puted spin densities are given in Table I.

Since the lower value of D to be associated with increased π delocalization would be expected to move the line to lower magnetic field, parallel changes of H and ρ^N are expected. For the phenyl, biphenylyl, naphthyl, and anthryl nitrenes, H is almost linearly related to both the SCF and Hückel spin densities. Benzenesulfonyl nitrene fits well if one assumes $\rho^N = 1$. For nitro and methoxyphenyl nitrenes, H has the same order as ρ^N_{asa}. Only the SCF spin densities agree with the slight shifts to higher fields observed with the meta derivatives.

More fruitful comparisons will be possible when D and E are accurately known. However, the main features of the correlation are unlikely to be altered. The isoelectronic aromatic methylenes, appear to be more suited for abstraction of these parameters and substituent effects in these are being investigated.[12]

TABLE I. Nitrogen π-electron spin density and the $\Delta m = 1$ line position for nitrenes.

Nitrene	H obs.	ρ^N_{asa}	ρ^N_k
benzenesulfonyl	7795	[1.0][c]	[1.0][c]
3-nitrophenyl	6857	0.760	0.571
3-methoxyphenyl[a,b]	6713	0.754	0.571
phenyl[a]	6701	0.752	0.571
4-nitrophenyl	6671	0.747	0.540
4-methoxyphenyl[a]	6618	0.729	0.513
4-biphenylyl	6526	0.739	0.516
2-naphthyl	6435	0.729	0.529
1-naphthyl[a]	6130	0.660	0.450
2-anthryl	6077	0.690	0.471
1-anthryl[a]	5754	0.610	0.381

[a] A $\Delta m = 2$ line is observed near 1620 G.
[b] Two lines are observed.
[c] An assumed spin density.

[12] R. W. Murray, L. C. Snyder, A. M. Trozzolo, and E. Wasserman (to be published).

REVIEWS OF MODERN PHYSICS VOLUME 35, NUMBER 3 JULY 1963

Optical Rotation

DENNIS J. CALDWELL AND HENRY EYRING
Department of Chemistry, University of Utah, Salt Lake City, Utah

THROUGHOUT the brief history of quantum-mechanical optical rotation theory there have developed two trends: exact, but lengthy, perturbation theory calculations applied to individual molecules, and less precise, but more general, calculations based on approximate expressions for the interaction between charges. Although the second method has led to the derivation of relatively simple formulas with wide generality, it has had only limited success in predicting signs and magnitudes of the optical rotation. The more exact calculations, on the other hand, have enjoyed a marked degree of success in predicting these quantities. In the following section we outline a method, which it is hoped, will embody the simplicity of the one and the precision of the other.

If one assumes isolated groups interacting through space and applies first-order perturbation theory to the appropriate zeroth-order wave functions in conjunction with the Rosenfeld[1] equation:

$$\beta = \frac{2}{3\pi}\sum_A \frac{R_A}{\nu_{OA}^2 - \nu^2} = \frac{2}{3\pi}\sum_A \mathrm{Im}\,\frac{\mathbf{p}_{OA}\cdot\mathbf{m}_{AO}}{\nu_{OA}^2 - \nu^2}, \quad (1)$$

one obtains[2]

$$\begin{aligned} R_A = \mathrm{Im}\,\mathbf{p}_{ioa}\cdot\mathbf{m}_{ioa} \quad & 2\sum_{j\neq i}\sum_{b\neq a} \\ \times & \frac{\mathrm{Im}\,V_{ioa;job}(\mathbf{p}_{ioa}\cdot\mathbf{m}_{jbo}\nu_a + \mathbf{p}_{job}\cdot\mathbf{m}_{iao}\nu_b)}{h(\nu_b^2 - \nu_a^2)} \\ - & \sum_{j\neq i}\sum_{b\neq a}\frac{\mathrm{Im}\,V_{iab;joo}(\mathbf{p}_{ioa}\cdot\mathbf{m}_{ibo} + \mathbf{p}_{iob}\cdot\mathbf{m}_{iao})}{h(\nu_b - \nu_a)} \\ - & \sum_{j\neq i}\sum_{b\neq a}\frac{\mathrm{Im}\,V_{iob;joo}(\mathbf{p}_{ioa}\cdot\mathbf{m}_{iab} + \mathbf{p}_{iab}\cdot\mathbf{m}_{iao})}{h\nu_b} \\ - & \sum_{j\neq i}\frac{\mathrm{Im}\,V_{ioa;joo}(\mathbf{p}_{iaa} - \mathbf{p}_{ioo})\cdot\mathbf{m}_{iao}}{h\nu_a} \\ - & \frac{2\pi}{c}\sum_{j\neq i}\sum_{b\neq a}\frac{V_{ioa;job}\nu_a\nu_b(\mathbf{R}_j - \mathbf{R}_i)\cdot(\mathbf{p}_{job}\times\mathbf{p}_{ioa})}{h(\nu_b^2 - \nu_a^2)}, \end{aligned} \quad (2)$$

where R_A is the rotational strength of the Ath transition in the molecule; $\mathbf{p}_{OA}$, $\mathbf{m}_{AO}$ are the electric and magnetic dipole moments of transitions in the molecule as a whole; $\mathbf{p}_{oa}$, $\mathbf{p}_{ob}$, $\mathbf{m}_{ao}$, $\mathbf{m}_{bo}$ are the electric and magnetic dipole moments of transitions in individual groups; ν_a, ν_b are group transition frequencies; $V_{ioa,job}$, etc. $= \int \psi_{io}\psi^*_{ia}\psi_{jo}\psi_{jb}V_{ij}d\psi_i d\psi_j$; and V_{ij} is the interaction between groups i and j.

The above equation gives the contribution of a single transition in a particular group of the molecule

[1] L. Rosenfeld, Z. Physik **52**, 161 (1928).

[2] I. Tinoco, Advan. Chem. Phys. **4**, 113 (1962).

to the total molecular rotation. It consists of the interaction of the transition under consideration, generally confined to a particular group, with all of the other transitions in the molecule both within the same group and in other groups. These interactions give rise to five types of terms. In Eq. (2) the first term is seen to measure the partial rotation of a transition in an isolated group and is, of course, zero unless the group itself is dissymmetric.

The second term arises from the interaction of an electric dipole transition in one group with a magnetic dipole transition in another. It may properly be called a coupled oscillator term, since it indicates a simultaneous motion of electrons in both groups.

The third and fourth terms are due to the interaction of electric and magnetic dipole transitions within the same group in the static or average field of the other groups. These are the one-electron terms, the third term coming from the perturbation of the excited states and the fourth from the perturbation of the ground state. Most investigators neglect the latter term due to the larger denominator $h\nu_b$ and the smaller interaction matrix element $V_{iob;joo}$; however, it is not always an order of magnitude lower than the former.

The fifth term measures the interaction between magnetic transitions and permanent dipole moments within the same group in the static field of the other groups. It is usually neglected for the same reasons as the preceding term. The last term accounts for the interactions of the electric dipole transitions of one group with those of all the others and is, again, a coupled oscillator term involving a simultaneous change in the electron distribution of both groups.

A detailed evaluation of any one of these terms is a formidable task and it would indeed be providential if one of them predominated over the others.

