Optical Activity of Saturated Ketones. Ab Initio Localized Orbital Analysis of a Model Ketone in the Random-Phase Approximation

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Abstract: The results of random-phase approximation calculations, which yield oscillator and rotatory strengths for electronic transitions correctly to first order in electron correlation, are reformulated in terms of localized molecular orbitals to allow interpretation of chromophoric excitations in terms of the interaction between a chromophore and its surroundings. Minimal basis set RPA calculations on a chiral conformation of diethyl ketone are presented in the localized picture, and the origins of the electric dipole transition moment of the n → π* transition are discussed. The calculated energy and rotatory strength for this excitation are in excellent agreement with experiment. Problems concerning the assignment of higher lying bands are discussed. The origin-independent part of the dipole length form of the rotatory strength is derived in an appendix.

I. Introduction

The rotatory intensity of the n→π* transition in chiral, saturated ketones has been the object of a great deal of theoretical and experimental attention over the years.[4] Both the sign and the magnitude of the observed rotatory intensity in the 290-nm spectral region are very sensitive to the disposition of the extrachromophoric portion of the molecule with respect to the local symmetry planes of the carbonyl group, and to a third surface, not determined by symmetry, that intersects the other two. The experimental sign correlations are summarized in the ketone octant rule,[5] which has proven to be a most valuable tool in determining the absolute configuration of a host of organic compounds. The magnitudes of the n→π* Cotton effect vary markedly with the position of a dissymmetric substituent within a given sign-determining region; moreover, recent studies have shown that the sign-determining regions originally proposed admit a number of exceptions.[6]

Although the signs of the rotatory strength can be predicted correctly from molecular orbital calculations for many conformationally rigid ketones, the calculated magnitudes are typically much too large, and thus the detailed structural information inherent in the experimental intensities is not mimicked by the calculations. Moreover, incorrect predictions of absolute configuration do occur.

It is now well known that a balanced treatment of electron correlation in both ground and excited states is crucial to the accurate determination of electronic intensities.[7] Correlation is typically introduced by expressing the pertinent states in terms of some sort of configuration interaction (CI) method.[8] Such procedures converge to reasonably good results—provided a good enough atomic orbital basis set—but the computational effort quickly becomes great, and the rate of convergence is slow. Since the CI method aims at optimizing the energies and wave functions of the individual states, much of the computational effort is misplaced as regards the spectroscopically observable energy differences and transition moments.

A physically appealing and efficient method for determining these properties directly, taking proper account of correlation, is the so-called random phase approximation (RPA).[9,10] Various versions of the method have been applied successfully to a number of molecules and spectroscopic properties, notably by Shibuya, McKoy, and co-workers,[11] and by Jørgensen, Oddershede, Linderberg, and co-workers.[10,12] We have recently applied the RPA method to the ab initio calculation of rotatory intensities of several simple optically active systems, with encouraging results for both signs and magnitudes.[13,14]

The results of such a calculation are normally obtained in terms of the canonical, i.e., fully delocalized set of molecular orbitals that one obtains from an SCF calculation.[15] Many molecules, however, are known from chemical and spectroscopic evidence to be describable in terms of a chromophore, which is responsible for the main features of the electronic absorption band of interest, and the remainder of the molecule which acts as a perturbation. Indeed, the ketone octant rule and all sector rules for optical activity assume that such a division is possible.[16] In order to extract the interaction between a chromophore and its surroundings from the results of a calculation, it is convenient to use a localized orbital basis,[17] rather than the delocalized canonical orbitals. Such localized orbitals have been used many times in discussions of ground-state properties and chemical bonding;[18] however, with the notable exception of the work by Langlet, Malrieu, and co-workers,[19] very little attention has been paid to the use of localized orbitals in discussions of spectroscopic properties.

The purpose of this paper is twofold: first, to show how the results obtained in canonical RPA calculations can be reformulated in terms of localized molecular orbitals, and second, to present the results of an ab initio RPA calculation of the low-lying valence shell excitations of a saturated ketone, where we use such a localized molecular orbital analysis to extract the chromophoric and the extrachromophoric contributions to the ordinary and rotatory intensities. The specific molecular system for these calculations is a chiral conformation of diethyl ketone, chosen to mimic the effects of 2-axial methyl groups in rigid, saturated ketones.

Section II contains a summary of the necessary intensity relations, including a brief outline of the general RPA relations. The formalism for the localized orbital analysis is derived in section III, and the actual method used to localize the occupied and the virtual orbitals is given in section IV. Section V contains the results of the calculations on the chiral conformation of diethyl ketone, and section VI contains discussion and concluding remarks.

II. Theoretical Intensity Considerations

The ordinary and rotatory intensities of an electronic transition from the ground state Ψ_0 to an excited state Ψ_q are given by the oscillator strength f_{0q} and the rotatory strength R_{0q},

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for which the following equivalent expressions are available:[20–22]

$$f_{0\mathrm{q}}{}^{(r)} = (2m/3\hbar^2)\Delta E_{0\mathrm{q}}|\langle 0|\sum_i \mathbf{r}_i|\mathrm{q}\rangle|^2 (\text{length form}) \quad (1)$$

$$f_{0\mathrm{q}}{}^{(r\nabla)} = (2/3)\ \langle 0|\sum_i \mathbf{r}_i|\mathrm{q}\rangle \cdot \langle 0\,|\sum_i \hat{\nabla}_i|\mathrm{q}\rangle\ (\text{mixed form}) \quad (2)$$

$$f_{0\mathrm{q}}{}^{(\nabla)} = (2\hbar^2/3m\Delta E_{0\mathrm{q}})|\langle 0\,|\sum_i \hat{\nabla}_i|\mathrm{q}\rangle|^2 (\text{velocity form}) \quad (3)$$

$$R_{0\mathrm{q}}{}^{(r)} = (e^2\hbar/2mc)\ \langle 0|\sum_i \mathbf{r}_i|\mathrm{q}\rangle \cdot \langle 0\,|\sum_i \mathbf{r}_i \times \hat{\nabla}_i|\mathrm{q}\rangle \quad (\text{length form}) \quad (4)$$

$$R_{0\mathrm{q}}{}^{(\nabla)} = (e^2\hbar^3/2m^2c\Delta E_{0\mathrm{q}})\ \langle 0\,|\sum_i \hat{\nabla}_i|\mathrm{q}\rangle \cdot \langle 0\,|\sum_i \mathbf{r}_i \times \hat{\nabla}_i|\mathrm{q}\rangle \quad (\text{velocity form}) \quad (5)$$

in cgs units. Here $\Delta E_{0\mathrm{q}}$ is the transition energy for the excitation $0 \rightarrow \mathrm{q}$, $\mathbf{r}_i$ and $\hat{\nabla}_i$ are respectively the position vector and gradient operator for the ith electron, and $\langle 0|\hat{A}|\mathrm{q}\rangle = \int \psi_0{}^*\hat{A}\psi_\mathrm{q}\,\mathrm{d}\tau$. The equivalence among the expressions in eq 1–3 and 4,5, respectively, follows from the relation

$$\frac{\hbar^2}{m}\langle 0|\sum_i \hat{\nabla}_i|\mathrm{q}\rangle = \langle 0|[\sum_i \mathbf{r}_i,\hat{H}]|\mathrm{q}\rangle = \Delta E_{0\mathrm{q}}\ \langle 0|\sum_i \mathbf{r}_i|\mathrm{q}\rangle \quad (6)$$

which is a special case of the off-diagonal hypervirial relation[23]

$$\langle 0|[\hat{F},\hat{H}]|\mathrm{q}\rangle = \Delta E_{0\mathrm{q}}\ \langle 0|\hat{F}|\mathrm{q}\rangle \quad (7)$$

for an arbitrary operator $\hat{F}$. In general, eq 1–3 and 4,5 will yield unequal results when approximate wave functions and energies are used; moreover, the length form of the rotatory strength $R_{0\mathrm{q}}{}^{(r)}$ may be dependent on the choice of coordinate origin if the vectors $\langle 0|\Sigma_i\mathbf{r}_i|\mathrm{q}\rangle$ and $\langle 0|\Sigma_i\hat{\nabla}_i|\mathrm{q}\rangle$ are not parallel.[22] In such cases, however, the quantity

$$R_{0\mathrm{q}}{}^{[r]} = (f_{0\mathrm{q}}{}^{(r\nabla)}/f_{0\mathrm{q}}{}^{(\nabla)})R_{0\mathrm{q}}{}^{(\nabla)} \quad (8)$$

(see Appendix) is origin independent, and is the part of $R^{(r)}$ that is determined by the quality of the wave functions.

