

Ab initio calculation and display of the rotatory strength tensor in the random phase approximation. Method and model studies

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Abstract

The theory of the rotatory strength tensor describing circular dichroism (CD) of electronic excitations in oriented molecules is summarized in length and velocity formulations, and we outline an ab initio implementation of the calculation of this tensor and its electric dipole – magnetic dipole and electric dipole – electric quadrupole components in the random phase approximation. Results are presented for the predominantly $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ type transitions in an ethylene molecule twisted into chiral D_2 conformations demonstrating the origin-sensitivity of the electric dipole–magnetic dipole and electric dipole–electric quadrupole contributions to the tensor, and demonstrating origin-invariance of the total tensor in the velocity formulation. The electric dipole–electric quadrupole contribution is small, but not insignificant for both transitions. We present a pictorial representation of the CD response, and its application to the total tensor and its components for the $\pi \rightarrow \pi^*$ excitation.

1. Introduction

Most investigations in the field of optical rotatory power [1], have dealt with isotropic situations where the individual molecules are randomly oriented [2,3]. The quantity governing isotropic optical rotatory power is the rotatory strength, which is proportional to the scalar product of electric and magnetic dipole transition moments [1,2]. A quantitative approach to orientational effects in chiroptical properties was formulated by Tinoco and Hammerle [4], based on a multipolar formulation of a rotatory strength tensor. The new aspect is that electric quadrupole and mag-

netic dipole terms enter on the same footing in the tensor, while the quadrupolar term vanishes for isotropic systems. In general multipolar formulations [5–9], a rotatory strength tensor appears alongside other electromagnetic response tensors. Avoiding multipolar expansions, Stephen [10] used quantized scattering theory to derive a fully retarded expression for optical rotatory power, while a semi-classical derivation was given by Hansen and Avery [11]. Fully retarded formulations explicitly contain the directional aspect, and are convenient points of departure for theoretical work on the rotatory strength tensor, see e.g. Refs. [12,13]. For exact wavefunctions, or if particular conditions (Eqs. (9a) and (9b), see below) are fulfilled, fully retarded formulations reproduce the multipolar formulation for molecules small compared to the wavelength.

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Despite interest in the rotatory strength tensor, and a history of computations of ordinary rotatory strength, see Refs. [2,14] and references therein, quantum chemical calculations of the tensor have not appeared. Here we present an ab initio approach to calculating this tensor for electronic transitions in the random phase approximation [2,14,15]. Results for a model system serve to illustrate the features of the tensor, and we apply a pictorial representation adapted from work on NMR tensors [16]. Results for larger molecules will appear elsewhere [17].

2. Theory

Circular dichroism (CD) is the difference in absorption coefficient for left and right circularly polarized radiation, and for the CD of a given excitation $0 \rightarrow n$ we find [11]

$$\Delta \kappa_{n0}(\mathbf{u}_3, \omega) = \frac{\pi e^2 N \rho(\omega)}{\epsilon_0 c m_e^2 \hbar \omega} i \mathbf{u}_3 \cdot [\boldsymbol{\eta}_{n0}^* \times \boldsymbol{\eta}_{n0}] \quad (1)$$

in SI units; Ref. [11] used cgs units. $\rho(\omega)$ is the density of final states, N the number of molecules per unit volume, \mathbf{u}_3 a unit vector along the direction of the light, $\boldsymbol{\eta}$ the retarded transition moment operator [11], and

$$\boldsymbol{\eta}_{n0} = \langle n | \boldsymbol{\eta} | 0 \rangle = \left\langle n \left| \sum_j \exp(i \omega c^{-1} \mathbf{u}_3 \cdot \mathbf{r}_j) \mathbf{p}_j \right| 0 \right\rangle \quad (2)$$