The third term is the only one which has ever been evaluated exactly for a given model, whereas the second and sixth have been evaluated approximately giving rise to concise expressions for the rotation in terms of molecular geometry and group polarizabilities, the most notable being the Kirkwood[3] formula. Although the exact evaluation of the third term in the manner of Kauzmann and Eyring[4] has provided very encouraging results, any model should include an exact evaluation of all terms to insure nothing has been neglected.

It is in the emphasis and the evaluation of the terms of Eq. (2) that the various theories of optical rotation have differed. In addition to the original literature, there are many excellent reviews[4-6] on the subject of past work in this field. In what follows we outline a program for determining the principal effect in optically active molecules and for obtaining relatively simple general expressions for the rotatory parameter.

It is generally agreed that the rotation arises from one or all of three terms in Eq. (2), the second, the third, and the sixth. The second and sixth terms account for the electronic motion induced in one group by that which has been induced in another by a light wave. The third term accounts for the alteration in the electronic paths of one group due to the average field of another. At this point, it is not apparent which effect, if any, will predominate. Accordingly, the first task is the selection of a tractable model which will lead to relatively simple and reasonably accurate expressions for the terms of Eq. (2).

The tractability of any particular model will depend on the form of the interaction potential between groups V_{ij}. If either a monopole or multipole expansion is used, one can sometimes develop formulas without explicitly representing the wave functions. The matrix elements involved consist of integrals of polynomials in the electronic coordinates multiplied by the appropriate wave functions and are relatively easy to evaluate.

If no such expansions are used, the computations are more difficult and wave functions suitable for the purpose are more limited. If one considers the fact that in most common optically active molecules the sum of average radii of the outer electron orbits in two groups is little smaller than the distance between them, it will be realized that the rapid convergence of a multipole expansion of the potential may not necessarily be relied upon.

From the above considerations it should be fruitful to explore the possible models which are amenable to such exact evaluations of the various integrals in Eq. (2). Of the feasible approaches two possibilities emerge, the use of harmonic oscillator wave functions or hydrogenlike wave functions.

In principle, the harmonic oscillator embodies all of the properties of any typical group. These group properties may be expressed in terms of the three force constants K_x, K_y, and K_z. For example, the polarizability at frequency v is given by

$$\alpha_z = \frac{e^2}{K_z - (2\pi)^2 m\nu^2}. \tag{3}$$

[3] J. G. Kirkwood, J. Chem. Phys. **5**, 479 (1937).
[4] W. J. Kauzmann, J. E. Walter, and H. Eyring, Chem. Rev. **3**, 339 (1940).
[5] E. U. Condon, Rev. Mod. Phys. **9**, 432 (1937).
[6] A. Moscowitz, Advan. Chem. Phys. **4**, 67 (1962).

The first-order expression for the polarizability consists of one term and, whenever one uses an harmonic oscillator model for a group, he is tacitly assuming that the group polarizability may be approximated by a one-term expansion. In most cases, this is not an unreasonable assumption. Since the force constants may be expressed in terms of physical constants, the final equation for the rotatory parameter of such a model will contain quantities expressible in terms of the physical constants of the individual groups.

Although the integrals which arise from this treatment are not prohibitively difficult, the approximations which would be required to express the final result in a useful form are of such a nature as to suggest a parallel approach.

In the most general case, a group will be anistropic and will possess an infinite series of electric and magnetic dipole transitions. In any given region of the spectrum the major contribution to the rotation will be accounted for by only a few of these transitions. Since certain approximations will inevitably be involved, it is possible to retain the advantages of the harmonic oscillator treatment in a hydrogenlike orbital treatment with the further important advantage that the integrals are much more tractable. In considering the role of electric transitions, one is no worse off in assuming that only the first term of the series for the polarizability need be considered, than in assuming a model in which the series consists of a single term.

We will, accordingly, carry out this investigation with hydrogenlike wave functions. There will be two cases to consider, one in which a group has a magnetic dipole transition near the visible and one in which it does not. It is necessary to recognize that the properties of a group such as polarizability computed from wave functions tailored to represent a particular transition important to the optical rotation may differ markedly from the experimental values. This means that a wave function which is satisfactory for a group in its capacity as a chromophore may not adequately give its effect as a vicinal group.

In the second and sixth terms of Eq. (2) both groups are acting in the capacity of chromophores, since transition moments in both occur in these terms. In the third, fourth, and fifth terms one group behaves as a chromophore and the other as a vicinal group. The methods for handling these two types of terms will differ somewhat.

In the treatment of actual molecules and groups one is hampered by a lack of knowledge of the complete spectrum. As a result one must search for a way of using all of the information that is available to the best possible advantage. First, all of the electric and magnetic dipole transitions which are known to occur in the group should be tabulated.

We shall have occasion to distinguish between particular state wave functions and average state wave functions. All of these states connected by well-defined electric or magnetic dipole transitions near the visible should be described by particular state wave functions. The second and third terms of Eq. (2) will be used exclusively for those cases in which one or both of the interacting transitions are well known. The sixth term of Eq. (2) may be evaluated, in part, by particular state wave functions and by average state functions depending on the form of the final result, as will be seen below.

To illustrate, the most general case will be outlined: the optical rotation arising from the interaction of two groups one of which has a magnetic dipole transition near the visible and the other of which has an electric dipole transition in this region. In addition to those two transitions, both groups will be assumed to have an array of electric dipole transitions in the ultraviolet. In the course of the calculation the following hydrogenlike wave functions will be used:

$\psi_{Ao}^{(m)}$, $\psi_{Aa}^{(m)}$—the ground- and excited-state wave functions for the magnetic dipole transition in group A;

$\psi_{Bo}^{(p)}$ $\psi_{Bb}^{(p)}$—the ground- and excited-state wave functions for the electric dipole transition in group B;

$\psi_{Ao}^{(P)}, \psi_{Ax}^{(P)}, \psi_{Ay}^{(P)}, \psi_{Az}^{(P)}$—the average state ground- and excited-state wave functions describing the overall behavior of *all* electric dipole transitions in group A;

$\psi_{Bo}^{(P)}$, $\psi_{Bx}^{(P)}$, $\psi_{By}^{(P)}$, $\psi_{Bz}^{(P)}$—the corresponding average wave functions for group B;

$\psi_{Ak}^{(p)}$—the hydrogenlike wave function with the same Z as $\psi_{Aa}^{(m)}$ and $n' = n + 1$ which has an electric moment between itself and $\psi_{Ao}^{(m)}$ parallel to $\mathbf{m}_{oa}^{(A)}$;

$\psi_{Bl}^{(m)}$—the hydrogenlike wave function with the same n as $\psi_{Bo}^{(p)}$ and $Z' < Z$ which has a magnetic moment between itself and $\psi_{Bo}^{(p)}$ parallel to $\mathbf{p}_{ob}^{(B)}$.

In addition, let N_A be number of electrons in outer shell of group A; N_B be number of electrons in outer shell of group B; n_A be quantum number of the outer shell of group A; n_B be quantum number of the outer shell of group B; ν_{Aoa}, ν_{Bob} be the frequencies of the magnetic and electric dipole transitions in question; $I_A^{(m)}$ be the ionization energy of the electron involved in the magnetic dipole transition of group A; $I_B^{(p)}$ be the ionization energy of the electron involved in the

electric dipole transition of group B; α_A, β_A be the average polarizability and anisotropy factor of group A; α_B, β_B be the average polarizability and anisotropy factor of group B.

