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Calculation of Optical Rotational Strength by Means of Various Types of Molecular Orbitals

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The optical rotational strengths of the methyl derivatives of cyclohexanone were calculated by means of various types of molecular orbitals, which were converted from those used in the CNDO/2 method. One of them is represented as a Sla ter-basis atomic orbital transformed from molecular orbitals on a CNDO basis by using the overlap matrix. Another was obtained only by modifying the normalization coefficient of the molecular orbitals. From the results, the two-center matrix elements in the calculation of rotational strengths was found to be not negligible, hence, the above-mentioned transformation was indicated to be indispensable. Good agreement with the experimental results was found for the transformed molecular orbitals, especially for those with a modification of the normalization coefficient. The theoretical grounds for these transformations are discussed. The formulae for the matrix elements of the gradient operator which are necessary for the calculation of the rotational strength are given in the appendix.

Recently, several studies of the calculation of the rotational strength by means of molecular orbital theories have been published. Pao and Santry first calculated the rotational strength of methyl-substituted cyclohexanones by the CNDO method,[1] neglecting all the two-center matrix elements.[2] Although only a few experimental data are available, the calculated values agree fairly well with the experimental results. On the other hand, the extended Hückel method[3] was applied to the same molecule, without neglecting the two-center matrix element, by Gould and Hoffmann.[4] Their results seem to be slightly too large.[5] They also calculated the rotational strength of the skewed butadiene chromophore by Pariser-Parr-Pople π-electron-only SCF calculation, with configuration interaction in order to emphasize the importance of the configurational mixing. The rotational strength of the skewed glyoxal at various rotational angles was also calculated[6] by the extended Hückel and CNDO methods, with and without configuration interactions, and with and without the inclusion of two-center matrix elements. This gives the correct sign of the rotational strength for the various α-diketones which were substituted for the skewed glyoxal as a model compound. However, the absolute value of the rotational strength depends remarkably upon the approximations used, that is, whether it is the extended Hückel method or the CNDO method, with or without configuration mixings, and with or without inclusion of two-center integrals. Similar calculations using the Pariser-Parr-Pople method were carried out for skewed butadiene and acrolein by Cheong *et al.*[7] For more complex molecules, the coupled oscillator theory[8] or the method of the composite molecule[9] was employed to find good agreement with the experimental results.

Although the molecular orbital approach to the calculation of the rotational strength is significantly used at present, the quantitative agreement between the calculated and observed values is not always satisfactory. In connection with this, various approximations used in the above calculation should be investigated. For example, the extended Hückel method includes all the overlap integrals; hence, the inclusion of the two-center integrals used for the calculation of the rotational strength is consistent with the approximation of the extended Hückel method However, as is well known, this method is not appropriate for the calculation of polar molecules because of the neglect of the electron-electron repulsion terms. On the other hand, the CNDO method can be expected to give a reasonable wave function for polar molecules, while the inclusion of two-center integrals for the rotational strength is in conflict with the complete neglect of the differential overlap.

In the present investigation, the rotational strength for a few methyl derivatives of cyclohexanone for which experimental data are available were calculated in the CNDO/2 method.[1] The molecular orbital obtained by means of the CNDO/2 method was transformed to that of the Slater-basis set in order to overcome the conflict between the inclusion of two-center integrals in the calculation of the rotational strength and the complete neglect of the differential overlap. The procedure used for the transformation of the molecular orbital from the CNDO basis to the Slater basis will be described in detail in the following section. The rotational strengths thus calculated are in good agreement with the experimental data. The

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[1] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, s129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, s136 (1965); J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

[2] Yoh-han Pao and D. P. Santry, *J. Amer. Chem. Soc.*, **88**, 4157 (1966).

[3] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[4] R. R. Gould and R. Hoffmann, *J. Amer. Chem. Soc.*, **92**, 1813 (1970).

[5] In Eq. (6) of Ref. 4, the factor of two is missing on the right side of the equation (private communication). Therefore, the calculated values in Table 1 should be multiplied by two, leading to a slightly large calculated value in comparison with the experimental value.

[6] W. Hug and G. Wagniere, *Theor. Chim. Acta*, **18**, 57 (1970).