The degree of agreement among eq 1–3 and 4,5 may be used as an index of the degree to which the excitations are properly described in the calculation. The RPA method, which is employed in this paper, has the appealing features that it deals directly with excitation quantities such as transition energies and transition moments, and that, in the limit of a complete Hartree–Fock basis set, the off-diagonal hypervirial relation, eq 7, is fulfilled for an arbitrary one-electron operator, so that the equivalent expressions in fact yield identical results. On the other hand, the conventional, variationally optimized CI description of the individual states is not in general balanced sufficiently well to yield transition moments which fulfill eq 6 and 7.

The RPA method is usually derived either from so-called equations of motion or from polarization propagators, in both cases via a second-quantized formalism. We have shown elsewhere that the RPA equations can be derived within a CI formulation provided that we require that the transition moments fulfill eq 7.[24] For convenience we present a brief outline of the latter approach below.

Let the states Ψ_0 and Ψ_q be represented by the approximate forms

$$\Psi_0 = D_0|\Delta_0\rangle + 1/4 \sum_{(lm)}\sum_{(l'm')} D_{(lm),(l'm')} \left|\begin{matrix} l' \rightarrow m' \\ l \rightarrow m \end{matrix}\right\rangle \quad (9)$$

$$\Psi_\mathrm{q} = \sum_{(lm)} C^\mathrm{q}{}_{(lm)}|l \rightarrow m\rangle \quad (10)$$

where $|\Delta_0\rangle$ is the exact Hartree–Fock single Slater determinant $|\phi_1\phi_2\cdots\phi_l\cdots\phi_{l'}\cdots\phi_N|$ of molecular spin orbitals ϕ_i, $|l \rightarrow m\rangle$ is a singly excited configuration $|\phi_1\phi_2\cdots\phi_m\cdots\phi_{l'}\cdots\phi_N|$, and D_0, $D_{(lm),(l'm')}$, and $C^\mathrm{q}{}_{(lm)}$ are numerical coefficients labeled by the paired indexes in parentheses (lm), $(l'm')$. Here l and l' refer to orbitals occupied in the Hartree–Fock ground state (with "less" energy than the bonding level), and m and m' refer to unoccupied (virtual) orbitals (with "more" energy than the occupied ones). The form of eq 9 follows from the Brillouin relation,[25] $\langle\Delta_0|\hat{H}|l \rightarrow m\rangle = 0$, and thus the most important correlation corrections to $|\Delta_0\rangle$ are from the doubly excited configurations

$$\left|\begin{matrix} l' \rightarrow m' \\ l \rightarrow m \end{matrix}\right\rangle$$

The transition moment $\langle 0|\hat{F}|\mathrm{q}\rangle$ induced by a one-electron operator $\hat{F} = \Sigma_i\hat{f}_i$ is then given by

$$\langle 0|\hat{F}|\mathrm{q}\rangle = D_0{}^* \sum_{(lm)} C^\mathrm{q}{}_{(lm)}\ \langle\Delta_0|\hat{F}|l \rightarrow m\rangle + \sum_{(lm)}\sum_{(l'm')} D^*{}_{(lm),(l'm')} \times C^\mathrm{q}{}_{(l'm')} \left\langle\begin{matrix} l' \rightarrow m' \\ l \rightarrow m \end{matrix}\ |\hat{F}|\Delta_0\right\rangle \quad (11)$$

or

$$\langle 0|\hat{F}|\mathrm{q}\rangle = \sum_{(lm)} \{f_{lm}X^\mathrm{q}{}_{(lm)} + f_{ml}Y^\mathrm{q}{}_{(lm)}\} \quad (12)$$

where we have let $X^\mathrm{q}{}_{(lm)} = D_0{}^*C^\mathrm{q}{}_{(lm)}$ and $Y^\mathrm{q}{}_{(lm)} = \Sigma_{(l'm')}D^*{}_{(lm),(l'm')}C^\mathrm{q}{}_{(l'm')}$, and we have used the Slater–Condon rules[26] to reduce the matrix elements of $\hat{F}$ between Slater determinants to their one-electron equivalents $f_{ij} = \int\phi_i{}^*(1)\hat{f}(1)\phi_j(1)\mathrm{d}\tau_1$. Note that the correlation coefficients $D_{(lm),(l'm')}$ occur in the transition moment expression only in fixed combinations with the $C^\mathrm{q}{}_{(lm)}$, so that the number of coefficients to be determined in order to compute the intensities is much smaller than that required to describe the separate states.

The requirement that the hypervirial relation, eq 7, be obeyed, that is, that the alternative intensity expressions yield the same result, together with Brillouin's relation, leads to the following equations for the coefficients $X^\mathrm{q}{}_{(lm)}$:

$$\sum_{(lm)} \{A_{(lm),(l'm')}X^\mathrm{q}{}_{(l'm')} + B_{(lm),(l'm')}Y^\mathrm{q}{}_{(l'm')}\} = \Delta E_{0\mathrm{q}}X^\mathrm{q}{}_{(lm)} \quad (13)$$

$$\sum_{(lm)} \{B^*{}_{(lm),(l'm')}X^\mathrm{q}{}_{(l'm')} + A^*{}_{(lm),(l'm')}Y^\mathrm{q}{}_{(l'm')}\} = -\Delta E_{0\mathrm{q}}Y^\mathrm{q}{}_{(lm)} \quad (14)$$

where $A_{(lm),(l'm')} = \langle l \rightarrow m|\hat{H}|l' \rightarrow m'\rangle$ is the matrix element of the Hamiltonian between singly excited configurations, and

$$B_{(lm),(l'm')} = \left\langle\begin{matrix} l' \rightarrow m \\ l \rightarrow m \end{matrix}\ |\hat{H}|\Delta_0\right\rangle$$

is the matrix element connecting ground and doubly excited configurations. In matrix form

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & -\mathbf{A}^* \end{pmatrix}\begin{pmatrix} \mathbf{X}^\mathrm{q} \\ \mathbf{Y}^\mathrm{q} \end{pmatrix} = \Delta E_{0\mathrm{q}}\begin{pmatrix} \mathbf{X}^\mathrm{q} \\ \mathbf{Y}^\mathrm{q} \end{pmatrix} \quad (15)$$

This non-Hermitian eigenvalue problem can be solved by standard matrix diagonalization procedures, involving for real orbitals the diagonalization of $\mathbf{A} \pm \mathbf{B}$,[10] and the calculation involves manipulation of matrices no larger than $N \times N$, where N is the number of singly-excited configurations, whereas an equivalent CI procedure would involve matrices of size ca. $N^2 \times N^2$. It is important to note that the coefficients $X^q_{(lm)}$ and $Y^q_{(lm)}$ are not the same as those that would have been obtained from a variational solution of eq 9 and 10. What the RPA method does is to sacrifice some of the energy optimization of the individual states in order to achieve a more balanced description of the excitation process, and the implied wave functions of eq 9 and 10 really only have heuristic value. The operators we shall deal with in computing the intensities are either Hermitian or anti-Hermitian. For a real basis set, eq 12 specializes to

$$\langle 0|\hat{F}|q\rangle = \sum_{(lm)} f_{lm}\{X^q_{(lm)} \pm Y^q_{(lm)}\} \qquad (16)$$

where the upper sign holds if $\hat{F}$ is Hermitian, such as $\Sigma_i \mathbf{r}_i$, while the lower sign obtains if $\hat{F}$ is anti-Hermitian, such as $\Sigma_i \hat{\nabla}_i$ and $\Sigma_i \mathbf{r}_i \times \hat{\nabla}_i$.