Then explicit expressions for the above wave functions may be written in terms of these quantities.

$$\psi_{Ao}^{(m)} = \frac{1}{\pi^{\frac{1}{2}}}\left(\frac{Z_{Ao}}{n_A a_0}\right)^{\frac{3}{2}} y_A e^{-Z_{Ao}r_A/n_A a_0}, \tag{4a}$$

$$\psi_{Aa}^{(m)} = \frac{1}{\pi^{\frac{1}{2}}}\left(\frac{Z_{Aa}}{n_A a_0}\right)^{\frac{3}{2}} x_A e^{-Z_{Aa}r_A/n_A a_0}, \tag{4b}$$

$$\psi_{Ak}^{(p)} = \left(\frac{2}{3\pi}\right)^{\frac{1}{2}}\left[\frac{Z_{Aa}}{(n_A+1)a_0}\right]^{\frac{7}{2}} y_A z_A e^{-Z_{Aa}r_A/(n_A+1)a_0}, \tag{4c}$$

$$\psi_{Bo}^{(p)} = \frac{1}{\pi^{\frac{1}{2}}}\left[\frac{Z_{Bo}}{n_B a_0}\right]^{\frac{5}{2}} y_B e^{-Z_{Bo}r_B/n_B a_0}, \tag{4d}$$

$$\psi_{Bb}^{(p)} = \left(\frac{2}{3\pi}\right)^{\frac{1}{2}}\left[\frac{Z_{Bo}}{(n_B+1)a_0}\right]^{\frac{7}{2}} y_B z_B e^{-Z_{Bo}r_B/(n_B+1)a_0}, \tag{4e}$$

$$\psi_{Bl}^{(m)} = \frac{1}{\pi^{\frac{1}{2}}}\left(\frac{Z_{Bl}}{n_B a_0}\right)^{\frac{5}{2}} x_B e^{-Z_{Bl}r_B/n_B a_0}, \tag{4f}$$

$$\psi_{Ao}^{(P)} = \frac{1}{\pi^{\frac{1}{2}}}\left(\frac{Z_{AP}}{n_A a_0}\right)^{\frac{3}{2}} e^{-Z_{AP}r_A/n_A a_0}, \tag{4g}$$

$$\psi_{Ax,y,z}^{(P)} = \frac{1}{\pi^{\frac{1}{2}}}\left[\frac{Z_{AP}}{(n_A+1)a_0}\right]^{\frac{5}{2}} (x_A,y_A,z_A) e^{-Z_{AP}r_A/(n_A+1)a_0}, \tag{4h}$$

$$\psi_{Bo}^{(P)} = \frac{1}{\pi^{\frac{1}{2}}}\left(\frac{Z_{BP}}{n_B a_0}\right)^{\frac{3}{2}} e^{-Z_{BP}r_B/n_B a^0}, \tag{4i}$$

$$\psi_{Bx,y,z}^{(P)} = \frac{1}{\pi^{\frac{1}{2}}}\left[\frac{Z_{BP}}{(n_B+1)a_0}\right]^{\frac{5}{2}} (x_B,y_B,z_B) e^{-Z_{BP}r_B/(n_B+1)a_0}. \tag{4j}$$

The optical rotation will be given in terms of the quantities Z_{Ao}, Z_{Aa}, Z_{Bo}, Z_{Bl}, Z_{AP}, and Z_{BP}, which, in turn, will be functions of certain physical properties of the groups. Although further refinements may well become necessary, the following relationships appear useful in the initial treatment of the problem:

$$Z_{Ao}^2 = \frac{2a_0 n_A^2 I_A^{(m)}}{e^2}, \tag{5a}$$

$$Z_{Ao}^2 - Z_{Aa}^2 = \frac{2a_0 n_A^2 h\nu_{AOa}}{e^2}, \tag{5b}$$

$$Z_{Bo}^2 = \frac{2a_0 n_B^2 I_B^{(P)}}{e^2}, \tag{5c}$$

$$Z_{AP} = \frac{8a_0 n_A^2 (n_A+1)^2}{(2n_A+1)^3}\left[\frac{N_A(2n_A+1)n_A}{(n_A+1)a_0\alpha_A}\right]^{\frac{1}{4}}, \tag{5d}$$

$$Z_{BP} = \frac{8a_0 n_B^2 (n_B+1)^2}{(2n_B+1)^2}\left[\frac{N_B(2n_B+1)n_B}{(n_B+1)a_0\alpha_B}\right]^{\frac{1}{4}}. \tag{5e}$$

Equations (5a), (5b), and (5c) relate Bohr energies to transition frequencies and ionization energies. Equation (5d) or (5e) is derived by using the wave functions (4g) and (4h) or (4i) and (4j) in the polarizability expression

$$\alpha = \frac{2}{3h}\sum_a \frac{\nu_{oa}|P_{oa}|^2}{\nu_{oa}^2 - \nu}, \tag{6}$$

where only the transitions $Ao \rightarrow Ax$, Ay, Az or $Bo \rightarrow Bx$, By, Bz are considered; the term depending on frequency ν has been neglected.

The quantity Z_{Bl} presents a problem and no general formula for it may be suggested. Only in rare cases does one have detailed information about both an electric and a magnetic dipole transition undergone by the same electron. (In this approximation transitions of different electrons in the same group are not mixed with one another by the perturbing field of the other groups.) When it is the magnetic dipole transition that is known to occur, one may safely assume that a companion electric dipole transition occurs between the ground state and an excited state with quantum number $n_A + 1$ polarized along the z direction (where the magnetic dipole transition involves a shift of charge from y direction with $Z = Z_{Ao}$, $n = n_A$ to the x direction with $Z = Z_{Aa} < Z_{Ao}$, $n = n_A$). It may also be mentioned that there is nothing to prevent one from assuming that an infinite array of such transitions exist to states with $n = n_A + 1, n_A + 2, \cdots$. It will be seen below that the sum of the contributions of such an array is finite, as must be the case.

The situation is not so simple when an electric dipole transition is under consideration. Here there is the problem of determining whether a companion magnetic dipole transition even exists; and, if so, what is to be its frequency? Neither the frequency of the electric dipole transition nor the ionization energy of the electron will necessarily have any relation to the energy of this companion state. If the group may be considered cylindrically symmetric, electric dipole transitions along the axis of symmetry will have no companion magnetic dipole transitions, for all radial directions are equivalent. Although one may formally describe parallel radial electric dipole and magnetic dipole transitions, there is no preferred direction and no net contribution for the optical rotation. From these considerations one may assume that the contribution due to the interaction of cylindrically symmetric groups will be given by the sixth term of Eq. (2).

