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CRITIQUE OF THE THEORY OF OPTICAL ACTIVITY OF HELICAL POLYMERS

By WILLIAM MOFFITT

DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY

AND

DONALD D. FITTS* AND JOHN G. KIRKWOOD

STERLING CHEMISTRY LABORATORY,† YALE UNIVERSITY

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1. *Introduction.*—In a series of recent articles,[1–4] we have severally attempted to use coupled-oscillator theory in order to understand the optical activity of polypeptides. This approach, the development of which stems from Born[5] and Kuhn,[6] was first used in quantum mechanics by Kirkwood[7] as the basis for his polarizability theory of rotatory power. In recent months we have been clarifying the relationship between our respective treatments, leaving out of account differences which stem from the specific means by which we have attained tractability. As a result, we have been able to show that a general formula, derived by Kirkwood[7] under special (nondegenerate) conditions which do not apply to polymers, has a wider range of validity and may also be used in the present context. But, paradoxically enough, we have thereby found an error in Moffitt's work,[3] one of the purposes of which was to acknowledge explicitly the degenerate nature of this problem.

In the following section, Kirkwood's formula is rederived under conditions appertaining to a sequence of identical residues. And in a final section this prescription is more specifically applied to helices. Some discussion is given of the way in which the result may be used. It appears that a particularly important factor $(A_{\sigma\sigma})$ is composed of two terms, one of which $(A_{\sigma\sigma}^{(1)})$ was correctly assessed by Moffitt, whereas the other $(A_{\sigma\sigma}^{(2)})$ was absent from his earlier derivation. The reason for this omission is analyzed and shown to originate, somewhat unexpectedly, in the failure of the Born–von Kármán boundary conditions which he had used in the course of his exciton treatment.

We are forced to conclude that the close agreement between the data presented by Moffitt and Yang,[8] and Moffitt's calculations for the α-helix,[4] is illusory and does not enable a definite screw sense to be assigned to these polypeptides. Moffitt's calculations were based on certain $A_{\sigma\sigma}^{(1)}$ terms alone, and our estimates indicate that the corresponding $A_{\sigma\sigma}^{(2)}$ contributions are of the same order but of opposite sign. However, since the qualitative form of the dispersion shown by the various partial rotations was correctly described in his work, this quantitative failure in no way vitiates the empirical correlations put forward by Moffitt and Yang; any

reservations we may have on this score have already been enumerated by these authors.

2. *Degenerate Coupled-Oscillator Theory.*—In this section we shall rederive Kirkwood's formula in such a way as to include, explicitly, the case of identical residues. It is convenient to use a modified form of the notation employed by Moffitt;[3] thus we adopt Section 2 of that paper, with only a change of phases (see below), and those parts of Section 3 which precede the paragraph containing equation (24). We shall avoid specifying the particular geometry of the polymer at this stage, so that our results are equally valid for random coils and for helices.

Our polymer therefore consists of an array of N identical residues, each of which is identified by a serial index m. The ground and excited states of the mth residue are represented by the real functions ψ_{0m} and $\psi_{\sigma m}$, respectively.[9] It is supposed that the interaction between different residues is sufficiently weak—or that the symmetry of the array is sufficiently high—that the respective excitation energies $\epsilon_{\sigma m} = \epsilon_\sigma$ are the same for all residues.

The ground state of the polymer as a whole is represented, in zeroth-order, by the simple product $\prod_m \psi_{0m}(\tau_m)$, which we call $|0)$; τ_m symbolizes the co-ordinates of the electrons associated with the mth residue.   At first, its excited states are also represented by simple products; if only one residue is excited ("fundamentals"),

$$| \sigma m) = | 0) (\psi_{0m})^{-1} \psi_{\sigma m}; \tag{1}$$

if two or more residues are excited ("overtones" and "combinations"),

$$\begin{aligned} | \sigma m \tau n) &= | 0) (\psi_{0m} \psi_{0n})^{-1} \psi_{\sigma m} \psi_{\tau n} \\ &\equiv | \tau n \sigma m), \qquad (n \neq m); \end{aligned} \tag{2}$$