[7] Kam-Khow Cheong, A. Oshita, D. J. Caldwell, and H. Eyring, *Proc. Nat. Acad. Sci. USA*, **67**, 1727 (1970).

[8] W. H. Inskeep, D. W. Miles, and H. Eyring, *J. Amer. Chem. Soc.*, **92**, 3866 (1970).

[9] S. Hagishita and K. Kuriyama, This Bulletin, **44**, 617 (1971).

difference between the rotational strengths calculated as the CNDO basis and as the Slater basis will be considered in connection with the nature of the atomic basis used in the molecular orbital. Moreover, theoretical grounds for the transformation of the molecular orbitals will be discussed.

Method

Molecular Orbitals. The molecular orbitals employed for the calculation of the rotational strengths were calculated by the CNDO/2 method.[1] The parameters included in the method were the same as those proposed by Pople *et al.*[1] The molecular orbitals thus obtained were transformed to those on the Slater basis in the following way: the molecular orbitals on the CNDO basis were assumed to be represented by the orthogonalized atomic basis defined by Löwdin;[10] hence, the atomic orbitals on the CNDO basis can be represented as an appropriate linear combination of Slater-type atomic orbitals effected by the transformation, so that the atomic orbitals on the CNDO basis are orthogonal with each other. The reverse transformation was already carried out by Pople *et al.* in order to compare the results obtained by the use of the CNDO method with those obtained by the use of the non-empirical method.[1] By making use of Pople's notation, the Slater basis set of atomic orbitals, ϕ', is given as;

$$\phi' = \phi S^{1/2} \tag{1}$$

where ϕ is the CNDO-basis set of atomic orbitals and where S is the overlap matrix calculated by use of the Slater-type atomic orbitals.

Another conversion of molecular orbitals was carried out as the assumption that the ratio of the coefficient in a given molecular orbital remains unaltered, while the corresponding normalizing coefficient of the molecular orbital was calculated including the overlap integrals, which were obtained as if the atomic orbital on the CNDO basis were a Slater-type atomic orbital. Therefore, the new coefficient of the atomic orbital can be obtained by dividing the old one by the normalizing coefficient. For occupied orbitals, the new coefficient is usually less in magnitude than the old one because of the bonding character of the orbitals, but the reverse is true for vacant orbitals because of their antibonding character. The physical meanings of these transformations are given below, along with the results calculated for the rotational strength.

Calculation of the Optical Rotational Strength. The optical rotational strength of the molecule, $\mathbf{R}$, can be calculated as follows[11]

$$\mathbf{R} = Im\{\langle\Psi_0|\boldsymbol{\mu}|\Psi_e\rangle\cdot\langle\Psi_e|\mathbf{m}|\Psi_0\rangle\} \tag{2}$$

where Ψ_0 and Ψ_e are wave functions of the ground and the excited states respectively, and where $\boldsymbol{\mu}$ and $\mathbf{m}$ are the electric and magnetic moment vectors respectively. In order to avoid the origin dependence of the rotational strength,[12] the matrix element of the electric dipole moment is converted into the dipole velocity formalism, as has already been done by Hoffmann *et al.*,[4]

$$\langle\phi_i|\mathbf{r}|\phi_j\rangle = \frac{\hbar^2}{m}\langle\phi_i|\nabla|\phi_j\rangle/(E_j-E_i) \tag{3}$$

where ϕ_i denotes an i-th molecular orbital, and E_i, its energy. By making use of Eqs. (2) and (3), the reduced rotational strength, $[R_{ij}]$, for the $i\rightarrow j$ transition, in which an electron in the i-th molecular orbital is excited to the j-th molecular orbital, is given by Eq. (4);

$$[R_{ij}] = \frac{-7313}{E_j-E_i}\langle\phi_i|\nabla|\phi_j\rangle\cdot\langle\phi_j|\mathbf{r}\times\nabla|\phi_i\rangle, \tag{4}$$

where energy is represented in eV units, and the gradient operator, in Å units. In the LCAO MO approximation, the matrix element included in Eq. (4) can be expanded into those between atomic orbitals. Therefore,

$$\langle\phi_i|\nabla|\phi_j\rangle = \sum_r\sum_s C_{ir}C_{js}\langle\chi_r|\nabla|\chi_s\rangle, \tag{5}$$