\mathbf{r}_j is the position vector and \mathbf{p}_j the linear momentum for electron j . Focusing on natural CD, we assume that the molecular wavefunctions are purely real, and for wavelengths much larger than molecular dimensions, the transition moment can be expanded to first order in ω/c to yield

$$\Delta \kappa_{n0}(\mathbf{u}_3, \omega) = \frac{4 \pi \omega_{n0} N \rho(\omega)}{3 \epsilon_0 c^2 \hbar} \mathbf{u}_3 \cdot \mathbf{R}_{n0} \cdot \mathbf{u}_3, \quad (3)$$

where

$$\mathbf{R}_{n0} \equiv -\frac{3e^2}{2m_e^2 \omega_{n0}} \mathbf{p}_{0n} \times (\mathbf{pr})_{n0} \quad (4)$$

is the rotatory strength tensor for the excitation. $\omega_{n0} = (E_n - E_0)/\hbar$ and the dyadic notation in Eq. (4) implies the Cartesian elements

$$\begin{aligned} & [\mathbf{p}_{0n} \times (\mathbf{pr})_{n0}]_{\alpha\beta} \\ &= \sum_{\gamma\delta} \epsilon_{\alpha\gamma\delta} \langle 0 | \sum_i p_{i,\gamma} | n \rangle \langle n | \sum_j p_{j,\delta} r_{j,\beta} | 0 \rangle. \end{aligned} \quad (5)$$

Writing the dyadic tensor $(\mathbf{pr})_{n0}$ as a sum of a symmetric and an anti-symmetric part, Eq. (4) becomes

$$\mathbf{R}_{n0}^v = \mathbf{R}_{n0}^{Qv} + \mathbf{R}_{n0}^{mv} \quad (6)$$

where the electric dipole–electric quadrupole component is

$$\mathbf{R}_{n0}^{Qv} = -\frac{3e^2}{4m_e^2 \omega_{n0}} \mathbf{p}_{0n} \times (\mathbf{pr} + \mathbf{rp})_{n0}, \quad (7)$$

while the electric dipole–magnetic dipole tensor component is

$$\mathbf{R}_{n0}^{mv} = \frac{3e^2}{4m_e^2 \omega_{n0}} [(\mathbf{L}_{n0} \cdot \mathbf{p}_{n0}) \mathbf{I} - \mathbf{L}_{n0} \mathbf{p}_{n0}]. \quad (8)$$

$\mathbf{L} = \sum_j \mathbf{r}_j \times \mathbf{p}_j$ is the angular momentum. The electric dipole and quadrupole moments contain the momentum \mathbf{p} , and Eqs. (6)–(8) are hence referred to as velocity (v) forms.

Equivalent forms follow by use of the hypervirial relations

$$(i/m_e) \mathbf{p}_{0n} = \langle 0 | [\mathbf{r}, H] | n \rangle / \hbar = \omega_{n0} \mathbf{r}_{0n}, \quad (9a)$$

$$\begin{aligned} (i/m_e) (\mathbf{pr} + \mathbf{rp})_{n0} &= \langle n | [\mathbf{rr}, H] | 0 \rangle / \hbar \\ &= -\omega_{n0} (\mathbf{rr})_{n0}, \end{aligned} \quad (9b)$$

where H is the electronic Hamiltonian. These can be inserted into Eqs. (7) and (8) to generate the length or multipolar (r) forms,

$$\mathbf{R}_{n0}^r = \mathbf{R}_{n0}^{Qr} + \mathbf{R}_{n0}^{mr}, \quad (10)$$

$$\mathbf{R}_{n0}^{Qr} = -\frac{3}{4} \omega_{n0} e^2 \mathbf{r}_{0n} \times (\mathbf{rr})_{n0}, \quad (11)$$

$$\mathbf{R}_{n0}^{mr} = -\frac{3ie^2}{4m_e} [(\mathbf{L}_{n0} \cdot \mathbf{r}_{0n}) \mathbf{I} - \mathbf{L}_{n0} \mathbf{r}_{0n}]. \quad (12)$$

Eqs. (7) and (11) are traceless, and the traces of Eqs. (8) and (12) hence lead to expressions for the ordinary rotatory strength [2],

$$R_{n0}^v = \frac{1}{3} \text{tr}\{\mathbf{R}_{n0}^v\} = \frac{1}{3} \text{tr}\{\mathbf{R}_{n0}^{mv}\} = \frac{e^2}{2m_e^2 \omega_{n0}} \mathbf{p}_{0n} \cdot \mathbf{L}_{n0}, \quad (13)$$

$$R_{n0}^r = \frac{1}{3} \text{tr}\{\mathbf{R}_{n0}^r\} = \frac{1}{3} \text{tr}\{\mathbf{R}_{n0}^{mr}\} = -\frac{ie^2}{2m_e} \mathbf{r}_{0n} \cdot \mathbf{L}_{n0}. \quad (14)$$

