

Regular article

Rationalization of the optical rotatory power of chiral molecules into atomic terms: a study of N_2H_4

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Received: 5 September 2002 / Accepted: 29 May 2003 / Published online: 10 October 2003
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Abstract. We applied a strategy to assign the individual contributions that atoms make to the optical rotation angle and, more generally, to the molecular chirality. The method resolves the optical rotatory power tensor into atomic contributions employing the formalism of the acceleration gauge for the electric dipole and the torque formalism for the magnetic dipolar moment. The gross atomic isotropic contributions have been evaluated for nitrogen and hydrogen in hydrazine, employing Gaussian basis sets of very good quality, in order to achieve the Hartree–Fock limit.

Keywords: Rotatory power – Chirality – Atomic contributions

Introduction

The idea that molecular properties can be rationalized in terms of atomic contributions, transferable from molecule to molecule, constitutes a subject of interest from the early days of chemistry. The idea of specific transferable magnetic atomic susceptibilities is due to Pascal [1]. Attempts have also been made to define the resolution of electric dipole polarizability into atomic terms, see for instance the sets of transferable contributions determined by Denbigh [2] and Vogel [3].

Alternative partitions have been proposed, adopting simple quantum mechanical methods based on molecular orbital localization procedures [4]. Bader et al. [5] introduced the concept of atoms in molecules (AIM) [6],

as spatial domains bounded in space, to demonstrate the additivity of group polarizabilities and susceptibilities.

In this context we are testing an additive scheme for resolving the average optical rotatory power of a molecule into atomic contributions, via the average operator method (OAM) employed previously to describe atomic magnetic susceptibilities [7], atomic electric polarizabilities [8, 9], and gross atomic populations [10].

The optical rotatory power is related to the rotation of plane-polarized light by a solution of chiral molecules. At a single frequency the rotation angle of plane-polarized light arises from the difference in the index of refraction for left- and right-circularly polarized light.

The rotatory power is a frequency-dependent property, and because of that it is very interesting to give further insight into the possibility of its partitioning into atomic contributions consistent with the equilibrium geometry.

In a previous paper [11] we applied a partitioning scheme based on rigorous definitions of quantum mechanical operators suitable to investigate the optical rotatory power of hydrogen peroxide [12]. Related theoretical procedures and algorithms have been implemented within the SYSMO suite of computer programs [13]. This time we are investigating the partition into atomic contributions of the hydrazine optical rotatory power tensor by employing the same method. This molecule exhibits optical activity because the nitrogen is a chiral center. A wide numerical test has been performed in order to document the transferability of the optical rotatory power in N_2H_4 , a very simple model, in frozen chiral arrangements of the nuclei, into atomic contributions. The behavior of the total molecular property and its atomic contributions with a change of the molecular structure, i.e., rotation about the bond between the heavier atoms, is also investigated. A brief outline of the theoretical methods employed in the calculation is given in Sects. 3 and 4. Numerical calculations are presented and discussed in Sect. 5.

From the Proceedings of the 28th Congreso de Químicos Teóricos de Expresión Latina (QUITEL 2002)

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Tensors related to optical rotatory power

In a molecule with n electrons with charge $-e$, mass m_e , and coordinates r_i , respect to an arbitrary origin, the canonical and angular momenta of the i th electron are indicated by p_i and l_i ; $l_i = r_i \times p_i$, $i = 1 \dots n$.

The corresponding quantities for the N nuclei are $Z_I e$, M_I , R_I , etc. The electronic global operators are R for position, P for total canonical momentum, and L for angular momentum. The electric, $\mu = -eR$, and magnetic, $m = -(e/2m_e c)L$, dipole moments are also defined. The R and L operators are defined with respect to an explicit origin, r_0 , of the coordinate system:

$$R_\alpha(r_0) = \sum_{i=1}^n (r_{i\alpha} - r_{0\alpha}), \quad (1)$$

$$L_\alpha(r_0) = \sum_{i=1}^n l_{i\alpha}(r_0) = \varepsilon_{\alpha\beta\gamma} \sum_{i=1}^n (r_{i\beta} - r_{0\beta}) p_{i\gamma}. \quad (2)$$

A sum over repeated Greek suffixes is implied, and $\varepsilon_{\alpha\beta\gamma}$ is the Levi-Civita unit tensor.