In other cases, where a magnetic dipole transition parallel to the electric dipole transition in question is possible, it may be possible to write down a reasonable wave function which has a magnetic dipole transition to the ground state with the same Z as the excited state having the electric dipole transition to the

ground state. Such a situation is encountered in benzene derivatives where the ground and the lowest excited states are connected by electric dipole transitions and are described by LCAO functions of $2pz$ orbitals with a given Z. The companion state with the required symmetry to give rise to optical rotation is found to be an LCAO orbital with $3p(3z^2 - r^2)$ wave functions having the same Z as the known excited states. In this case, symmetry automatically requires a state which necessarily has higher energy to be mixed with the excited state wave function.

On the other hand, if one is considering a chromophore such as the carbon double bond, symmetry does not give any indication of the energy of the required excited state with a magnetic dipole transition to the ground state. There is need for further experimental and theoretical work in this area. If there is no magnetic dipole transition of importance to optical rotation, then the rotation of a compound such as methyl cyclopentene should be given by the sixth term of Eq. (2). Any large discrepancy between the theoretical value so calculated and the experimental value may be attributed to such a magnetic dipole transition and the magnitude of the discrepancy may be useful in further investigation of the chromophore.

In the derivation of the general formulas we have treated the groups as though they consisted of one atom. For small groups such as $-CH_3$, $-OH$, $-SH$, etc., the behavior will be dominated by one large central atom. For more complex groups like phenyl it may be advisable to subdivide the group; no detailed general procedure appears plausible at this point.

One may now carry out an explicit evaluation of Eq. (2) with the wave functions of Eq. (4). First the third term will be calculated since it is the easiest. One obtains

$$\mathbf{m}_{Aao} = \frac{e\hbar}{2mci}\mathbf{k}\int \psi_{Aa}^{(m)}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\psi_{Ao}^{(m)}d\tau = \frac{e\hbar}{2mci}\frac{(Z_{Ao}Z_{Aa})^{\frac{5}{2}}}{[\frac{1}{2}(Z_{Ao}+Z_{Aa})]^5}\mathbf{k}, \tag{7}$$

$$\mathbf{p}_{Aok} = e\mathbf{k}\int \psi_{Ao}^{(m)} z \psi_{Ak}^{(m)} d\tau = \left(\frac{3}{2}\right)^{\frac{1}{2}} 2^7 \frac{Z_{Ao}^{\frac{5}{2}} Z_{Aa}^{\frac{7}{2}}}{n_A^5 (n_A+1)^{\frac{7}{2}}}\left(\frac{Z_{Ao}}{n_A} + \frac{Z_{Aa}}{n_A+1}\right)^{-7} e a_0 \mathbf{k}. \tag{8}$$

The potential of interaction to be used in the evaluation of the one electron term for the magnetic dipole transition is

$$V = N_B e^2\left[\frac{1}{r_{12}} - \frac{1}{r_{B1}}\right] - \frac{Q_B e^2}{r_{B1}}, \tag{9}$$

where Q_B is the net charge on group B. The ground-state wave function for group B will be the average state function

$$\psi_{Bo}^{(P)} = \frac{1}{\pi^{\frac{1}{2}}}\left(\frac{Z_{BP}}{n_{Ba_0}}\right)^{\frac{3}{2}} e^{-Z_{BP}r_{B2}/n_B a_0}. \tag{10}$$

The matrix element of interaction $V_{Aak;Boo}$ is given by

$$V_{Aak;Boo} = \frac{1}{\pi^2}\left(\frac{2}{3}\right)^{\frac{1}{2}} \frac{Z_{Aa}^6}{a_0^9} Z_{BP}^3 \frac{N_B e^2}{n_A^5 (n_A+1)^{\frac{7}{2}} n_B^3} \times \iint \left\{x_A y_A z_A e^{-2b_1 r_{A1} - 2b_2 r_{B2}}\left[\frac{1}{r_{12}} - \frac{1}{r_{B1}}\right]\right\} d\tau_1 d\tau_2 - \frac{1}{\pi}\sqrt{\frac{2}{3}} \frac{Z_{Aa}^6 Q_B e^2}{a_0^6 n_A^5 (n_A+1)} \int \frac{x_A y_A z_A e^{-2b_1 r_{A1}}}{r_{B1}} d\tau_1, \tag{11}$$

where

$$b_1 = \frac{Z_{Aa}}{2a_0}\left(\frac{1}{n_A} + \frac{1}{n_A+1}\right)$$

and

$$b_2 = Z_{Bp}/a_0 n_B.$$

A rotation of axes to make the Z_A axis coincident with the line of centers transforms $x_A y_A z_A$ into $\gamma_x\gamma_y\gamma_z(z'^2 - 3x'^2)z'$, where $\gamma_x\gamma_y\gamma_z$ are the direction cosines of group B in the coordinate system of A. The correct distance dependence of the net charge effect is obtained only when the x'^2z' term is included in the calculation. The final result is

$$\begin{aligned} V_{Aak;Boo} = &-\left(\frac{2}{3}\right)^{\frac{1}{2}} \frac{Z_{Aa}^6 Q_B e^2}{a_0^6 n_A^5 (n_A+1)^{\frac{7}{2}} b_1^5} \gamma_x\gamma_y\gamma_z \left\{\frac{45}{b_1^4 R^4}\right. \\ &- e^{-2b_1 R}\left[(b_1R)^3 + 4(b_1R)^2 + 12(b_1R) + 30 + \frac{60}{b_1R} + \frac{90}{(b_1R)^2} + \frac{90}{(b_1R)^3} + \frac{45}{(b_1R)^4}\right]\Bigg\} - \left(\frac{2}{3}\right)^{\frac{1}{2}} \frac{{}^6Z_{Aa} N_B e^2}{a_0^6 n_A^5 (n_A+1)^{\frac{7}{2}}} \\ &\times \gamma_x\gamma_y\gamma_z \left\{e^{-2b_1 R}\left[\frac{R^3(2b_2^2 - b_1^2)}{(b_2^2 - b_1^2)^2} - \frac{4b_1(3b_2^2 - b_1^2)R^2}{(b_2^2 - b_1^2)^3} + \frac{12b_1^2(4b_2^2 - b_1^2)R}{(b_2^2 - b_1^2)^4} - \frac{6b_1(-15b_2^4 + 36b_1^2b_2^2 - 5b_1^4)}{(b_2^2 - b_1^2)^5} + \frac{12b_1^2}{R}\frac{(9b_2^4 - 14b_1^2b_2^2 - 5b_1^4)}{(b_2^2 - b_1^2)^6} - \frac{90b_1}{R^2} \times \frac{(b_1^4 - 6b_1^2b_2^2 + b_2^4)}{(b_2^2 - b_1^2)^6} + \frac{90b_1^2(4b_2^2 - b_1^2)}{R^3(b_2^2 - b_1^2)^6} + \frac{45b_1}{R^4}\frac{(6b_2^2 - b_1^2)}{(b_2^2 - b_1^2)^6}\right] \end{aligned}$$

$$+ e^{-2b_2R}\left[- \frac{24b_1b_2^4}{(b_2^2 - b_1^2)^5} - \frac{60b_1b_2^3(3b_2^2 - b_1^2)}{R(b_2^2 - b_1^2)^6} - \frac{90b_1b_2^2(5b_2^2 - b_1^2)}{R^2(b_2^2 - b_1^2)^6} - \frac{45b_1b_2(11b_2^2 - b_1^2)}{R^3(b_2^2 - b_1^2)^6} - \frac{45b_1(6b_2^2 - b_1^2)}{R^4(b_2^2 - b_1^2)^6}\right]\Bigg\}. \quad (12)$$

Although the form of Eq. (12) is correct, the authors cannot completely vouch for the accuracy of all the coefficients, since the theory is still in the process of development.