It should be emphasized at this point that the fact that the molecular orbitals are solutions to the Hartree–Fock equations is important for the RPA method in the sense that Brillouin's relation $\langle \Delta_0|\hat{H}|l \rightarrow m\rangle = 0$ is crucial for the construction of the expressions in eq 11. However, the orbitals need not be the canonical solutions, i.e., the orbital set which diagonalizes the Fock matrix. Any unitary transformation within the occupied set $\{\phi_l\}$ and/or within the virtual set $\{\phi_m\}$ will leave the Brillouin relation unaffected, so that the RPA expressions can be formulated in terms of noncanonical orbitals. In the present context the particular noncanonical orbitals we have in mind are localized ones, and in the following section we shall present the formalism for the transformation of eq 12 and 13–15 into configurations corresponding to such localized orbitals.

III. Localized Orbital Analysis of the RPA Solutions

Let $\{\phi_{li}\}$ be the set of occupied canonical molecular spin orbitals, where $i = \alpha$ or β spin, $\{\phi_{mi}\}$ the set of canonical virtual orbitals, $\{\phi_{\lambda i}\}$ the set of noncanonical (here, localized) occupied orbitals, and $\{\phi_{\mu i}\}$ the set of localized virtual orbitals. We shall discuss the method for obtaining $\{\phi_{\lambda i}\}$ and $\{\phi_{\mu i}\}$ in the next section. Greek indexes are used throughout to refer to the localized orbitals. The canonical and the localized sets are related through unitary transformations:

$$\phi_{\lambda i} = \sum_l \phi_{li} T_{l\lambda} \qquad \phi^*_{\lambda i} = \sum_l T^\dagger_{\lambda l}\phi^*_{li} \qquad (17)$$

$$\phi_{\mu i} = \sum_m \phi_{mi} S_{m\mu} \qquad \phi^*_{\mu i} = \sum_m S^\dagger_{\mu m}\phi^*_{mi} \qquad (18)$$

where, for any unitary matrix $\mathbf{W}$, $\Sigma_j w^\dagger_{ij} w_{jk} = \Sigma_j w_{ij} w^\dagger_{jk} = \delta_{ik}$, and $w^\dagger_{ij} = w^*_{ji}$.

An integral of a one-electron operator $\hat{f}$ over the localized orbitals can be written

$$f_{\lambda\mu} = \langle \lambda|\hat{f}|\mu\rangle = \sum_l \sum_m T^\dagger_{\lambda l}\langle l|\hat{f}|m\rangle S_{m\mu} \qquad (19)$$

with the inverse

$$f_{lm} = \langle l|\hat{f}|m\rangle = \sum_\lambda \sum_\mu T_{l\lambda}\langle \lambda|\hat{f}|\mu\rangle S^\dagger_{\mu m} \qquad (20)$$

so that the RPA transition moment, eq 12, becomes

$$\langle 0|\hat{F}|q\rangle = \sum_{\lambda,\mu}\{f_{\lambda\mu}[\sum_{ml} T_{l\lambda}S^\dagger_{\mu m}X^q_{(lm)}] + f_{\mu\lambda}[\sum_{ml} T^\dagger_{\lambda l}S_{m\mu}Y^q_{(lm)}]\} \qquad (21)$$

It is convenient to introduce a unitary matrix $\mathbf{V}$ with elements

$$V_{(lm),(\lambda\mu)} = T^\dagger_{\lambda l}S_{m\mu} = T^*_{l\lambda}S_{m\mu} \qquad (22)$$

This matrix represents the transformation from the canonical (i.e., delocalized) configuration set labeled by the pair index (lm) into the noncanonical (i.e., localized) configuration set labeled by the pair index $(\lambda\mu)$. In terms of the matrix $\mathbf{V}$ we observe that eq 19 and 21 provide the following transformation relations:

$$f_{\lambda\mu} = \sum_{(lm)} f_{lm} V_{(lm),(\lambda\mu)} \qquad (23)$$

$$f_{\mu\lambda} = \sum_{(lm)} f_{ml} V^*_{(lm),(\lambda\mu)} \qquad (24)$$

$$\chi^q_{(\lambda\mu)} = \sum_{(lm)} X^q_{(lm)} V^*_{(lm),(\lambda\mu)} \qquad (25)$$

$$\gamma^q_{(\lambda\mu)} = \sum_{(lm)} Y^q_{(lm)} V_{(lm),(\lambda\mu)} \qquad (26)$$

To see how the $\mathbf{A}$ and $\mathbf{B}$ matrices transform into their localized counterparts, we write out the expressions for the matrix elements for spin-singlet excitations in terms of the canonical MOs:[9]

$$A_{(lm),(l'm')} = \delta_{ll'}\delta_{mm'}(\epsilon_m - \epsilon_l) + 2(ml|l'm') - (mm'|l'l) \qquad (27)$$

$$B_{(lm),(l'm')} = 2(lm|m'l') - (ml'|m'l) \qquad (28)$$

where ϵ_m and ϵ_l are the Hartree–Fock orbital energies, and the integral $(ij|kl)$ is defined as

$$(ij|kl) = \iint \phi_i^*(1)\phi_j(1)\frac{1}{r_{12}}\phi_k^*(2)\phi_l(2)\,d\tau_1\,d\tau_2 \qquad (29)$$

The integral $(ml|l'm')$, for example, transforms in the following way:

$$(\mu\lambda|\lambda'\mu') = \sum_{lm}\sum_{l'm'} S^\dagger_{\mu m}T_{l\lambda}T^\dagger_{\lambda' l'}S_{m'\mu'}(ml|l'm') = \sum_{(lm)}\sum_{(l'm')} V^*_{(lm),(\lambda\mu)}(ml|l'm')V_{(l'm'),(\lambda'\mu')} \qquad (30)$$

The remaining quantities appearing in $A_{(lm),(l'm')}$ can be seen to transform in the same way, so that

$$\mathcal{A}_{(\lambda\mu),(\lambda'\mu')} = \sum_{(lm)}\sum_{(l'm')} V^*_{(lm),(\lambda\mu)}A_{(lm),(l'm')} \times V_{(l'm'),(\lambda'\mu')} \qquad (31)$$

For the $\mathbf{B}$ matrix, we consider the integral $(ml|m'l')$:

$$(\mu\lambda|\mu'\lambda') = \sum_{lm}\sum_{l'm'} S^\dagger_{\mu m}T_{l\lambda}S^\dagger_{\mu' m'}T_{l'\lambda'}(ml|m'l') = \sum_{(lm)}\sum_{(l'm')} V^*_{(lm),(\lambda\mu)}(ml|m'l')V^*_{(l'm'),(\lambda'\mu')} \qquad (32)$$

so that we finally obtain

$$\mathcal{B}_{(\lambda\mu),(\lambda'\mu')} = \sum_{(lm)}\sum_{(l'm')} V^*_{(lm),(\lambda\mu)}B_{(lm),(l'm')} \times V^*_{(l'm'),(\lambda'\mu')} \qquad (33)$$

in the localized basis.

