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Degenerate states in optical rotation and time-reversal invariance

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The consequence of time-reversal symmetry in a general *second-order* optical process between degenerate initial and final states is elucidated. The principle is applied to the pseudoscalar natural-optical-rotation operator ($R_L \cdot M_L$), which involves the interference of an electric-multipole (R_L) transition and a magnetic-multipole (M_L) transition. In addition to deriving point-group selection rules, time-reversal effects on matrix elements between degenerate states of a chiral versus an achiral molecule are compared and contrasted. Other non—time-reversal-degenerate states in chiral versus achiral molecules (D_3 versus C_{3v} and D_4 versus D_{2d}) are also compared. The analogy to the Jahn-Teller effect, which also involves (albeit *first-order* vibronic) matrix elements over degenerate states, is mentioned, especially with regard to the formal "splitting" of the degenerate levels by the pseudoscalar optical-rotation operator. A comprehensive search among the point groups for degenerate-state self-products that will give rise to the pseudoscalar function is conducted. Detailed results for the coupling of (degenerate) irreducible representations for important point groups (and their subgroups) are worked out for T_d (T), O, D_{6d} (D_6, D_3, C_{6v}, C_{3v}, C_6, C_3, D_{2d}), and D_{4d}. The couplings to give dipolar ($L=1$), quadrupolar ($L=2$), and octopolar ($L=3$) pseudoscalars are shown explicitly. Attention is called to the *differences in the transformation* of a magnetic-multipole operator and an electric-multipole operator, even though they both belong to the same irreducible representation. The resulting *differences in coupling coefficients* for degenerate states are given to help determine nonvanishing optical-rotation matrix elements. A summary and a discussion of the conservation of parity and time symmetry in optical rotation are given.

I. INTRODUCTION

Natural optical rotation in random molecular systems is due to intrinsically chiral molecules.[1,2] The observed rotatory strength is proportional to the matrix element[3–8] over $R \cdot M$ which is a pseudoscalar and is parity odd. In terms of point-group-symmetry selection rules, the symmetry of the state wave-function self-products must match the symmetry of the pseudoscalar operator $R \cdot M$ for this matrix element to be nonzero. Since most ground-state molecules are nondegenerate, the direct self-product of these ground-state wave functions yields the totally symmetric irreducible representation. Therefore, the observed pseudoscalar quantity $R \cdot M$ also belongs to the same totally symmetric representation in naturally optically active *chiral* molecules, as is well known.[9–11] Few studies have been made on degenerate ground or excited states serving as the initial or intermediate states. For many degenerate states, the direct self-product can yield the symmetry to match that of the pseudoscalar operator $R \cdot M$ whether the molecule is *chiral* or not. For example, in an achiral molecule of C_{3v} symmetry, $R \cdot M$ belongs to A_2 and $E \otimes E (=A_1+A_2+E)$ also contains A_2. Will point-group symmetry alone be sufficient to ensure the observation of optical activity in a molecule? This is especially pertinent when some degenerate states are time-reversal degenerate[12–14] (e.g., E of C_4). Will time symmetry be needed? In the case of the Jahn-Teller effect, which is proportional to the *first-order* vibronic matrix element $\langle \Gamma_j \mid (\partial H/\partial Q_i) Q_i \mid \Gamma_j \rangle$, time symmetry is needed to determine the selection rules. Even though some direct-product representation of the degenerate state Γ_j may satisfy the point-group-symmetry selection rule, having the same symmetry as the vibration Q_i, some matrix elements may still be zero.[9,14,15] This is because of the "hidden" time-reversal symmetry which requires the states with an even number of electrons to select only the (permutationally) symmetric direct product $[\Gamma_j^2]$. However, the Jahn-Teller effect is a *first-order* process while optical rotation is a *second-order* optical process. The time reversal of the latter involving four state vectors has not been formally treated. Time reversal in first-order matrix elements is relatively well known and some second-order processes have also been treated as pseudo—first order[7,16] by lumping the two perturbations and the intermediate states together as a single effective perturbation operator. The questions we ask in this work are as follows.

(1) When a point-group-symmetry selection rule is satisfied, will the degenerate states of achiral molecules produce natural optical rotation or not, and why? Similarly, how will the degenerate states of chiral molecules give optical rotation? Will the contributions of the degenerate components cancel or reinforce each other?

(2) In the case of time-reversal degenerate states, will point-group symmetry be sufficient? What is the consequence of introducing time symmetry? Because a single component of the time-reversal degenerate state lacks time symmetry, will a time-nonconserving property be observ-

able for this component? What is this property? How does it differ from the usual optical rotation due to the parity-odd pseudoscalar $R\cdot M$?

(3) In the introduction of time-reversal symmetry, how does the time reversal in a *second-order* matrix element involving four state vectors differ from that of the first order? What are the requirements for the permutational symmetries of the degenerate components?

(4) A pseudoscalar operator for natural optical rotation comes from the scalar contraction of one electric (E_L) and one magnetic (M_L) multipole.[10] When degenerate states are considered, will each degenerate state contain *all orders* ($L=1,2,3,\ldots$) of multipoles? If not, which degenerate state can contain which multipole? (The latter affects the magnitude of rotatory strength.) What are the irreducible representations of these higher multipoles in various point groups?

(5) The higher magnetic multipoles are functions that contain angular momentum l in addition to the usual positional variables and are seldom studied. How do these mixed functions differ from the usual pure electric multipoles in transformation and coupling characteristics? The latter determine the selection rules.

We shall start by deriving the effect of time reversal in second-order processes in Sec. II [to answer (3) above]. Then we will apply the principle to optical rotation of degenerate states in Sec. III [to answer (1) and (2) above]. We will then deduce the electric and magnetic multipoles contained in the degenerate states in Sec. IV. We will elucidate their symmetries, selection rules, and coupling coefficients with each other in the same section [to answer (4) and (5) above].

II. TIME-REVERSAL INVARIANCE IN SECOND-ORDER OPTICAL PROCESSES

To consider time reversal, we introduce a general term I in a second-order matrix element over the perturbation H':

$$I=H'^{jk}_{m\mu}H'^{kj}_{\nu n}\equiv(\psi^j_m,H'\psi^k_\mu)(\psi^k_\nu,H'\psi^j_n)\ , \tag{1}$$

where j is the initial and (identical) final degenerate-state irreducible representation; μ,ν,m,n are the degenerate components; and k is the intermediate degenerate-state irreducible representation. In the absence of spin, the time-reversal operator K reduces to complex conjugation K_0 (or the Wigner's time-reversal operator). In the presence of spin, the operator becomes $K=UK_0=\sigma_y K_0$, where σ_y is the Pauli spin matrix. With time invariance, the operation of K on a component will give rise either to the same component, except for a phase δ when it is nondegenerate, or to another degenerate component[13] multiplied by a phase factor, specifically when operating on the spin functions $K\binom{\alpha}{\beta}=\binom{i\beta}{-i\alpha}$.

Therefore, there is no loss of generality in considering another matrix element I', which is proportional to I and which can be rearranged by applying the "turn-over rule" for matrices:[14]

$$\begin{aligned} I\propto I'=H'^{\bar{j}k}_{m\mu}H'^{\bar{k}j}_{\nu n}&\equiv(K\psi^j_m,H'\psi^k_\mu)(K\psi^k_\nu,H'\psi^j_n)\\ &=(H'^{\dagger}K\psi^j_m,\psi^k_\mu)(H'^{\dagger}K\psi^k_\nu,\psi^j_n)\ . \end{aligned} \tag{2}$$

The operation by K which is an antiunitary operator yields

$$\begin{aligned} KI'&=(K\psi^k_\mu,KH'^{\dagger}K\psi^j_m)(K\psi^j_n,KH'^{\dagger}K\psi^k_\nu)\\ &=(K\psi^k_\mu,KH'^{\dagger}K^{-1}K^2\psi^j_m)(K\psi^j_n,KH'^{\dagger}K^{-1}K^2\psi^k_\nu)\\ &=a_1\kappa^2(K\psi^k_\mu,H'\psi^j_m)a_2\kappa^2(K\psi^j_n,H'\psi^k_\nu)\\ &=a_1a_2\kappa^4H'^{\bar{k}j}_{\mu m}H'^{\bar{j}k}_{n\nu}\ , \end{aligned} \tag{3}$$

where a_1 and a_2 are, respectively, the "eigenvalues" for $KH'^{\dagger}K^{-1}=aH'$ for the first and second H'.

a_1 and a_2 are both unity if H' is the radiative interaction operator $-(e/mc)A\cdot P$. This is because both the vector potential and the momentum change sign under time reversal (and the charge e is not changed). a is also $+1$ for the vibronic operator $(\partial H/\partial Q)Q$. $\kappa^2=(\pm i)^{2N}=(-1)^N$ with N equal to the number of electron spins and is also the eigenvalue for the twofold repeated operation of time reversal on any wave function, $K^2\psi=\kappa^2\psi$.