The optical rotatory power of a chiral molecule can be rationalized via the tensor [11]

$$\kappa_{\alpha\beta}(\omega) = -\frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 - \omega^2} \text{Im}(\langle a | \mu_\alpha | j \rangle \langle j | m_\beta | a \rangle), \quad (3)$$

where Im takes the imaginary part of the term within the parentheses, ω_{ja} are the natural transition frequencies of the molecule in the reference state $|\psi_a^{(0)}\rangle \equiv |a\rangle$, with energy eigenvalue $E_a^{(0)}$, excited-state energies $E_j^{(0)}$, determined by solving the Schrödinger equation for the unperturbed Hamiltonian $H^{(0)}$, and ω is the angular frequency of a monochromatic electromagnetic wave incident on the molecule.

The trace of the tensor defined in Eq. (3) is a pseudoscalar, changing sign under inversion of the coordinate system because μ and \mathbf{m} are, respectively, a polar and an axial vector. The α optical rotatory parameter is measured experimentally [14] and is related to the tensor κ by

$$[\alpha]_D = 1.343 \times 10^{-4} \kappa v^2 (n^2 + 2) / 3\text{MW}, \quad (4)$$

where MW is the molar mass, n is the refractive index of the medium, and v is the frequency of the sodium D line.

Equation (3) defines a second-order property in the length-angular momentum R - L picture, i.e., $(R, L): \kappa(R, L)(\omega) = \kappa(\omega)$. Using the expressions for the total force of the nuclei on the electrons

$$\frac{i}{\hbar} [H^{(0)}, P] = F_n^N = -e^2 \sum_{l=1}^N Z_l \sum_{i=1}^n \frac{r_i - R_l}{|r_i - R_l|^3}, \quad (5)$$

the torque about the origin acting on the electrons

$$\begin{aligned} \frac{i}{\hbar} [H^{(0)}, L(r_0)] &= K_n^N(r_0) \\ &= e^2 \sum_{l=1}^N Z_l \sum_{i=1}^n \frac{r_i - R_l}{|r_i - R_l|^3} \times (R_l - r_0), \end{aligned} \quad (6)$$

and taking into account that the total force and torque can also be conveniently rewritten in terms of the electric field

$$E_l^i = e \sum_{i=1}^n \frac{r_i - R_l}{|r_i - R_l|^3}, \quad (7)$$

on nucleus I , arising from electron i , alternative definitions for the rotatory power tensor can immediately be arrived at by off-diagonal hypervirial relationships [15]. The hypervirial relationships, within the notation of Ref. [12], are

$$\begin{aligned} \langle a | R_\alpha | j \rangle &= \frac{i}{m_e} \omega_{ja}^{-1} \langle a | P_\alpha | j \rangle = \frac{1}{m_e} \omega_{ja}^{-2} \langle a | F_{n\alpha}^N | j \rangle \\ &= \frac{e}{m} \omega_{ja}^{-2} \sum_{l=1}^N Z_l \langle a | E_{l\alpha}^n | j \rangle \end{aligned} \quad (8)$$

and

$$\langle a | L_\alpha | j \rangle = i \omega_{ja}^{-1} \langle a | K_{n\alpha}^N | j \rangle. \quad (9)$$