and so on. Owing to the possibility of synchronizing the instantaneous charge distributions in different residues, these functions must be combined linearly to give the correct zeroth-order functions, namely,

$$\begin{aligned} | \sigma K) &= \sum_m | \sigma m) (\sigma m | \sigma K), \\ | \sigma \tau K) &= \sum_m \sum_{n \neq m} | \sigma m \tau n) (\sigma m \tau n | \sigma \tau U), \end{aligned} \tag{3}$$

where the concomitant transformations are all unitary and serve to diagonalize the Hamiltonian locally: typically,

$$(\sigma K | \mathcal{3C} | \sigma K') = E_{\sigma K} \delta_{KK'}. \tag{4}$$

The stationary states of the polymer, correct to first-order terms, are now represented by

$$\begin{aligned} |0\rangle &= | 0) + \sum_\rho \sum_\tau \sum_U | \rho \tau U) (\rho \tau U \| 0), \\ | \sigma K \rangle &= | \sigma K) + \sum_{\tau \neq \sigma} | \tau L) (\tau L \| \sigma K) + \sum_\tau \sum_\rho \sum_W | \sigma \tau \rho W) (\sigma \tau \rho W \| \sigma K), \end{aligned} \tag{5}$$

with similar expressions for the upper states of combinations bands.   Here

$$\begin{aligned} (\rho \tau U \| 0) &= -(\rho \tau U | \mathcal{3C} | 0)/(\epsilon_\rho + \epsilon_\tau), \\ (\tau L \| \sigma K) &= -(\tau L | \mathcal{3C} | \sigma K)/(\epsilon_\tau - \epsilon_\sigma), \\ (\sigma \tau \rho W \| \sigma K) &= -(\sigma \tau \rho W | \mathcal{3C} | \sigma K)/(\epsilon_\rho + \epsilon_\tau), \end{aligned} \tag{6}$$

and it has been assumed that the numerators are first-order small quantities with respect to the denominators.

We now compute, correct to first order, the matrix elements of a typical "one-electron" operator $\mathcal{P}$, such as the linear or angular momentum, corresponding to the excitation of a fundamental. Setting

$$
\begin{aligned}
V_{mn}{}^{\sigma\tau} &= (\tau n \,|\, \mathcal{3C} \,|\, \sigma m), \\
\mathcal{P}_{\sigma m} &= (0\,|\,\mathcal{P}\,|\,\sigma m) = (\sigma m\,|\,\mathcal{P}\,|\,0)^{*},
\end{aligned}
\tag{7}
$$

we find, after a little rearrangement, that

$$
\langle 0|\,\mathcal{P}\,|\,\sigma K\rangle = \sum_{m}\Big\{\mathcal{P}_{\sigma m} - \sum_{n\neq m} V_{mn}{}^{\sigma\sigma}\mathcal{P}_{\sigma n}{}^{*}/2\epsilon_{\sigma} \\
- \sum_{\tau\neq\sigma}\sum_{n\neq m} V_{mn}{}^{\sigma\tau}[\mathcal{P}_{\tau n}{}^{*}/(\epsilon_{\tau}+\epsilon_{\sigma}) + \mathcal{P}_{\tau n}/(\epsilon_{\tau}-\epsilon_{\sigma})]\Big\}\,(\sigma m\,|\,\sigma K). \tag{8}
$$

With our phase choice, we may enumerate two particular forms which this expression may take, depending on whether $\mathcal{P}_{\sigma m}$ is real or imaginary. If $\mathcal{P}$ is to represent the total linear momentum $\boldsymbol{P} = \sum_{m}\boldsymbol{p}_{m}$ (or, again, the total angular momentum $\boldsymbol{L}$), $\mathcal{P}_{\sigma m} = \boldsymbol{p}_{\sigma m}$ is imaginary and therefore

$$
\langle 0|\,\boldsymbol{P}\,|\,\sigma K\rangle = \sum_{m}\Big\{\boldsymbol{p}_{\sigma m} + \sum_{n\neq m}\boldsymbol{p}_{\sigma n}V_{mn}{}^{\sigma\sigma}/2\epsilon_{\sigma} \\
- 2\sum_{\tau\neq\sigma}\sum_{n\neq m} V_{mn}{}^{\sigma\tau}\boldsymbol{p}_{\tau n}\epsilon_{\sigma}/(\epsilon_{\tau}{}^{2}-\epsilon_{\sigma}{}^{2})\Big\}\,(\sigma m/\sigma K). \tag{9}
$$