The term proportional to Q_B/R^4 represents a monopole–octapole interaction. Terms similar to this one have been derived by Condon, Altar, and Eyring[7] and Jones[8] with the use of the multipole expansion; in this more accurate treatment all the additional terms have an exponential dependence. In handling the net charge effect the use of the multipole expansion causes an error of about 20%.

The terms proportional to N_B, all of which are exponential, describe the incomplete screening effect of the vicinal group. Although the effect is that of a positive charge, the distance dependence is seen to differ markedly from that describing the effect of a true net charge. This term represents the results of Kauzmann's[4] work in explicit form.

In many cases it may be sufficient to take only the leading terms of Eq. (12). This gives a contribution to R_A of

$$R_A^{\text{static field}} = -\gamma_x\gamma_y\gamma_z\left\{\frac{e\hbar}{2mc}\frac{(Z_{Ao}Z_{Aa})^{\frac{5}{2}}}{[\frac{1}{2}(Z_{Ao}+Z_{Aa})]^5}\right\} \times\left[ea_0\left(\frac{3}{2}\right)^{\frac{1}{2}}\frac{2^7Z_{Ao}^{\frac{5}{2}}Z_{Aa}^{\frac{7}{2}}}{n_A^{\frac{5}{2}}(n_A+1)^{\frac{7}{2}}}\left(\frac{Z_{Aa}}{n_A}+\frac{Z_{Aa}}{n_A+1}\right)^{-7}\right] \times\left[\frac{e^2}{2a_0}Z_{Aa}^2\left(\frac{1}{n_A^2}-\frac{1}{(n_A+1)^2}\right)\right]^{-1} \times\left\{\left[\frac{(\frac{2}{3})^{\frac{1}{2}}Z_{Aa}^6e^2}{a_0^6n_A^{\frac{5}{2}}(n_A+1)^{\frac{7}{2}}}\right] \times\left[\frac{45Q_B}{b_1^9R^4}+\frac{N_B(2b_2^2-b_1^2)}{(b_2^2-b_1^2)^2}R^3e^{-2b_1R}\right]\right\}. \quad (13)$$

The terms in e^{-2b_2R} have been neglected because b_1 is sufficiently smaller than b_2 to make them negligible. (In Kauzmann's treatment of methyl cyclopentanone $b_1 \sim \frac{1}{2}\, b_2$.)

At present, there is no reason to believe that the interaction of a magnetic dipole transition with the electric dipole transitions of the same electron should be confined to only one instance. Accordingly, one may include the interactions with the infinite array of electric dipole transitions to states $n' = n_A + 2, \cdots$. In Eq. (13) $n_A + 1$ will be replaced successively by $n_A + 2$, $n_A + 3$, etc. The series will behave for large n' like $\Sigma n'[1/(n')^{\frac{3}{2}}]$, which converges rapidly.

The fourth term of Eq. (2) may not necessarily give a contribution excessively smaller than that of the third. The value of $V_{1ob;2oo}$ may be found from Eq. (12) by replacing

$$b_1 = \frac{Z_{Aa}}{2a_0}\left(\frac{1}{n_A}+\frac{1}{n_A+1}\right)$$

by

$$b_1' = \frac{1}{2a_0}\left(\frac{Z_{Ao}}{n_A}+\frac{Z_{Aa}}{n_A+1}\right).$$

For the carbonyl group $b_1 = 1.25$, $b_2 = 1.4$; in methyl cyclopentanone this leads to the result that $V_{Aok;Boo} \cong \frac{1}{3}\, V_{Aak;Boo}$. The ratio $\nu_b - \nu_a/\nu_b$ is not quite $\frac{1}{2}$, from which one concludes that the term arising from perturbing the ground state increases the over-all result by a factor of about $\frac{1}{6}$. In a thorough analysis of a molecule it is wise to retain this term, since there appears to be several terms involving such increments.

If one is treating, say, a two atom group such as carbonyl, in which the magnetic dipole transition involves the transfer of an electron centered on one of the atoms to an orbital on both, it may be desirable to use a two center orbital for the excited state. The over-all effect is to decrease the magnitude of the rotation primarily through the lower value of the transition's magnetic moment.

As partial compensation for this, however, there will be an appreciable difference in permanent electric dipole moment between the ground and excited states which will interact with the magnetic dipole transition in an analagous manner to the interaction by a transition electric moment. This is the effect taken into account by the fifth term of Eq. (2). For the same reasons as those given in the discussion of the fourth term this should contribute about $\frac{1}{6}$ of the magnitude of the third term to the total rotation in the carbonyl case.

The remaining two terms of Eq. (2), the second and the sixth describe the coupled oscillator effects. In the initial stage of the calculation there will be no need to specify whether the wave function of the vicinal group is describing one particular transition or the net effect of all electric dipole transitions in a certain direction. It will be found that both forms are useful.

[7] E. U. Condon, W. Altar, and H. Eyring, J. Chem. Phys. 5, 753 (1937).
[8] L. L. Jones, thesis, Department of Chemistry, University of Utah, 1961 (unpublished).

In the second term, we will begin by considering the interaction of an arbitrary electric dipole transition in group B with a certain magnetic dipole transition in group A. The ground- and excited-state wave function for group A will be given once again by Eqs. (4a) and (4b) and the ground- and excited-state wave function for the transition in group B will be given by

$$\psi_{Bo}^{(p)} = (1/\pi^{\frac{1}{2}})b_2^{\frac{3}{2}}e^{-b_2 r_{B2}}, \tag{14a}$$

$$\psi_{Bz}^{(p)} = (1/\pi^{\frac{1}{2}})b_2'^{\frac{5}{2}}z_B e^{-b'_2 r_{B2}}, \tag{14b}$$

where the z_B direction is for an arbitrary transition and b_2 and b_2' are for the moment unspecified.

The quantity $\mathbf{m}_{Aao}$ is given, as before, by Eq. (7) and $\mathbf{p}_{BOZ}$ is given by

$$\mathbf{p}_{BOZ} = \frac{2^5 e b_2^{\frac{3}{2}} b_2'^{\frac{5}{2}}}{(b_2 + b_2')^5}\,\mathbf{k}_B, \tag{15}$$

where $\mathbf{k}_B$ is the transition's direction of polarization.

