Thomas–Reiche–Khun populations in X–CH$_3$ and X–C$_2$H$_5$ series of molecules

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Abstract

Calculations of nuclear electric shieldings, equivalent to dipole moment geometric derivatives, and related to atomic polar tensors, are presented for X–CH$_3$ and X–C$_2$H$_5$ molecules with X = NH$_2$, OH and F. The electric shielding tensors satisfy a constraint for the electrostatic equilibrium, i.e., the mixed length–acceleration Thomas–Reiche–Khun sum rule, which gives important indications on the reliability of theoretical predictions of IR intensities and leads to the definition of atomic populations. Numerical evidence was found for the additivity and transferability of atomic populations, within the X-substituted alkane series. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In a previous paper [1], atomic populations have been defined in a molecule via the Thomas–Reiche–Khun (TRK) sum rule for oscillator strengths expressed within the acceleration gauge.

The variations in a group property in a series of molecules are sometimes so slight as to put into evidence that there exists a group transferability scheme for that property, and it is this feature which is employed to define a functional group in chemistry. The earliest and most studied systems exhibiting such additivity and transferability schemes are molar volumes, polarizabilities, heats of formation, magnetic susceptibilities, etc., in a series of homologous compounds, e.g., the alkane series.

The idea of electron population of a given atom within a molecule, its importance, and influence on observable properties have been extensively discussed in the literature [2]. The analyses of Mulliken and Löwdin constitute widely accepted attempts to define electron populations via quantum-mechanical methods [3].

A discussion of theoretical schemes proposed so far to furnish suitable representations of electron populations via quantum-mechanical methods is available in Section 1 of Ref. [1]. Among them the contributions of Meyer [4,5], inspired by the

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Mulliken conceptions, and the natural population analysis (NPA) developed by Reed, Weinstock and Weinhold [6] are worth mentioning.

The topological analysis developed by Bader within the theory of atoms-in-molecules [7–11] deserves special attention. The atomic population is simply the integral of the density within the atomic basin defined by asymptotic lines in the vector field $\nabla \rho(\mathbf{r})$, i.e., the gradient of the electron density. This technique is elegant and well-sound from the theoretical point of view.

The relative performance of different methods for describing atomic populations has been sometimes analysed, see, for instance, a recent paper [12]: their merits and quirks seem to be well understood nowadays [2].

Biarge, Herranz and Morcillo et al. [13,14] have introduced the idea of displacement polar tensors, or simply atomic polar tensors (APT). Adopting a set of Cartesian nuclear coordinates $\mathbf{R}_I$, the polar tensor associated with atom I is defined as

$$P_{\beta\alpha}^I = \frac{\partial \mathcal{M}_\beta}{\partial R_{I\alpha}}, \tag{1}$$

where $\mathcal{M}_\beta$ is a component of the electric dipole moment of the molecule. The APT is related to the electric dipole shielding of nuclei, theoretically discussed by Sambe for the first time [15], and widely studied in connection with other first- and second-order properties [16–20].

The general purpose of this paper is to employ quantum-mechanical relationships involving the APT and the related nuclear electric shielding, which provide clearcut recipes to evaluate atomic populations in molecules within the dipole acceleration formalism of quantum mechanics, by rewriting the TRK sum rule [21] in mixed length–acceleration gauge [22]. A more specific aim is that of proving the practicality of the method, first applied to the alkane series [1], also for X–CH_3 and X–C_2H_5 molecules, with X = NH_2, OH and F. These molecular systems are larger, and more interesting from a chemical point of view: a successful test of the transferability of atomic terms would permit predictions of atomic populations in other members, larger than those studied here, of the X-substituted alkane series.

