficient. This casts some doubt on the low value for CuBr reported in conjunction with CuCl. In the case of the linear *e-o* coefficient in HMT, Heilmeyer's[13] value $d_{123} = 32 \times 10^{-9}$ esu is the most recent and reliable.

The average of all the s.h.g. data is $\Delta = 3.3 \times 10^{-6}$ esu, and only two coefficients d_{123} in HMT and d_{333} in $LiNbO_3$ exceed 6×10^{-6} esu by more than the probable error. One coefficient d_{222} in $LiNbO_3$ is unambiguously less than 1×10^{-6} esu. The sole accurate rectification coefficient, Δ_{123} in NH_4HPO_4, is 3×10^{-6} esu which is remarkably close to the values 3.15 and 3.2×10^{-6} esu for s.h.g. and the electro-optic effect.

Whereas the s.h.g. data have a rather compact distribution about 3×10^{-6} esu the linear *e-o* data are more straggled. The mean value is 2.3×10^{-6} esu but there are a considerable number of materials with $\Delta < 1 \times 10^{-6}$ esu. The difference between the averages $\bar{\Delta}_{shg}$ and $\bar{\Delta}_{eo}$ is not due to the different materials in the two lists, it persists if we

Table IV—Electro-optic Coefficients

Units of d 10^{-9} esu Units of Δ 10^{-6} esu

Material	Class	λ	d_{123}	Δ								Ref.
HMT $= N_4(CH_2)_6$	$\bar{4}3m$	0.5	32	14								10
HMT $= N_4(CH_2)_6$	$\bar{4}3m$		6	2.3								11
HMT $= N_4(CH_2)_6$	$\bar{4}3m$		55	21								12
$Bi_4(GeO_4)_3$	$\bar{4}3m$		22	0.8 assumed $\epsilon = 6$								13
Sodalite	$\bar{4}3m$		9.5	1.8								14
CuCl	$\bar{4}3m$		28	0.75								16
CuCl	$\bar{4}3m$		110	3								15
CuBr	$\bar{4}3m$		22	0.4 assumed $\epsilon = 10$								16
ZnS	$\bar{4}3m$	0.65	74	0.9								17
ZnSe	$\bar{4}3m$	0.55	120	0.8								18
ZnTe	$\bar{4}3m$	0.60	440	1.5								19
GaP	$\bar{4}3m$	0.63	150	0.3								20
GaAs	$\bar{4}3m$	1.02	215	0.3								21
$NaClO_3$	23	0.59	2.5	0.6								22
$K_2Mg_2(SO_4)_3$	23		$< .26$	<0.1 assumed $\epsilon = 6$								23
$(NH_4)_2Mn_2(SO_4)_3$	23		4.3	0.5 assumed $\epsilon = 9$								24
$(NH_4)_2Cd_2(SO_4)_3$	23		5.7	0.6								24
$NaVO_2(CH_3COO)_3$	23		5.3	1.3 assumed $\epsilon = 6$								25
$Na_3SbS_4 \cdot 9H_2O$	23		10	2								26
Tren Chloride	23		9.5	2.7								27
			d_{333}	Δ	d_{113}	Δ						
ZnO	6mm	0.63	50	1.5	26	0.8	$\frac{d_{113}}{d_{333}}$ neg.					28
ZnS	6mm	0.63	67	0.9	34	0.45						28
CdS	6mm	0.63	110	1.2	48	0.55						28
Material	Class	λ	d_{123}	Δ	d_{321}	Δ						Ref.
KH_2PO_4	$\bar{4}2m$	0.55	+65	4.0	−50	1.7	constant stress					29
KH_2PO_4	$\bar{4}2m$		60	3.7			constant strain					30
KD_2PO_4	$\bar{4}2m$		160	4.0			constant stress					31
KH_2AsO_4	$\bar{4}2m$		77	3.7	84	1.7	constant stress					32
RbH_2AsO_4	$\bar{4}2m$		92	3.5			constant stress					32
$NH_4H_2PO_4$	$\bar{4}2m$		+55	4.4	−146	3.4	constant stress					32,29
$NH_4H_2PO_4$	$\bar{4}2m$		36	3.2			constant strain					29
			d_{333}	Δ	d_{311}	Δ	d_{113}			Δ	$\frac{d_{113}}{d_{333}}$	
$BaTiO_3$	4mm	0.63	1000	1			320			0.3	+	33
					3.3×10^4	1.4		constant strain				34
					6.6×10^4	1.9		constant stress				35
			d_{333}	Δ	d_{311}	Δ	d_{113}	Δ	d_{222}	Δ	$\frac{d_{113}}{d_{333}}$	
$LiNbO_3$	3m	0.63	860	4.3	840	2.5	280	1.2	110	0.3	+	36
			d_{111}	Δ								
SiO_2	32	0.5	3.2	0.9								22
$K_2S_2O_6$	32	0.55	1.4	0.4	assumed $\epsilon = 6$							11
$S_rS_2O_6 \cdot H_2O$	32	0.55	0.65	0.15								11
$C_6H_{12}O_6NaBr \cdot H_2O$	32	0.55	0.65	0.15								11
$CsC_4H_4O_6$	32	0.55	7	1.4								11
			d_{312}	Δ								
$C(CH_2OH)_4$	$\bar{4}$		9.7	7								37