The matrix element I' may be expressed as the average of (2) and (3) as follows:

$$I'=\tfrac{1}{2}(1+K)I'=\tfrac{1}{2}(H'^{\bar{j}k}_{m\mu}H'^{\bar{k}j}_{\nu n}+a_1a_2\kappa^4H'^{\bar{k}j}_{\mu m}H'^{\bar{j}k}_{n\nu})\ , \tag{4}$$

where we have taken care to keep the same order for the first and second H' and where $1+K$ is the projection operator which generates the totally symmetric irreducible representation of time inversion. The fact that we can project out a nonzero time-invariant (time-symmetric) component is, of course, a prerequisite (selection rule) for the existence of the matrix element. It is seen that because of the simultaneous permutation of m,n and μ,ν, there is no clear-cut symmetry or antisymmetry in the appearance of the indices, *even if the first and second H''s are identical.* However, if either the intermediate state or the initial state is nondegenerate, we can rewrite Eq. (4) for $\psi^k_\mu=\psi^k_\nu=\psi^k_0$ as follows (the ensuing arguments also apply to the sum over the *same* component serving as the intermediate state):

$$I'=\tfrac{1}{2}(H'^{\bar{j}k}_{m0}H'^{\bar{k}j}_{0n}+a_1a_2\kappa^4H'^{\bar{k}j}_{0m}H'^{\bar{j}k}_{n0})\ . \tag{5}$$

This has permutation symmetry if the first H' is the same as the second. For the radiative interaction $H'=-(e/mc)A\cdot P$, this means that after the photon creation and annihilation contained in A have been evaluated,[4,10] the first and second $A\cdot P$ are replaced by the *same* multipole-transition operator[10,17] to give T_LT_L which may be equal to R_1R_1 (both photons in the electric-dipole mode), to M_1M_1 (both photons in the magnetic-dipole mode), to R_2R_2 (both photons in the electric-quadrupole mode), etc. These processes can give rise to Rayleigh optical activity[18–20] and optical rotation in oriented systems.[21] The time-reversal projection operator in Eqs. (4) and (5) may be replaced by the following permutation projection operator:

$$\tfrac{1}{2}(1+K)=\tfrac{1}{2}(1+a_1^2\kappa^4P_{mn})\ , \tag{6}$$

where $\kappa^4=(\pm 1)^{4N}=1$ and where for the second-order transition with identical operators $\langle T_L\rangle\langle T_L\rangle$, $a_1^2=1$. Therefore, *only the symmetric permutation,* coming from $\frac{1}{2}(1+P_{mn})$, of the degenerate-state direct product *is permitted* in the time-reversal selected second-order matrix element between the *same* initial and final degenerate states, *regardless of* whether the *number* of electrons is *even* or *odd.* If one had taken an antisymmetric permutation for the wave function using the projection operator $\frac{1}{2}(1-P_{mn})$, then superposition of the symmetric projection operator $\frac{1}{2}(1+K)$ required by time-reversal invariance would give a "null" matrix element. The necessary wave functions, direct products for R_1R_1, M_1M_1, and R_2R_2 for the point groups, are derivable from character tables. For a first-order matrix element involving only two state vectors such as that in the Jahn-Teller effect, with $a_1=1$, $\kappa^2=(\pm i)^{2N}=(-1)^N$, our results reduce to

$$\begin{aligned}I&=\tfrac{1}{2}(1+K)H'^{\,\bar{j}j}_{mn}\\&=\tfrac{1}{2}(1+a_1\kappa^2P_{mn})H'^{\,\bar{j}j}_{mn}\\&=\tfrac{1}{2}[1+(-1)^NP_{mn}]H'^{\,\bar{j}j}_{mn}\ .\end{aligned}\tag{7}$$

In other words, only the symmetric direct product for an even number of electrons and the antisymmetric product for an odd number are permitted—a result in agreement with that of Jahn and Teller.[22,23]

III. TIME-REVERSAL INVARIANCE AND THE MATRIX ELEMENT OVER TIME-REVERSAL-DEGENERATE STATES

This permutation symmetry will not exist if the first and second H''s are different multipole operators. Optical rotation for a randomly oriented (isotropic) system of molecules[10] is the case in which the first $H'=R$ (electric dipole) and the second $H'=M$ (magnetic dipole). Because the time-reversal operator is antiunitary[14] and reverses the order of states in a matrix, we choose to write the optical-rotatory strength[10] in a more symmetrical form as follows:

$$\begin{aligned}\phi_0&=-\frac{2\pi kN_0}{3}\sum_b[(E_j-E_b+\hbar ck)^{-1}+(E_j-E_b+\hbar ck)^{-1}](\langle j\,|\,\mathscr{E}_1\,|\,b\rangle\cdot\langle b\,|\,M\,|\,j\rangle+\langle j\,|\,M\,|\,b\rangle\cdot\langle b\,|\,\mathscr{E}_1\,|\,j\rangle)\\&=\mathscr{K}(\langle Kj'\,|\,\mathscr{E}_1\,|\,b\rangle\cdot\langle Kb'\,|\,l\,|\,j\rangle+\langle Kj'\,|\,l\,|\,b\rangle\cdot\langle Kb'\,|\,\mathscr{E}_1\,|\,j\rangle)\\&=\mathscr{K}'(\langle Kj'\,|\,R_1\,|\,b\rangle\cdot\langle Kb'\,|\,M\,|\,j\rangle-\langle Kj'\,|\,M\,|\,b\rangle\cdot\langle Kb'\,|\,R_1\,|\,j\rangle)\ ,\end{aligned}\tag{8}$$

where the $\mathscr{K}$'s stand symbolically for all the constants and summations over appropriate states. $Kj'=j$, $Kb'=b$, $k=2\pi\nu/c$, $M=(e/2mc)l$ is the magnetic-dipole operator, and $\langle j\,|\,\mathscr{E}_1\,|\,b\rangle$ is antisymmetric when the indices j,b of its matrix elements are permuted. This is because of its proportionality to the antisymmetric energy factor (E_j-E_b), viz. [Ref. 10, Eqs. (17) and (A13)],

$$\begin{aligned}\langle j\,|\,\mathscr{E}_{1\mu}\,|\,b\rangle&=(E_j-E_b)\Big\langle j\,\Big|\sum_i er_i\left[\frac{4\pi}{3}\right]^{1/2}\\&\qquad\times Y_{1\mu}(\theta_i\phi_i)\,\Big|\,b\Big\rangle\Big/\hbar ck\\&\equiv(E_j-E_b)\langle j\,|\,R_{1\mu}\,|\,b\rangle/\hbar ck\ .\end{aligned}\tag{9a}$$

As a result, under complex conjugation as well as under time reversal, an artificial negative sign must be added, making the transformation of the "effective" electric dipole, which is derived from momentum P, the same as that of the magnetic dipole, as it should:

$$\begin{aligned}\langle j\,|\,\mathscr{E}_1\,|\,b\rangle^*&=(E_j-E_b)\langle j\,|\,R_1\,|\,b\rangle^*/\hbar ck\\&=(E_j-E_b)\langle R_1^\dagger j\,|\,b\rangle^*/\hbar ck\\&=(E_j-E_b)\langle b\,|\,R_1\,|\,j\rangle/\hbar ck\\&=-\langle b\,|\,\mathscr{E}_1\,|\,j\rangle\ ,\end{aligned}\tag{9b}$$

$$\begin{aligned}K\langle Kj'\,|\,\mathscr{E}_1\,|\,b\rangle&=K\langle\mathscr{E}_1^\dagger Kj'\,|\,b\rangle\\&=\langle Kb\,|\,K\mathscr{E}_1^\dagger K^{-1}\,|\,K^2j'\rangle\\&=-\kappa^2\langle Kb\,|\,\mathscr{E}_1\,|\,j'\rangle\ ,\end{aligned}\tag{9c}$$

$$\begin{aligned}K\langle Kj'\,|\,l\,|\,b\rangle&=K\langle l^\dagger kj'\,|\,b\rangle\\&=\langle Kb\,|\,Kl^\dagger K^{-1}\,|\,K^2j'\rangle\\&=-\kappa^2\langle Kb\,|\,l\,|\,j'\rangle\ .\end{aligned}\tag{9d}$$

To illustrate the effect of degenerate states, we first use the pair of C_4 and S_4 groups. The results for other groups are given in tables. From Table I we see that in C_4 the pseudoscalars R_+l_- and R_-l_+ (derived from $\mathscr{E}_{1+}l_-$ and $\mathscr{E}_{1-}l_+$) belong to A, where $R_\pm=\mp R_{1\pm1}$. The degenerate-state components $\psi_\pm$ $(=K\psi_\mp)$ may be generated by time reversal from each other. The degenerate-state product $E\otimes E$ contains $\psi^*_+\psi_+\pm\psi^*_-\psi_-=\Pi_-\Pi_+\pm\Pi_+\Pi_-$ with the upper sign corresponding to the time-symmetric component and the lower sign corresponding to the time-antisymmetric component. But *both* components belong to point-group symmetry A. *Because of this ambivalence of two A's, point-group symmetry* is not sufficient to determine a nonvanishing matrix element with respect to a pseudoscalar which also belongs to A. Therefore, time-reversal symmetry is necessary to determine which A, the one with symmetric combination or

TABLE I. Transformation of electric and magnetic dipolar operator products and self-products of degenerate states and the matrix elements[a,b] thereof.