Five alternative expressions are found for the rotatory power tensor, see Refs. [11, 12]:

$$\begin{aligned} \kappa_{\alpha\beta}^{(R,K)}(\omega) &= \frac{e^2}{2m_e c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 (\omega_{ja}^2 - \omega^2)} \text{Re}(\langle a | R_\alpha | j \rangle \langle j | K_{n\beta}^N | a \rangle), \end{aligned} \quad (10)$$

$$\begin{aligned} \kappa_{\alpha\beta}^{(P,L)}(\omega) &= -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja} (\omega_{ja}^2 - \omega^2)} \text{Re}(\langle a | P_\alpha | j \rangle \langle j | L_\beta | a \rangle), \end{aligned} \quad (11)$$

$$\begin{aligned} \kappa_{\alpha\beta}^{(P,K)}(\omega) &= -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 (\omega_{ja}^2 - \omega^2)} \text{Im}(\langle a | P_\alpha | j \rangle \langle j | K_{n\beta}^N | a \rangle), \end{aligned} \quad (12)$$

$$\begin{aligned} \kappa_{\alpha\beta}^{(F,L)}(\omega) &= \frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^2 (\omega_{ja}^2 - \omega^2)} \text{Im}(\langle a | F_{n\alpha}^N | j \rangle \langle j | L_\beta | a \rangle), \end{aligned} \quad (13)$$

$$\begin{aligned} & \kappa_{\alpha\beta}^{(F,K)}(\omega) \\ &= -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^3 (\omega_{ja}^2 - \omega^2)} \operatorname{Re} \left(\langle a | F_{nz}^N | j \rangle \langle j | K_{nz}^N | a \rangle \right). \end{aligned} \quad (14)$$

As F_{nz}^N and K_{nz}^N are, respectively, polar and axial vectors, and the operator $\kappa_{\alpha\beta}(\omega)$ is a pseudotensor, this character is unaffected by the change of picture.

All these definitions are equivalent in quantum mechanics, as a consequence of the invariance of the theory in a canonical transformation. However, the numerical estimates of a property do not depend on the chosen formalism, and only if the eigenfunctions $|a\rangle$ and $|j\rangle$ are the exact eigenstates to a model Hamiltonian [14], a condition that is hardly met in a calculation based on the algebraic approximation, values arrived at by Eq. (3) and Eqs. (10), (11), (12), (13) and (14) can be appreciably different: their numerical agreement gives a benchmark of basis set completeness and an *a priori* quality criterion. When that agreement is met in self-consistent-field (SCF) calculations, we commonly say that the Hartree–Fock limit has been achieved.

The rotatory power tensor depends on the origin assumed for the multipole expansion. For instance, in a change of origin, $r'' \rightarrow r' + d$, the rotatory power tensor changes according to the relationship [11]

$$\begin{aligned} \kappa_{\alpha\beta}(r'') &= \kappa_{\alpha\beta}(r') - \frac{1}{2c} \varepsilon_{\alpha\beta\gamma} d_\delta \alpha_{\alpha\gamma}, \\ \operatorname{Tr}\{\kappa(r'')\} &= \operatorname{Tr}\{\kappa(r')\}. \end{aligned} \quad (15)$$

Equation (15) is valid, and the trace of the tensor stays the same, if the hypervirial relations, Eqs. (8) and (9), are satisfied exactly. For instance, to fulfill this requirement within the algebraic approximation, i.e., employing the coupled Hartree–Fock method and random-phase approximation (RPA) [11] a complete basis set should be used [14]. In any practical calculation adopting a truncated basis, the equations describing the origin dependence of molecular tensors must be properly interpreted. If the optical activity tensor is defined via Eq. (3), then in Eq. (15) the electric polarizability in mixed length–velocity gauge [11] must be used. If only gaugeless basis sets are available, the trace of the tensor in the (P,L) gauge, Eq. (11), will be invariant, but its quality always depends on the quality of the basis set. Another way of solving the problem of the gauge invariance is provided by basis sets of London orbitals [16], i.e., gauge-including atomic orbitals (GIAO), as they were renamed for the first time by Hansen and Bouman [17]. GIAO calculations of optical rotatory power are implemented in the Dalton program [18].

Atomic contributions to optical rotatory power

The chiroptical phenomena in molecules have been known since the early days of quantum mechanics.