On the other hand, taking $\mathcal{P} = \boldsymbol{Q} = \sum_{m}\boldsymbol{q}_{m}$, where $\boldsymbol{q}_{m}$ is the sum of the position vectors of all the electrons in residue m, we see that $\boldsymbol{q}_{\sigma m}$ is real, so that

$$
\langle 0|\,\boldsymbol{Q}\,|\,\sigma K\rangle = \sum_{m}\Big\{\boldsymbol{q}_{\sigma m} - \sum_{n\neq m}\boldsymbol{q}_{\sigma n}V_{mn}{}^{\sigma\sigma}/2\epsilon_{\sigma} \\
- 2\sum_{\tau\neq\sigma}\sum_{n\neq m} V_{mn}{}^{\sigma\tau}\boldsymbol{q}_{\tau n}\epsilon_{\tau}/(\epsilon_{\tau}{}^{2}-\epsilon_{\sigma}{}^{2})\Big\}\,(\sigma m/\sigma K). \tag{10}
$$

Since ψ_{0m}, $\psi_{\sigma m}$ are the eigenfunctions of a self-consistent field operator $\mathcal{3C}_{m}$,

$$
\boldsymbol{p}_{\sigma m} = (m_{e}/i\hbar)\epsilon_{\sigma}\boldsymbol{q}_{\sigma m}, \tag{11}
$$

where m_{e} is the electronic mass. Using this relation and the properties derived above, it is now easily verified that, correct to the first order,

$$
\langle 0|\,\boldsymbol{P}\,|\,\sigma K\rangle = (m_{e}/i\hbar)E_{\sigma K}\langle 0|\,\boldsymbol{Q}\,|\,\sigma K\rangle, \tag{12}
$$

where, for simplicity, we have taken as origin for the energy that of the ground state in zeroth-order. Thus the internal consistency of our model allows us to use with impunity either the dipole moment or the dipole velocity expressions relating to the optical properties of the polymer.

It is a straightforward matter at this stage to write down, correct to first-order, the rotational strength associated with any transition in the polymer. Since this quantity is the scalar product of two vector matrix elements, namely, of $\boldsymbol{Q}$ and of $\boldsymbol{L}$, it is clear that, to our approximation, at least one of these elements must be non-vanishing in zeroth-order. Accordingly, we may ignore the contributions from overtones and combinations, confining ourselves to the fundamentals whose rotational strengths are typified by

$$R_{\sigma K} = (e^2/2m_e c) Im [\langle 0| \mathbf{Q} | \sigma K \rangle \cdot \langle \sigma K | \mathbf{L} | 0 \rangle]. \qquad (13)$$

Since $\mathbf{L}$ is referred to a fixed origin, we write $\mathbf{L} = \sum_m \mathbf{k}_m$, preferring to reserve the symbol $\mathbf{l}_m$ for the angular momentum of the electrons of the mth residue, referred to an origin in that residue; we note that