Finally, among other expressions [2], the oscillator strength can be written as

$$f_{n0}^v = (2i/3\hbar) \mathbf{p}_{0n} \cdot \mathbf{r}_{n0}. \quad (15)$$

Consider now a translation of the reference frame along a vector \mathbf{a} , i.e. $\mathbf{r}_j \rightarrow \mathbf{r}_j - \mathbf{a}$ and $\mathbf{p}_j \rightarrow \mathbf{p}_j$. Orthogonality makes Eq. (15) invariant, while Eqs. (6)–(8) yield

$$\mathbf{R}_{n0}^{Qv} \rightarrow \mathbf{R}_{n0}^{Qv} + \frac{3e^2}{4m_e^2 \omega_{n0}} [\mathbf{p}_{0n} \times \mathbf{a}] \mathbf{p}_{n0}, \quad (16a)$$

$$\mathbf{R}_{n0}^{mv} \rightarrow \mathbf{R}_{n0}^{mv} - \frac{3e^2}{4m_e^2 \omega_{n0}} [\mathbf{p}_{0n} \times \mathbf{a}] \mathbf{p}_{n0}. \quad (16b)$$

The total tensor in velocity form is hence invariant, while its electric quadrupole and magnetic dipole components change with origin [18–20]. For Eqs. (10)–(12) we find in a similar manner

$$\mathbf{R}_{n0}^{Qr} \rightarrow \mathbf{R}_{n0}^{Qr} + \frac{3}{4} e^2 \omega_{n0} [\mathbf{r}_{0n} \times \mathbf{a}] \mathbf{r}_{n0}, \quad (17a)$$

$$\mathbf{R}_{n0}^{mr} \rightarrow \mathbf{R}_{n0}^{mr} + \frac{3ie^2}{4m_e} \{(\mathbf{a} \cdot [\mathbf{p}_{n0} \times \mathbf{r}_{0n}]) \mathbf{I} - [\mathbf{p}_{0n} \times \mathbf{a}] \mathbf{r}_{n0}\}, \quad (17b)$$

$$\mathbf{R}_{n0}^r \rightarrow \mathbf{R}_{n0}^r + \frac{3}{4} e^2 \times \{[(\omega_{n0} \mathbf{r}_{0n} - (i/m_e) \mathbf{p}_{0n}) \times \mathbf{a}] \mathbf{r}_{n0} + (i/m_e) (\mathbf{a} \cdot [\mathbf{p}_{n0} \times \mathbf{r}_{0n}]) \mathbf{I}\}. \quad (17c)$$

In length form the total tensor is hence invariant only if Eq. (9a) is fulfilled. However, since the trace of the translational terms in Eq. (17c) is proportional to $[\mathbf{p}_{n0} \times \mathbf{r}_{0n}]$, it is sufficient for invariance of the length form of the (scalar) rotatory strength, Eq. (14), that \mathbf{p}_{0n} and \mathbf{r}_{0n} are parallel [21] (e.g. as a result of symmetry [22], see Section 3).

The above summarizes the theory and establishes our notation. The tensor appears in a variety of forms in the literature [4–13,17]. Apart from the present use of SI units, our Eqs. (10)–(12) are identical to Eqs. (8a) and (9a) of Snir and Schellman [12] while Eqs. (8) and (9) of Ref. [12], which are advocated by the latter authors, represent a ‘mixed’ formulation, where the electric dipole is in length form and the electric quadrupole is in velocity form. The present expressions are consistent in the sense that the velocity and length forms, Eqs. (6)–(8) and (10)–(12), respectively, can be derived directly from Hamiltonians related by a gauge transformation, see e.g. Refs. [17,23].