Rosenfeld [19] made the quantum mechanical description of the rotation angle. Kirwood and other authors [20, 21] proposed models based on polarizable interacting atoms or chemical groups. These models do not provide a general strategy for assigning the contributions of individual atoms. The numerical estimates of atomic contributions have become available [11], and have been successfully applied very recently [10]. The method is simple: the total force and the torque of the nuclei on the electrons, appearing in Eqs. (12), (13), and (14) can be partitioned as sums of corresponding atomic operators:

$$\begin{aligned} F_n^N &= \sum_{I=1}^N F_n^I = \sum_{i=1}^n F_i^N, \\ F_i^I &= -e^2 Z_I \frac{r_i - R_I}{|r_i - R_I|^3}, \end{aligned} \quad (16)$$

and

$$\begin{aligned} K_n^N &= \sum_{I=1}^N K_n^I = \sum_{i=1}^n K_i^N, \\ K_i^I &= -e^2 Z_I \frac{r_i - R_I}{|r_i - R_I|^3} \times R_I. \end{aligned} \quad (17)$$

Accordingly, the trace of the tensor for optical activity can be partitioned into atomic terms. For instance, in the low-frequency limit, i.e., $\kappa_{\alpha\alpha}(\omega \approx 0) = \kappa_{\alpha\alpha}(0) = \kappa_{\alpha\alpha}$, we can introduce an $[RK(I)]$ scheme

$$\begin{aligned} \kappa_{\alpha\alpha} &= \sum_{I=1}^N \kappa_{\alpha\alpha}^{[RK(I)]}, \\ \kappa_{\alpha\alpha}^{[RK(I)]} &= \frac{e^2}{2m_e c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^3} \operatorname{Re} \left(\langle a | R_\alpha | j \rangle \langle j | K_{nz}^I | a \rangle \right), \end{aligned} \quad (18)$$

a $[PK(I)]$ scheme

$$\begin{aligned} \kappa_{\alpha\alpha} &= \sum_{I=1}^N \kappa_{\alpha\alpha}^{[PK(I)]}, \\ \kappa_{\alpha\alpha}^{[PK(I)]} &= -\frac{e^2}{2m_e c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^4} \operatorname{Im} \left(\langle a | P_\alpha | j \rangle \langle j | K_{nz}^I | a \rangle \right), \end{aligned} \quad (19)$$

an $[F(I)L]$ scheme

$$\begin{aligned} \kappa_{\alpha\alpha} &= \sum_{I=1}^N \kappa_{\alpha\alpha}^{[F(I)L]}, \\ \kappa_{\alpha\alpha}^{[F(I)L]} &= -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^4} \operatorname{Im} \left(\langle a | F_{nz}^I | j \rangle \langle j | L_\alpha | a \rangle \right), \end{aligned} \quad (20)$$

an $[F(I)K]$ scheme

$$\begin{aligned} \kappa_{\alpha\alpha} &= \sum_{I=1}^N \kappa_{\alpha\alpha}^{[F(I)K]}, \\ \kappa_{\alpha\alpha}^{[F(I)K]} &= -\frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^5} \operatorname{Re} \left(\langle a | F_{nz}^I | j \rangle \langle j | K_{nz}^N | a \rangle \right), \end{aligned} \quad (21)$$

and an $[FK(I)]$ scheme

$$\begin{aligned} \kappa_{\alpha\alpha} &= \sum_{I=1}^N \kappa_{\alpha\alpha}^{[FK(I)]}, \\ \kappa_{\alpha\alpha}^{[FK(I)]} &= \frac{e^2}{2m_e^2 c \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^5} \operatorname{Re} \left(\langle a | F_{nz}^N | j \rangle \langle j | K_{nz}^I | a \rangle \right). \end{aligned} \quad (22)$$

These expressions involve transition matrix elements of nuclear-centered operators, without a partition of the molecule into overlapping atoms: the operators are averaged over the total system (OAM, based on referee's remarks on Ref. [22]), and because of this the atomic contributions to a molecular property (i.e., dipole polarizability) are not transferable like those obtained using Bader's AIM, because the operator-averaging will extend into what are in reality basins of neighboring atoms. The atomic contributions are transferable between members of a homologous serial, and the method relies on completely general and simple quantum mechanical recipes. The atom domain is defined by the actual domain of atomic operators like F_{nz}^N and K_{nz}^N . Such a domain is not uniquely defined; it depends on the form of the operator itself. That means that each operator, F_{nz}^I and K_{nz}^I , weights differently the molecular domain leading to different definitions of effective atomic basins. A detailed discussion of the OAM [6, 7, 8, 9, 22] and Bader's AIM [5] is included in Ref. [10].