$$\langle\phi_j|\mathbf{r}\times\nabla|\phi_i\rangle = \sum_r\sum_s C_{jr}C_{is}\langle\chi_r|\mathbf{r}\times\nabla|\chi_s\rangle, \tag{6}$$

where the molecular orbital, ϕ_i, is represented as in Eq. (7), using the atomic orbital χ_r:

$$\phi_i = \sum_r C_{ir}\chi_r. \tag{7}$$

Calculation of the Matrix Element between Atomic Orbitals. The problem now is to calculate the matrix elements between atomic orbitals. One-center integrals will be considered first. The one-center integrals necessary for the calculation are the gradient and the magnetic moment integrals. These integrals have already been given in a previous paper;[2] hence, only the results will be indicated in this paper, with slight modifications. For a gradient operator, the following equations are obtained by using Slater-type atomic orbitals;

$$\begin{aligned}\int\chi_{2s}\nabla_x\chi_{2px}\mathrm{d}\tau &= -\int\chi_{2px}\nabla_x\chi_{2s}\mathrm{d}\tau\\ &= \frac{1}{\sqrt{3}\,a_0}\frac{(\delta_1\delta_2)^{5/2}}{(\delta_1+\delta_2)}(24\delta_1-8\delta_2)\end{aligned} \tag{8}$$

where a_0 is the Bohr radius and where:

$$\chi_{2s} = \frac{1}{\sqrt{3\pi}}\left(\frac{\delta_1}{a_0}\right)^{5/2} r\exp\left(-\frac{\delta_1}{a_0}r\right), \tag{9}$$

$$\chi_{2px} = \frac{1}{\sqrt{\pi}}\left(\frac{\delta_2}{a_0}\right)^{5/2} x\exp\left(-\frac{\delta_2}{a_0}r\right). \tag{10}$$

If the $2s$ and $2p$ orbitals have the same Slater exponent, Eq. (8) becomes simpler (Eq. (11)):

$$\int\chi_{2s}\nabla_x\chi_{2px}\mathrm{d}\tau = -\int\chi_{2px}\nabla_x\chi_{2s}\mathrm{d}\tau = \frac{\delta}{2\sqrt{3}\,a_0}, \quad (\delta=\delta_1=\delta_2). \tag{11}$$

It is apparent that the same formulae are given for the matrix elements between $2s$ and $2py$ or $2pz$ atomic orbitals and that the matrix elements between $2p$ orbitals and those between $1s$ orbitals should vanish because of their symmetrical properties. It should be mentioned that when the matrix element is re-

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[10] P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).

[11] L. Rosenfeld, *Z. Phys.*, **52**, 161 (1928).

[12] A. Moscowitz, "Modern Quantum Chemistry," Vol. 3, ed. by O. Sinanoğlu, Academic Press, New York (1965), p. 31.

presented in atomic units, a_0 (Bohr radius) in the denominator of Eqs. (8) and (11) is unnecessary.

The one-center matrix elements for the magnetic-moment operator can be rewritten as follows:

$$\int \chi_r(\mathbf{r}\times\nabla)\chi_s \mathrm{d}\tau = \mathbf{R}_A\times\int\chi_r\nabla\chi_s\mathrm{d}\tau+\int\chi_r(\mathbf{r}_A\times\nabla)\chi_s\mathrm{d}\tau, \tag{12}$$

where $\mathbf{R}_A$ is the position vector of the atom, A, to which the χ_r and χ_s atomic orbitals belong, and where $\mathbf{r}_A\times\nabla$ is the magnetic moment operator on the A atom. The second term of the right-hand side of Eq. (12) can be calculated by using the following equations:

$$\left.\begin{aligned}
&(\mathbf{r}_A\times\nabla)\chi_{1s}=0\\
&(\mathbf{r}_A\times\nabla)\chi_{2s}=0\\
&(\mathbf{r}_A\times\nabla)\chi_{2px}=\mathbf{j}\chi_{2pz}-\mathbf{k}\chi_{2py}\\
&(\mathbf{r}_A\times\nabla)\chi_{2py}=\mathbf{k}\chi_{2px}-\mathbf{i}\chi_{2pz}\\
&(\mathbf{r}_A\times\nabla)\chi_{2pz}=\mathbf{i}\chi_{2py}-\mathbf{j}\chi_{2px}
\end{aligned}\right\}, \tag{13}$$

where **i**, **j**, and **k** are the unit vectors in the x, y, and z directions. By combining Eq. (12) with Eq. (13) and Eq. (8) or Eq. (11), all kinds of one-center matrix elements for the magnetic-dipole operator can easily be calculated.