eliminate all materials not common to both lists and may therefore, be either a real effect or a systematic error.

A few materials [e.g., $SrS_2O_6 \cdot H_2O$, $C_6H_{12}O_6NaBr \cdot H_2O$ and $K_2Mg_2(SO_4)_3$] have very low values of Δ. The latter is especially interesting since the isomorphous $(NH_4)_2Cd_2(SO_4)_3$ and $(NH_4)_2Mn_2(SO_4)_3$ salts have somewhat larger values. The ammonium cadmium salt is known to be ferro-electric at very low temperatures and the ammonium manganese salt is also suspected of ferro-electricity (Jona and Shirane[28]). More significant, perhaps, is the fact that the divalent ions have very nearly regular octahedral coordination (Zemann and Zemann[30]) and so form a unit with near inversion symmetry and contribute little to d. The main contribution comes from the monovalent ions and their irregularly placed neighbors. The difference between the potassium and ammonium salts would then be due to the difference in the polarizability of the two ions. For K^+ the refractivity is 2.45 ccs and for NH_4^+ it is 4.05 ccs (see Le Fevre[12]). If this enters d as a cube the expected ratio of the d coefficients would be 4.5. The observed value is greater than about 5. Note also that NH_4^+ itself lacks inversion symmetry.

The tabulated values of Δ show that Miller's rule is an excellent rough guide to the probable value of d. If the component is allowed by symmetry

$$| d_{ijk}^{\alpha\beta\gamma} | \approx 3 \times 10^{-6} X_{ii}^{\alpha} X_{jj}^{\beta} X_{kk}^{\gamma} \text{ esu.} \qquad (136)$$

However, the rule by itself is not infallible. Occasionally, a value of d much higher than that predicted by (136) will occur. In some cases, (e.g., d_{333} in $LiNbO_3$) this is accompanied by a very low value of another coefficient and it is then plausible to assume that this is due to a particularly critical geometric configuration. In other cases, (e.g., HMT) it is quite clearly due to the coincidence of a number of favorable factors. The atoms, the molecule and the crystal all have the same symmetry and moreover, as we saw in Section 1, all the separate contributions to d have the same sign. Thus, it is likely that the value of $\Delta \approx 15 \times 10^{-6}$ esu for HMT represents something of an upper limit to what is possible.

More often (136) will overestimate d. This is especially likely to occur if the molecules themselves, or large sections of the molecule have near inversion symmetry, but it may also occur if the crystal structure itself departs only very slightly from a centro-symmetric structure.

VII. CONCLUSION

If reasonably good ground state wave functions are available, the direct perturbation method of Section II seems most suitable as a basis for calculating the magnitudes of the coefficients. It gives the intrinsic nonlinear coefficient

$$d^a_{ijk} = \frac{3\chi^a}{a_o e} \frac{T_{ijk}}{n} \tag{137}$$

in terms of the intrinsic low-frequency limit of the optical susceptibility χ^a and a cubic moment in the ground state. If the electrons are uncorrelated, this can be replaced by

$$d^a_{ijk} = \frac{3\chi^a}{a_o e} t_{ijk} \tag{138}$$

and t_{ijk} can be obtained from the charge distribution. From (138) we obtain the reduced tensor

$$\Delta_{ijk} = \frac{3}{a_o e} \frac{t_{ijk}}{(\chi^a)^2} \tag{139}$$

and we can then incorporate this directly in Miller's rule using the observed susceptibilities χ^α_{ii}, etc. to obtain $d^{\alpha\beta\gamma}_{ijk}$.