Finally, it must be recalled that the atomic contributions to the optical rotatory power depend on the gauge of the vector potential. The molecular rotatory power is gauge-invariant if the hypervirial relations, Eqs. (8) and (9), are satisfied exactly.

Results and discussion

The molecular equilibrium geometry of hydrazine employed in the calculations was optimized at the 6-31G* SCF level of accuracy via the GAMESS code [23]. Isomers of hydrazine were found by internal rotation about the N-N bond. The rotation was performed rigidly (keeping fixed the equilibrium bond distances) from $\Phi=0^\circ$ (C_{2v} , eclipsed) to $\Phi=180^\circ$ (C_{2h} , staggered). The equilibrium configuration corresponds to $\Phi=90.2^\circ$ (C_2 point group), in accordance with Refs. [24, 25]. In all the calculations of the κ optical rotatory power tensor the origin of the coordinate system is in the center of mass.

Four basis sets of increasing extension and quality were used in the calculation of the rotatory power tensor and its average atomic contributions. Basis set 1 is (18s18p7d/7s7p)/[6s6p2d/2s2p] designed in Ref. [26], to yield accurate representation of force operators, has been successfully used to predict near-Hartree-Fock estimates of nuclear electric shieldings [25, 27]. Basis sets 2-4 correspond to different contractions of basis set 1: basis set 2 is the same as basis set 1 with uncontracted d and p functions on the oxygen and hydrogen atoms, respectively; basis set 3 is (18s18p7d/7s7p)/[10s10p7d/7s7p]. The use of step p functions, obtained by allowing the 18p subset to vary freely, is recommended to improve the representation of the force operator [28, 29]. Basis set 4 is (18s18p7d/7s7p), a fully free set.

The results of our calculations are reported in Tables 1 and 2 and Figs. 1, 2, 3, 4, and 5. All the calculations were done by employing the RPA via various formalisms, implemented in the SYSMO code

Table 1. Average rotatory power tensor of N_2H_4 at equilibrium geometry. The number of contracted Gaussian-type orbitals is given in *parentheses* for Gaussian basis sets 1-4 (in parts per thousand atomic units). The self-consistent-field (SCF) energy is given in bohr

Formalism ^a	Basis set			
	1 (104)	2 (224)	3 (284)	4 (340)
(R,L)	-0.364	-0.255	-0.249	-0.257
(P,L)	-0.202	-0.243	-0.247	-0.245
(F,L)	-0.022	-0.073	-0.132	-0.132
(R,K)	-0.328	-0.229	-0.240	-0.248
(P,K)	-0.161	-0.217	-0.239	-0.236
(F,K)	0.011	-0.050	-0.124	-0.124
E_{SCF}	-111.193894	-111.231341	-111.233610	-111.233849

^aSee Eqs. (10), (11), (12), (13), and (14)

Table 2. Partition of the average rotatory power of N_2H_4 at equilibrium geometry, $\kappa(\omega)=1/3\kappa_{xx}(\omega)$ (in parts per thousand atomic units), into atomic contributions versus the angular frequency, ω , of the perturbing monochromatic wave. The results are from basis set 4, with the origin at the center of mass. The values of ω (in atomic units) are given in *parentheses*