The two-center integrals will be considered next. For the calculation of the two-center matrix elements for the gradient operator, two atoms are assumed to be located on the local coordinate Z axis at the distance of R from one another, as is shown in Fig. 1.

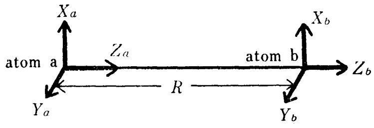

Fig. 1. Local coordinate system.

Then, the matrix elements between the two atomic orbitals on each atom are classified for calculation into several groups according to their symmetrical character, that is, the σ and π characteristics along the Z axis for the atomic orbitals and the gradient operator. The calculation of these matrix elements is followed by the transformation of the coordinate to obtain the matrix element between the atomic orbitals whose coordinates, x, y, and z are defined in the whole molecule. The formulae for the transformation have already been given in the paper by Suzuki *et al.*[13] In Table 1, the equations for the transformation are given; they can be applied by making use of the direction cosines of the local Z-axis with respect to the x, y, z-coordinate system. The two-center gradient matrix elements in the local coordinate can be calculated by using the prolate spheroidal coordinate system, as has already been done by Ehrenson and Phillipson.[14] In this paper, the formulae, which will be given in the appendix, are represented in terms of A and B functions, which are the auxiliary functions frequently used for the calculation of the overlap integrals.[15]

For the calculation of the two-center matrix elements for the magnetic moment operator, the displacement of the origin of the coordinate is necessary, as is shown in the following equation:

$$\int\chi_r(\mathbf{r}\times\nabla)\chi_s\mathrm{d}\tau = \mathbf{R}_A\times\int\chi_r\nabla\chi_s\mathrm{d}\tau+\int\chi_r(\mathbf{r}_A\times\nabla)\chi_s\mathrm{d}\tau \tag{14}$$

where $\mathbf{R}_A$ is the position vector of the atom, A, to which the atomic orbital, χ_s, belongs, and where $\mathbf{r}_A\times\nabla$ is the operator centered on the A atom. The first term of Eq. (14) is easily obtained, since the values of the matrix element for the gradient operator have been calculated in the preceeding step. The second term converts to the calculation of the overlap integrals for p orbitals, but vanishes for s orbitals, according to Eq. (13).

The matrix elements between atomic orbitals thus calculated are substituted into Eqs. (5) and (6) to obtain the rotational strength of the molecules. In order to check the numerical values of these matrix elements, the following equations, which are valid for both the one-center and two-center integrals, should be useful:

$$\int\chi_r\nabla_k\chi_s\mathrm{d}\tau = -\int\chi_s\nabla_k\chi_r\mathrm{d}\tau \tag{15}$$

TABLE 1. FORMULAE FOR THE TRANSFORMATION OF TWO-CENTER GRADIENT INTEGRALS

$$(s|\nabla_i|s)=\gamma_i(S|\nabla_Z|S)$$

$$(s|\nabla_i|p_i)=\gamma_i^2(S|\nabla_Z|P_Z)+(1-\gamma_i^2)(S|\nabla_X|P_X)$$

$$(p_i|\nabla_i|s)=\gamma_i^2(P_Z|\nabla_Z|S)+(1-\gamma_i^2)(P_X|\nabla_X|S)$$

$$(s|\nabla_i|p_j)=\gamma_i\gamma_j\{(S|\nabla_Z|P_Z)-(S|\nabla_X|P_X)\}$$

$$(p_j|\nabla_i|s)=\gamma_i\gamma_j\{(P_Z|\nabla_Z|S)-(P_X|\nabla_X|S)\}$$

$$(p_i|\nabla_i|p_i)=\gamma_i[\gamma_i^2(P_Z|\nabla_Z|P_Z)+(1-\gamma_i^2)\{(P_Z|\nabla_X|P_X)+(P_X|\nabla_Z|P_X)+(P_X|\nabla_X|P_Z)\}]$$