Operator/ states	Definition	C_3	C_4	S_4	C_{3v}	D_3	D_4	D_{2d}
$\Pi_+ = x+iy$	$R_+ = \Psi_+$							
$\Pi_- = x-iy$	$R_- = \Psi_-$	E	E	E	E	E	E	E
$l_+ = l_x + il_y$	$= M_+$							
$l_- = l_x - il_y$	$= M_-$	E	E	E	E	E	E	E
$xx+yy$	$[\Psi\cdot\Psi]^+$	A	A	A	A_1	A_1	A_1	A_1
$xy-yx$	$[\Psi\times\Psi]^-$	A	A	A	A_2	A_2	A_2	A_2
$xy+yx$	$[\Psi\times\Psi]^+$	E	B	B	E	E	B_2	B_2
$xx-yy$	$[\Psi\cdot\Psi]^-$	E	B	B	E	E	B_1	B_1
xl_x+yl_y	$[R\cdot M]^+$	A	A	B	A_2	A_1	A_1	B_1
xl_y-yl_x	$[R\times M]^-$	A	A	B	A_1	A_2	A_2	B_2
xl_y+yl_x	$[R\times M]^+$	E	B	A	E	E	B_2	A_2
xl_x-yl_y	$[R\cdot M]^-$	E	B	A	E	E	B_1	A_1
$\Pi_+\Pi_-\pm$	$(\Psi\cdot\Psi)^+$	A	A	A	A_1	A_1	A_1	A_1
$\Pi_-\Pi_+$	$(\Psi\cdot\Psi)^-$	A	A	A	A_2	A_2	A_2	A_2
$\Pi_-\Pi_-\pm$	$(\Psi\times\Psi)^+$	E	B	B	E	E	B_1	B_1
$\Pi_+\Pi_+$	$(\Psi\times\Psi)^-$	E	B	B	E	E	B_2	B_2
$R_+l_-\pm$	$(R\cdot M)^+$	A	A	B	A_2	A_1	A_1	B_1
R_-l_+	$(R\cdot M)^-$	A	A	B	A_1	A_2	A_2	B_2
$R_-l_-\pm$	$(R\times M)^+$	E	B	A	E	E	B_1	A_1
R_+l_+	$(R\times M)^-$	E	B	A	E	E	B_2	A_2
$(xl_x)_{xx}$	$=$	$(yl_y)_{yy}$	$(yl_y)_{yy}$	$-(yl_y)_{yy}$	0	$(yl_y)_{yy}$	$(yl_y)_{yy}$	$-(yl_y)_{yy}$
$(yl_y)_{xx}$	$=$	$(xl_x)_{yy}$	$(xl_x)_{yy}$	$-(xl_x)_{yy}$	0	0	0	0
$(xl_y)_{xx}$	$=$	$-(yl_x)_{yy}$	$-(yl_x)_{yy}$	$(yl_x)_{yy}$	$-(yl_x)_{yy}$	0	0	0
$(yl_x)_{xx}$	$=$	$-(xl_y)_{yy}$	$-(xl_y)_{yy}$	$(xl_y)_{yy}$	0	0	0	0
$(\Pi_-l_+)_{++}$	$=$	$\neq 0$	$\neq 0$	0	$-(\Pi_+l_-)_{--}$	$(\Pi_+l_-)_{--}$	$(\Pi_+l_-)_{--}$	0
$(\Pi_+l_-)_{++}$	$=$	0	0	0	0	0	0	0
$(\Pi_-l_-)_{++}$	$=$	0	0	$\neq 0$	0	0	0	$\neq 0$
$(\Pi_+l_+)_{++}$	$=$	0	0	0	0	0	0	0

[a] By definition $(yl_y)_{xx} = \langle 0|y|x\rangle\langle x|ly|0\rangle$ and $(\Pi_-l_+)_{++} = \langle 0|\Pi_-|\Psi_+\rangle\langle\Psi_+|l_+|0\rangle$, where 0 stands for the totally symmetric (A or A_1) state.

[b] From this table under D_3, we see that (using additional matrix elements by permutation of indices) $R_{xx} = (xl_x)_{xx} + (xl_x)_{yy} = (yl_y)_{xx} + (yl_y)_{yy} = R_{yy}$, in agreement with L. D. Barron (private communication).

the one with antisymmetric combination, will give the matrix element. We may write the rotatory strength for each degenerate component separately. After taking the average of time reversal [assuming the intermediate state ψ_0 $(=K\psi_0)$ is nondegenerate] in the manner of Eqs. (1)—(4), we get the angle of rotation for the ψ_+ component, proportional to $\langle\psi_+|\mathscr{E}_1\cdot l|\psi_+\rangle$ $(=\langle K\psi_-|\mathscr{E}_1\cdot l|\psi_+\rangle)$, as

$$\begin{aligned}\phi_0^+ &= \tfrac{1}{2}(1+K)\mathscr{K}(\langle K\psi_-|\mathscr{E}_1|0\rangle\cdot\langle K0|l|\psi_+\rangle + \langle K\psi_-|l|0\rangle\cdot\langle K0|\mathscr{E}_1|\psi_+\rangle)\\ &= \tfrac{1}{2}\mathscr{K}(\langle K\psi_-|\mathscr{E}_1|0\rangle\cdot\langle K0|l|\psi_+\rangle + \langle K\psi_-|l|0\rangle\cdot\langle K0|\mathscr{E}_1|\psi_+\rangle\\ &\quad + \langle K\psi_+|l|0\rangle\cdot\langle K0|\mathscr{E}_1|\psi_-\rangle + \langle K\psi_+|\mathscr{E}_1|0\rangle\cdot\langle K0|l|\psi_-\rangle)\,,\end{aligned} \tag{10a}$$

where we have made use of Eqs. (8) and (9) and $\kappa^4 = (\pm i)^{4N} = (-1)^{2N} = 1$, regardless of an even or odd number of electrons. For an odd number of electrons, however, because the operators are spin independent, care must be exercised to use the states of the same spin for the matrix element. Similarly, we can write down the angle of rotation for the ψ_- component,

$$\begin{aligned}\phi_0^- &= \tfrac{1}{2}(1+K)\mathcal{K}(\langle K\psi_+ | \mathcal{E}_1 | 0\rangle \cdot \langle K0 | l | \psi_-\rangle + \langle K\psi_+ | l | 0\rangle \cdot \langle K0 | \mathcal{E}_1 | \psi_-\rangle) \\ &= \tfrac{1}{2}\mathcal{K}(\langle K\psi_+ | \mathcal{E}_1 | 0\rangle \cdot \langle K0 | l | \psi_-\rangle + \langle K\psi_+ | l | 0\rangle \cdot \langle K0 | \mathcal{E}_1 | \psi_-\rangle \\ &\quad + \langle K\psi_- | l | 0\rangle \cdot \langle K0 | \mathcal{E}_1 | \psi_+\rangle + \langle K\psi_- | \mathcal{E}_1 | 0\rangle \langle K0 | l | \psi_+\rangle)\,, \end{aligned} \tag{10b}$$

which is seen to be identical to (10a). Therefore, in the symmetrical combination of the state self-product $[A]=\psi_+^*\psi_+ + \psi_-^*\psi_- = (K\psi_-)^*\psi_+ + (K\psi_+)^*\psi_-$, the two angles of rotations *add* to give nonvanishing optical rotation for the time-reversal E state of a C_4 molecule. In the antisymmetric state product $\{A\}$, the two contributions to angles subtract to give a zero matrix element. This is so even though the apparent point-group selection rule is still satisfied; a similar use of time reversal also applies to other time-reversal-degenerate states. For example, in the E state of the T group, for which $E \otimes E = A + \{A\} + E$, only the symmetric $A = E_+^* E_+ + E_-^* E_-$ will give optical rotation. This result implies that the two opposite components of E have the same natural optical activity for random systems. This is different from the finding of Atkins and Gomes[24] for the opposite rotational optical activity for $|JM\rangle$-vs-$|J\text{-}M\rangle$ components for *oriented* rotators (see below).

For a molecule belonging to the S_4 point group, we see from Table I that the pseudoscalars $R_+ l_-$ and $R_- l_+$ belong to B. Similarly, the $E \otimes E$ state products $\psi_+^*\psi_- = \Pi_-\Pi_-$ and $\psi_-^*\psi_+ = \Pi_+\Pi_+$ both belong to B and both are symmetric. However, these products do not have cancelled phases and are not the usual intermediate $|\psi_\pm\rangle\langle\psi_\pm|$ in second-order perturbation, nor are they the usual $\langle\psi_\pm|\psi_\pm\rangle$ which belong to A, with coherent phase, in the optical activity expression $\phi_0 = \mathcal{K}\,\mathrm{Im}(\langle\psi_\pm | R | 0\rangle \cdot \langle 0 | M | \psi_\pm\rangle)$. This is one reason for the absence of optical rotation in the degenerate E state in S_4. To see the effect of time reversal, we take the first state product $\psi_+^*\psi_- = (K\psi_-)^*\psi_-$ and write the matrix element for the "rotatory-strength" operation:

$$\begin{aligned}\phi_0 &= \tfrac{1}{2}(1+K)\mathcal{K}(\langle K\psi_- | \mathcal{E}_1 | 0\rangle \cdot \langle K0 | l | \psi_-\rangle \\ &\qquad + \langle K\psi_- | l | 0\rangle \cdot \langle K0 | \mathcal{E}_1 | \psi_-\rangle) \\ &= \mathcal{K}(\langle K\psi_- | \mathcal{E}_1 | 0\rangle \cdot \langle K0 | l | \psi_-\rangle \\ &\qquad + \langle K\psi_- | l | 0\rangle \cdot \langle K0 | \mathcal{E}_1 | \psi_-\rangle) \\ &= \langle\psi_+ | \mathcal{E}_1 | 0\rangle \cdot \langle 0 | l | \psi_-\rangle \\ &\quad + \langle\psi_+ | l | 0\rangle \cdot \langle 0 | \mathcal{E}_1 | \psi_-\rangle\,. \end{aligned} \tag{11}$$

Strictly speaking, this is not a legitimate expression for optical rotation as an observable because the "initial" (ψ_-) and "final" (ψ_+) states have incoherent phases. However, it will be a valid observable when it is squared and the phase difference cancels as in Rayleigh and Raman intensity formulas. Formally, since the optical-rotation "perturbation" connects the two degenerate components ψ_+ and ψ_-, it therefore splits the energy as in the Jahn-Teller effect.

Even though S_4 symmetry means an achiral molecule, it is seen that time reversal gives no obvious reason for the lack of optical rotation. Furthermore, the apparent point-group selection rule for S_4 is satisfied and the matrix elements are not required to be zero. Because of the phase-coherence criterion required for an observable, this nonzero matrix element does not represent the usual inherent natural optical rotation for chiral molecules (see Table II). Instead, it represents the splitting of degeneracy by the optical-rotation operator. From the same table and based on the above reasons, it can be concluded that none of the degenerate states of achiral molecules gives optical rotation, although the overt point-group selection rule is satisfied. It may also be concluded that in chiral molecules (C_n and T) the time-reversal-degenerate states ψ_+ and ψ_- have the same optical-rotatory strengths. In achiral molecules ($S_{2(2n+2)}$) the two time-reversal-degenerate states are connected and are formally "split" by the optical-rotatory-strength operator.