Atom Formalism	K(0.0)	K(0.20)	K(0.24)	K(0.27)	K(0.28)	K(0.30)
(R,L)	-0.257	-0.201	1.263	419.7	151.7	27.4
GIAO ^a	-0.262	-0.206	1.262	419.8	151.9	27.3
(P,L)	-0.245	-0.183	1.347	421.0	151.5	27.5
N (R,K^N)	0.017	0.235	0.947	54.17	4.24	0.206
H1 (R,K^{H1})	1.042	3.248	8.177	196.35	-33.71	-12.940
H3 (R,K^{H3})	-1.184	-3.570	-8.471	-40.48	104.92	26.390
Total (R,K)	-0.247	-0.174	1.306	420.10	150.90	27.390
N (P,K^N)	0.027	0.243	0.961	54.330	4.237	0.233
H1 (P,K^{H1})	1.042	3.252	8.203	196.77	-33.770	-12.958
H3 (P,K^{H3})	-1.181	-3.563	-8.459	-40.382	104.890	26.420
Total (P,K)	-0.236	-0.137	1.411	421.4	150.7	27.390
N (E^N,L)	0.525	0.818	2.229	275.4	69.8	-8.20
H1 (E^{H1},L)	0.045	-1.613	-6.641	-162.9	100.25	53.92
H3 (E^{H3},L)	-0.636	0.828	5.307	99.55	-96.17	-32.54
Total (F,L)	-0.132	0.065	1.790	424.10	147.7	26.40
N (E^N,K)	0.519	0.817	2.247	275.55	69.34	-8.310
H1 (E^{H1},K)	0.059	-1.587	-6.62	-162.75	100.10	53.940
H3 (E^{H3},K)	-0.638	0.82	5.307	99.39	-95.95	-32.5
Total (F,K)	-0.124	0.089	1.850	424.50	147.0	26.2
N (F,K^N)	0.040	0.279	0.995	54.63	3.95	0.17
H1 (F,K^{H1})	1.062	3.291	8.270	197.18	-33.94	-12.91
H3 (F,K^{H3})	-1.166	-3.524	-8.389	-39.992	105.06	24.15
Total (F,K)	-0.124	0.089	1.850	424.5	147.0	26.2

^aCalculations made using the Dalton program [18] using a basis set of gauge-including atomic orbitals corresponding to the same basis set

[30]. The average trace of the rotatory power tensor $\kappa(\omega)=1/3\kappa_{xx}(\omega)$ in the low-frequency limit, $\omega=0$, is reported in Table 1 for the molecular equilibrium geometry. The results corresponding to basis set 4 are expected to be close to the Hartree-Fock limit for the property. The results corresponding to formalisms (P,L), (R,K), and (P,K) are close to (R,L) only for basis sets 3 and 4.

The results corresponding to formalisms (F,L) and (F,K) suffer greater deviations. They improve very much on enlarging the basis set from 1 to 4, as it can be easily

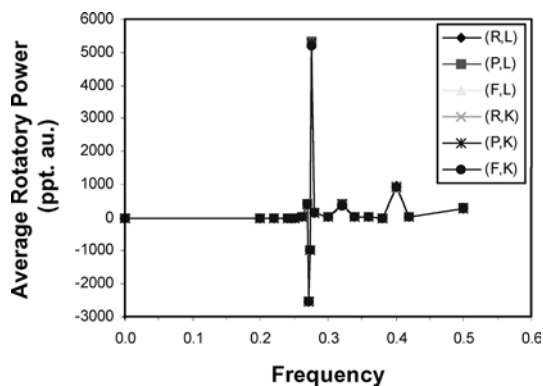


Fig. 1. The average rotatory power of N_2H_4 , expressed as $1/3\text{Tr}\kappa(\omega)$, in various formalisms, as a function of the frequency ω (in parts per thousand atomic units)