$$(p_i|\nabla_j|p_j)=\gamma_i[(1-\gamma_j^2)(P_Z|\nabla_X|P_X)+\gamma_j^2\{(P_Z|\nabla_Z|P_Z)-(P_X|\nabla_Z|P_X)-(P_X|\nabla_X|P_Z)\}]$$

$$(p_i|\nabla_j|p_i)=\gamma_j[(1-\gamma_i^2)(P_X|\nabla_Z|P_X)+\gamma_i^2\{(P_Z|\nabla_Z|P_Z)-(P_Z|\nabla_X|P_X)-(P_X|\nabla_X|P_Z)\}]$$

$$(p_i|\nabla_i|p_j)=\gamma_j[(1-\gamma_i^2)(P_X|\nabla_X|P_Z)+\gamma_i^2\{(P_Z|\nabla_Z|P_Z)-(P_Z|\nabla_X|P_X)-(P_X|\nabla_Z|P_X)\}]$$

$$(p_i|\nabla_j|p_k)=\gamma_i\gamma_j\gamma_k\{(P_Z|\nabla_Z|P_Z)-(P_Z|\nabla_X|P_X)-(P_X|\nabla_Z|P_X)-(P_X|\nabla_X|P_Z)\}$$

i or j or k denotes one of x or y or z. Small letter indicates the atomic orbitals defined in the coordinate of the whole molecule, and large letter the local coordinate in which the Z axis coincides with the line combining two atoms (Fig. 1). γ_i is the direction cosine of the Z axis with respect to the coordinate system x, y and z defined in molecule.

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13) M. Suzuki, Y. Nihei, and H. Kamada, This Bulletin, **42**, 323 (1969).

14) S. Ehrenson and P. E. Phillipson, *J. Chem. Phys.*, **34**, 1224 (1961).

15) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

$$\int \chi_r(\mathbf{r}\times\nabla)_k\chi_s d\tau = -\int \chi_s(\mathbf{r}\times\nabla)_k\chi_r d\tau, \tag{16}$$

where k denotes either the x, y, or z component of the operator. These equations can easily be proved by using integration by parts. Therefore, Eqs. (17) and (18) can also be obtained:

$$\langle\phi_i|\nabla_k|\phi_j\rangle = -\langle\phi_j|\nabla_k|\phi_i\rangle \tag{17}$$

$$\langle\phi_i|(\mathbf{r}\times\nabla)_k|\phi_j\rangle = -\langle\phi_j|(\mathbf{r}\times\nabla)_k|\phi_i\rangle. \tag{18}$$

In our test calculation, the numerical values for the matrix elements were checked against those in Ref. 6, where the numerical values of the z component of the magnetic moment operator of glyoxal are given together with the coordinates of the atoms. It was also confirmed that the rotational strength thus calculated does not vary with the transformation of the coordinate and the displacement of the origin of the coordinate.

Results and Discussion

In Table 2, the calculated rotational strengths of the methyl derivatives are listed for various methods, together with the experimental values. The coordinates of the atoms used for the calculation are the same as those in Ref. 2. By any method, fairly good agreement with the experimental values is found. However, the calculations with only one-center integrals give too large values for 7-, 13-dimethyl cyclohexanone. In other words, the neglect of the two-center integrals results in a large effect on the value of the rotational strength. Therefore, it should be concluded that the rotational strength has to be calculated by the inclusion of two-center integrals, even in the CNDO method.