The above results, Eqs. (10) and (11), are all for random systems. For an *oriented* molecule, if the ψ_+ and ψ_- of E can be separated, we consider the electric-dipole—electric-dipole scattering (versus the electric-dipole—magnetic-dipole scattering of natural optical activity) of light propagating along the quantization axis z. If we define optical activity as being proportional to the difference in scattering of right versus left-circularly polarized light we obtain a result similar to that of Atkins and Gomes:[24]

$$\begin{aligned}\phi_0 \sim \mathcal{C}(&\langle j | R_+ | b\rangle\langle b | R_- | j\rangle \\ &- \langle j | R_- | b\rangle\langle b | R_+ | j\rangle)\,, \end{aligned} \tag{12a}$$

where $\mathcal{C}$ is a symbolic constant. This antisymmetric combination of operator products $(R_+R_- - R_-R_+)$ belongs to the irreducible representation A in C_4. As mentioned before, the time-symmetric and antisymmetric state products $\psi_+^*\psi_+ \pm \psi_-^*\psi_-$ also belong to A in C_4. Therefore, *point-group symmetry is not sufficient,* because again there is an *ambivalence. Only the time-reversal operator can resolve this.* We start by writing the matrix element over the ψ_+ component as in Eqs. (10) and then note its relationship to the matrix element of the ψ_- component:

$$\begin{aligned}\phi_0^+ &= \tfrac{1}{2}(1+K)\mathcal{C}(\langle\psi_+ | R_+ | 0\rangle\langle 0 | R_- | \psi_+\rangle - \langle\psi_+ | R_- | 0\rangle\langle 0 | R_+ | \psi_+\rangle) \\ &= \tfrac{1}{2}\mathcal{C}(\langle K\psi_- | R_+ | 0\rangle\langle K0 | R_- | \psi_+\rangle - \langle K\psi_- | R_- | 0\rangle\langle K0 | R_+ | \psi_+\rangle \\ &\quad + \langle K\psi_+ | R_- | 0\rangle\langle K0 | R_+ | \psi_-\rangle - \langle K\psi_+ | R_+ | 0\rangle\langle K0 | R_- | \psi_-\rangle) \\ &= -\phi_0^-\,, \end{aligned} \tag{12b}$$

TABLE II. Matrix elements of pseudoscalar operators over self-products of degenerate states.[a–c]

	C_3	C_4	S_4	C_{3v}	D_3	D_4	D_{2d}
Rectangular coordinates							
$[R\cdot M]^+$ over $[\Psi\cdot\Psi]^+$	$\underline{A\times A}$	$\underline{A\times A}$	$B\times A$	$A_2\times A_1$	$\underline{A_1\times A_1}$	$\underline{A_1\times A_1}$	$B_1\times A_1$
$[R\cdot M]^+$ over $[\Psi\cdot\Psi]^-$	$A\times E$	$A\times B$	$\underline{B\times B}$	$A_2\times E$	$A_1\times E$	$A_1\times B_1$	$\underline{B_1\times B_1}$
$[R\cdot M]^+$ over $[\Psi\times\Psi]^+$	$A\times E$	$A\times B$	$\underline{B\times B}$	$A_2\times E$	$A_1\times E$	$A_1\times B_2$	$B_1\times B_2$
$[R\cdot M]^+$ over $[\Psi\times\Psi]^-$	$\underline{A\times A}$	$\underline{A\times A}$	$B\times A$	$\underline{A_2\times A_2}$	$A_1\times A_2$	$A_1\times A_2$	$B_1\times A_2$
Polar coordinates							
$(R\cdot M)^+$ over $(\Psi\cdot\Psi)^+$	$\underline{A\times A}$	$\underline{A\times A}$	$B\times A$	$A_2\times A_1$	$\underline{A_1\times A_1}$	$\underline{A_1\times A_1}$	$B_1\times A_1$
$(R\cdot M)^+$ over $(\Psi\cdot\Psi)^-$	$\underline{A\times A}$	$\underline{A\times A}$	$B\times A$	$\underline{A_2\times A_2}$	$A_1\times A_2$	$A_1\times A_2$	$B_1\times A_2$
$(R\cdot M)^+$ over $(\Psi\times\Psi)^+$	$A\times E$	$A\times B$	$\underline{B\times B}$	$A_2\times E$	$A_1\times E$	$A_1\times B_2$	$\underline{B_1\times B_1}$
$(R\cdot M)^+$ over $(\Psi\times\Psi)^-$	$A\times E$	$A\times B$	$\underline{B\times B}$	$A_2\times E$	$A_1\times E$	$A_1\times B_1$	$B_1\times B_2$

[a] By definition $[R\cdot M]^+$ over $[\Psi\cdot\Psi]^-$ means four terms: $(xl_x)_{xx}-(xl_x)_{yy}+(yl_y)_{xx}-(yl_y)_{yy}$. Refer to Table I, footnote a, for detailed definitions.

[b] See Table I for definition of the operators and degenerate-state products. In the entries here the direct products represent the symmetry of integrands in the matrix element. Nonvanishing matrix elements over off-diagonal components mean the formal splitting of the degeneracy.

[c] Underlined terms represent possible nonvanishing matrix elements. However, note that for achirality (C_{3v}, S_4, and D_{2d}) none of these matrix elements represents the diagonal matrix elements with canceling coherent phases and contains the (symmetric) sum (rather than difference) of degenerate components. These latter conditions are required for natural inherent optical activity (see the terms in inherently active chiral groups, C_3, C_4, D_3, D_4, for comparison).

where we have made use of the relationships $KR_{\pm}K^{-1}=R_{\pm}^{\dagger}$ and $R_{\pm}^{\dagger}=R_{\mp}$, which also account for the fact that $R_+R_- - R_-R_+$ is Hermitian and time odd. Equation (12) shows that the two opposite components of E in C_4, when oriented and separated, will have opposite optical rotation expressible through the electric-dipole—electric-dipole polarizability. This is in agreement with the results of the Faraday effect in which the two degenerate components are separated by application of an external magnetic field. The same should be true of the components of E_1 and E_2 of C_5 and C_6, etc., up to the limit of C_∞. In the limit of continuous symmetry this approaches the case of separated and oriented rotors $|JM\rangle$ and $|J-M\rangle$, which was shown by Atkins and

TABLE III. Irreducible representations and degenerate base products of electric and magnetic dipoles and quadrupoles[a] in hexagonal groups and subgroups.

Multipoles and products	Bases and products	D_{6d}	D_6	C_{6v}	D_{2d}	D_3	C_{3v}	C_6/C_3
R_1	Z	B_2	A_2	A_1	B_2	A_2	A_1	A/A
	$(x,y)\equiv(E_{1x},E_{1y})$	E_1	E_1	E_1	E	E	E	E_1/E
M_1	l_z	A_2	A_2	A_2	A_2	A_2	A_2	A/A
	$(l_x,l_y)\equiv(E_{5l_x},E_{5l_y})$	E_5	E_1	E_1	E	E	E	E_1/E
$R_1\otimes M_1$	(xl_z-zl_x,yl_z-zl_y)	$E_1=E_1\otimes A_2=B_2\otimes E_5$	E_1	E_1	E	E	E	E_1/E
$M_2\subset R_1\otimes M_1$	$[\frac{3}{2}(xl_z+zl_x),\frac{3}{2}(yl_z+zl_y)]$ $\equiv[E_{1\eta},E_{1\xi}]$	$E_1=E_1\otimes A_2=B_2\otimes E_5$	E_1	E_1	E	E	E	E_1/E
$M_2\subset R_1\otimes M_1$	$[\frac{3}{2}(xl_y+yl_x),\frac{3}{2}(xl_x-yl_y)]$ $\equiv[E_{4x},E_{4y}]$	$E_4\subset E_1\otimes E_5$	E_2	E_2	$[A_2,A_1]$	E	E	E_2/E
$M_2\subset R_1\otimes M_1$	$\frac{1}{2}(zl_z-xl_x-yl_y)$	$B_1=B_2\otimes A_2$ $B_1\subset E_1\otimes E_5$	A_1	A_2	B_1	A_1	A_2	A/A
$R_1\otimes M_1$	xl_y-yl_x	$B_2\subset E_1\otimes E_5$	A_2	A_1	B_2	A_2	A_1	A/A
R_2	$[xy,\frac{1}{2}(x^2-y^2)]\equiv[E_{2s},E_{2c}]$	E_2	E_2	E_2	$[B_2,B_1]$	E	E	E_2/E
R_2	$[xz,yz]\equiv[E_{5\eta},E_{5\xi}]$	E_5	E_1	E_1	E	E	E	E_1/E
R_2	$\frac{1}{2}(3z^2-r^2)\equiv A_{1z^2}$	A_1	A_1	A_1	A_1	A_1	A_1	A/A

[a] Transformations were first obtained in D_{6d}. Symmetries in lower point groups are obtained from correlation tables. (D_{2d} has C_2' axis along x axis.) For correlation see J. A. Salthouse and M. J. Ware, *Point-Group Character Tables and Related Data* (Cambridge University, Cambridge, England, 1972) and C. J. H. Schutte, *The Theory of Molecular Spectroscopy 1* (North-Holland, Amsterdam, 1976).

Gomes[24] to have opposite optical rotation for light propagating along the quantization axis. However, neither our $\psi_\pm$ pair (though they have no parity) nor Atkin's $|J\pm M\rangle$ pair (which have parity) can be called true chiral enantiomers according to Barron,[16] in the sense of chiral isomers giving natural optical rotation by the usual $R\cdot M$ or *electric-dipole—magnetic-dipole* mechanism. Barron defined an enantiomer of a truly chiral object as that obtained by charge conjugation plus space inversion (see below).