The transformed RPA equations are then

$$\begin{pmatrix} \mathcal{A} & \mathcal{B} \\ -\mathcal{B}^* & -\mathcal{A}^* \end{pmatrix}\begin{pmatrix} \chi^q \\ \gamma^q \end{pmatrix} = \Delta E_{0q}\begin{pmatrix} \chi^q \\ \gamma^q \end{pmatrix} \qquad (34)$$

where the transformed quantities are defined in eq 25, 26, 31, and 33. The canonical RPA problem is symmetry adapted, that is, the $\mathbf{A}$ and $\mathbf{B}$ matrices are block diagonal, with matrices $\mathbf{A}^{(\Gamma)}$, $\mathbf{B}^{(\Gamma)}$ connecting singly excited configurations belonging to irreducible representation Γ of the molecular point group. The $\mathbf{V}$ matrix is therefore also symmetry blocked into rectangular blocks $\mathbf{V}^{(\Gamma)}$. Equations 23–26 are seen to reduce further, for an excited state of symmetry **Γ**,

$$f_{\lambda\mu} = \sum_{\Gamma} \sum_{(lm)\epsilon\Gamma} f^{(\Gamma)}{}_{lm} V^{(\Gamma)}{}_{(lm),(\lambda\mu)} \tag{35}$$

$$\chi^{q(\Gamma)}{}_{(\lambda\mu)} = \sum_{(lm)\epsilon\Gamma} X^{q(\Gamma)}{}_{(lm)} V^{*(\Gamma)}{}_{(lm),(\lambda\mu)} \tag{36}$$

with similar equations for $f_{\mu\lambda}$ and $\gamma^{q(\Gamma)}{}_{(\lambda\mu)}$. The transformations of **A** and **B** are somewhat simplified, and reduce to a sum over symmetries:

$$\mathcal{A} = \sum_{\Gamma} \mathbf{V}^{\dagger(\Gamma)}\mathbf{A}^{(\Gamma)}\mathbf{V}^{(\Gamma)} \tag{37}$$

$$\mathcal{B} = \sum_{\Gamma} \mathbf{V}^{\dagger(\Gamma)}\mathbf{B}^{(\Gamma)}\mathbf{V}^{*(\Gamma)} \tag{38}$$

IV. Determination of Localized Orbitals

Equations 17 and 18, relating canonical and noncanonical molecular orbital sets by unitary transformations, are a consequence of the invariance of a Slater determinantal wave function to such a transformation.[27] Various criteria have been advanced for determining the transformation of the occupied orbital set to localized orbitals, the most common of which are the Edmiston–Ruedenberg method[18] and the Foster–Boys method.[17]

The Edmiston–Ruedenberg procedure requires an expensive transformation of electron repulsion integrals, and has thus remained largely unexploited for medium-sized or large molecules. The localized orbitals yielded by the two methods are actually quite similar,[18] except that the Foster–Boys method produces "banana" bonds instead of the more conventional σ–π orbitals for multiple bonds (see below). In the absence of compelling evidence favoring one procedure over the other on some absolute scale, we have opted for the Foster–Boys method on the basis of its computational simplicity.

The Foster-Boys criterion for the unitary matrix T is that the quantity $\Sigma_\lambda\langle\phi_\lambda\phi_\lambda|r_{12}{}^2|\phi_\lambda\phi_\lambda\rangle$, which they refer to as "the quadratic self-repulsion", be minimized. This has been shown[17] to be equivalent to minimizing the sum

$$J \equiv \sum_{\lambda} \langle\phi_\lambda|\,|\mathbf{r} - \mathbf{R}_\lambda|^2|\phi_\lambda\rangle = a - \sum_{\lambda} R_\lambda{}^2$$
$$= b - (2N_\lambda)^{-1} \sum_{\lambda}\sum_{\lambda'} |\mathbf{R}_\lambda - \mathbf{R}_{\lambda'}|^2 \tag{39}$$

Here $\mathbf{R}_\lambda \equiv \langle\phi_\lambda|\mathbf{r}|\phi_\lambda\rangle$, and N_λ denotes the number of orbitals in the set $\{\phi_\lambda\}$. The values of a and b are unchanged by a unitary transformation of the orbitals.

It is seen from the first expression in (39) that J may be taken as a measure of the average diffuseness of the orbitals. Thus the minimization of J produces the most compact orbitals (with this particular definition of the concept) that can be reached within a unitary transformation.

Very little attention has been paid in previous work to the localization of the virtual orbital set. The added complication encountered in this case is that density of the orbitals is not the only condition that must be met. In order to have intensity contributions concentrated into a few configurations it is further necessary that each of the localized virtual orbitals has large differential overlap with only one (or a few) of the localized occupied orbitals, i.e., that each of the virtual orbitals be localized in the same region as one (or a few) of the occupied orbitals. The same criterion also ensures that electron correlation effects are most efficiently accounted for. Since both of these aspects are of interest in the present work, localizing the virtual orbitals in the same fashion as the occupied ones would not necessarily be optimal. Instead we adopt the extension of the Foster–Boys scheme that has been proposed by Coffey.[28] In this method the unitary transformation S of the virtual orbitals is required to minimize the sum

$$K \equiv \sum_{\mu=1}^{n} |\mathbf{R}_\mu - \boldsymbol{\rho}_\mu|^2 = \sum_{\mu=1}^{n} \{\langle\phi_\mu|\,|\mathbf{r} - \boldsymbol{\rho}_\mu|^2|\phi_\mu\rangle$$
$$- \langle\phi_\mu|\,|\mathbf{r} - \mathbf{R}_\mu|^2|\phi_\mu\rangle\} \tag{40}$$

where n is the number of virtual orbitals to be localized ($n \le N_\mu$), and the $\boldsymbol{\rho}_\mu$ vectors point to the centroid positions of the relevant localized occupied orbitals.

Let us for the moment assume that $n = N_\mu$ and that we have started out by localizing the virtual orbitals by the same criterion as used for the occupied ones, i.e., minimization of eq 39 with the set $\{\phi_\mu\}$ substituted for $\{\phi_\lambda\}$. Focusing next on K as given by the second expression in (40) it is seen that the last summation will vary slowly if the S matrix required to minimize K is reasonably close to the one that minimizes J, i.e., if the $\boldsymbol{\rho}_\mu$'s do not differ too much from the $\mathbf{R}_\mu$'s obtained from the minimization of J. The Coffey procedure thus constitutes a desirable compromise: a presumably minor part of the density of the virtual orbitals is sacrificed in order to shift the centroid closer to those of the selected occupied orbitals.

Our computer program for localizing the virtual orbitals proceeds through the two steps outlined above, namely, an initial localization using the Foster–Boys criterion, followed by a retransformation to accomplish the pairing with the occupied orbitals. Our experience so far has confirmed that the second step causes only small readjustments of the orbitals obtained in the initial step (θ values less than 0.05 rad). Lone-pair centroids, which have no virtual counterparts in minimal basis set calculations, of course do not enter the pairing process.