Theoretically speaking, the molecular orbital employed for the calculation of the rotational strengths including the two-center matrix elements should not be the molecular orbital calculated in the approximation of the complete neglect of the differential overlap, that is, by the CNDO method. In order to overcome this difficulty, the molecular orbitals obtained by the CNDO method were converted to those on the Slater basis or those with a modification of the normalization coefficient described in the previous section. The bonding parameters, β, in the CNDO method were originally determined by corresponding the non-empirically calculated molecular orbitals with those on the Slater basis, which were converted from those on the CNDO basis for diatomic molecules.[1] In this sense, the molecular orbitals on the Slater basis by the CNDO method seem to be appropriate for the calculation of the rotational strength by procedure including two-center matrix elements. However, it should be emphasized that the atomic orbital on the CNDO basis should have a considerable mixing of Slater-type atomic orbitals other than that of the atom considered if the atomic orbital on the CNDO basis is assumed to be the orthogonalized atomic orbital proposed by Löwdin and if the overlap integrals between Slater-type atomic orbitals are relatively large. On the other hand, the bonding parameters are appropriate for diatomic molecules. Therefore, the Slater-type atomic orbitals converted from those on the CNDO basis may not correspond to the Slater-type atomic orbitals used in non-empirical calculations for large molecules. This may be the reason why the rotational strengths calculated by using the molecular orbital on the Slater basis are slightly different from the experimental values.

TABLE 2. ROTATIONAL STRENGTHS OF METHYL DERIVATIVES OF CYCLOHEXANONE FOR n-π^* TRANSITION[a]

Method \ Molecule		7-, 13- CH_3 cyclo-hexanone	7-, 8-, 13- CH_3 cyclo-hexanone
CNDO basis	total	+1.65	+7.26
	one-center[b]	+4.95	+3.64
Slater basis	total	+4.10	+5.28
	one-center[b]	+11.44	+5.77
CNDO normalized[c]	total	+1.95	+8.63
	one-center[b]	—	—
Experimental[16]		+1.8	+6.7
Extended Hückel[4]		+11.06	+12.72

a) The rotational strengths are calculated by using the value of 4 eV for the n-π^* excitation energy.

b) The rotational strength with the one-center matrix element only.

c) CNDO normalized is the method in which the molecular orbital is normalized by using overlap integrals.

Another approach to the calculation of rotational strengths is to use the molecular orbital in which the normalization coefficient is recalculated by including overlap integrals, while the ratio of the coefficients of atomic orbitals in a molecular orbital is assumed to be the same as that in the CNDO method, as has been mentioned in the previous section. Even in this method, there are some faults, one of which is the fact that the molecular orbitals in the CNDO method are calculated in an approximation and with a complete neglect of the differential overlap, contrary to the inclusion of overlap integrals in the recalculation of the normalization coefficient. This discrepancy can be overcome if the ratio of the coefficients of the atomic orbitals in a molecular orbital does not depend upon either the inclusion or neglect of the differential overlap in the CNDO calculation, which cannot be theoretically proved. Another fault included in this method is the non-orthogonality, that is, the molecular orbitals obtained by a modification of the normalization coefficient are usually not orthogonal with each other. However, if the molecular orbitals have different symmetries, even incompletely different ones, such as in the n-π^* transition in methylcyclohexanones, this orthogonality between molecular orbitals is approximately retained. Generally speaking, this non-orthogonal character may not have serious effects on the rotational strength, since the bonding character for occupied orbitals and the antibonding character for vacant orbitals give rise to relatively small overlap integrals between occupied and the vacant orbitals, although the contribution of this overlap term

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[16] H. Moffitt and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959).

may not be negligible in some cases. At any rate, as may be seen in Table 2, this molecular orbital with a modification of the normalization coefficient seems to give a remarkably good agreement with the experimental results.

In connection with the modification of the molecular orbitals in the CNDO method, we would like to mention that the calculation of the rotational strength with only a one-center matrix element is not always consistent with the approximation in the CNDO method, contrary to the discussion given in a previous paper.[2] The reason for this is that the atomic orbital on the CNDO basis, which can be considered to be the orthogonalized atomic orbital proposed by Löwdin, usually gives non-vanishing two-center matrix elements for the gradient and the magnetic moment operators, even if the corresponding overlap integral vanishes. This is probably supported by the fact that the rotational strengths with only one-center matrix elements calculated by the CNDO molecular orbital (first row of Table 2) are considerably different from those with both one- and two-center matrix elements calculated by the molecular orbitals on the Slater basis (third row of Table 2).

In conclusion, the rotational strengths calculated by the molecular orbitals in the CNDO method with a modification of the normalization coefficients have been found to be in excellent agreement with the experimental result. However, the validity of this treatment must be extensively investigated for various molecules, although the lack of the experimental values of the rotational strength makes it impossible to do so in the present investigation.