$$\mathbf{k}_{\sigma m} \equiv (0| \mathbf{L} | \sigma m), \qquad (14)$$

like $\mathbf{p}_{\sigma m}$, is a pure imaginary vector. Accordingly,

$$R_{\sigma K} = (ie^2/2m_e c) \sum_m \sum_{m'} (\sigma m | \sigma K) (\sigma K | \sigma m')$$
$$\times \{ \mathbf{q}_{\sigma m} \cdot \mathbf{k}_{\sigma m'} + (2\epsilon_\sigma)^{-1} [\sum_{n \neq m'} \mathbf{q}_{\sigma m} \cdot \mathbf{k}_{\sigma n} V_{m'n}{}^{\sigma\sigma} - \sum_{n \neq m} \mathbf{q}_{\sigma n} \cdot \mathbf{k}_{\sigma m'} V_{mn}{}^{\sigma\sigma}]$$
$$- 2 \sum_{\tau \neq \sigma} (\epsilon_\tau{}^2 - \epsilon_\sigma{}^2)^{-1} [\sum_{n \neq m'} \mathbf{q}_{\sigma m} \cdot \mathbf{k}_{\tau n} \epsilon_\sigma V_{m'n}{}^{\sigma\tau} + \sum_{n \neq m} \mathbf{q}_{\tau n} \cdot \mathbf{k}_{\sigma m'} \epsilon_\tau V_{mn}{}^{\sigma\tau}] \}. \qquad (15)$$

The partial rotation, per residue, due to this transition is therefore

$$[m_{\sigma K}] = \left(\frac{\hbar c F_\nu}{e^2 N} \right) \frac{\nu^2 R_{\sigma K}}{(\nu_{\sigma K}{}^2 - \nu^2)}, \qquad (16)$$

where $\nu_{\sigma K} = E_{\sigma K}/hc$ is expressed in wave numbers and we have set

$$F_\nu = \frac{48 N_0 e^2}{\hbar^2 c^2} \left(\frac{n_\nu{}^2 + 2}{3} \right), \qquad (17)$$

N_0 being Avogadro's number and n_ν being the refractive index of the medium at frequence ν.

If the frequency of the incident light is not too close to $\nu_\sigma = \epsilon_\sigma/hc$, so that, for all K, $|\nu_\sigma - \nu| \gg |\nu_{\sigma K} - \nu_\sigma|$, then the contribution to the residue rotation from transitions to all states K in the exciton band $\psi_0 \rightarrow \psi_\sigma$ is proportional to

$$\frac{\nu^2 \sum_K R_{\sigma K}}{(\nu_\sigma{}^2 - \nu^2)} - \frac{2\nu^2 \nu_\sigma{}^2}{(\nu_\sigma{}^2 - \nu^2)^2} \sum_K R_{\sigma K} (E_{\sigma K} - \epsilon_\sigma)/\epsilon_\sigma.$$

The summation in the first term reduces to

$$(ie^2/2m_e c) \sum_m \{ \mathbf{q}_{\sigma K} \cdot \mathbf{k}_{\sigma m} - 2 \sum_{\tau \neq \sigma} \sum_{n \neq m} (\epsilon_\tau{}^2 - \epsilon_\sigma{}^2)^{-1} V_{mn}{}^{\sigma\tau}$$
$$\times (\epsilon_\sigma \mathbf{q}_{\sigma m} \cdot \mathbf{k}_{\tau n} + \epsilon_\tau \mathbf{q}_{\tau m} \cdot \mathbf{k}_{\sigma m}) \},$$

and, dropping second-order terms, the summation in the second becomes

$$(ie^2/2m_e c) \epsilon_\sigma{}^{-1} \sum_m \sum_{m'} \mathbf{q}_{\sigma m} \cdot \mathbf{k}_{\sigma m'} \sum_K (\sigma m | \sigma K) \langle \sigma K | \mathcal{K} - \epsilon_\sigma | \sigma K \rangle (\sigma K | \sigma m').$$

Since $\mathcal{K}$ is locally diagonal, the last line is just

$$\sum_K \sum_{K'} (\sigma m | \sigma K) \langle \sigma K | \mathcal{K} - \epsilon_\sigma | \sigma K' \rangle (\sigma K' | \sigma m') = (\sigma m | \mathcal{K} - \epsilon_\sigma | \sigma m') = V_{mm'}{}^{\sigma\sigma}$$

which vanishes if $m = m'$. Accordingly, the summation in the second term becomes

$$(ie^2/2m_e c) \sum_m \sum_{n \neq m} \epsilon_\sigma{}^{-1} V_{mn}{}^{\sigma\sigma} \mathbf{q}_{\sigma m} \cdot \mathbf{k}_{\sigma n}.$$

As a last transformation, we now put

$$k_{\sigma m} = l_{\sigma m} + r_m \times p_{\sigma m} = l_{\sigma m} + (m_e \epsilon_\sigma / i\hbar) r_m \times q_{\sigma m}, \tag{18}$$

where $l_{\sigma m}$ is the appropriate vector matrix element of the angular momentum referred to a point r_m, fixed in the mth residue.