The localization of orbitals proceeds by successive 2 * 2 unitary transformations of the type

$$\phi'_{\nu1} = \phi_{\nu1}\cos\theta - \phi_{\nu2}\sin\theta$$
$$\phi'_{\nu2} = \phi_{\nu1}\sin\theta + \phi_{\nu2}\cos\theta$$

The condition that J be stationary as a function of θ leads to the equation[17]

$$\tan 4\theta = \mathbf{A}\cdot\mathbf{B} \Big/ \left(\frac{1}{4}A^2 - B^2\right) \tag{41}$$

where $\mathbf{A} \equiv \mathbf{R}_{\nu1} - \mathbf{R}_{\nu2}$ and $\mathbf{B} \equiv \langle\phi_{\nu1}|\mathbf{r}|\phi_{\nu2}\rangle$. If $\nu1 \le n$ and $\nu2 \le n$ the condition of immobility of K reads

$$\left(\frac{1}{4}A^2 - B^2\right)\sin 4\theta + (\mathbf{A}\cdot\mathbf{B})\cos 4\theta$$
$$+ \left(\frac{1}{2}\mathbf{A}\sin 2\theta + \mathbf{B}\cos 2\theta\right)\cdot(\boldsymbol{\rho}_{\nu2} - \boldsymbol{\rho}_{\nu1}) = 0 \tag{42}$$

This is essentially the equation given by Coffey[28] (however, there appears to be a misprint in ref 28 where the above equation shows an extra factor 1/2 on the cos 2θ term). For the case $\nu1 \le n$ and $\nu2 > n$ we obtain the equation

$$\left(\frac{1}{4}A^2 - B^2\right)\sin 4\theta + (\mathbf{A}\cdot\mathbf{B})\cos 4\theta$$
$$+ \left(\frac{1}{2}\mathbf{A}\sin 2\theta + \mathbf{B}\cos 2\theta\right)\cdot(\mathbf{R}_{\nu1} + \mathbf{R}_{\nu2} - 2\boldsymbol{\rho}_{\nu1}) = 0 \tag{43}$$

Both eq 41 and 42 are easily solved by numerical methods and the solution corresponding to the minimum is found by inspection.

The minimization of J converges rapidly, and is continued until J becomes stationary to within 10^{-14}. The process requires only a few seconds of computer time, and the dipole length matrix elements over atomic orbitals are already available for the intensity calculations. The localized functions so obtained correspond closely to chemical intuition in the case of the σ bonds in the saturated parts of the molecules. On the other hand, for double bonds the Foster–Boys procedure yields

Table I. Atomic Coordinates (Å) for Diethyl Ketone[a]

atom	index	X	Y	Z
O	1	0.0	0.0	1.220
C	2	0.0	0.0	0.0
C_{α}	3 (10)	0.0	−1.258	−0.889
$H_{\alpha\epsilon}$	4 (11)	0.0	−2.148	−0.260
$H_{\alpha a}$	5 (12)	0.889	−1.258	−1.518
C_{β}	6 (13)	−1.258	−1.258	−1.778
$H_{\beta ax}$	7 (14)	−2.148	−1.258	−1.149
$H_{\beta 3}$	8 (15)	−1.258	−0.369	−2.407
$H_{\beta eq}$	9 (16)	−1.258	−2.148	−2.407

[a] Only one of the two ethyl groups is given; coordinates for the other are obtained by changing the signs of X and Y. Atom numbers in parentheses refer to the symmetry-related atoms not given explicitly.

a pair of banana orbitals, and the lone-pair orbitals come out essentially as sp^2 hybrids. The latter results can be expected from the structure of the last term in eq 39, and are in fact well-known features of the Foster–Boys procedure. However, for the analysis of the results it is much more convenient to use localized orbitals that reflect as closely as possible the local symmetry of a chromophore (e.g., the C_{2v} local symmetry of the carbonyl group). Such (pseudo)symmetry-adapted orbitals can be generated by a procedure which we call *redelocalization,* in which the set of localized orbitals to be (pseudo)symmetry adapted is subjected to a new unitary transformation where the criterion is that J of eq 39 be *maximized* for this set of orbitals. In the diethyl ketone calculations reported in the next section, we use this procedure to generate the customary local σ, π, and nonbonding orbitals for the carbonyl fragment.

V. Diethyl Ketone. Computations and Results

In order to apply the present method to chiral systems, we have chosen to examine the low-lying valence-shell spectrum of a chiral conformation of diethyl ketone, in which the methyl groups are held in positions corresponding to 2-axial methyl groups in cyclohexanone. The conformation is such that a twofold rotational symmetry axis is maintained about the carbonyl group, in order to allow some symmetry blocking in the calculations.

The positions of the carbon and hydrogen atoms were taken to correspond to those in a rigid, idealized chair-cyclohexane geometry; that is, all CCC, HCC, and HCH angles are tetrahedral, all $r_{CC} = 1.54$ Å, all $r_{CH} = 1.09$ Å, and $r_{CO} = 1.22$ Å. These coordinates are not greatly different from those found in conformationally rigid ketones.[5] The right-handed Cartesian coordinate system used has its origin on the carbonyl carbon, the oxygen along the $+Z$ axis, and the two α carbons in the Y–Z plane. Atomic coordinates are given in Table I.

The canonical molecular orbitals for the ground state were determined using the GAUSSIAN 70 system of computer programs[29] and the STO-4G minimal basis set of Pople et al.[30] The orbital exponents used for the Slater orbital mimics were $\zeta_C(1s) = 5.67$, $\zeta_C(2s) = \zeta_C(2p) = 1.72$, $\zeta_O(1s) = 7.66$, $\zeta_O(2s) = \zeta_O(2p) = 2.25$, and $\zeta_H(1s) = 1.24$. The basis set yielded a total Hartree–Fock ground-state energy of −268.5959 au.

The set of 18 valence-shell occupied and 16 virtual MOs supports a total of 288 singly excited configurations, which can be divided into 144 of A symmetry and 144 of B symmetry in the C_2 point group. All valence-shell configurations were included in the calculations of excitation properties. Canonical RPA calculations were performed for singlet excitations of each symmetry, and for comparison, the ^{1}A excitations were also computed in singly-excited CI, also known as the Tamm–Dancoff approximation (TDA), and in the simple virtual-orbital, or single-transition approximation (STA).[9] The TDA corresponds to neglecting the $Y^{q}{}_{(lm)}$ coefficients entirely, and formally setting the **B** matrix equal to zero, i.e., using an uncorrelated ground state.

We summarize the excitation properties of the lowest three singlet excitations in Table II. The overall agreement among the calculated intensities is seen to be quite good in the RPA, considering the small basis set used. Deviations from exact equivalence in the RPA are a consequence of a truncated basis set, since the RPA method guarantees satisfaction of the hypervirial relation only for exact Hartree–Fock orbitals.[24] Table II also shows a comparison of the results for the ^{1}A states in TDA and STA, as well as comparisons with experiment. One sees that the rotatory strength calculated for the lowest ($n \rightarrow \pi^*$) state is much too high in STA, as is typical of such calculations, while the RPA, and in this case also the TDA, yields energies and intensities that are in very good agreement with experimental estimates.[6] It is this agreement, particularly between the dipole length and dipole velocity forms of the intensities, that leads us to place some confidence in our minimal-basis RPA results. RPA calculations are known to suffer from certain instabilities in approximate calculations, and these instabilities are closely related to instabilities in the approximate Hartree–Fock ground state.[43] In the present case, we conclude from the results that the ground state is sufficiently well described to warrant application of the RPA method to the lowest lying singlet excitations, and in particular the 290-nm transition, which is generally agreed to be a valence-shell excitation.

The ^{1}B ($\sigma \rightarrow \pi^*$) state correlates well with the $\sigma \rightarrow \pi^*$ excitation computed at 9.2 eV in formaldehyde by Yeager and McKoy,[31] and found experimentally at 8.9 eV.[32] The ^{1}A ($\pi \rightarrow \pi^*$) band, which is autoionizing in formaldehyde but seems to appear at the limits of the vacuum UV in aliphatic ketones, is calculated to lie somewhat too high in energy,[32] and the TDA oscillator strengths disagree violently, while the RPA results are in reasonably good agreement. This feature of TDA-computed intensities has been observed frequently especially for $\pi \rightarrow \pi^*$-type excitations.[13,14]

The molecular orbitals were localized according to the modified Foster–Boys–Coffey procedure outlined in the previous section; the carbonyl σ, π, and nonbonding orbitals were generated by separate redelocalizations of the two CO double bond banana orbitals and the two sp^2-type lone pair hybrids. The convergence for the localization of virtual orbitals turned out to be slow. In our calculations all the virtual orbitals were localized (i.e., $n = N_{\mu}$ in eq 39), and K was minimized to within 10^{-12}; the process required some 30 s of IBM 370/155 computer time. Special techniques were invoked in order to avoid breaking the overall molecular symmetry since this proved to be restored only at a rather slow rate. The centroids of the occupied σ and π orbitals of the CO group were close together, and it was decided to localize the corresponding virtual orbitals with respect to the midpoint between these two centroids. This resulted immediately in virtual orbitals of σ^* and π^* character, and subsequent redelocalization, in the sense defined above, had essentially no effect on these orbitals.