IV. HIGHER MULTIPOLE PSEUDOSCALAR AND SELECTION RULES OVER DEGENERATE STATES

In this section we explore the distinction between different degenerate states (e.g., E_2 versus E_1 in D_6) in their self-product in generating different pseudoscalars (dipole $R_1\cdot M_1$, quadrupole $R_2\cdot M_2$, and octopole $R_3\cdot M_3$). We derive the transformations of the electric (R_n) and magnetic (M_n) dipoles ($n=1$) and quadrupole ($n=2$) and octopole ($n=3$) operators in point groups D_{6d}, T_d, and D_{4d} and then show how they transform in subgroups of these reference groups. These are shown in Tables III—VII. It is found that in chiral groups (for example, C_6 and D_6) E_2 cannot generate a dipole pseudoscalar but can generate quadrupole and octopole pseudoscalars. In achiral groups, the higher the symmetry, the fewer degenerate-state self-products that will give the pseudoscalar function. For example, in D_{6d}, only E_3^2 (not E_1^2 or E_2^2) will give the pseudoscalar B_1 and then only for the octopole scalar. In T_d, only E^2 (not F_1^2 or F_2^2) will give the pseudoscalar A_2. In S_8, E_2^2 contains the quadrupole and octopole but not the dipole component. The various pseudoscalar products in D_{6d} are, using the symbols defined in Tables III and IV, given by

$$R_1\cdot M_1=\frac{e^2\hbar}{2mc}(xl_x+yl_y+zl_z)=\frac{e^2\hbar}{2mc}(E_{1x}E_{5lx}+E_{1y}E_{5ly}+B_2\cdot A_2)\subset B_1, \tag{13a}$$

$$\begin{aligned}R_2\cdot M_2=\frac{2e^2\hbar}{3mc}[&\tfrac{1}{2}(x^2-y^2)\tfrac{3}{2}(xl_x-yl_y)+xy\tfrac{3}{2}(xl_y+yl_x)+xz\tfrac{3}{2}(xl_z+zl_x)\\ &+yz\tfrac{3}{2}(yl_z+zl_y)+\tfrac{1}{2}(3z^2-r^2)\tfrac{1}{2}(2zl_z-xl_x-yl_y)]\\ =\frac{2e^2\hbar}{3mc}&(E_{2c}E_{4y}+E_{2s}E_{4x}+E_{5\eta}E_{1\eta}+E_{5\xi}E_{1\xi}+A_{1z^2}B_1)\subset B_1\ ,\end{aligned} \tag{13b}$$

TABLE IV. Irreducible representations and degenerate base products of electric and magnetic octopoles in hexagonal groups and subgroups.[a]

Multipoles and products	Bases and products	D_6/D_3	C_{6v}/C_{3v}	D_{2d}	D_{6d}	C_6/C_3
$R_{3,0}$	$\frac{1}{2}z(5z^2-3r^2)$	A_2/A_2	A_1/A_1	B_2	B_2	A/A
$R_{3,\pm1}$	$[x(5z^2-r^2),y(5z^2-r^2)]$ $\equiv[E_{1xz^2},E_{1yz^2}]$	E_1/E	E_1/E	E	E_1	E_1/E
$R_{3,\pm3}$	$[y(3x^2-y^2),x(x^2-3y^2)]$ $\equiv[E_{3\theta},E_{3\epsilon}]$	B_2B_1/A_2A_1	B_2B_1/A_2A_1	E	E_3	BB/AA
$R_{3,\pm2}$	$[xyz,\frac{1}{2}z(x^2-y^2)]\equiv[E_{4\theta},E_{4\epsilon}]$	E_2/E	E_2/E	$[A_1,A_2]$	E_4	E_2/E
$M_{3,\pm3}$	$\{[5l_x(x^2-y^2)-10l_yxy],$ $[10l_xxy+5l_y(x^2-y^2)]\}$ $\equiv\{E_{3u}''',E_{3v}'''\}$	B_1B_2/A_1A_2	B_2B_1/A_2A_1	E	$E_3'''\subset E_5\otimes E_2$	BB/AA
$M_{3,\pm1}$	$\{[-l_x(x^2-y^2)-2l_yxy],$ $[-2l_xxy+l_y(x^2-y^2)]\}$ $\equiv\{E_{5u},E_{5v}\}$	E_1/E	E_1/E	E	$E_5\subset E_5\otimes E_2$	E_1/E
$M_{3,\pm1}$	$[2l_x(3z^2-r^2),2l_y(3z^2-r^2)]$ $\equiv[E_{5xu},E_{5yv}]$	E_1/E	E_1/E	E	$E_5\subset E_5\otimes A_1$	E_1/E
$M_{3,\pm1}$	$[8l_zxz,8l_zyz]\equiv[E_{5\eta u},E_{5\xi v}]$	E_1/E	E_1/E	E	$E_5\subset A_2\otimes E_5$	E_1/E
M_{30}	$4l_z(3z^2-r^2)\equiv A_2^a$	A_2/A_2	A_2/A_2	A_2	$A_2=A_2\otimes A_1$	A/A
M_{30}	$-8(l_xxz+l_yyz)\equiv A_2^e$	A_2/A_2	A_2/A_2	A_2	$A_2\subset E_5\otimes E_5$	A/A
$M_1\times R_2$	l_xyz-l_yxz	A_1/A_1	A_1/A_1	A_1	$A_1\subset E_5\otimes E_5$	A/A
$M_{3\pm2}$	$[40(l_xyz+l_yxz),40(l_xxz-l_yyz)]$ $\equiv[E_{2u},E_{2v}]$	E_2/E	E_2/E	$[B_1,B_2]$	$E_2\subset E_5\otimes E_5$	E_2/E
$M_{3\pm2}$	$[40l_zxy,20l_z(x^2-y^2)]$ $\equiv[E_{2u}''',E_{2v}''']$	E_2/E	E_2/E	$[B_1,B_2]$	$E_2'''=A_2\otimes E_2$	E_2/E

[a] As a price to pay for insisting on the same degenerate components as base functions in the correlation from D_{6d} to nondegenerate representation in C_{6v}/C_{3v} (e.g., for E_3), one must choose a different x axis and let σ_v pass through it in C_{6v}/C_{3v}. There is no loss of generality. However, D_{2d} has a C_2' axis along the x axis, the same as D_6 and D_{6d}. Superscripts e and a on A's denote the origin of A as coming from the product of E's or the product of A's. Triple primes denote different transformation matrices for the E's.

TABLE V. Irreducible representations from degenerate base products of electric and magnetic dipoles (R_1, M_1) and quadrupoles $(R_2, M_2)^a$ in T_d, O, T, and S_4.

Multipoles and products	Degenerate bases and products	T	O	T_d	S_4
R_1	(x,y,z)	F	F_1	F_2	E,B
M_1	(l_x,l_y,l_z)	F	F_1	F_1	E,A
$R_1 \cdot M_1$	$xl_x+yl_y+zl_z$	$A\subset F\otimes F$	$A_1\subset F_1\otimes F_1$	$A_2\subset F_2\otimes F_1$	B
$R_1\otimes M_1$	$[(yl_z-zl_y),(zl_x-xl_z),(xl_y-yl_x)]$	$[F]\subset F\otimes F$	$[F_1]\subset F_1\otimes F_1$	$F_2\subset F_2\otimes F_1$	E,B
$M_2\subset R_1\otimes M_1$	$[(yl_z+zl_y),(zl_x+xl_z),(xl_y+yl_x)]$ $\equiv[M_{2\xi},M_{2\eta},M_{2\zeta}]$	$F\subset F\otimes F$	$F_2\subset F_1\otimes F_1$	$F_1\subset F_2\otimes F_1$	E,A
$M_2\subset R_1\otimes M_1$	$[\frac{1}{2}(2zl_z-xl_x-yl_y),(\sqrt{3}/2)(xl_x-yl_y)$ $\equiv[e_u''',e_v''']$	$E\subset F\otimes F$	$E\subset F_1\otimes F_1$	$E'''\subset F_2\otimes F_1$	A,B
R_2	$[\frac{1}{2}(3z^2-r^2),(\sqrt{3}/2)(x^2-y^2)]=[e_u,e_v]$	$E\subset F\otimes F$	$E\subset F_1\otimes F_1$	$E\subset F_2\otimes F_2$	A,B
R_2	$(yz,zx,xy)\equiv(\xi,\eta,\zeta)$	$F\subset F\otimes F$	$F_2\subset F_1\otimes F_1$	$F_2\subset F_2\otimes F_2$	E,B
$M_2 \cdot R_2$	$e_u'''e_u+e_v'''e_v$	$A\subset E\otimes E$	$A_1\subset E\otimes E$	$A_2\subset E'''\otimes E$	B
$M_2\otimes R_2$	$e_u'''e_v-e_v'''e_u$	$[A]\subset E\otimes E$	$[A_2]\subset E\otimes E$	$A_1\subset E'''\otimes E$	A
$M_2\otimes R_2$	$[(1/\sqrt{2})(-e_u'''e_u+e_v'''e_v),$ $(1/\sqrt{2})(e_u'''e_v+e_v'''e_u)]$	$E\subset E\otimes E$	$E\subset E\otimes E$	$E\subset E'''\otimes E$	A,B
$M_2\otimes R_2$	$M_{2\xi}\xi+M_{2\eta}\eta+M_{2\zeta}\zeta$	$A\subset F\otimes F$	$A_1\subset F_2\otimes F_2$	$A_2\subset F_1\otimes F_2$	B
$M_2\otimes R_2$	$[\frac{1}{2}(2M_{2\zeta}\zeta-M_{2\xi}\xi-M_{2\eta}\eta)$ $(\sqrt{3}/2)(M_{2\xi}\xi-M_{2\eta}\eta)]$	$E\subset F\otimes F$	$E\subset F_2\otimes F_2$	$E'''\subset F_1\otimes F_2$	A,B
$M_2\otimes R_2$	$[(M_{2\eta}\zeta+\eta M_{2\zeta}),(M_{2\zeta}\xi+\zeta M_{2\xi}),$ $(M_{2\xi}\eta+\xi M_{2\eta})]$	$F\subset F\otimes F$	$F_2\subset F_2\otimes F_2$	$F_1\subset F_1\otimes F_2$	E,A
$M_2\otimes R_2$	$[(M_{2\eta}\zeta-\eta M_{2\zeta}),(M_{2\zeta}\xi-\zeta M_{2\xi}),$ $(M_{2\xi}\eta-\xi M_{2\eta})]$	$[F]\subset F\otimes F$	$[F_1]\subset F_2\otimes F_2$	$F_2\subset F_1\otimes F_2$	E,B

[a] E''' denotes a different transformation matrix from E.