2. Discussion of the results

Within the notation of Ref. [1], the TRK sum rule within mixed dipole length–dipole acceleration formalism is written in the form

$$\sum_{I=1}^{N} Z_I \gamma_{(R)\alpha\beta}^I = n\delta_{\alpha\beta}, \tag{2}$$

where

$$\gamma_{(R)\alpha\beta}^I = \frac{e}{\hbar} \sum_{j\neq a} \frac{2}{\omega_{ja}} \Re\left(\langle a|E_{I\alpha}^n|j\rangle\langle j|R_\beta|a\rangle\right) \tag{3}$$

is the electric shielding of nucleus I in dipole length formalism. Alternative representations of the same tensors are obtained, allowing for hypervirial relationships [19], within dipole velocity, (P), and dipole acceleration, (F), gauges, i.e.,

$$\gamma_{(P)\alpha\beta}^I = \frac{e}{m_e\hbar} \sum_{j\neq a} \frac{2}{\omega_{ja}^2} \Im\left(\langle a|E_{I\alpha}^n|j\rangle\langle j|P_\beta|a\rangle\right), \tag{4}$$

$$\gamma_{(F)\alpha\beta}^I = -\frac{e}{m_e\hbar} \sum_{j\neq a} \frac{2}{\omega_{ja}^3} \Re\left(\langle a|E_{I\alpha}^n|j\rangle\langle j|F_{n\beta}^N|a\rangle\right), \tag{5}$$

where $\Re$ ($\Im$) means real (imaginary). If the molecular wave functions are exact eigensolutions to a model Hamiltonian, then $\gamma_{(R)\alpha\beta}^I = \gamma_{(P)\alpha\beta}^I = \gamma_{(F)\alpha\beta}^I \equiv \gamma_{\alpha\beta}^I$.

The nuclear electric shielding is related to the atomic polar tensor [1] by

$$\frac{\partial \mathcal{M}_\beta}{\partial R_{I\alpha}} = Z_I(\delta_{\alpha\beta} - \gamma_{\alpha\beta}^I), \tag{6}$$

the quantities $Z_I \gamma_{\alpha\beta}^I$ can be referred to as TRK population tensors [22], and the average trace $1/3 Z_I \gamma_{\alpha\alpha}^I$ is immediately interpreted as a *scalar atomic population* (repeated Greek indices imply summation over these indices).

An accurate calculation of nuclear electric shielding tensors and TRK sum rules has been carried out employing the random-phase approximation (RPA) [23], equivalent to coupled Hartree–Fock (CHF) method [24], using algorithms implemented previously in the SYSMO package [17].

The molecular geometries have been optimized, using the HF approximation and a 6-31G* basis

Table 1
Specification of basis sets and SCF energies (hartree)

Basis set	Contraction scheme		Number of GTOs	Number of CGTOs	SCF energy
	GTO	CGTO			
CH_3NH_2					
I	(14s14p5d/5s5p/14s14p5d)	[6s6p2d/2s2p/6s6p2d]	272	112	−95.216264
II	(13s8p4d/8s2p/13s8p4d)	[8s6p4d/6s2p/8s6p4d]	192	160	−95.256659
CH_3OH					
I	(14s14p5d/5s5p/14s14p5d)	[6s6p2d/2s2p/6s6p2d]	252	104	−115.051546
II	(13s8p4d/8s2p/15s8p3d)	[8s6p4d/6s2p/10s6p3d]	174	144	−115.098135
CH_3F					
I	(14s14p5d/5s5p/14s14p5d)	[6s6p2d/2s2p/6s6p2d]	232	96	−139.056525
II	(13s8p4d/8s2p/13s8p4d)	[8s6p4d/6s2p/8s7p4d]	164	139	−139.105888
$C_2H_5NH_2$					
I	(14s14p5d/5s5p/14s14p5d)	[6s6p2d/2s2p/6s6p2d]	398	164	−134.249637
II	(13s8p4d/8s2p/13s8p4d)	[8s6p4d/6s2p/8s6p4d]	281	234	−134.303106
C_2H_5OH					
I	(14s14p5d/5s5p/14s14p5d)	[6s6p2d/2s2p/6s6p2d]	378	156	−154.087489
II	(13s8p4d/8s2p/15s8p3d)	[8s6p4d/6s2p/10s6p3d]	263	218	−154.147184
C_2H_5F					
I	(14s14p5d/5s5p/14s14p5d)	[6s6p2d/2s2p/6s6p2d]	358	148	−178.094190
II	(13s8p4d/8s2p/13s8p4d)	[8s6p4d/6s2p/8s7p4d]	253	213	−178.156609