The centroids for the resulting localized orbitals are given in Table III. Because of the close relationship between the local symmetry of the chromophore and the overall molecular symmetry for the conformation of diethyl ketone we have chosen, it proved to be convenient to symmetry adapt the localized orbitals with respect to the molecular twofold rotation axis. This amounts simply to taking the combinations $2^{-1/2}(\phi_1 + \phi_2)$ for A symmetry and $2^{-1/2}(\phi_1 - \phi_2)$ for B symmetry, where ϕ_1 and ϕ_2 are localized orbitals related by the C_2 operation. The analysis of contributions to the overall transition moments by individual configurations built from this final set of localized orbitals is simplified, in that canceling contributions from opposite sides of the molecule are excluded auto-

Table II. Calculated Spectroscopic Properties for the Lowest Three Singlet Excitations for Diethyl Ketone[f]

state	method	ΔE^a	$f^{(r)}$	$f^{(r\nabla)}$	$f^{(\nabla)}$	$R^{[r]\,b}$	$R^{(\nabla)\,b}$	β_{0q}, deg
^{1}A (n→π*)	STA	5.36	0.0013	0.0015	0.0018	+30.5	+35.7	0
	TDA	4.44	0.0001	0.0001	0.0001	+7.7	+7.9	0
	RPA	4.34	0.0001	0.0001	0.0001	+8.3	+6.4	0
	expt[c]	4.3		$\sim 10^{-4}$			+9 ± 2	
^{1}B (σ→π*)	RPA	9.05	0.0017	0.0063	0.0275	−2.7	−11.6	20.9
	expt[d]	8.9						
^{1}A (π→π*)	STA	13.95	1.208	0.488	0.197	+11.7	+4.7	0
	TDA	11.47	0.395	−0.0008	1.6×10^{-6}	+26.1	−0.05	0
	RPA	10.77	0.289	0.143	0.071	+14.7	+7.3	0
	expt[e]	~8.1						

[a] Energies in eV; experimental energies are vertical transition energies. [b] Units of R are $D\beta/100 = 1.08 \times 10^{40} R$ (cgs). [c] Reference 6. [d] Estimated value in formaldehyde, ref 32. [e] Estimated for diethyl ketone, ref 38. [f] See text and Appendix for definitions of symbols and notation.

Table III. Modified Foster–Boys Localized Occupied MOs and Foster–Boys–Coffey Localized Virtual Orbitals[a]

index	atom(s)	centroid coordinates, Å		
		x	y	z
1	1-2 (π)	0	0	0.7127
2	1-2 (σ)	0	0	0.6952
4 (3)	2-3 (2-10)	0.0025	−0.6426	−0.4405
6 (5)	3-4 (10-11)	−0.0001	−1.8643	−0.4598
7 (8)	3-5 (10-12)	0.6056	1.2540	−1.3111
9 (10)	3-6 (10-13)	−0.6252	−1.2492	−1.3247
12 (11)	6-7 (13-14)	−1.8664	−1.2578	−1.3484
13 (14)	6-8 (13-15)	−1.2587	−0.6516	−2.2094
15 (16)	6-9 (13-16)	−1.2564	−1.8656	−2.2058
17	1	0	0	1.4990
18	1	0	0	1.1615
19	1-2 (σ*)	0	0	0.5706
20	1-2 (π*)	0	0	0.4641
22 (21)	2-3 (2-10)	−0.0006	−0.6395	−0.4369
24 (23)	3-4 (10-11)	−0.0076	−1.8562	−0.4592
25 (26)	3-5 (10-12)	0.5975	−1.2466	−1.3128
27 (28)	3-6 (10-13)	−0.6297	−1.2453	−1.3275
30 (29)	6-7 (13-14)	−1.8522	−1.2584	−1.3529
31 (32)	6-8 (13-15)	−1.2534	−0.6611	−2.1986
33 (34)	6-9 (13-16)	−1.2549	−1.8547	−2.1966

[a] In each case the orbital index, atoms, and coordinates of the orbital centroid are given. Orbitals related by a C_2 rotation to those given are indexed in parentheses.

Table IV. Indexes, Symmetry Designations, and Descriptions of Symmetry-Adapted Localized Orbitals[a]

description	occupied	virtual
C=O π_x	1b	20b
C=O σ	2a	19a
O lone pair (sp_z)	17a	
O lone pair (p_y)	18b	
C-C_α	3a, 4b	21a, 22b
C_α-$H_{\alpha eq}$	5b, 6a	23a, 24b
C_α-$H_{\alpha ax}$	7b, 8a	25a, 26b
C_α-C_β	9a, 10b	27a, 28b
C_β-$H_{\beta ax}$	11b, 12a	29a, 30b
C_β-$H_{\beta 3}$	13a, 14b	31a, 32b
C_β-$H_{\beta eq}$	15b, 16a	33b, 34a

[a] The symmetry label immediately follows the orbital index in each case.

Table V. Analysis of the ^{1}A (n→π*) Excitation Eigenvector (RPA) in Terms of the Symmetry-Adapted Localized Orbital Set of Table IV

$X^q_{\lambda\mu}$	$Y^q_{\lambda\mu}$	excitation (λ→μ)	% of total
−0.889 74	0.053 83	18→20	78.9
−0.414 39	0.017 73	4→20	17.1
0.107 96	−0.006 02	18→28	3.7
−0.063 15	0.002 84	10→20	
−0.098 12	0.005 48	18→26	
−0.066 75	0.002 76	7→20	
0.059 35	−0.002 63	4→28	
−0.053 69	0.002 41	4→26	
0.050 60	−0.001 83	15→20	0.3
0.038 91	−0.000 70	5→20	−0.1
0.007 63	−0.054 88	1→22	
			99.7

matically. The centroids of the symmetry-adapted localized of course all lie along the z axis. The descriptions of these orbitals, together with their associated indexes and symmetry labels, are given in Table IV.

From the transformation matrices for the localization, with additional modifications as described above, the transformation matrix **V** of eq 22 was constructed, and the canonical RPA coefficients $\mathbf{X}^q$ and $\mathbf{Y}^q$ and the MO transition moment integrals **f** were transformed according to eq 23-26.

The ^{1}A (n→π*) Excitation. In the localized orbital picture, this excitation is seen to consist predominantly of a combination of promotions from the $2p_Y$ "lone pair" orbital on oxygen and the antisymmetric combination of the carbonyl carbon-α carbon bonds into the π* orbital (Table V). Small contributions come from excitations into and out of the α-axial bonds and the β-equatorial bond. The excitation is magnetic dipole allowed and the two main configurations in the excitation eigenvector account for 97% of the total magnetic transition

Table VI. Localized Analysis of the Electric Moment of the ^{1}A (n→π^*) Excitation[a]

configuration description	z	∇_z
LE in C=O (4 conf)	0.005 78	0.003 07
C_α–C ↔ C=O CT (6 conf)	−0.000 94	0.002 46
LE in C_2H_5 (14 conf)	−0.009 21	−0.003 10
C_α bonds ↔ C=O (18 conf)	−0.002 71	0.000 08
nearest-neighbor CT in C_2H_5 (48 conf)	−0.003 54	−0.001 61
non-nearest-neighbor CT (54 conf)	−0.017 59	−0.004 44
total	−0.028 21	−0.003 48
zigzag orbitals only	−0.026 95	−0.002 84
LE in zigzag	−0.000 38	0.000 61
CT in zigzag	−0.026 57	−0.003 45
nearest neighbor CT	−0.004 47	0.000 52
non-nearest-neighbor CT	−0.022 10	−0.003 97

[a] "LE" means locally excited configuration, and "CT" means charge transfer. See text for description of zigzag.

moment (in the chosen coordinate system) of −1.15 μ_B.