TABLE VI. Irreducible and degenerate base products of electric and magnetic octopoles in T_d and S_4.

Multipoles and products	Bases and products	S_4	T_d
R_3	$30xyz$	A	A_1
R_3	$\{\frac{1}{4}x[(5z^2-r^2)+(x^2-3y^2)],-\frac{1}{4}y[(5z^2-r^2)+(y^2-3x^2)],(y^2-x^2)z\}$ $=\{(z^2-y^2)x,(x^2-z^2)y,(y^2-x^2)z\}\equiv\{T_{1x},T_{1y},T_{1z}\}$	$\{E,A\}$	T_1
R_3	$\{-\frac{1}{4}x[3(5z^2-r^2)-5(x^2-3y^2)],-\frac{1}{4}y[3(5z^2-r^2)-5(y^2-3x^2)],(5z^2-3r^2)z\}$ $=\{(5x^2-3r^2)x,(5y^2-3r^2)y,(5z^2-3r^2)z\}\equiv\{T_{2x},T_{2y},T_{2z}\}$	$\{E,B\}$	T_2
M_{32}	$\frac{4}{3}(yzl_x+zxl_y+xyl_z)$	B	$A_2\subset F_2\otimes F_1$
$M_{33}M_{31}M_{30}$	$[(xyl_y+xzl_z),(yzl_z+xyl_x),(xzl_x+yzl_y)]\equiv[F_{1x},F_{1y},F_{1z}]$	$[E,A]$	$F_1\subset F_2\otimes F_1$
$M_{33}M_{31}M_{32}$	$[(xyl_y-xzl_z),(yzl_z-xyl_x),(xzl_x-yzl_y)]\equiv[F_{2x},F_{2y},F_{2z}]$	$[E,B]$	$F_2\subset F_2\otimes F_1$
$E_2\otimes M_1$	$[\frac{1}{2}(2xyl_z-yzl_x-zxl_y),(\sqrt{3}/2)(yzl_x-zxl_y)]$	$[A,B]$	$E\subset F_2\otimes F_1$
$M_{33}M_{32}M_{31}$ $\subset R_2\otimes M_1$	$\{[(-\sqrt{3}/2)e_u-\frac{1}{2}e_v]l_x,[(\sqrt{3}/2)e_u-\frac{1}{2}e_v]l_y,e_vl_z\}$ $=[(\sqrt{3}/2)(y^2-z^2)l_x,(\sqrt{3}/2)(z^2-x^2)l_y,(\sqrt{3}/2)(x^2-y^2)l_z]$ $\equiv[F'_{2_x},F'_{2_y},F'_{2_z}]$	$[E,B]$	$F'_2\subset E\otimes F_1$
$M_{33}M_{31}M_{30}$ $\subset R_2\otimes M_1$	$\{[-\frac{1}{2}e_u+(\sqrt{3}/2)e_v]l_x,[-\frac{1}{2}e_u-(\sqrt{3}/2)e_v]l_y,e_ul_z\}$ $=[\frac{1}{2}(3x^2-r^2)l_x,\frac{1}{2}(3y^2-r^2)l_y,\frac{1}{2}(3z^2-r^2)l_z]$ $\equiv[F'_{1_x},F'_{1_y},F'_{1_z}]$	$[E,A]$	$F'_1\subset E\otimes F_1$
M_3	$\{[-(20/\sqrt{3})F'_{2_x}-20F_{2_x}],[-(20/\sqrt{3})F'_{2_y}-20F_{2_y}],[-(20/\sqrt{3})F'_{2_z}-20F_{2_z}]\}$ $\equiv[F''_{2_x},F''_{2_y},F''_{2_z}]$	$[E,B]$	F''_2
M_3	$[(4F'_{1_x}-4F_{1_x}),(4F'_{1_y}-4F_{1_y}),(4F'_{1_z}-4F_{1_z})]$ $\equiv[F''_{1_x},F''_{1_y},F''_{1_z}]$	$[E,A]$	F''_1

[a] Both T and F are used to denote the three-dimensional irreducible representation, T for electric octopole, F for magnetic.

[b] Primes and double primes here are used to denote different bases for the same irreducible representation with the same matrix of transformation.

[c] The definition of e_u, e_v from electric quadrupoles has been given in Table V.

$$R_3\cdot M_3=\sum_{m=-3}^{3}(-1)^m R_{3m}M_{3-m}$$

$$=\frac{3e^2\hbar}{32mc}[B_2(A_2^e+A_2^a)+E_{1xz^2}(E_{5u}+E_{5\eta u}+E_{5xu})+E_{1yz^2}(E_{5v}+E_{5\xi v}+E_{5yv})$$

$$+E_{3\theta}E_{3v}'''E_{3\epsilon}E_{3u}'''+E_{4\theta}(E_{2u}+E_{2u}''')+E_{4\epsilon}(E_{2v}+E_{2v}''')]\subset B_1\ . \tag{13c}$$

The various pseudoscalar products in T_d are, using the symbols defined in Tables V and VI, given by

$$R_1\cdot M_1=\sum_{m=-1}^{1}(-1)^m R_{1m}M_{1-m}=F_2\cdot F_1\subset A_2\ , \tag{14a}$$

$$R_2\cdot M_2=\frac{2e^2\hbar}{3mc}\left[\frac{1}{2}(3z^2-r^2)\frac{1}{2}(2zl_z-xl_x-yl_y)+\frac{\sqrt{3}}{2}(x^2-y^2)\frac{\sqrt{3}}{2}(xl_x-yl_y)\right.$$

$$\left.+\frac{3}{2}[yz(yl_z+zl_y)+zx(zl_x+xl_z)+xy(xl_y+yl_x)]\right]$$

$$=\frac{2e^2\hbar}{3mc}(e_ue_u'''+e_ve_v'''+F_{2\xi}F_{1x}+F_{2\eta}F_{1y}+F_{2\xi}F_{1z})\subset A_2\ , \tag{14b}$$

$$R_3\cdot M_3=\frac{3e^2\hbar}{32mc}(A_1\cdot A_2+T_{1x}F_{2x}''+T_{1y}F_{2y}''+T_{1z}F_{2z}''+T_{2x}F_{1x}''+T_{2y}F_{1y}''+T_{2z}F_{1z}'')\subset A_2\ . \tag{14c}$$

The pseudoscalar products in D_{4d} are obtained from Tables III, IV, and VII as follows:

$$R_1\cdot M_1=\frac{e^2\hbar}{2mc}(E_{1x}E_{3l_x}+E_{1y}E_{3l_y}+B_2A_2)\subset B_1\ , \tag{14d}$$

$$R_2\cdot M_2=\frac{2e^2\hbar}{3mc}(E_{2s}E_{2x}+E_{2c}E_{2y}+E_{3\eta}E_{1\eta}+E_{3\xi}E_{1\xi}+A_{1z^2}B_1)\subset B_1\ , \tag{14e}$$

$$R_3\cdot M_3=\frac{3e^2\hbar}{3mc}[B_2(A_2^e+A_2^a)+E_{1xz^2}(E_{3u}+E_{3\eta u}+E_{3xu})+E_{1yz^2}(E_{3v}+E_{3\xi v}+E_{3yv})+E_{3\theta}E_{1v}'''+E_{3\epsilon}E_{1u}'''$$

$$+E_{2\theta}(E_{2u}+E_{2u}''')+E_{2\epsilon}(E_{2v}+E_{2v}''')]\subset B_1\ . \tag{14f}$$

The correlations to lower point groups are given in the corresponding tables. The "selection rules" of these pseudoscalars over the components may be perceived from the definitions of the electric (R_n) and magnetic (M_n) multipoles,[10,25]

$$R_{n,-M}=er^n\left[\frac{4\pi}{2n+1}\right]^{1/2}Y_{n,-M}(\theta,\phi)\ , \tag{15a}$$

$$M_{n,M}=\frac{e\hbar}{m_ec}(4\pi n)^{1/2}$$

$$\times\sum_{m=-1}^{1}C(n-1,1,n;M-m,m,M)$$

$$\times r^{n-1}Y_{n-1,M-m}(\theta,\phi)\left[\frac{L_m}{n+1}+S_m\right]\ , \tag{15b}$$

where C is the Clebsch-Gordan coefficient and L_m and S_m are orbital and spin angular momentum operators, respectively, with $m=+1$, -1, and 0 corresponding to raising, lowering, and z-component operators. The matrix element we consider is symbolically [referring to Eq. (8)] given by

TABLE VII. Equivalence of the symmetry designations[a] of electromagnetic multipoles in D_{6d} and D_{4d}.