The partial rotation $[m_\sigma]$ may therefore be written as follows:

$$[m_\sigma] = [m_{\sigma i}] + [m_{\sigma j}] + [m_{\sigma h}] + [m_{\sigma h'}] + [m_{\sigma j'}], \tag{19}$$

where

$$[m_{\sigma i}] = \left(\frac{i\hbar F_\nu}{2m_e N}\right) \frac{\nu^2}{(\nu_\sigma{}^2 - \nu^2)} \sum_m q_{\sigma m} \cdot l_{\sigma m},$$

$$[m_{\sigma j}] = -\left(\frac{F_\nu}{N}\right) \frac{\nu^2}{(\nu_\sigma{}^2 - \nu^2)} \sum_m \sum_{n \neq m} \sum_{\tau \neq \sigma} \frac{\epsilon_\sigma \epsilon_\tau}{(\epsilon_\tau{}^2 - \epsilon_\sigma{}^2)} V_{mn}{}^{\sigma \tau} (r_m - r_n) \cdot (q_{\sigma m} \times q_{\tau n}),$$

$$[m_{\sigma h}] = -\frac{1}{2}\left(\frac{F_\nu}{N}\right) \frac{\nu^2 \nu_\sigma{}^2}{(\nu_\sigma{}^2 - \nu^2)^2} \sum_m \sum_{n \neq m} V_{mn}{}^{\sigma\sigma} (r_m - r_n) \cdot (q_{\sigma m} \times q_{\sigma n}), \tag{20}$$

$$[m_{\sigma h'}] = -\left(\frac{i\hbar F_\nu}{m_e N}\right) \frac{\nu^2 \nu_\sigma{}^2}{(\nu_\sigma{}^2 - \nu^2)} \sum_m \sum_{n \neq m} \epsilon_\sigma{}^{-1} V_{mn}{}^{\sigma\sigma} q_{\sigma m} \, l_{\sigma n},$$

$$[m_{\sigma j'}] = -\left(\frac{i\hbar F_\nu}{m_e N}\right) \frac{\nu^2}{(\nu_\sigma{}^2 - \nu^2)} \sum_m \sum_{n \neq m} \sum_{\tau \neq \sigma} (\epsilon_\tau{}^2 - \epsilon_\tau{}^2)^{-1} V_{mn}{}^{\sigma\tau}$$
$$\times (\epsilon_\sigma q_{\sigma m} \cdot l_{\tau n} + \epsilon_\tau q_{\tau n} \cdot l_{\sigma m})$$

$[m_{\sigma i}]$ represents the intrinsic partial rotations of the individual residues, whose electrons are subject to slightly asymmetric Hartree fields, arising from any asymmetric centers they may possess or from their polymeric environment. If the transition $\psi_0 \rightarrow \psi_\sigma$ is associated with a large change in magnetic moment, and therefore a small dipole moment,[10] it is said to have a high dissymmetry factor;[11] for such bands, $[m_{\sigma i}]$ dominates the partial rotation, and the remaining terms in $[m_\sigma]$ may safely be dropped. $[m_{\sigma j}]$, which shows the same dispersive behavior as $[m_{\sigma i}]$, arises from the first-order corrections, $\{| \rangle - |)\}$, due to the correlative interaction between states in different exciton bands.   For strong electronic bands, this term can be large; in general, it is of the same order as $[m_{\sigma i}]$, though, in coupled-oscillator theory, one is inclined to hope that it outweighs $[m_{\sigma i}]$.   The third contribution, namely, $[m_{\sigma h}]$, shows different dispersion and is a unique feature of the degenerate case; it arises from the correlative interaction between different residues, within the same exciton band.   It was at this term that Moffitt attempted to direct attention.[3]   The last two terms $[m_{\sigma h'}]$ and $[m_{\sigma j'}]$, are small with respect to their imprimed counterparts, namely, $[m_{\sigma h}]$ and $[m_{\sigma j}]$, by a factor $d_\sigma / |r_m - r_n|$, where d_σ is the distance of r_m from the partial optic axis of the transition $\psi_{0m} \rightarrow \psi_{\sigma m}$.[3] Following Kirkwood,[7] we therefore drop both of these.