Numerical calculations were carried out on the HITAC 5020E Computation Center of the University of Tokyo and on the HITAC 8300 Computer at the National Cancer Center.

Appendix

Formulae of the two-center matrix elements for the gradient operator. As is shown in Fig. 1, the Z axis directs from the a atom to the b atom. R is the distance between a and b atoms in Å units, while P and t are given by the following equation:

$$P=\frac{R}{2a_0}(\delta_a+\delta_b) \tag{A-1}$$

$$t=\frac{\delta_a-\delta_b}{\delta_a+\delta_b} \tag{A-2}$$

where a_0 is the Bohr radius and where δ_a and δ_b are the Slater exponents of the two atomic orbitals, a and b. The auxiliary functions, A_k and B_k, are defined as usual:[15]

$$A_k(P)=\int_1^{\infty}x^k e^{-Px}dx \tag{A-3}$$

$$B_k(Pt)=\int_{-1}^{1}x^k e^{-Ptx}dx. \tag{A-4}$$

The formulae of various types of matrix elements for the gradient operator are given below:

$$\begin{aligned}(1S_a|\nabla_Z|1S_b)=&-\frac{P^4}{4R}(1-t^2)^{3/2}(1-t)\\&[A_2B_1+A_1(B_2-B_0)-A_0B_1]\end{aligned}$$

$$\begin{aligned}(2S_a|\nabla_Z|1S_b)=&-\frac{P^5}{8\sqrt{3}R}(1-t^2)^{5/2}\\&[A_3B_1+A_2(2B_2-B_0)+A_1(B_3-2B_1)-A_0B_2]\end{aligned}$$

$$\begin{aligned}(1S_a|\nabla_Z|2S_b)=&\frac{\delta_b}{8\sqrt{3}a_0}P^4(1-t^2)^{3/2}(1-t)\\&[-A_3B_1+A_2B_0+A_1B_3-A_0B_2]\\&+\frac{P^4}{4\sqrt{3}R}(1-t^2)^{3/2}(1-t)\\&[A_2B_1+A_1(B_2-B_0)-A_0B_1]\end{aligned}$$

$$\begin{aligned}(2P_{Za}|\nabla_Z|1S_b)=&-\frac{P^5}{8R}(1-t^2)^{5/2}[A_3B_2+A_2B_3\\&-A_1B_0-A_0B_1]\end{aligned}$$

$$\begin{aligned}(1S_a|\nabla_Z|2P_{Zb})=&\frac{\delta_b}{4a_0}P^3(1-t^2)^{3/2}(A_2B_0-A_0B_2)\\&-\frac{P^5}{8R}(1-t^2)^{3/2}(1-t)^2[A_3B_2+A_2\\&\times(B_3-2B_1)+A_1(B_0-2B_2)+A_0B_1]\end{aligned}$$

$$\begin{aligned}(2P_{Xa}|\nabla_X|1S_b)=&-\frac{P^5}{16R}(1-t^2)^{5/2}[A_3(B_0-B_2)\\&+A_2(B_1-B_3)+A_1(B_2-B_0)+A_0(B_3-B_1)]\end{aligned}$$

$$\begin{aligned}(1S_a|\nabla_X|2P_{Xa})=&\frac{\delta_b}{4a_0}P^3(1-t^2)^{3/2}(A_2B_0-A_0B_2)\\&-\frac{P^5}{16R}(1-t^2)^{3/2}(1-t)^2[A_3(B_0-B_2)\\&+A_2(B_1-B_3)+A_1(B_2-B_0)+A_0(B_3-B_1)]\end{aligned}$$

$$\begin{aligned}(2S_a|\nabla_Z|2S_b)=&\frac{\delta_b}{48a_0}P^5(1-t^2)^{5/2}[A_3(B_0-B_2)\\&+A_1(B_4-B_2)+B_1(A_2-A_4)+B_3(A_2-A_0)]\\&+\frac{P^5}{24R}(1-t^2)^{5/2}[A_3B_1+A_2(2B_2-B_0)\\&+A_1(B_3-2B_1)-A_0B_2]\end{aligned}$$