D_{6d}	D_{4d}	Equivalent transformation matrix in D_{4d}
B_2	B_2	
(E_{1x},E_{1y})	(E_{1x},E_{1y})	
A_2	A_2	
(E_{5l_x},E_{5l_y})	$(E_3l_xE_3l_y)$	
$(E_{1\eta},E_{1\xi})$	$(E_{1\eta},E_{1\xi})$	
(E_{4x},E_{4y})	(E_{2x},E_{2y})	
B_1	B_1	
(E_{2s},E_{2c})	(E_{2s},E_{2c})	
$(E_{5\eta},E_{5\xi})$	$(E_{3\eta},E_{3\xi})$	
A_{1z^2}	A_{1z^2}	
(E_{1xz^2},E_{1yz^2})	(E_{1xz^2},E_{1yz^2})	(E_{1x},E_{1y})
$(E_{3\theta},E_{3\epsilon})$	$(E_{3\theta},E_{3\epsilon})$	$(E_{3\eta}E_{3\xi})$
$(E_{4\theta},E_{4\epsilon})$	$(E_{2\theta},E_{2\epsilon})$	
(E_{3u}''',E_{3v}''')	(E_{1u}''',E_{1v}''')	$(E_{1\xi},E_{1\eta})$
(E_{5u},E_{5v})	(E_{3u},E_{3v})	(E_{3l_x},E_{3l_y})
(E_{5xu},E_{5yv})	(E_{3xu},E_{3yv})	
$(E_{5\eta u},E_{5\xi v})$	$(E_{3\eta u},E_{3\xi v})$	
A_2^a	A_2^a	
A_2^e	A_2^e	
(E_{2u},E_{2v})	(E_{2u},E_{2v})	
(E_{2u}''',E_{2v}''')	(E_{2u}''',E_{2v}''')	

[a] See the definitions in Tables III and IV.

$$\phi_0 \cong \sum_n C_n \langle \Gamma | R_n \cdot M_n | \Gamma \rangle$$

$$= C_1 \langle \Gamma | R_1 \cdot M_1 | \Gamma \rangle + \cdots$$

$$= C_1 \left\langle \Gamma \left| \frac{e^2 \hbar}{2mc} \left[\frac{4\pi}{3} \right]^{1/2} \times \sum_{M=-1}^{1} (-1)^M r Y_{1,-M} L_M \right| \Gamma \right\rangle + \cdots , \qquad (16a)$$

where the C_n's are constants.[10,25] The general selection rule is $\Delta l \le 2n-1$, $\Delta m_l = 0$ if the intermediate state is a function of r only. The largest contribution will come from the leading dipolar-pseudoscalar term shown explicitly. The latter has the selection rule $\Delta l = \pm 1$ and $\Delta m_l = 0$. For the D_6 point group, the E_1 irreducible representations contain $Y_{1\pm1}$ (or, x,y) as well as $Y_{2,\pm1}$ (or xz,yz) and $Y_{3,\pm1}$ (xz^2, yz^2, etc.). The wave function $|\Gamma\rangle$ may therefore be represented symbolically as a linear combination,

$$|\Gamma\rangle = \psi_{E1} = p_1 \varphi_1^{(1)}(r) Y_{1\pm1} + d_1 \varphi_2^{(1)}(r) Y_{2\pm1} + \cdots , \qquad (16b)$$

where p_1 and d_1 are constant coefficients and the φ's are functions in radial coordinates, all of which are special to the particular potentials of the molecule. The relative amount of s, p, d, or f orbitals (proportional to $Y_{0,0}$, $Y_{1,m}$, $Y_{2,m}$, or $Y_{3,m}$) in a given linear combination of atomic orbitals (-molecular orbitals) belonging to the E_1 irreducible representation may be estimated, for example, from the perturbed united-atom Rydberg orbitals to which these E_1's correlate.[26,27] The leading dipolar pseudoscalar matrix element is then proportional to

$$\phi^0_{E_1} \cong C_1 p_1 d_1 \langle \varphi_1^{(1)}(r) Y_{1\pm1} | R_1 \cdot M_1 | \varphi_2^{(1)}(r) Y_{2,\pm1} \rangle + \cdots , \qquad (17)$$

we assume from now on that the intermediate state has no angular dependence. This may be compared with the E_2 irreducible representation in the same D_6 point group, in which the lowest spherical harmonics are second order, i.e., $Y_{2,\pm2}$ (as x^2-y^2, xy). Thus,

$$|\Gamma\rangle = \psi_{E_2} = d_2 \varphi_2^{(2)}(r) Y_{2,\pm2} + f_2 \varphi_3^{(2)}(r) Y_{3,\pm2} + \cdots , \qquad (18a)$$

$$\phi^0_{E_2} \cong C_1 d_2 f_2 \langle \varphi_2^{(2)}(r) Y_{2,\pm2} | R_1 \cdot M_1 | \varphi_3^{(2)}(r) Y_{3,\pm2} \rangle + \cdots , \qquad (18b)$$

where d_2 and f_2 are constant coefficients.

When intermediate states are considered, the coupling coefficients in Table VIII and other direct-product

TABLE VIII. Coupling of multipole degenerate irreducible representations[a,b] in D_{6d} and D_{4d}.

Mixed electric and magnetic multipoles	Pure electric multipoles	Transformation[b] matrix "Pure" D_{4d}	"Mixed" D_{6d}	"Mixed" D_{4d}
$E_{3\theta}E'''_{3v}+E_{3\epsilon}E'''_{3u}$	$E_{3\theta}E_{3\theta}-E_{3\epsilon}E_{3\epsilon}$	$E_{2\theta}$	B_1	B_1
$E_{3\theta}E'''_{3u}-E_{3\epsilon}E'''_{3v}$	$E_{3\theta}E_{3\epsilon}+E_{3\epsilon}E_{3\theta}$	$E_{2\epsilon}$	B_2	B_2
$E_{3\theta}E'''_{3u}+E_{3\epsilon}E'''_{3v}$	$E_{3\theta}E_{3\epsilon}-E_{3\epsilon}E_{3\theta}$	A_2	A_2	E_{2x}
$E_{3\theta}E'''_{3v}-E_{3\epsilon}E'''_{3u}$	$E_{3\theta}E_{3\theta}+E_{3\epsilon}E_{3\epsilon}$	A_1	A_1	E_{2y}
$E_{4\theta}E_{2v}+E_{4\epsilon}E_{2u}$	$E_{4\theta}E_{2c}+E_{4\epsilon}E_{2s}$	A_1	E_{2s}	A_2
$E_{4\theta}E_{2u}-E_{4\epsilon}E_{2v}$	$E_{4\theta}E_{2s}-E_{4\epsilon}E_{2c}$	A_2	E_{2c}	A_1
$E_{4\theta}E_{2u}+E_{4\epsilon}E_{2v}$	$E_{4\theta}E_{2c}-E_{4\epsilon}E_{2s}$	B_1	B_1	B_1
$E_{4\theta}E_{2v}-E_{4\epsilon}E_{2u}$	$E_{4\theta}E_{2s}+E_{4\epsilon}E_{2c}$	B_2	B_2	B_2
$E_{1x}E_5l_y+E_{1y}E_5l_x$	$E_{1x}E_{5\xi}+E_{1y}E_{5\eta}$	$E_{2\theta}$	E_{4x}	E_{2x}
$E_{1x}E_5l_x-E_{1y}E_5l_y$	$E_{1x}E_{5\eta}-E_{1y}E_{5\xi}$	$E_{2\epsilon}$	E_{4y}	E_{2y}
$E_{1x}E_5l_x+E_{1y}E_5l_y$	$E_{1x}E_{5\xi}-E_{1y}E_{5\eta}$	B_1	B_1	B_1
$E_{1x}E_5l_y-E_{1y}E_5l_x$	$E_{1x}E_{5\eta}+E_{1y}E_{5\xi}$	B_2	B_2	B_2
$l_x\xi-l_y\eta$	$\eta\eta+\xi\xi$	A_1	A_1	A_1
$l_x\eta+l_y\xi$	$\eta\xi-\xi\eta$	A_2	A_2	A_2
$l_x\xi+l_y\eta$	$\eta\xi+\xi\eta$	E_{2s}	E_{2u}	E_{2u}
$l_x\eta-l_y\xi$	$\eta\eta-\xi\xi$	E_{2c}	E_{2v}	E_{2v}
$E_{4\theta}E_{4y}+E_{4\epsilon}E_{4x}$	$E_{4\theta}E_{4\epsilon}+E_{4\epsilon}E_{4\theta}$	B_2	$E_{4\theta}$	B_1
$E_{4\theta}E_{4x}-E_{4\epsilon}E_{4y}$	$E_{4\theta}E_{4\theta}-E_{4\epsilon}E_{4\epsilon}$	B_1	$E_{4\epsilon}$	B_2
$E_{4\theta}E_{4x}+E_{4\epsilon}E_{4y}$	$E_{4\theta}E_{4\epsilon}-E_{4\epsilon}E_{4\theta}$	A_2	A_2	A_2
$E_{4\theta}E_{4y}-E_{4\epsilon}E_{4x}$	$E_{4\theta}E_{4\theta}+E_{4\epsilon}E_{4\epsilon}$	A_1	A_1	A_1

[a] The definitions of the degenerate components are given in Tables III and IV.

[b] The degenerate transformation matrix is given only for the mixed electric- and magnetic-multipole case in D_{6d}. (The pure electric-multipole product has a 2×2 matrix differing by a sign from the mixed case for c'_2 and σ_d.) Corresponding definitions in D_{6d} and D_{4d} are in Table VII.

tables[26,28,29] will aid the determination of selection rules. The symmetries of the multipole pseudoscalars given in the tables not only serve to deduce the selection rules, but also will guide the derivation of magnetic pseudoscalar potentials[30] for asymmetric perturbations.[31]

V. CONCLUSIONS AND DISCUSSIONS

We have searched among common point groups of interest for degenerate-state self-products that contain the pseudoscalar symmetry. These degenerate states are given in Table IX. The pseudoscalar operator is found to parallel the vibronic operator of Jahn and Teller[22,23] in that it can connect components of degenerate states. For these degenerate states we can now answer the questions raised in the Introduction. The answers are summarized below.