This continuation of the basic perturbation calculation with Miller's rule appears to be the most straight-forward approach to the coefficients. Apart from the cubic moment t_{ijk} it involves only experimental quantities.

The analogy with the classical anharmonic oscillator established in Section IV seems most likely to be fruitful in qualitative discussions of the general behavior of the coefficients. It appears to have both empirical and theoretical justification.

Obviously, on this basis further generalizations of Miller's rule are possible. For example, we might expect the fourth rank tensor $d^{\alpha\beta\gamma\delta}_{ijkl}$ which describes induced second harmonic generation, the Kerr effect, etc. to satisfy a relation of the form

$$d^{\alpha\beta\gamma\delta}_{ijkl} = X^\alpha_{ii} X^\beta_{jj} X^\gamma_{kk} X^\delta_{ll} \Delta_{ijkl} \,. \tag{140}$$

A calculation based on fourth-order perturbation theory and a lavish use of sum rules leads to

$$\Delta_{ijkl} \approx 1.5 \times 10^4 \frac{a_o}{e^2} \langle r^2 \rangle^{\frac{3}{2}} \frac{Q_{ijkl}}{\langle r^2 \rangle^2} \,, \tag{141}$$

where $\langle r^2 \rangle$ is the mean square radius of the charge distribution and Q_{ijkl} is the semi-invariant

$$Q_{ijkl} = \langle x_i x_j x_k x_l \rangle - 2\langle x_i x_j \rangle \langle x_k x_l \rangle \tag{142}$$

if we assume that all odd moments vanish.

If we take $\langle r^2 \rangle^{\frac{1}{2}}$ as 1 Å this gives

$$\Delta_{ijkl} \approx 3 \times 10^{-10} \frac{Q_{ijkl}}{\langle r^2 \rangle^2} \text{ esu}. \tag{143}$$

We have seen that in the lower-order processes T/r^3 is of the order of 2×10^{-2}. This does not imply that Q/r^4 is of the order $(2 \times 10^{-2})^{4/3} \sim 5 \times 10^{-3}$ for whereas T is nonzero only because of asymmetric molecular and intermolecular forces, Q is nonzero even for free atoms or ions. For example, in the hydrogen atom $Q_{iiii}/\langle r^2 \rangle^2 = 5/18$ and $Q_{iijj}/\langle r^2 \rangle^2 = 1/9$ so that we expect Δ to be of the order of 3×10^{-11} to 10^{-10} esu. For calcite with $\chi_{\text{optical}} = 0.1$ and $\chi_{\text{dc}} = 0.55$ this gives a value of d between 3×10^{-14} and 10^{-13} esu. Bjorkholm and Siegman[31] have measured 3×10^{-14} esu.

We have seen that the reduced tensor Δ_{ijk} is proportional to the cubic moment,

$$T_{ijk} = \langle \hat{x}_i \hat{x}_j \hat{x}_k \rangle$$

and it is therefore clearly symmetric in all its indices. This is in agreement with Kleinman's[2] hypothesis and follows from the origin of the nonlinear behavior in the electronic motion.

Finally, we remark that nothing increases d like large values of the linear susceptibilities yet, although, the values of most allowed reduced tensor components Δ_{ijk} are near 3×10^{-6} esu they can vary by a factor 100:1. The molecular geometry will often indicate which end of the range is likely to apply to a particular material.

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APPENDIX

We have throughout adopted a notation, originally introduced by Bloembergen[15] and his colleagues, in which two fields with complex time dependence $E_j^{\beta} e^{i\beta t}$ and $E_k^{\gamma} e^{i\gamma t}$ produce a polarization $P_i^{\alpha} e^{i\alpha t}$ at the algebraic sum frequency $\alpha = \beta + \gamma$ according to

$$P_i^{\alpha} e^{i\alpha t} = d_{ijk}^{\alpha\beta\gamma} E_j^{\beta} E_k^{\gamma} e^{i(\beta+\gamma)t}. \tag{144}$$

If the actual fields vary as $\cos \omega_1 t$ and $\cos \omega_2 t$ there will be terms in P at $\omega_1 + \omega_2$ and $\omega_1 - \omega_2$ obtained from (144) by letting $\beta = \omega_1, \bar{\omega}_1$, etc. where $\bar{\omega}_1 = -\omega_1$.