$$\begin{aligned}(2P_{Za}|\nabla_Z|2S_b)=&-\frac{\delta_b}{16\sqrt{3}a_0}P^5(1-t^2)^{5/2}\\&[B_2(A_0+A_4)-A_2(B_0+B_4)]\\&+\frac{P^5}{8\sqrt{3}R}(1-t^2)^{5/2}\\&\times[A_3B_2+A_2B_3-A_1B_0-A_0B_1]\end{aligned}$$

$$\begin{aligned}(2S_a|\nabla_Z|2P_{Zb})=&\frac{\delta_b}{8\sqrt{3}a_0}P^4(1-t^2)^{3/2}(1+t)\\&(A_3B_0+A_2B_1-A_1B_2-A_0B_3)\\&-\frac{P^6}{16\sqrt{3}R}(1-t^2)^{5/2}(1-t)\\&\times[A_4B_2+2A_3(B_3-B_1)+A_2(B_4-4B_2+B_0)\\&+2A_1(B_1-B_3)+A_0B_2]\end{aligned}$$

$$\begin{aligned}(2P_{Xa}|\nabla_X|2S_b)=&-\frac{\delta_b}{32\sqrt{3}a_0}P^5(1-t^2)^{5/2}\\&\times[A_4(B_0-B_2)+A_2(B_4-B_0)+A_0(B_2-B_4)]\\&+\frac{P^5}{16\sqrt{3}R}(1-t^2)^{5/2}[A_3(B_0-B_2)\\&+A_2(B_1-B_3)+A_1(B_2-B_0)+A_0(B_3-B_1)]\end{aligned}$$

$$
\begin{aligned}
(2S_a|\nabla_X|2P_{Xb}) = {} & \frac{\delta_b}{8\sqrt{3}\,a_0}P^4(1-t^2)^{3/2}(1+t) \\
& \times[A_3B_0+A_2B_1-A_1B_2-A_0B_3] \\
& -\frac{\sqrt{3}P^6}{96R}(1-t^2)^{5/2}(1-t) \\
& \times[A_4(B_0-B_2)+2A_3(B_1-B_3) \\
& +A_2(2B_2-B_4-B_0)+2A_1(B_3-B_1) \\
& +A_0(B_4-B_2)]
\end{aligned}
$$

$$
\begin{aligned}
(2P_{Za}|\nabla_Z|2P_{Zb}) = {} & \frac{\delta_b}{8a_0}P^4(1-t^2)^{3/2}(1+t) \\
& \times[A_3B_1+A_2B_0-A_1B_3-A_0B_2] \\
& -\frac{P^6}{16R}(1-t^2)^{5/2}(1-t) \\
& \times[A_4B_3+A_3(B_4-B_2)-A_2(B_3+B_1) \\
& +A_1(B_0-B_2)+A_0B_1]
\end{aligned}
$$

$$
\begin{aligned}
(2P_{Xa}|\nabla_X|2P_{Zb}) = {} & -\frac{P^6}{32R}(1-t^2)^{5/2}(1-t) \\
& \times[A_4(B_1-B_3)+A_3(2B_2-B_4-B_0) \\
& +2A_2(B_3-B_1)+A_1(B_4-2B_2+B_0) \\
& +A_0(B_1-B_3)]
\end{aligned}
$$

$$
\begin{aligned}
(2P_{Za}|\nabla_X|2P_{Xb}) = {} & \frac{\delta_b}{8a_0}P^4(1-t^2)^{3/2}(1+t) \\
& [A_3B_1+A_2B_0-A_1B_3-A_0B_2] \\
& -\frac{P^6}{32R}(1-t^2)^{5/2}(1-t)[A_4(B_1-B_3) \\
& +A_3(B_0-B_4)+A_1(B_4-B_0)+A_0(B_3-B_1)]
\end{aligned}
$$

$$
\begin{aligned}
(2P_{Xa}|\nabla_Z|2P_{Xb}) = {} & -\frac{P^6}{32R}(1-t^2)^{5/2}(1-t) \\
& [A_4(B_1-B_3)+A_3(2B_2-B_4-B_0) \\
& +2A_2(B_3-B_1)+A_1(B_4-2B_2+B_0) \\
& +A_0(B_1-B_3)]
\end{aligned}
$$