Approximate calculations in general do not fulfil Eq. (9). Hence velocity and length results generally do not agree, and the translational term in Eq. (17c) becomes nonvanishing, making the length formulation translationally non-invariant. The random phase approximation (RPA) [2,15] is a post-Hartree–Fock approach where one-electron hypervirial relations are fulfilled in the Hartree–Fock limit. Assuming real matrix elements the various transition moments are

$$\langle 0 | \mathbf{r} | n \rangle = \sqrt{2} \sum_{\alpha,i} \langle \Delta_0 | \mathbf{r} | \alpha^i \rangle \{X_{\alpha i}^n + Y_{\alpha i}^n\}, \quad (18)$$

$$\langle 0 | \nabla | n \rangle = \sqrt{2} \sum_{\alpha,i} \langle \Delta_0 | \nabla | \alpha^i \rangle \{X_{\alpha i}^n - Y_{\alpha i}^n\}, \quad (19)$$

$$\langle 0 | \mathbf{r} \times \nabla | n \rangle = \sqrt{2} \sum_{\alpha,i} \langle \Delta_0 | \mathbf{r} \times \nabla | \alpha^i \rangle \{X_{\alpha i}^n - Y_{\alpha i}^n\}, \quad (20)$$

$$\langle 0 | \mathbf{r} \mathbf{r} | n \rangle = \sqrt{2} \sum_{\alpha,i} \langle \Delta_0 | \mathbf{r} \mathbf{r} | \alpha^i \rangle \{X_{\alpha i}^n + Y_{\alpha i}^n\}, \quad (21)$$

$$\langle 0 | \nabla \mathbf{r} + \mathbf{r} \nabla | n \rangle = \sqrt{2} \sum_{\alpha,i} \langle \Delta_0 | \nabla \mathbf{r} + \mathbf{r} \nabla | \alpha^i \rangle \{X_{\alpha i}^n - Y_{\alpha i}^n\}, \quad (22)$$

for singlet excitations. $|\Delta_0\rangle$ is the Hartree–Fock ground state, $|\alpha^i\rangle$ is obtained by promoting an electron from occupied orbital α to virtual orbital i , and \mathbf{X}^n and \mathbf{Y}^n are eigenvectors of the RPA eigenvalue problem whose eigenvalues are the transition energies. The sign combinations reflect the Hermitian or anti-Hermitian form of the operators. This approach is implemented in the RPAC Program [24],

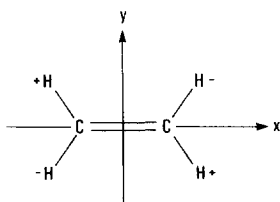


Fig. 1. The right-handed c.m. coordinate frame for 10° twisted ethylene; the sense of twist is contained in the + and – signs referring to positive and negative z coordinates, respectively.

extending the machinery outlined in Ref. [25] to the quadrupole integrals required for Eqs. (21) and (22).

3. A model calculation

Nonvanishing rotatory strengths, Eqs. (13) and (14), require chiral molecules, i.e. the absence of S_n improper axes [2], while it is apparent from Eqs. (6)–(8), (10)–(12) that off-diagonal elements of the tensor can be nonvanishing for achiral (e.g. plane symmetric) systems. Here we wish to exploit high symmetry and chirality, and have chosen ethylene twisted into a D_2 conformation, assuming bond lengths $r_{CH} = 1.09$ Å and $r_{CC} = 1.34$ Å, CCH angles = 120°, and a 10° angle of twist, Fig. 1. This sense of twist corresponds to that of (+)-trans-cyclooctene [26], but is opposite to that of previous model studies [27]. To study the interplay of basis set quality and origin sensitivity, we report results for three different basis sets and two locations of the molecule relative to the coordinate system. The basis sets are, A:

STO-5G, B: [3s2p/2s] and C: [5s4p2d/3s1p]; basis C results from B [28] by adding two s, two p and two d functions ($\alpha_s = 0.044, 0.017$; $\alpha_p = 0.04, 0.016$; $\alpha_d = 0.03, 0.01$) on carbon, and one s and one p function ($\alpha_s = 0.03, \alpha_p = 0.03$) on hydrogen. The coordinate systems are the center-of-mass (c.m.) system in Fig. 1 with axes coinciding with the C_2 axes of D_2 , and a system obtained by translating the coordinate frame by a vector $\mathbf{a} = (1, 1, 1)$ in Å (the molecular center is at $(-1, -1, -1)$ in the translated system).