The only nonvanishing term of $\mathbf{V}_{Aoa;BoZ}$ is

$$V_{Aoa;Boz} = C_{Ao}C_{Aa}C_{Bo}C_{Bz} \times \iint \frac{x_{A1}y_{A1}z_{B2}\exp(-2\bar{b}_1 r_{A1} - 2\bar{b}_2 r_{B2})}{r_{12}}\,d\tau_1 d\tau_2, \tag{16}$$

where

$$C_{Ao} = \frac{1}{\pi^{\frac{1}{2}}}\left(\frac{Z_{Ao}}{n_A a_0}\right)^{\frac{5}{2}}, \quad C_{Aa} = \frac{1}{\pi^{\frac{1}{2}}}\left(\frac{Z_{Aa}}{n_A a_0}\right)^{\frac{5}{2}},$$

$$C_{Bo} = \frac{1}{\pi^{\frac{1}{2}}}b_2^{\frac{3}{2}}, \quad C_{Bz} = \frac{1}{\pi^{\frac{1}{2}}}b_2'^{\frac{5}{2}},$$

$$\bar{b}_1 = \frac{Z_{Ao} + Z_{Aa}}{2n_A a_0}, \quad \bar{b}_2 = \tfrac{1}{2}(b_2 + b_2').$$

By a twofold rotation of axes this integral becomes

$$\iint \Big\{[\sigma_x\gamma_y(1 - 2\gamma_x^2) + \sigma_y\gamma_z(1 - 2\gamma_y^2) - 2\sigma_z\gamma_x\gamma_y\gamma_z] \times x'_{A1}z'_{A1}x'_{B2} + [\gamma_x\sigma_x + \gamma_y\sigma_y + \gamma_z\sigma_z]\gamma_x\gamma_y \times (z'^2_{A1} - x'^2_{A1})z'_{B2}\Big\} \times \frac{\exp(-2\bar{b}_1 r_{A1} - 2\bar{b}_2 r_{B2})}{r_{12}}\,d\tau_1 d\tau_2, \tag{17}$$

where γ_x, γ_y, γ_e are the direction cosines of group B in the coordinate system of group A and σ_x, σ_y, σ_e are the direction cosines of $\mathbf{k}_B$ in this coordinate system.

This is first integrated over the coordinates of electron 2 with the aid of the usual Neumann expansion

$$\frac{1}{r_{12}} = \sum_{n=0}^{\infty}\sum_{m=-n}^{m=+n}\frac{(n - |m|)!}{(n + |m|)!}\frac{r_<^n}{r_>^{n+1}}P_n^{|m|}(\theta_1)P_n^{|m|}(\theta_2) \times e^{im(\varphi_1 - \varphi_2)}, \tag{18}$$

where $r_<$ is the lesser of r_{B1} and r_{B2} and $r_>$ the greater. The angles θ_1 and θ_2 are measured from the x' axis for the $x_{A1}z_{A1}x_{B2}$ term and from the z' axis for the $(z'^2_{A1} - x'^2_{A1})z'_{B2}$ term. The net result is to replace x'_{B2}, z'_{B2} by x'_{B1}, z'_{B1}, in Eq. (17) and $e^{-2b_2 r_{B2}}$ by

$$\left[\frac{3}{4\bar{b}_2^5 r_{B1}^3} - \left(\frac{3}{4\bar{b}_2^2} + \frac{3}{2\bar{b}_2^3 r_{B1}} + \frac{3}{2\bar{b}_2^4 r_{B1}^2} + \frac{3}{4\bar{b}_2^5 r_{B1}^3}\right) \times \exp(-2\bar{b}_2 r_{B1})\right].$$

The integration over the coordinates of electron 1 is best handled by retaining the variables r_{B1} and r_{B2} along with the dihedral angle ϕ. A convenient cancellation gives rise to a completely elementary, though cumbersome, integral.

The integration over the terms multiplied by $\exp(-2\bar{b}_1 r_{A1} - 2\bar{b}_2 r_{B1})$ will give expressions proportional to $\exp(-2\bar{b}_1 R)$ and $\exp(-2\bar{b}_2 R)$. The result of integrating the $3/4\bar{b}_2^5 r_{B1}^3$ term gives, for its leading term when substituted into the second term of Eq. (2) and then into the expression for the rotatory parameter β,

$$\beta_{oa,oz}^{\text{mag-elec}} = -\frac{b_{1g}}{b_{1a}}\frac{e^2\hbar}{2mc}\left(\frac{c}{3\pi h}\right)\frac{1}{\nu_{Aoa}^2 - \nu^2}\frac{3}{2}\frac{b_{1g}}{b_{1a}R^4}\Big\{\frac{2}{h} \times e^2\frac{b_{2g}^8\mathbf{k}_A\cdot\mathbf{k}_B}{b_{2a}^{10}(\nu_{Bob}^2 - \nu^2)} \times [15\sigma_z\gamma_x\gamma_y\gamma_z + \sigma_y(15\gamma_x\gamma_y^2 - 3\gamma_x) + \sigma_x(15\gamma_y\gamma_x^2 - 3\gamma_y)]\Big\}, \tag{19}$$

where

$$b_{1g} = \left[\left(\frac{Z_{Ao}}{n_A a_0}\right)\left(\frac{Z_{Ao}}{n_A a_0}\right)\right]^{\frac{1}{2}},$$

$$b_{1a} = \frac{1}{2n_A a_0}(Z_{Ao} + Z_{Aa}),$$

$$b_{2g} = b_2^{\frac{3}{5}}b_2'^{\frac{5}{5}}, \quad b_{2a} = \tfrac{1}{2}(b_2 + b_2').$$

When the results of Eq. (19) are added for all electric dipole transitions in group B, noting that $\sigma_z = \mathbf{k}_A\cdot\mathbf{k}_B$, $\sigma_y = \mathbf{j}_A\cdot\mathbf{k}_B$, $\sigma_x = \mathbf{i}_A\cdot\mathbf{k}_B$ and $b_{1g}/b_{1a} \cong 1$ this becomes

$$B_{Aoa,B}^{\text{mag-elec}} = -\frac{3}{2}\left(\frac{e^2\hbar}{2mc}\right)\left(\frac{c}{3\pi h}\right)\frac{1}{b_{1a}^2R^4}\frac{1}{\nu_{A_{oa}}^2 - \nu^2} \times \{\mathbf{k}_A\cdot\boldsymbol{\alpha}_B\cdot\mathbf{k}_A 15\gamma_x\gamma_y\gamma_z + \mathbf{k}_A\cdot\boldsymbol{\alpha}_B\cdot\mathbf{j}_A \times [15\gamma_x\gamma_y^2 - 3\gamma_x] + \mathbf{k}_A\cdot\boldsymbol{\alpha}_B\cdot\mathbf{i}_A \times [15\gamma_y\gamma_x^2 - 3\gamma_y]\}, \tag{20}$$

where $\boldsymbol{\alpha}_B$ is the polarizability tensor of group B.

This is the only term which does not have an exponential dependence and for large distances will

be the dominant one; however, the distance R for which the exponential terms are significant may well be in the range of common integral distances for optically active molecules.

Equation (20) has also been derived by means of the multipole expansion in a more general fashion.[8] When R is small it is hoped that the exponential terms arising from the complete evaluation of Eq. (17) will properly correct the result in Eq. (20).