It may be noticed that, on summing over all exciton bands, the residue rotation may now be written

$$[m] = \sum_\sigma [m_\sigma] = \sum_\sigma [m_{\sigma i}]$$
$$+ \frac{1}{N} F_\nu \sum_m \sum_{n > m} \sum_\sigma \sum_\tau \frac{\nu^2 \nu_\sigma \nu_\tau V_{mn}{}^{\sigma\tau}}{(\nu_\sigma{}^2 - \nu^2)(\nu_\tau{}^2 - \nu^2)} (r_n - r_m) \cdot (q_{\sigma m} \times q_{\tau n}), \tag{21}$$

where, by combining the $[m_{\sigma j}]$ and $[m_{\sigma h}]$ contributions, we have removed the restriction $\tau \neq \sigma$ from the summation over τ.   Since $\nu_\sigma = \nu_{\sigma m}$, $\nu_\tau = \nu_{\tau n}$ for all m, n,

it will be recognized that this formula is identical with that obtained by Kirkwood.[7] But, whereas the validity of the original derivation was confined to the nondegenerate case, we see that this restriction has been removed by the present treatment. If $V_{mn}{}^{\sigma\tau}$ is replaced by an appropriate dipole-dipole approximation, the more particular results of the polarizability theory follow immediately.

3. *Application to Helices.*—Let us now specialize our discussion and suppose that the successive residues are arranged to form a right-handed helix. The monomers may then be located by the equivalent points r_m in each, namely, by

$$r_m = \rho \cos \alpha_m \, i + \rho \sin \alpha_m \, j + mZk, \tag{22}$$

where P is the number of residues per turn (and not necessarily integral), PZ is the pitch of the helix, and $\alpha_m = 2\pi m/P$. Similarly, we may put $q_{\sigma m} = |q_\sigma| e_{\sigma m}$, where $e_{\sigma m}$ is a unit vector whose radial, tangential, and vertical components, relative to the circumscribed cylinder, are $e_{\sigma r}$, $e_{\sigma t}$, and $e_{\sigma v}$, respectively:

$$e_{\sigma m} = (e_{\sigma r} \cos \alpha_m - e_{\sigma t} \sin \alpha_m)i + (e_{\sigma r} \sin \alpha_m + e_{\sigma t} \cos \alpha_m)j + e_{\sigma v}k. \tag{23}$$

We suppose the helix is sufficiently long that we may neglect end effects. To simplify the discussion, we confine our attention to two transitions, $\psi_0 \to \psi_1$ and $\psi_0 \to \psi_2$, say, supposing that contributions from these dominate the residue rotation. The optical rotatory dispersion is then described by

$$[m] = \left\{ [m_{1i}] + \frac{\nu^2 \nu_1 \nu_2 (A_{12} + A_{21})}{(\nu_1{}^2 - \nu^2)(\nu_2{}^2 - \nu_1{}^2)} \right\} + \frac{\nu^2 \nu_1{}^2 A_{11}}{(\nu_1{}^2 - \nu^2)^2}$$
$$+ \left\{ [m_{2i}] + \frac{\nu^2 \nu_2 \nu_1 (A_{21} + A_{12})}{(\nu_2{}^2 - \nu^2)(\nu_1{}^2 - \nu_2{}^2)} \right\} + \frac{\nu^2 \nu_2{}^2 A_{22}}{(\nu_2{}^2 - \nu^2)^2}, \tag{24}$$