RPAC calculations presuppose solution of the Hartree–Fock equations [24] for which we use the GAUSSIAN 92 system [29], and the RHF ground state energies in the three bases are A: -77.7751415 au, B: -78.0080525 au and C: -78.0099314 au. The RPAC results show an increasing number of transitions going from basis A to C, and increased complexity of the amplitudes. We focus on two easily identified and robust excitations, the predominantly $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ type transitions, Table 1. Both are of B_3 symmetry, and are hence electric and magnetic dipole polarized along the x axis with the $yz = zy$ elements as the only nonvanishing parts of the electric quadrupole transition moment.

Table 1 reports electric dipole and quadrupole transition moments in energy scaled form (see Eq. (9))

$$\rho_{0n}^r \equiv \omega_{n0}^{1/2} \mathbf{r}_{0n}, \quad \rho_{0n}^v \equiv \omega_{n0}^{-1/2} \nabla_{0n}, \quad (23a)$$

$$\kappa_{0n}^r \equiv \omega_{n0}^{1/2} (\mathbf{r}\mathbf{r})_{0n}, \quad \kappa_{0n}^v \equiv \omega_{n0}^{-1/2} (\nabla\mathbf{r} + \mathbf{r}\nabla)_{0n}. \quad (23b)$$

Table 1

Excitation energies oscillator and rotatory strengths and transition moments for 10° twisted ethylene in the c.m. frame of Fig. 1

Exc. basis	ΔE (eV)	f^a rv	R^b		ρ_x^c		$(\mathbf{r} \times \nabla)_x^a$	κ_{yz}^c	
			r	v	r	v		r	v
$\pi \rightarrow \pi^*$									
A	9.86	0.25	0.22	0.13	0.786	0.476	0.337	0.124	−0.012
B	7.62	0.35	0.25	0.21	0.792	0.657	0.335	0.206	0.177
C	7.34	0.34	0.21	0.18	0.772	0.650	0.285	0.215	0.192
$\sigma \rightarrow \pi^*$									
A	11.36	0.05	−0.32	−0.20	0.331	0.210	−1.235	−0.377	−0.042
B	9.38	0.04	−0.32	−0.27	0.280	0.238	−1.339	−0.496	−0.333
C	9.28	0.03	−0.23	−0.21	0.219	0.193	−1.245	−0.496	−0.404

^a Dimensionless.

^b Atomic units, to convert to SI and cgs units multiply by 1572.3×10^{-55} J C m T^{–1} and 471.4×10^{-40} erg esu cm gauss^{–1}, respectively.

^c Atomic units (see Eq. (23)).

Table 2
Rotary strength tensors ^a for 10° twisted ethylene in the c.m. frame of Fig. 1

Rotary strength tensors for π^0 twisted ethylene in the same frame as Fig. 1							
Exc. basis	Comp. ^b	$R_{\pi 0}^Q$		$R_{\pi 0}^m$		$R_{\pi 0}$	
		r	v	r	v	r	v
$\pi \rightarrow \pi^*$							
A	yy	0.073	−0.004	0.330	0.199	0.403	0.195
	zz	−0.073	0.004	0.330	0.199	0.257	0.204
B	yy	0.122	0.087	0.376	0.312	0.498	0.399
	zz	−0.122	−0.087	0.376	0.312	0.254	0.225
C	yy	0.124	0.093	0.318	0.267	0.442	0.361
	zz	−0.124	−0.093	0.318	0.267	0.194	0.174
$\sigma \rightarrow \pi^*$							
A	yy	−0.094	−0.007	−0.475	−0.301	−0.568	−0.308
	zz	0.094	0.007	−0.475	−0.301	−0.381	−0.294
B	yy	−0.104	−0.060	−0.479	−0.407	−0.583	−0.467
	zz	0.104	0.060	−0.479	−0.407	−0.375	−0.348
C	yy	−0.082	−0.059	−0.351	−0.309	−0.432	−0.368
	zz	0.082	0.059	−0.351	−0.309	−0.269	−0.250

^a Atomic units, see Table 1, footnote b.

^b Only yy and zz components are nonvanishing (see text).