(1) Degenerate states of achiral molecules will not yield natural optical activity, even if their self-products contain the pseudoscalar symmetry thus satisfying the point-group selection rule. This is because only incoherent products of (different) components constitute the pseudoscalar symmetry component. This point is made clear by contrasting chiral versus achiral point groups (Tables I and II), C_4 versus S_4 (both of order 4), D_3 versus C_{3v} (both of order 6), and D_4 versus D_{2d} (both of order 8). It is also quantitatively illustrated for E of S_4 in Sec. III. In Sec. III it is shown that the two degenerate components of C_4 contribute equal natural optical-rotatory strength in random molecular arrangements. The same is true for other E degenerate states of C_3, D_3, and D_4 molecules (Tables I and II). Thus, the two components reinforce each other.

(2) For time-reversal-degenerate components, e.g., the ψ_+ and ψ_- of C_3 and C_4, it is shown (Sec. III) that point-group symmetry alone is not sufficient to arrive at the above result. There is an ambivalence which only the time-reversal operation, converting $\psi_\pm$ to $\psi_\mp$, can resolve. In addition to the natural optical activity proportional to the pseudoscalar $R \cdot M$, the time-reversal component is shown (Sec. II) to have "oriented" optical activity proportional to $R_+R_- - R_-R_+$ when light propagates along the quantization axis of ψ_+ and ψ_-. The former ($R \cdot M$), which is parity odd, is observable because of the chiral molecule's lack of parity symmetry. The latter ($R_+R_- - R_-R_+$), which is time odd, is observable because of the single time-reversal component's (ψ_+ or ψ_-) lack of time symmetry. It is also seen that the lack of time symmetry in one of the time-reversal-degenerate components, such as ψ_+ in the E, is not the source of isotropic *natural* activity in C_4. This is because the similar component of E in S_4 produces no natural optical activity.

(3) In Sec. II, we show that for a second-order optical interaction, time reversal does not give additional spin selection rules as in the Jahn-Teller effect.[22,23] It is shown that the permutation of degenerate components, however, is meaningful when the operators in each of the second-order processes are the same, e.g., for Rayleigh scattering when both radiative interactions are in the electric-dipole mode. The formalism developed in this section permits the later consideration of optical rotation in degenerate states with even and odd numbers of electrons.

(4) The various degenerate states differ in the order of the electromagnetic multipoles they contain. We have de-

TABLE IX. Degenerate irreducible representations and pseudoscalar self-products.

Γ^2 does not contain a pseudoscalar: C_{nh}, D_{nh}, $D_{2n+1,d}$, $S_{2(2n+1)}$, O_h.
Γ^2 contains a pseudoscalar.

CHIRAL GROUPS

No time-reversal degeneracy:
contains dipole pseudoscalar A_1: $D_3(E)$, $D_6(E_1)$, $T(F)$, $O(F_1)$.
contains quadrupole pseudoscalar A_1: $D_3(E)$, $D_6(E_1,E_2)$, $O(E,F_2)$, $T(F)$.
contains octopole pseudoscalar A_1: $D_3(E)$, $D_6(E_1,E_2)$.

Time-reversal degeneracy:
contains dipole pseudoscalar A: $C_3(E)$, $C_6(E_1)$, $C_4(E)$.
contains quadrupole pseudoscalar A: $C_3(E)$, $C_6(E_1,E_2)$, $T(E)$, $C_4(E)$.
contains octopole pseudoscalar A: $C_6(E_1,E_2)$, $C_4(E)$.

ACHIRAL GROUPS

No time-reversal degeneracy:
contains dipole pseudoscalar B_1 or $A_2(\Sigma^-)$: $C_{3v}(E)$, $C_{6v}(E_1)$, $D_{2d}(E)$.
contains quadrupole pseudoscalar B_1 or $A_2(\Sigma^-)$: $C_{3v}(E)$, $C_{6v}(E_1,E_2)$, $D_{2d}(E)$, $D_{4d}(E_2)$, $T_d(E)$.
contains octopole pseudoscalar B_1 or $A_2(\Sigma^-)$: $C_{3v}(E)$, $C_{6v}(E_1E_2)$, $D_{2d}(E)$, $D_{6d}(E_3)$, $D_{4d}(E_2)$.

Time-reversal degeneracy:
contains dipole pseudoscalar B: $S_4(E_1)$.
contains quadrupole pseudoscalar B: $S_8(E_2)$.
contains octopole pseudoscalar B: $S_8(E_2)$.

rived self-products of degenerate states that not only give rise to a dipolar pseudoscalar ($R_1 \cdot M_1$), but also quadrupolar ($R_2 \cdot M_2$) and octopolar ($R_3 \cdot M_3$) pseudoscalars in important point groups (Sec. III). Because the occurrence of these pseudoscalars differs from group to group, we have derived the most general pseudoscalar products in a higher symmetry and exhibited their correlation upon descent into groups of lower symmetry [Sec. III, Eqs. (13) and (14), and Tables III and VI]. Furthermore, since different-order pseudoscalars represent natural optical activity of different orders of magnitude, we considered the selection rules (Sec. IV) for various degenerate states which have a unique correspondence to a given order of pseudoscalar (e.g., in D_6 and D_{4d}, $E_2 \otimes E_2$ admits only quadrupolar and octopolar pseudoscalars and not dipolar pseudoscalars [see Table IX and Eq. (18)]).

(5) In order to handle the direct products involving a new type of basis function (the magnetic multipoles), we have derived the difference in transformation between two functions which belong to the same irreducible representation, but one of which has the axial vector (L) incorporated [e.g., M_n of Eq. (15)] while the other has none [e.g., R_n of Eq. (15)]. The resulting difference in coupling coefficients (Table VIII) is important in the selection rule due to pseudoscalar-potential perturbations of achiral molecules.

Last, we would like to offer a few words in a philosophical vein. Throughout this work, the chiral molecules we consider are molecules without parity (no S_n symmetry), yet interactions with polarized light in optical rotation and (degenerate) electronic energetic considerations in chemistry all involve electromagnetic interactions which conserve parity. We are, therefore, assuming that optical isomers with given handedness belonging to the chiral groups (see Table IX) all have long lifetimes (compared to radiative *interaction* time) due to a high potential barrier for inversion (i). Namely, the molecules are prepared in a left- or right-handed state ψ_L or ψ_R. Only a linear combination[8,32] generated by the parity projection operator will give truly parity-conserved states $\overline{\Psi}^{\pm}$:

$$\overline{\Psi}^{\pm} = \frac{1}{\sqrt{2}}(\psi_L \pm \psi_R) e^{-iE_{\pm}t/\hbar} \equiv \psi^{\pm} e^{-iE_{\pm}t/\hbar} , \qquad (19)$$

where $E_{\pm}$ is the energy for the even (+) or odd (−) parity state. At any given time, an arbitrary state is a linear combination of the two parity-conserved states $\overline{\Psi}^{\pm}$ with appropriate time developments. Thus by inverting Eq. (19) we get

$$\begin{aligned} \psi &= \frac{1}{\sqrt{2}}(\overline{\Psi}^{+} + \overline{\Psi}^{-}) \\ &= \frac{1}{\sqrt{2}}(\psi^{+} + \psi^{-} e^{-i(E_{-}-E_{+})t/\hbar}) e^{-iE_{+}t/\hbar} , \qquad (20) \end{aligned}$$

which yields ψ_L at $t=0$ and ψ_R at $t=h/[2(E_{-}-E_{+})]$. The latter is the time for inversion. This is the classic double-well potential problem[33,34] and $E_{-}-E_{+}$ is the splitting due to "tunneling" and is dependent on the height of the barrier separating the two wells. For an infinite barrier, the splitting $E_{-}-E_{+}=0$ and the inversion time is infinite. For most such molecules the inversion barrier is of a vibrational nature. For molecules belonging to the D_3 group (e.g., twisted C_2H_6) or C_3 group (twisted CCl_3CH_3), it would be interesting to look into the rotational barrier for interconversion, especially for C_3, which has time-reversal degeneracy. In any case, allowing for inversion of left-to-right isomers and vice versa takes into account conservation of parity for electromagnetic interactions. The concomitant time-reversal symmetry[35,36] for such an interaction is also adopted. It is within this framework that we used the time-reversal operator to search for additional selection rules (Secs. I and II). Strictly speaking, left- and right-handed isomers in the real world may not be of the same energy, and the linear combination coefficients in Eq. (19) may not be equal (i.e., $\neq 1/\sqrt{2}$), thus destroying the parity of the states. This is due to the weak neutral-current coupling[8,37–39] of the electromagnetic interaction to the weak nuclear interaction V_{pnc}, which is parity nonconserving. However, since we confine ourselves to one isomer, all of our symmetry arguments for optical rotation remain valid. This weak neutral-current coupling mainly operates on the electron-spin singlet S through spin-orbit interaction ($V_{\text{s.o.}}$) and an intermediate spin triplet T state,[8,38,39] viz.,

$$\begin{aligned} &\langle S \mid V_{\text{pnc}} \mid T \rangle \langle T \mid V_{\text{s.o.}} \mid S \rangle / \Delta E \\ &\quad \approx \langle S \mid \sigma \cdot p \mid T \rangle \langle T \mid \sigma \cdot l \mid S \rangle / \Delta E \\ &\quad \Longrightarrow \langle S \mid p \mid T \rangle \cdot \langle T \mid l \mid S \rangle / \Delta E + \cdots , \qquad (21) \end{aligned}$$

where p is the linear momentum, l is the orbital angular momentum, σ is the Pauli spin operator, and the matrix element is different for left and right isomers. The operator $p \cdot l$ is *also a pseudoscalar*. Therefore, the selection rules for the natural-optical-rotation operator over degenerate states *also apply to this coupling*. It is conceivable that this coupling may also give a nonzero matrix element for the two time-reversal-degenerate components of achiral molecules, thus splitting the degeneracy by a magnitude[39] of around 10^{-16} eV.

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