The electric dipole transition moment, on the other hand, is zero in formaldehyde, and thus the observed optical activity of this transition in chiral systems is governed by the dissymmetry-induced electric moment. Table VI shows the breakdown of the electric moment into local and charge transfer contributions. It is seen that the overall transition moment is a result of a large number of small contributions of both kinds; however, a number of regularities emerge from a closer analysis.

In Table VII, which displays the contributions of each bond orbital to the electric moment, the largest noncanceling terms arise from the β-equatorial local excitation and from long-range charge transfer between this bond and the carbonyl group. The bonds involved in the large contributions lie on a W-shaped path extending outward from the carbonyl group; this path is identical with what Kirk and Klyne have denoted a "primary zigzag" of bonds.[6] On empirical grounds, these authors have determined that substituents extending the zigzag path contribute much more to the total rotatory strength than those that break the pattern, for example, in the β-axial position. Recent theoretical studies have shown a similar effect.[4,33] The zigzag pathway, over which quite long-range effects on the carbonyl group are observed, is reminiscent of the phenomenon called W-coupling in NMR.[6,34]

Table VI shows that the contributions from the zigzag bonds are in fact sufficient to account for most of the induced electric transition moment, but also that long-range couplings are much more significant than would be expected from their contribution to the normalization of the excitation eigenvector. The zigzag behavior can be seen most clearly in the C–H bond contributions of the terminal methyl groups. The β-axial position actually interacts so as to reduce the net transition moment; experimentally, this corresponds to the "antioctant" behavior of a β-axial substituent.[35]

The importance of the zigzag path can be discerned already in the transition moment integrals over the localized molecular orbitals. Table VIII shows selected integrals involving the three methyl C–H orbitals. The difference in the long-range coupling shown by the three bonds is striking, and in accord with available experimental evidence.[6] The long-range coupling may be classed as "charge transfer" in the sense that contributions from two-center terms outside the main part of the localized orbitals far outweigh the one- and two-center terms linking the atomic orbitals in the head of the orbital with the same atomic orbitals in the tail of the other. The contributions along the tails of the localized orbitals are significant, however, and may not be ignored. Tables VI and VIII show further that the contributions to the transition moment from local mixing of carbonyl n and π^* orbitals is small at the MO level and actually of the opposite sign to the final moment at the RPA level.[33]

Finally, it is of interest to note that, of the 144 ^{1}A configurations contributing to the electric transition moment, the contributions from those arising from b→b MO excitations far outweigh the terms from a→a excitations. Of the total dipole length transition moment of −0.028 21 au, the b→b excitations account for −0.025 80 au. For the dipole velocity form, the proportion is −0.002 94 out of −0.003 48 au. An RPA calculation was carried out using only the 72 b→b configurations, and the results for the n→π^* excitation were ΔE = 4.34 eV, $R^{(r)} = +7.3$, $R^{(\nabla)} = +5.1$. This result can be un-

Table VII. Analysis of $2^{-1/2} \times 10^4 \langle 0|\nabla_z|q\rangle$ for the ^{1}A (n→π^*) Excitation in Terms of Bond Orbital Contributions[a]

	C=O	C–C_α	C_α–H_{eq}	C_α–H_{ax}	C_α–C_β	C_β–H_{eq}	C_β–H_{ax}	C_β–H_3
C=O	22							
C—C_α	18	−5						
C_α–H_{eq}								
C_α–H_{ax}	65	37	−5	29				
C_α–C_β	−64	−45	4	4	−30			
C_β–H_{eq}	−21	−6		−2	−10	−11		
C_β–H_{ax}					2		1	
C_β–H_3					3	−2		−5

[a] Terms less than 1 in these units have been omitted for clarity.

Table VIII. Selected Localized MO Integrals $\langle\lambda|z|\mu\rangle$ ($\langle\lambda|\nabla_Z|\mu\rangle$ in Parentheses)[a]

	1. β-Methyl Group Interactions		
	β-eq H	β-ax H	β-H_3
to π^*	−0.152 72 (−0.031 41)	−0.008 65 (−0.012 82)	−0.023 05 (−0.003 98)
to C-C_α	−0.141 85 (−0.045 57)	−0.046 22 (−0.018 10)	+0.006 52 (0.036 51)
from α-eq H	−0.018 41 (0.001 47)	−0.049 55 (−0.019 82)	−0.161 55 (−0.054 46)
	11. C=O Group Interactions		
$\langle\pi|Z(\nabla_Z)|\pi^*\rangle$	= 1.146 64 (0.213 66)		
$\langle p_Y|Z(\nabla_Z)|\pi^*\rangle$	= −0.005 25 (−0.002 67)		
$\langle CC_\alpha|Z(\nabla_Z)|\pi^*\rangle$	= −0.002 92 (−0.005 97)		
$\langle p_Y|Z(\nabla_Z)|CC_\alpha^*\rangle$	= 0.562 20 (0.191 39)		
$\langle CC_\alpha|Z(\nabla_Z)|CC_\alpha^*\rangle$	= 0.730 37 (0.339 70)		

[a] Only the b→b combinations are shown.

derstood with reference to the C_{2v} local symmetry of the carbonyl chromophore, in which the n→π* transition is of $b_1 \times b_2 = A_2$ symmetry, corresponding to $b \times b = A$ in the C_2 case.

Higher Energy Valence Excitations. Because the adequacy of a minimal basis set can easily be questioned for higher lying transitions, we shall make only a few observations about them.

The second excitation we compute is ^{1}B, and consists in the localized orbital picture of a combination of promotions from $sp_Z(O)$, σ_{CO}, and σ_{CC_α} (orbitals 17, 2, and 3) into π* (orbital 20). The magnetic moment is computed to be large and Y polarized, while the electric moment comes out mostly in the X direction. The question arises to what extent our ^{1}B excitation can be identified with the 190-nm band in saturated ketones.[36,39] The corresponding bands in formaldehyde and acetone have been studied extensively,[31,32,37] and the prevailing opinion at the present time is that the transition is Rydberg-like, n→3s. Barnes and Simpson,[38] on the other hand, present spectra for both acetone and diethyl ketone in which the former clearly shows Rydberg peaks but the latter does not. Our calculations do not support an earlier, valence-shell, n→σ* assignment for this band;[40] the n→σ* transition we compute is the fourth ^{1}B transition, occurring at 15.9 eV. However, since our basis set contains no diffuse functions, we are not in a position to address the Rydberg assignments. On the basis of the limited experimental and theoretical evidence for ketones larger than acetone, we believe that a definitive assignment of the 190-nm band for such molecules remains to be achieved.[41]

The ^{1}A, π→π* excitation is found, as expected, to be dominated by the local, carbonyl π→π* transition, with a tail consisting of the antisymmetric combinations of the α-axial σ bonds. The most important additional contribution to the electric transition moment comes from the local carbonyl σ→σ* excitation, even though it contributes very little to the excitation eigenvector. Its effect is to reduce the transition moment generated by the π→π* configuration by about one-third; TDA calculations of this type of excitation appear characteristically to overemphasize the σ→σ* contribution, especially in the dipole velocity form, thus leading to anomalously low intensities calculated for this transition.[9,13]

VI. Concluding Remarks

A random-phase approximation calculation of electronic intensities treats electron correlation correctly to first order, and the agreements among the various intensity expressions are limited only by the atomic orbital basis set used. The analysis of such a calculation in terms of localized orbitals, which we have introduced in the present work, allows interpretation of the low-lying excitations in terms of a chromophore interacting with its surroundings, and thus provides a firmer theoretical base for approximate models of optical activity of inherently symmetric but dissymmetrically perturbed functional groups.