Since length and velocity results are identical in the Hartree–Fock limit, deviations between the energy scaled moments are a measure of basis set quality, and will expectedly diminish with basis set size, as found in the table. The electric quadrupole moments are quite basis set sensitive; in fact the quadrupole velocity results in basis A are unreliable. The magnetic dipole moments are computed as angular momentum elements. Numerically attractive alternatives have not been suggested, and the quality of the

magnetic dipole moments can be gauged only by convergence with basis set size, Table 1. The excitations have retained most of their planar nature, and the $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ excitations are largely electric dipole allowed and largely magnetic dipole and electric quadrupole allowed, respectively. As before [27], they yield large oppositely signed rotatory strengths.

Table 2 reports the yy and zz elements of the rotatory strength tensor, and its electric quadrupole

Table 3
Nonvanishing components ^a of the ‘translational’ tensor ^b.

Exc. basis	Ω_{yx}^Q		Ω_{yx}^m		Ω_{yx}	
	<i>r</i>	<i>v</i>	<i>r</i>	<i>v</i>	<i>r</i>	<i>v</i>
$\pi \rightarrow \pi^*$						
A	−0.876	−0.320	0.530	0.320	−0.346	0.000
B	−0.888	−0.611	0.737	0.611	−0.151	0.000
C	−0.846	−0.599	−0.711	0.599	−0.134	0.000
$\sigma \rightarrow \pi^*$						
A	−0.155	−0.062	0.098	0.062	−0.057	0.000
B	−0.111	−0.080	0.095	0.080	−0.017	0.000
C	−0.068	−0.053	0.060	0.053	−0.008	0.000

^a See Eq. (24), only $\Omega_{yx} = -\Omega_{xx}$ components are nonvanishing.

^b Atomic units, see Table 1, footnote b.

and magnetic dipole parts; by symmetry these are the only nonvanishing elements in the c.m. frame. Basis sets B and C again improve length and velocity agreements, and the electric quadrupole components are traceless, in accord with Eqs. (7) and (11). We note that *in the c.m. frame* the magnetic dipole component is significantly larger than the electric quadrupole component for both excitations.

From Eq. (16) and (17), the effect of translation can be written

$$\mathbf{R}_{n0} \rightarrow \mathbf{R}_{n0} + \mathbf{\Omega}_{n0} \quad (24)$$

for the total tensor and its electric quadrupole and magnetic dipole components. By the electric dipole selection rule for B_3 transitions, only the yx and zx components of the translational $\mathbf{\Omega}$ tensor are non-zero; in addition $\Omega_{yx} = -\Omega_{zx}$. This is indeed found in the calculations, and Table 3 shows the values for these non-vanishing $\mathbf{\Omega}$ elements found as differences between results obtained in the c.m. frame and in the frame translated as described above. We note the expected basis set improvements, and that cancellations of electric quadrupole and magnetic dipole terms in velocity form make the total velocity tensor invariant regardless of basis set quality, Eq. (16), while incomplete cancellations in the length tensor leave it non-invariant. On the other hand, since symmetry makes the trace of $\mathbf{\Omega}$ vanish for both transitions, or alternatively forces electric and magnetic dipole transition moments to be parallel [21,22], the length form of the rotatory strength, Eq. (14), is in fact origin invariant in this case.

4. Display of the rotatory strength tensor

From Eq. (3) it follows that the circular dichroism, $\Delta\kappa_{n0}(\mathbf{u}_3, \omega)$, for a light beam propagating along a direction \mathbf{u}_3 relative to an oriented molecule is proportional to the quantity

$$\begin{aligned} \Gamma_{n0}(\theta, \phi) &\equiv \mathbf{u}_3 \cdot \mathbf{R}_{n0} \cdot \mathbf{u}_3 \\ &= \sin^2\theta \left[R_{xx}^{n0} \cos^2\phi + R_{yy}^{n0} \sin^2\phi \right. \\ &\quad \left. + \frac{1}{2}(R_{xy}^{n0} + R_{yx}^{n0}) \sin 2\phi \right] \\ &\quad + \sin 2\theta \left[\frac{1}{2}(R_{xz}^{n0} + R_{zx}^{n0}) \cos \phi \right. \\ &\quad \left. + \frac{1}{2}(R_{yz}^{n0} + R_{zy}^{n0}) \sin \phi \right] + \cos^2\theta R_{zz}^{n0}, \end{aligned} \quad (25)$$