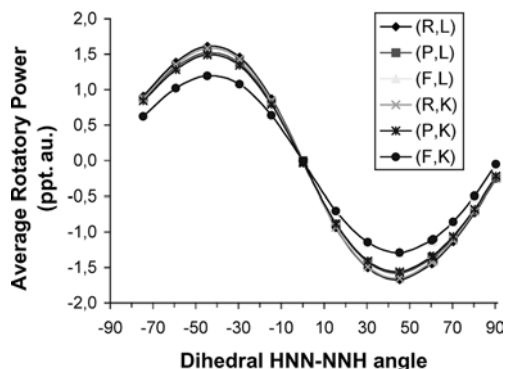


Fig. 2. The average rotatory power of N_2H_4 , $1/3\text{Tr}\kappa(\omega)$, in the limit $\omega=0$, in various formalisms, as a function of the HNN-NNH dihedral angle (in parts per thousand atomic units)

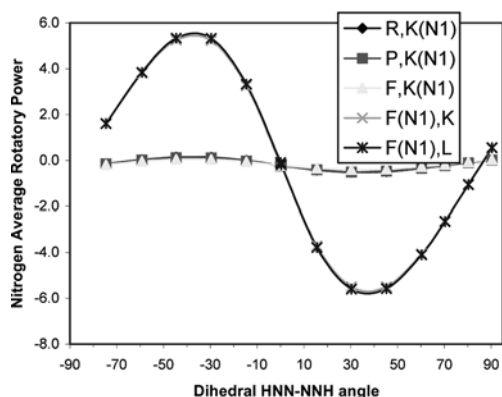


Fig. 3. Contribution of one nitrogen atom to the average rotatory power of N_2H_4 in the limit $\omega=0$, in various formalisms, as a function of the HNN-NNH dihedral angle (in parts per thousand atomic units)

verified. However basis set 4 is not good enough to represent properly the force operator.

The nonequivalent hydrogen, nitrogen, and total contributions to the average $k(\omega)$ tensor are displayed in Table 2 for frequencies up to 0.3 au and basis set 4.

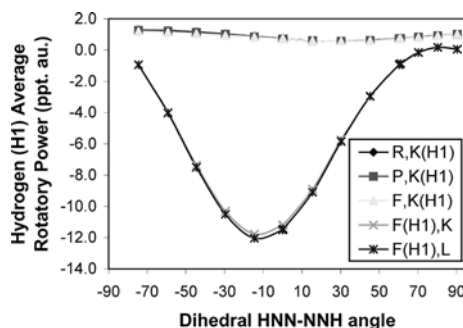


Fig. 4. Contribution of one hydrogen (H1) atom to the average rotatory power of N_2H_4 in the limit $\omega=0$, in various formalisms, as a function of the HNN-NNH dihedral angle (in parts per thousand atomic units)

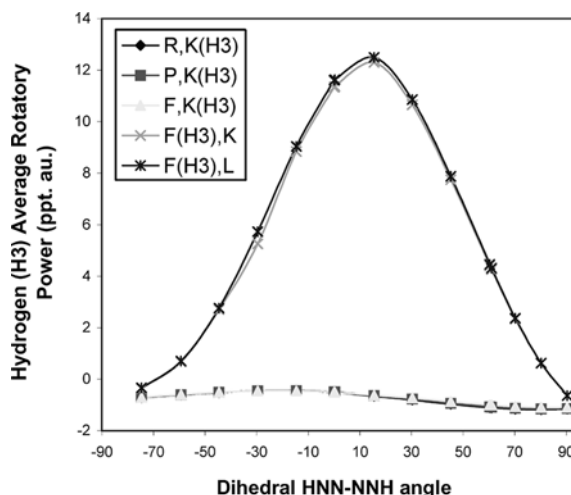


Fig. 5. Contribution of one hydrogen (H3) atom to the average rotatory power of N_2H_4 in the limit $\omega=0$, in various formalisms, as a function of the HNN-NNH dihedral angle (in parts per thousand atomic units)

Comparison with values obtained by the Dalton code [17] for the (R,L) formalism using GIAO basis sets is included. Excellent agreement is observed between the DALTON and SYSMO results for this representation. This agreement indicates that basis set 4 is close to the Hartree-Fock limit for the property. Remember that (R,L) estimates from DALTON calculations are independent of the origin; only (P,L) are independent of it for the gaugeless basis sets employed here. (P,L) , (R,K) , and (P,K) results agree with (R,L) results.