or, equivalently, by

$$[m] = [m_{1i}] + [m_{2i}]$$
$$+ \left\{ \frac{\nu^2 \nu_1{}^2 A_{11}}{(\nu_1{}^2 - \nu^2)^2} + \frac{\nu^2 \nu_1 \nu_2 (A_{12} + A_{21})}{(\nu_1{}^2 - \nu^2)(\nu_2{}^2 - \nu^2)} + \frac{\nu^2 \nu_2{}^2 A_{22}}{(\nu_2{}^2 - \nu^2)^2} \right\}, \tag{25}$$

where

$$A_{\sigma\tau} = F_\nu \sum_{n(>m)} V_{mn}{}^{\sigma\tau}(r_n - r_m) \cdot (q_{\sigma m} \times q_{\tau n}). \tag{26}$$

In making a theoretical analysis of the "observed" dispersion curves for such an idealized system, one may adopt several different viewpoints which it is as well to enumerate.

It should be recognized, first of all, that the calculation of terms involving $A_{\sigma\tau}$ presents a very different problem from that of computing the $[m_{\sigma i}]$'s. The so-called one-electron theory[11] is primarily concerned with the latter task, whereas the coupled-oscillator theory is best suited to the former. For the present, we cannot attempt to assess the intrinsic rotatory parameters and are forced to regard these as outside the scope of our work. We are therefore faced with two alternatives.

On the one hand, we may hope that the $[m_{\sigma i}]$'s are appreciably smaller than the coupled-oscillator terms. In this case, we attribute the main part of the optical rotation to those terms of equation (25) which have been inclosed in braces. We

then base our calculations on the polarizability theory or make some other use of the optical properties of the individual residues—in particular, of their absorption spectra. This approach has been adopted by Fitts and Kirkwood in their work on polypeptides.[1, 2]

Alternatively, we may observe that $[m_{1i}]$ shows the same frequency dependence, namely, $\nu^2/(\nu_1{}^2 - \nu^2)$, as the term accompanying it in braces in equation (24); and similarly for $[m_{2i}]$. The other two terms, which involve A_{11} and A_{22}, show an unusual dispersive behavior, however. We may therefore hope, on the basis of the observed frequency dependence, to distinguish between these two different sets of dispersive terms. Adopting this approach, we attempt empirically to separate contributions to the rotation due to the terms in braces from those due to the remainder of equation (24). The latter are amenable to calculation, and we are enabled to avoid the $[m_{\sigma i}]$ difficulty without having to neglect it. This avenue has been explored by Moffitt and Yang[3] in the present context.

It should perhaps be added that neither method is very satisfactory. Thus it may be questioned whether the existing data actually succeed in separating the abnormally dispersing terms from their normal counterparts. And, again, it is by no means clear that the $[m_{\sigma i}]$'s make a negligible contribution to the observed rotation. However, while making these reservations, we continue to pursue such work, since it is unlikely that progress is to be made in any other way.

Returning to the helical problem, we evaluate $A_{\sigma\sigma}$ by using equations (22) and (23). It is found that

$$
\begin{aligned}
A_{\sigma\sigma} &= A_{\sigma\sigma}{}^{(1)} + A_{\sigma\sigma}{}^{(2)}, \\
A_{\sigma\sigma}{}^{(1)} &= -4F_\nu |q_\sigma|^2 \rho e_{\sigma t} e_{\sigma v} \sum_{n(>m)} V_{mn}{}^{\sigma\sigma} \sin^2 [\pi(n-m)/P], \\
A_{\sigma\sigma}{}^{(2)} &= F_\nu |q_\sigma|^2 Z(e_{\sigma r}{}^2 + e_{\sigma t}{}^2) \sum_{n(>m)} (n-m) V_{mn}{}^{\sigma\sigma} \sin [2\pi(n-m)/P]. \quad (27)
\end{aligned}
$$

This expression for $A_{\sigma\sigma}$ should be compared with that derived by Moffitt,[3] under the same assumptions. (It will be recalled that this term arises from correlative interactions within the same exciton band and is therefore directly related to the correct zeroth-order functions $|\sigma K\rangle$.) He found only the term $A_{\sigma\sigma}{}^{(1)}$, so that his analysis is in error. Since his mistake is rather interesting, we shall conclude by showing how it arose.