This notation has several advantages in theoretical calculations for much the same reason that the use of complex numbers simplifies ac circuit theory, and for much the same reason it has a number of disadvantages in calculating numerical values. For this reason, it has not gained general acceptance by experimentalists who tend to use a number of different notations, some of which, especially in electro-optics, are of respectable antiquity. The difference between the two notations introduces various factors of 2. These are independent of the general reluctance of physicists to state unequivocally whether they are using peak or rms fields. In particularly fertile ground, these various factors can luxuriate and blossom as factors of 8 in the final answer. We use peak fields in all our definitions.

If the applied field is

$$\underline{F}(t) = (0,\ F_2 \cos \omega t,\ F_3 \cos \Omega t), \tag{145}$$

it has components $E_2^{\bar{\omega}} = E_2^{\omega} = \frac{1}{2}F_2$, $E_3^{\bar{\Omega}} = E_3^{\Omega} = \frac{1}{2}F_3$ and the 1 component of $\underline{P}(t)$ is

$$\begin{aligned} P_1(t) &= \tfrac{1}{4}\{d_{123}^{\omega\Omega}F_2F_3e^{i(\omega+\Omega)t} + cc\} + \tfrac{1}{4}\{d_{132}^{\Omega\omega}F_3F_2e^{i(\omega+\Omega)t} + cc\} \\ &\quad + \tfrac{1}{4}\{d_{123}^{\omega\bar{\Omega}}F_2F_3e^{i(\omega-\Omega)t} + cc\} + \tfrac{1}{4}\{d_{132}^{\Omega\bar{\omega}}F_3F_2e^{i(\omega-\Omega)t} + cc\}, \end{aligned} \tag{146}$$

where we have used $d_{123}^{abc} = d_{123}^{\overline{\bar{a}\bar{b}\bar{c}}}$ and suppressed the first superscript, which is always the algebraic sum of the second and third superscripts.

We can also write (146) as

$$\begin{aligned} P_1(t) &= \tfrac{1}{2}\{d_{123}^{\omega\Omega} + d_{132}^{\Omega\omega}\}F_2F_3 \cos(\omega + \Omega)t \\ &\qquad + \tfrac{1}{2}\{d_{123}^{\omega\bar{\Omega}} + d_{132}^{\Omega\bar{\omega}}\}F_2F_3 \cos(\omega - \Omega)t. \end{aligned} \tag{147}$$

If $\omega = \Omega$, this gives

$$P_1(t) = \tfrac{1}{2}\{d_{123}^{2\omega\omega\omega} + d_{132}^{2\omega\omega\omega}\}F_2F_3 \cos 2\omega t + \tfrac{1}{2}\{d_{123}^{0\omega\bar{\omega}} + d_{132}^{0\bar{\omega}\omega}\}F_2F_3\,. \tag{148}$$

Now the usual experimental definition would be

$$P_1(t) = (d_{123}^{2\omega} + d_{132}^{2\omega})F_2F_3 \cos 2\omega t + (d_{123}^{0} + d_{132}^{0})F_2F_3 \tag{149}$$

and so we see that

$$\text{s.h.g.} \quad d_{ijk}^{2\omega} = \tfrac{1}{2}d_{ijk}^{2\omega\omega\omega} \tag{150}$$

$$\text{rectification} \quad d_{ijk}^{0} = \tfrac{1}{2}d_{ijk}^{0\omega\bar{\omega}}. \tag{151}$$

If we let $\Omega = 0$, we have

$$P_1(t) = (d_{123}^{\omega\omega 0} + d_{132}^{\omega 0 \omega})F_2F_3 \cos \omega t. \tag{152}$$

The experimental definition reads

$$P_1(t) = d_{123}^{\omega}F_2F_3 \cos \omega t \tag{153}$$

i.e.,

$$\delta\chi_{12} = d_{123}^{\omega}F_3 , \tag{154}$$

so that it is possible to contract the last two suffices according to the scheme

$$11 \rightarrow 1 \;\; 22 \rightarrow 2 \;\; 33 \rightarrow 3, \quad 32 = 23 \rightarrow 4, \quad 31 = 13 \rightarrow 5, \quad 12 = 21 \rightarrow 6. \tag{155}$$

Thus, $d_{ip}^{2\omega}$ ($i = 1 \cdots 3$, $p = 1 \cdots 6$) represents $d_{ijk}^{2\omega}$ and, for example, $d_{25} \equiv d_{231} = d_{213}$.