The dependence of the average κ tensor with the frequency of the monochromatic wave is plotted in Fig. 1. A resonance between the frequency of the incident light and the natural frequencies ω_{ja} is clearly observed.

The results displayed in Table 2 show that the basis set is still poor to represent the average rotatory power tensor in the force gauge, as it was pointed out before; and the schemes based on torque (Eqs. 18, 19, 22) provide atomic contributions to the average tensor that are

similar among them, but different from those provided by the scheme based on force (Eqs. 20, 21). We bring these two observations together to emphasize that the quality of the basis set is not the reason for the disagreement between the schemes as will be explained in the following discussion.

Figure 2 shows the dependence of the average rotatory tensor κ on the HNN–NNH dihedral angle, i.e., the dependence on the rotation angle Φ about the N–N bond, evaluated with basis set 3 (all the results displayed in Figs. 2, 3, 4, 5 were evaluated with basis set 3, because of interest in the behavior of the property with the change in the geometry and not so much in the quality of the results, which can be analyzed from Tables 1, 2). Despite the problem of incomplete convergence, the six formalisms are close to one another. They would become the same if the hypervirial relationships (Eqs. 8, 9), were fulfilled. The overall measure of the systematic deviation of the curves for (F,L) and (F,K) estimates from the corresponding ones for (R,L) , (P,L) , (R,K) , and (P,K) is plotted. There are two separate sets of curves consistent with the numerical values of Table 1 for the equilibrium geometry.

Figures 3, 4, and 5 show the dependence of the atomic contributions to the rotatory average tensor $\kappa(0)$ with the HNN–NNH dihedral angle, for nitrogen and the nonequivalent hydrogen atoms, H1 and H3. $[RK(I)]$, $[PK(I)]$, and $[FK(I)]$ are close to one another in spite of using basis set 3, and define a homogeneous set of numerical values for the torque partitioning scheme. The force scheme, partitions $[F(I)L]$ and $[F(I)K]$, which would become the same in the Hartree–Fock limit, define another set of numerical values. The atomic contributions provided by the force scheme are systematically larger in absolute value than those given by the torque scheme. In Ref. [22] we proposed a definition of the I th atom in the molecule as that region of space which essentially coincides with the domain weighted by operators like those appearing in Eqs. (16) and (17). The present findings confirm those of the previous paper on H_2O_2 [10]: the basins of the operators $F_{n\alpha}^I$ and $K_{n\alpha}^I$ do not coincide. They define different AIM within the OAM approach. See the appendix in Ref. [10].

Figure 3 shows $[RK(N)]$, $[PK(N)]$, and $[FK(N)]$ are virtually the same on the scale of the plot, defining atomic contributions in the torque scheme. $[F(N)L]$ and $[F(N)K]$ curves are close to one another, but they are characterized by a different pattern with a minimum and a maximum, respectively, at conformations in the proximity of 45° after and before the eclipsed configuration ($\Phi=0$). Such a trend cannot be attributed to insufficient convergence of atomic contributions in the force gauge.

Similar conclusions are arrived at from inspection of Figs. 4 and 5, showing that the curves corresponding to $[RK(H)]$, $[PK(H)]$, and $[FK(H)]$ belong, for each hydrogen, to a set different from that defined by the $[F(H)L]$ and $[F(H)K]$ curves.

Another difference between Figs. 2, 3, and 4 is that the hydrogen contributions do not exhibit a minimum and a maximum in the force scheme; there is a minimum for the H1 contribution and a maximum for the contribution of the nonequivalent H3 hydrogen to the molecular property.

The AIM weighted by the force F_n^I and the torque K_n^I operators do not coincide, in general, for molecular properties. This can be explained by the different dependence of these operators on the inverse power of the electron–nucleus distance, see Eqs. (16) and (17).

Acknowledgements. Financial support from the University of Buenos Aires (UBACYT X098) and Consejo Nacional de Investigaciones Científicas y Técnicas (PIP 02151/01) is gratefully acknowledged.

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