If group B is cylindrically symmetric one may write

$$\alpha_B = \alpha_B[(1 - \beta_B)\mathrm{I} + \beta_B \mathbf{k}_B \mathbf{k}_B] .$$

Substitution into Eq. (20) gives

$$\begin{aligned} B^{\text{mag-elec}}_{Aoa,B} = &-\frac{3}{2}\left(\frac{c}{3\pi\hbar}\right)\left(\frac{e^2\hbar}{2mc}\right)\frac{1}{\nu^2_{Aoa} - \nu^2}\frac{\alpha_B}{\bar{b}^2_{1a}R^4} \\ &\times \{15\gamma_x\gamma_y\gamma_z[1 + \beta_B((\mathbf{k}_A\cdot\mathbf{k}_B)^2 - \tfrac{1}{3})] \\ &+ [15\gamma_x\gamma_y^2 - 3\gamma_x][\beta_B(\mathbf{k}_A\cdot\mathbf{k}_B)(\mathbf{k}_B\cdot\mathbf{j}_A)] \\ &+ [15\gamma_y\gamma_x^2 - 3\gamma_y][\beta_B(\mathbf{k}_A\cdot\mathbf{k}_B)(\mathbf{k}_B\cdot i_A)]\} . \end{aligned} \tag{21}$$

The first term of this expression is seen to be the most important; the other two contribute about $\frac{1}{10}$ of the magnitude of the first. This term contributes about 20° to the 130° total of the rotation in methyl cyclopentanone. If only the partial rotation due to the magnetic dipole transition is desired one uses the value of α_B and β_B at the frequency ν_{Aoa} rather than that of the incident light.

In the evaluation of exponential terms it will be expedient to let b_2' and b_2 be related to the longitudinal and transverse polarizabilities of group B as though the polarizability arose from just two transitions, one axial and one radial.

Finally, the sixth term may be evaluated by the same methods as used above. Once again it will be convenient to let the parameters in the wave function be unspecified until the final expressions are obtained. The interaction of two arbitrary electric dipole transitions, one in group A and one in group B will be considered. The wave functions of Eqs. (4g,h,i,j) will be used with $Z_{AP}/n_A a_o \rightarrow b_1$, $Z_{AP}/(n_A + 1)a_o \rightarrow b_1'$, $Z_{BP}/n_B a_o \rightarrow b_2$, and $Z_{BP}/(n_B + 1)a_o \rightarrow b_2'$. The Z_A and Z_B axes will be along the directions of polarization.

The integral required in the sixth term of Eq. (2) is

$$V_{Aoa,Boz} = C_{Ao}C_{Aa}C_{Bo}C_{Bz} \times \iint \frac{z_A z_B \exp(-2\bar{b}_1 r_{A1} - 2\bar{b}_2 r_{B2})}{r_{12}} d\tau_1 d\tau_2 . \tag{22}$$

When both the Z_A and Z_B axes are rotated so as to coincide with the line of centers, one obtains

$$\begin{aligned} V_{Aoa;Boz} = C_{Ao}C_{Aa}C_{Bo}C_{Bz} \iint (&\{(\mathbf{d}_1\cdot\mathbf{d}_2)[1 - (\mathbf{d}_1\cdot\mathbf{k}_{12})^2] \\ &- (\mathbf{d}_1\cdot\mathbf{k}_{12})[\mathbf{d}_2\cdot\mathbf{k}_{12} - (\mathbf{d}_1\cdot\mathbf{k}_{12})(\mathbf{d}_1\cdot\mathbf{d}_2)]\} x'_{A1}x'_{B2} \\ &+ \{(\mathbf{d}_1\cdot\mathbf{d}_2)(\mathbf{d}_1\cdot\mathbf{k}_{12})^2 + (\mathbf{d}_1\cdot\mathbf{k}_{12}) \\ &\times [\mathbf{d}_2\cdot\mathbf{k}_{12} - (\mathbf{d}_1\cdot\mathbf{k}_{12})(\mathbf{d}_1\cdot\mathbf{d}_2)]\} \\ &\times z'_{A1}z'_{B2}) \frac{\exp(-2\bar{b}_1 r_{A1} - 2\bar{b}_2 r_{B2})}{r_{12}} d\tau_1 d\tau_2 , \end{aligned} \tag{23}$$

where $\mathbf{d}_1$ and $\mathbf{d}_2$ are unit vectors in the two directions of polarization and $\mathbf{k}_{12}$ is a unit vector along the line of centers pointing from group A to group B. The x'_{A1} and x'_{B2} axes are parallel.

This integral may be evaluated with the expansion of Eq. (18) and the final integration performed in the (r_{A1}, r_{B1}, ϕ) coordinates rather than the usual confocal elliptic coordinates. Once again there will be a single $1/R^n$ term, where here $n = 3$, and the rest will be polynomials of R multiplied by $\exp(-2\bar{b}_1 R)$ or $\exp(-2\bar{b}_2 R)$. When all of the transitions are summed over the twofold infinite series as done by Kirkwood, one will obtain for the first term precisely the expression derived by him.[3]

At this writing it is not known exactly how much weight the various exponential terms will have in the final answer. From the results of previous one-electron calculations it will be seen that $1/R^n$ terms do not necessarily predominate over exponential terms. The relative magnitudes of these terms, of course, depend on the various constants involved. It is certainly true that for large distances the $1/R^n$ terms will predominate, and the question of whether the intergroup distances in simple optically active compounds is sufficiently large for this to occur should be answered when the integrations outlined above have been carried out.

It is to be noted that even if the multipole expansion terms require little correction in most cases, the incomplete screening effect, which still appears to be very important in magnetic dipole transitions, can only be handled by detailed calculations such as Kauzmann's and its generalization given above. In the one electron calculation the multipole expansion takes into account only the effect of a net static charge on the vicinal group such as contributes to the molecular dipole moment.

Our preliminary investigation indicates that there are cases when one or all of the terms of Eq. (2) may be substantial. The relative magnitude of the terms will depend on the types of transition in the interacting groups and their distance apart.

In summary, one may anticipate that the contribution to a molecule's rotatory power from two inter-

acting groups will be given by

$$[\alpha]_2 = \left\{ -\left[\frac{a\alpha_2 + bQ_2}{R^4} + P_1(R,\alpha_2)\exp(-2\bar{b}_1 R)\right] \times \gamma_x\gamma_y\gamma_z + \left[\frac{f(\alpha_2)}{R^3} + P_2(R,\alpha_2)e^{-2b_1 R}\right]\gamma_x\gamma_y \right\} \times \frac{1}{\nu_{Aoa}^2 - \nu^2} + \left\{ \tfrac{1}{6}\,\alpha_1\alpha_2\beta_1\beta_2 \frac{1}{R^3} \times \left[\mathbf{d}_1\cdot\mathbf{d}_2 - 3\frac{(\mathbf{d}_1\cdot\mathbf{R})(\mathbf{d}_2\cdot\mathbf{R})}{R^2}\right]\mathbf{R}\cdot(\mathbf{d}_1 + \mathbf{d}_2) + P_3(R,\mathbf{d}_1,\mathbf{d}_2,\alpha_1,\alpha_2)e^{-2p_1 R} + P_4(R,\mathbf{d}_1,\mathbf{d}_2,\alpha_1,\alpha_2)e^{-2p_2 R}\right\}, \quad (24)$$

where a and b do not depend on R or group 2. The quantities α_1, α_2, β_1, β_2 are the polarizability and anisotropy factors of the two groups. Group 1 is assumed to have a single magnetic dipole transition. The functions P_1, f, and P_2 also depend on the properties of the magnetic dipole transition.