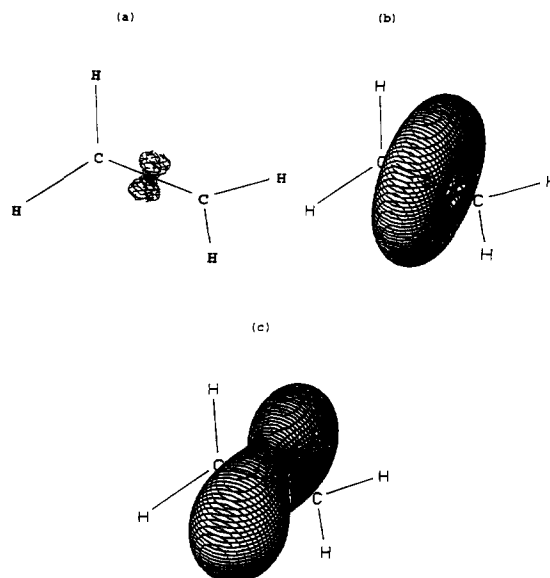


Fig. 2. Display of the quantity $\Gamma_{n0}(\theta, \phi)$, Eq. (25), for the total rotatory strength tensor (c) and for its electric quadrupole (a) and magnetic dipole (b) components for the $\pi \rightarrow \pi^*$ transition based on the basis C velocity results (Table 2) in the c.m. frame; dashed line surfaces corresponding to negative values of $\Gamma_{n0}(\theta, \phi)$. The scale is such that 1 Å is equivalent to 0.25 atomic units of rotatory strength. (The C=C bond length is 1.34 Å).

where θ and ϕ are spherical polar angles for \mathbf{u}_3 in the molecular coordinate system, see Ref. [16]. The rotatory strength tensor is not necessarily symmetric in the Cartesian indices, but only its symmetrized elements enter Eq. (25), implying that a principal axis system can be introduced [20], and that only $l=0$ and 2 spherical harmonics contribute to $\Gamma_{n0}(\theta, \phi)$. Eq. (25) can be applied both to the total tensor and to its magnetic dipole and electric quadrupole parts. For the quadrupole part the $l=0$ term vanishes since this tensor is traceless.

Eq. (25) lends itself easily to pictorial representations [16], and Fig. 2 displays the surfaces for the tensor and its components for the $\pi \rightarrow \pi^*$ transition using the basis C velocity results in the c.m. frame, Table 2. In these pictures, the distance from the origin to a surface along a given direction, and the sign of the surface, provide magnitude and sign for the circular dichroism for a light beam propagating along that direction. The plots are viewed from the fourth ($x > 0, y < 0, z > 0$) octant; see text to Fig. 2 for the scaling of the surfaces. Notice the $l=2$ (d

orbital-like) nature of the quadrupolar contribution, Fig. 2a, with oppositely signed contributions along the y and z axes (cf. Table 2). For the total tensor, Fig. 2c shows the vanishing CD response for light propagating along the C=C bond (the x axis), and the anisotropy of the response in the yz plane, caused by the rather dramatic effect of the small quadrupolar contribution. Except for sign changes, the corresponding pictures for the $\sigma \rightarrow \pi^*$ excitation are similar, see Table 2, and are therefore not shown.

5. Concluding remarks

We have presented *ab initio* calculations of the rotatory strength tensor using a twisted ethylene system as a model, and demonstrated the gauge origin invariance of the tensor obtained in the velocity formulation regardless of basis set quality, as contrasted to the non-invariance of the finite basis set results obtained in the length formulation. The electric dipole–magnetic dipole and the electric dipole–electric quadrupole contributions to the tensor are computed separately, and the calculations demonstrate how these contributions vary with gauge origin. For the transitions considered here the electric dipole–magnetic dipole contributions are larger than the electric dipole–electric quadrupole contributions in the c.m. frame; however the latter are by no means insignificant. We have shown also that the directional features of the CD spectra corresponding to a given rotatory strength tensor can be brought out in the display of the quantity $\Gamma_{n0}(\theta, \phi)$, Eq. (25), as in Fig. 2.

No symmetry constraints are imposed in these calculations, and the fact that the results respect symmetry and display the required basis set convergence for length and velocity results is a severe test of the implementation. The mutual cancellation of electric quadrupole and magnetic dipole terms in the velocity form of the translational tensor Ω (Table 3) is also significant since these components are computed by separate routes.

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