$$\begin{aligned} P_1 \cos 2\omega t &= (d_{123}^{2\omega} + d_{132}^{2\omega})F_2F_3 \cos 2\omega t \\ &= 2d_{123}^{2\omega}F_2F_3 \cos 2\omega t = d_{14}^{2\omega}\cdot 2F_2F_3 \cos 2\omega t. \end{aligned} \tag{156}$$

It is therefore common to define the "vector" $\mathfrak{F}$

$$\mathfrak{F} \equiv \mathfrak{F}_1 , \mathfrak{F}_2 , \mathfrak{F}_3 , \mathfrak{F}_4 , \mathfrak{F}_5 , \mathfrak{F}_6 = F_1^2 , F_2^2 , F_3^2 , 2F_2F_3 , 2F_3F_1 , 2F_1F_2 \tag{157}$$

so that

$$P_i = \sum_{p=1}^{6} d_{ip}\mathfrak{F}_p . \tag{158}$$

With this notation $d_{16}^{2\omega} = d_{123}^{2\omega} = d_{132}^{2\omega} \neq d_{123}^{2\omega} + d_{132}^{2\omega}$ but also $d_{11}^{2\omega} = d_{111}^{2\omega}$.

In the electro-optic case, the subscripts referring to optical fields can be contracted

$$2d_{ijk}^{\omega\omega 0} = d_{ijk}^{\omega} = d_{pk}^{\omega} \qquad p = 1 \cdots 6, \qquad k = 1.3. \tag{159}$$

The alternative ordering (155) leads to d_{kp}^{ω}.

Note that in this case, since d operates on two distinct fields, one optical the other dc, there is no possibility of constructing a "vector" such as $\mathfrak{F}$. The sum implied in the definition of d_{pk}^{ω} is

$$\delta\chi_p = \delta\chi_{ij} = \sum_{k=1}^{3} d_{pk}^{\omega}E_k^{dc}. \tag{160}$$

Electro-optic data are often presented as coefficients r_{pk} in the susceptibility ellipsoid. If n is the refractive index (assumed isotropic),

$$r_{pk} = -\frac{4\pi}{n^4} d^{\omega}_{pk} = -\frac{4\pi}{n^4} d^{\omega}_{ijk} = -\frac{8\pi}{n^4} d^{\omega\omega 0}_{ijk}. \tag{161}$$

The dimensions of d and r are those of an inverse field.

In the MKS system, the units are meters per volt, in the cgs system they are centimeters per stat-volt. One MKS unit is 3×10^4 esu and so numerical values of d in esu are the larger numbers.

We have not discussed the influence of a mixed use of rms and peak fields but we note that if rms fields are used throughout the values of the coefficients will all be $\sqrt{2}$ times larger than if peak fields are used throughout. No one is, however, likely to use an rms dc field.

Experimental values of the electro-optic coefficients are usually expressed in absolute units and the only ambiguity that can occur is associated with whether the measurements were made at constant stress (unclamped) or constant strain (clamped). It is safe to assume that constant stress is implied by the absence of any definite statement to the contrary.

Second harmonic coefficients are sometimes given in absolute units but more often relative to the coefficient $d^{2\omega}_{321}$ in KH_2PO_4. An absolute measurement of this by Ashkin, Boyd, and Diedzic[32] gave

$$d^{2\omega}_{321} = \tfrac{1}{2} d^{2\omega\omega\omega}_{321} = 3 \times 10^{-9} \text{ esu},$$

but this is now believed to be too large. The most recent measurements, Francois[5], Bjorkholm,[33] give

$$d^{2\omega}_{321} = \tfrac{1}{2} d^{2\omega\omega\omega}_{321} = 1.38 \times 10^{-9} \text{ esu} \pm 12 \text{ percent}$$

for the coefficient in $NH_4H_2PO_4$. Relative measurements show that it is identical in KDP and ADP. We have used a rounded off, compromise value

$$\text{KDP } d^{2\omega}_{321} = \tfrac{1}{2} d^{2\omega\omega\omega}_{321} = 1.5 \times 10^{-9} \text{ esu} \tag{162}$$

in compiling the tables. It affects all values of $d^{2\omega}$ at optical frequencies but not at 10.6 μ.

It will be apparent that in comparing theory or experiment with experiment, considerable care is needed to be sure that like definitions are being compared with like.

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