The second, third, and fourth terms of Eq. (2) are proportional to $\gamma_x\gamma_y\gamma_z$, the product of the direction cosines of group 2; the fifth term is proportional to $\gamma_x\gamma_y$ and the sixth term is the final term in braces of Eq. (24).

The middle term of Eq. (24) has significance when the chromophore electron ranges over more than one atom; the last term will always have potential significance, being small only in the case of cancellation among several pairwise interactions.

One cannot always say which of the three terms proportional to $\gamma_x\gamma_y\gamma_z$ will be dominant, the coupled oscillator, static charge, or incomplete screening. The coupled oscillator and incomplete screening terms will always be positive and should vary in the same way from group to group, but the static charge term may be of either sign and will depend on the electronegativity of the vicinal group and the nature of its linkage with the rest of the molecule. It is possible that in the case of a highly electronegative group with tightly bound electrons such as fluorine, the static charge term may be considerably larger than the others. Although one can explain the opposite sign of rotation of α-fluoro-cylcopentanone as compared with the bromo and chloro compounds by means of hydrogen's larger polarizability and incomplete screening, it is difficult to explain the comparable magnitudes on this basis. In the bromo and chloro derivatives there would be considerable cancellation between the positive coupled oscillator and incomplete screening terms and the negative net charge term with the former predominating; whereas in the fluoro compound the former terms are quite small and the net charge term is largest of all the halogens. This may be the way to explain the fact that, although bromine is nearly fifteen times more polarizable than fluorine, the magnitudes of the partial rotation due to the carbonyl transition of the α-halo-cyclopentanone are only in the ratio of about 2:1.[9]

A word may be said now by way of interpretation of certain aspects of the picture summarized in Eq. (24). In order to produce optical rotation there must be a net motion of charge in a helical or screw pattern; although these patterns exist in all molecules, it is only for dissymmetric ones that the effects do not cancel. It is easy to see how the circular motion of an electron undergoing a magnetic dipole transition in an isolated group acquires a linear drift and hence a helical motion in the presence of the electrostatic field of a vicinal group.

In the evaluation of the third term of Eq. (2) there occurs the integral

$$\int \frac{x_{A1}y_{A1}z_{A1}e^{-kr_{A1}}}{\gamma_{B1}}\,d\tau_1,$$

which is a two-center integral giving the energy of interaction between a point charge on B with the charge cloud on A. The product $x_{A1}y_{A1}z_{A1}$ changes sign eight times and divides group A into octants of alternating sign. This will be equivalent in form to the interaction of a monopole, or point charge with an octopole and gives rise to the familiar octant rule implicit in the work of Condon, Altar, and Eyring[7] and Kauzmann.[4] The leading term of the integral may be expected to vary as $1/R^4$, which is found to be the case. The other terms will depend on the exact nature of the charge cloud on A.

When considering the interaction of a magnetic dipole transition in one group and an electric dipole transition in another, the screw pattern will be seen to arise from the combined motion of two separate electrons in different groups. The phenomenon may be reduced to the equivalent situation of a single electron moving in the field of positive charge on the vicinal group in the following way:

The integral arising in the second term of Eq. (2) is

$$\iint \frac{x_{A1}y_{A1}z_{B2}e^{-kr_{A1}-k'r_{B2}}}{r_{12}}\,d\tau_1 d\tau_2,$$

which in analogy with the discussion above is seen to give the energy of interaction of a dipole on group B

[9] C. Djerassi, J. Osiecki, R. Riniker, and B. Riniker, J. Am. Chem. Soc. **80**, 1216 (1958).

with a quadrupole on group A. The leading term will again vary as $1/R^4$; furthermore, if one always chooses the positive direction of z_{B2} to point away from group A this dipole quadrupole interaction may be replaced by an equivalent monopole-octapole interaction between a positive charge on B with the same form of octapole distribution on A as above.

The magnitude of this equivalent positive charge will be seen from Eq. (24) to be $(a/b)\alpha_2$. This provides the physical basis for the many-electron model of Jones and Eyring.[10] One cannot make the same correspondence for the interaction of two electric dipole transitions, since a different distance and angular dependence is inherently involved, as may be seen from the integral in the sixth term of Eq. (2),

$$\iint \frac{Z_{A1}Z_{B2}e^{-kr_{A1}-k'r_{B2}}}{r_{12}} d\tau_1 d\tau_2 .$$

This gives the energy of interaction between two dipoles of charge and will lead to a $1/R^3$ dependence.

The helical pattern is once again formed by two separate electrons. The linear motion of a transition of group B becomes a circular motion as viewed from group A with A as center. Then one observes a linear motion of its own electron and a circular motion of the electron on B giving rise to a helical drift of charge. If one attempts to make the centers coincide, as was done in the previous discussion, the net motion of charge is linear and the effect vanishes.

It is accordingly best to visualize the effect of two electric dipole transitions in this way with the transitions remaining on different groups. The models of Kirkwood[3] and Kuhn[11] are particularly instructive. Although it is possible to set up equivalent monopole-quadrupole interactions, no simple correspondence with the static-charge, one-electron effect is feasible. It is observed that a right-handed screw pattern of polarizability does not always give dextro rotation, for the sign also depends on the angles which the symmetry axes make with the line of centers.

Preliminary calculations indicate that the exponential terms will be negative corrections involving 10–20% of the total rotation. Calculations with the Kirkwood polarizability formula[3] on hydrocarbons indicate that the coupled oscillator effect may account for less than one-half of the total rotation.

In the case of two methyl groups forming a screw pattern, it will be worthwhile to take into consideration the destruction of cylindrical symmetry of the groups by adjacent bonds. This will split the degeneracy for orbitals directed along radial directions enabling magnetic dipole transitions to occur with axial components of magnetic moment parallel to the electric dipole transitions known to occur. The method for doing this has been outlined by Condon, Altar and Eyring[7] in conjunction with the multipole expansion, which gives the net charge effect. For aliphatic carbon–carbon bonding the net charges will be nearly zero and the incomplete screening effect will predominate.

ACKNOWLEDGMENT

The authors express appreciation to the Army Ordnance for financial support of this research under Grant No. DA-ARO(D)-31-124-6298.

[10] L. L. Jones and H. Eyring, Tetrahedron **13**, 235 (1961).

[11] W. Kuhn, Z. Phys. Chem. **B4**, 14 (1929).

REVIEWS OF MODERN PHYSICS VOLUME 35, NUMBER 3 JULY 1963

Quantum Theory of Conjugated Systems

MICHAEL J. S. DEWAR*

George Herbert Jones Laboratory, University of Chicago, Chicago 37, Illinois

1. INTRODUCTION

As the previous papers have indicated, it is still an extremely difficult matter to treat even simple atoms and molecules by quantum-mechanical methods. The most useful treatments at present available can give binding energies with an accuracy little better than one percent. We are now going to consider the application of quantum-mechanical methods to complex organic molecules containing perhaps fifty or one hundred atoms, and we are also going to consider chemical problems in which an error of 0.1 eV would be intolerable. Stated in this way the problem seems quite hopeless. Even if the more refined "Group

* This work has been supported by the National Institutes of Health, U. S. Public Health Service, under grant No. GM-10123-01.