The calculation could equally well have been done directly in a basis of localized orbitals. (Equation 37 no longer holds for the A matrix elements in this case, however.) With configurations built from localized orbitals, correlation corrections to the local chromophoric excitations can be assumed to fall off with increasing distance from the chromophore. This property opens the possibility of truncation of the configurational basis set by criteria closely related to the intensities of the excitations. The effects of less important configurations can be included by perturbation theory. Studies using this approach are underway, and will be reported in due course.

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Appendix. Origin-Independent Part of $R^{(r)}_{0q}$

The magnetic transition moment varies under a translation of the origin of the Cartesian coordinate system by some vector **A** according to

$$\langle 0|\sum_i (\mathbf{r}_i + \mathbf{A}) \times \hat{\nabla}_i|q\rangle = \langle 0|\sum_i(\mathbf{r}_i \times \hat{\nabla}_i)|q\rangle + \mathbf{A} \times \langle 0|\sum_i \hat{\nabla}_i|q\rangle$$

It follows that the component of the magnetic moment along the direction of $\langle 0|\Sigma_i\hat{\nabla}_i|q\rangle$ is independent of **A**. This direction defines what Moffitt proposed as a "partial optic axis" for the transition 0 → q.[42]

Let $\mathbf{l}_{0q} = \langle 0|\Sigma_i(\mathbf{r}_i \times \hat{\nabla}_i)|q\rangle$, $\nabla_{0q} = \langle 0|\Sigma_i\hat{\nabla}_i|q\rangle$, and $r_{0q} = \langle 0|\Sigma_i\mathbf{r}_i|q\rangle$. Then $\mathbf{l}^{\nabla}_{0q} = l_{0q} \cdot (\nabla_{0q}/|\nabla_{0q}|)$ is the component of $\mathbf{l}_{0q}$ along ∇_{0q}, and $R^{[r]}_{0q} = \mathbf{r}_{0q}\cdot\mathbf{l}^{\nabla}_{0q}$ is independent of origin. In atomic units, we have

$$R^{[r]}_{0q} = \left(r_{0q} \cdot \frac{\nabla_{0q}}{|\nabla_{0q}|}\right)\left(\mathbf{l}_{0q} \cdot \frac{\nabla_{0q}}{|\nabla_{0q}|}\right) = \frac{(\mathbf{r}_{0q} \cdot \nabla_{0q})(\mathbf{l}_{0q} \cdot \nabla_{0q})}{(\nabla_{0q} \cdot \nabla_{0q})} = \frac{\left(\frac{3}{2}f^{(r\nabla)}{}_{0q}\right)(\Delta E R^{(\nabla)}{}_{0q})}{\frac{3}{2}\,\Delta E f^{(\nabla)}{}_{0q}}$$

or

$$R^{[r]}_{0q} = \mathrm{R}^{(\nabla)}{}_{0q}(f^{(r\nabla)}{}_{0q}/f^{(\nabla)}{}_{0q})$$

It is seen that $R^{[r]}_{0q} = R^{(r)}_{0q}$ if $\mathbf{r}_{0q}$ and ∇_{0q} are parallel. The origin-dependent part of $R^{(r)}_{0q}$ has been shown previously to be less than or equal (in cgs units) to

$$\Delta R^{(r)}{}_{0q} = \frac{3e^2\hbar}{4mc}\,|\mathbf{A}|\,|f^{(r\nabla)}{}_{0q}\tan\beta_{0q}|$$

where β_{0q} is the angle between $\mathbf{r}_{0q}$ and ∇_{0q}, and $|\mathbf{A}|$ is the magnitude of the translation vector.[13]

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Theoretical Relationship between Diamagnetic Susceptibility Exaltation and Aromatic Stabilization

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Abstract: The London theory of diamagnetism for aromatic compounds was reformulated by analogy with the graph theory of aromaticity. A relationship between diamagnetic susceptibility exaltation (DSE) and aromatic stabilization was theoretically clarified for these compounds. The role of the applied magnetic field was to make the total π-electron energy of a conjugated system slightly approach that of its olefinic reference structure. The total π-electron energy of the reference structure was free from the effect of the magnetic field. The DSE was found to reflect the sign of the resonance energy and, to a lesser extent, its magnitude. Now, we can safely use the DSE as a definite criterion of aromaticity.

Early in this century, Pascal found that, in general, the diamagnetic susceptibility of an organic compound is approximately an additive function of its constituent groups.[1] He constructed a system for estimating the diamagnetic susceptibility on this principle. However, benzene typically exhibited a rather larger susceptibility than was expected from a comparison with the values of alkenes. Many aromatic compounds were found to show an analogous response to the magnetic field. In this context, diamagnetic susceptibility exaltation (DSE) is defined as the difference between the susceptibility (χ) found for a compound and that (χ_0) for the olefinic reference structure.[2-4] Here, χ_0 is the value estimated on Pascal's additive principle.

In 1936, Pauling pointed out that the DSE arises from a circulation of fully delocalized π electrons (i.e., a ring current).[5] London developed a simple quantum mechanical description of this effect.[6,7] The contribution of fully delocalized π electrons to the magnetic susceptibility is termed the London diamagnetism. It is nothing other than the origin of the DSE. The London diamagnetism is strongly anisotropic, being large in the direction perpendicular to the ring plane and small or zero in the plane.

It has widely been accepted that DSE is not only a manifestation of the presence of fully delocalized π electrons in a compound but also a reliable criterion of aromaticity.[2-4] However, there have been no satisfactory theories which might justify a relationship between the DSE and the degree of aromatic stabilization. In this paper, I would like to develop the London theory of diamagnetism by analogy with the graph theory of aromaticity,[8-10] and present a theoretical basis for correlating the DSE concept with the theory of aromaticity. We hereafter refer to DSE only, and call it the diamagnetic susceptibility of a conjugated system for convenience's sake.

Graph Theoretical Formulation of the London Theory

In the London theory for aromatic hydrocarbons,[6,7] the effect of a uniform, external magnetic field, with a component perpendicular to the ring plane, is to perturb the original "field-free" Hückel secular determinant by modifying all the off-diagonal matrix elements, H_{ij}, in the original AO basis, by a complex factor

$$\omega_{ij} = \exp(i\theta_{ij}H) \tag{1}$$

where

$$\theta_{ij} = \frac{2\pi e s_{ij}}{hc} \tag{2}$$

Here, H is the magnitude of the component of the external magnetic field perpendicular to the ring plane, e, h, and c are the standard constants with these symbols, and s_{ij} is the signed (algebraic) area of the triangle formed by an arbitrary (but subsequently fixed) origin and atoms i–j in the conjugated system. Since s_{ij} is a signed area, $s_{ij} = -s_{ji}$, and therefore $\omega_{ij} = \omega_{ji}^*$.

Here, we consider the eigenvalue problem of conjugated hydrocarbons. To a first approximation, one may take H_{ij} to have a common value β for all C–C bonds. All the diagonal matrix elements, H_{ii}, may be set equal to α. The Hückel secular equation can then be reduced to

$$|\omega_{ij} - X\delta_{ij}| = 0 \tag{3}$$

where X is a dimensionless eigenvalue. It is linearly related to