Moffitt considered the helix as a one-dimensional crystal and employed exciton theory. By this method, the coefficients $(\sigma m/\sigma K)$ of equation (3), which determine the correct zeroth-order functions, are evaluated by adopting the Born–von Kármán cyclic condition, which leads to

$$
(\sigma m | \sigma K) = N^{-1/2} \exp (2\pi i m K/N), \quad (28)
$$

where K runs from 1 to N, the total number of residues. The procedure is standard in the treatment of the optical properties of molecular crystals, as well as in almost all of crystal physics. It is not, however, quite correct, when the crystal is not in fact re-entrant.

It is easy to see that the error incurred in the calculation of $(0 | Q | \sigma K)$ by adopting this boundary condition is of order $N^{-1/2}$, although the main part of this term is of order $N^{1/2}$ and correctly given. In computing oscillator strengths per residue, which are proportional to $N^{-1} |(0 | Q | \sigma K)|^2$, the error is therefore of order N^{-1},

which is indeed negligible.   However, in the present context, we wish to compute rotational strengths per residue, which are proportional to $N^{-1}(0|\boldsymbol{Q}|\sigma K)|(\sigma K|\boldsymbol{L}|0)$. Now $(\sigma K|\boldsymbol{L}|0)$ involves the moments of the electronic displacements about some fixed (but arbitrary) point in the molecule; it therefore contains terms of order $N^{3/2}$ as well as of order $N^{1/2}$.   (The former were innocuously symbolized by $N^{1/2}\alpha_\sigma$, $N^{1/2}\beta_\sigma$ in Moffitt's equations [48],[3] although, since the difficulty was not foreseen, they were not explicitly evaluated.)   The scalar product of the $N^{1/2}$ terms of $(\sigma K|\boldsymbol{L}|0)$ taken with the $N^{1/2}$ terms of $(0|\boldsymbol{Q}|\sigma K)$ vanishes identically—as, clearly, it must, because the residue rotation is not proportional to the number of residues. The predominant $N^{1/2}$ terms of $(0|\boldsymbol{Q}|\sigma K)$ and the $N^{1/2}$ terms of $(\sigma K|\boldsymbol{L}|0)$ yield a contribution to the residue rotation of order unity, namely, the term involving $A_{\sigma\sigma}^{(1)}$.   But the scalar product of the $N^{-1/2}$ errors of the former taken with the $N^{3/2}$ terms of the latter does not vanish and is therefore of order N; this again leads to a contribution of order unity to the residue rotation, namely, the neglected term $A_{\sigma\sigma}^{(2)}$.   It may be noticed that the $N^{3/2}$ terms of $(\sigma K|\boldsymbol{L}|0)$ can involve only perpendicularly polarized components of $\boldsymbol{q}_\sigma$, whose cylindrical direction cosines are $e_{\sigma r}$ and $e_{\sigma t}$.   These large moments are also perpendicularly directed, so that the neglected term cannot involve the vertical component $e_{\sigma v}$.   Looking at equations (27), it is therefore clear why $A_{\sigma\sigma}^{(1)}$ was correctly assessed but $A_{\sigma\sigma}^{(2)}$ was missing.

We may conclude that whereas the application of the Born–von Kármán boundary conditions leads to a correct picture of the spectra of molecular crystals, they may not be used with impunity.   In particular, they fail to give an accurate account of the optical rotatory properties of long helices.

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† Contribution No. 1421.

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[9] In the paper referred to in n. 3, the $\psi_{\sigma m}$ were defined to be pure imaginaries, so that the vectors used in discussing the properties of partial optic axes should all be real.

[10] For small groups the presence of a large magnetic moment virtually precludes a large electric moment and vice versa.

[11] Cf. E. U. Condon, *Rev. Mod. Phys.*, **9**, 432, 1937.