set [25], via the GAMESS program [26]. Two different Gaussian basis sets have been employed to make the calculations. Their contraction scheme and corresponding SCF energies are reported in Table 1. Basis sets of type I have been constructed following the indications of Sadlej et al. [27,28] to yield accurate representation of the force operator. They have been successfully used to provide near HF estimates of nuclear electric shieldings and IR intensities [29]. Similar basis sets have been previously used to predict atomic populations in the alkane series [1]. TRK sum rules evaluated via basis set I within the mixed length–acceleration formalism (R, F), for methane, ethane, propane and butane are quite accurate [1]. Therefore, corresponding atomic populations calculated by definition (3) in the length gauge (R), for the electric shielding are expected to be reliable.

The extended basis set II corresponds to the contraction scheme (13s8p4d)–[8s6p4d] for carbon, nitrogen, and fluorine nuclei, and (15s8p3d)–[10s6p3d] for oxygen. The (8s2p)–[6s2p] contraction scheme has been chosen for hydrogen. The s/p substratum has been taken from van Duijneveldt

tables [30]. The exponents of the 3d polarization functions are 1.61, 0.43, 0.15, and 0.062 on carbon nuclei; 1.67, 0.45, 0.16, and 0.065 on nitrogen; 1.59, 0.477, and 0.175 on oxygen; 1.89, 0.63, 0.21, and 0.070 on fluorine. The exponents of the 2p polarization functions on hydrogen are 1.845 and 0.429 for all the XC_mH_{2m-1} compounds. The contraction scheme and the exponents of the polarization functions of basis set II, more extended and flexible than basis set I, have been tested previously to obtain accurate values for a number of second-order properties, including electric dipole polarizabilities and magnetic susceptibilities in different formalisms.

The results of the calculations of nuclear electric shieldings and TRK sum rules are reported in Tables 2–8. Electric shieldings of hydrogen, carbon, nitrogen, oxygen and fluorine nuclei have been estimated within dipole length, velocity, and acceleration gauges. It is well known that only in the limit of a complete basis set the results corresponding to different formalisms coincide. The TRK sum rules (Table 8) within the (R, F) formalism deviate very little from the number of

Table 2
Nuclear electric shielding tensors for the CH_3NH_2[a] molecule

Formalism	Basis I				Basis II			
	γ_{xx}	γ_{yy}	γ_{zz}	γ_{Av}	γ_{xx}	γ_{yy}	γ_{zz}	γ_{Av}
C_1								
(R)	0.904	0.951	0.960	0.939	0.919	0.960	0.969	0.945
(P)	0.774	0.813	0.819	0.802	0.919	0.963	0.972	0.951
(F)	0.776	0.815	0.822	0.805	0.948	0.992	0.997	0.979
H_1								
(R)	1.193	1.042	0.958	1.064	1.170	1.027	0.935	1.044
(P)	1.108	0.943	0.813	0.955	1.169	1.022	0.925	1.038
(F)	1.114	0.947	0.818	0.960	1.209	1.018	0.913	1.047
H_2								
(R)	1.016	1.059	1.125	1.067	0.998	1.040	1.106	1.048
(P)	0.876	0.951	1.055	0.961	0.991	1.034	1.103	1.042
(F)	0.878	0.955	1.058	0.964	0.974	1.051	1.113	1.053
N_1								
(R)	1.077	1.094	1.043	1.072	1.080	1.097	1.044	1.074
(P)	0.928	0.918	0.888	0.912	1.082	1.091	1.045	1.073
(F)	0.929	0.920	0.890	0.913	1.098	1.111	1.056	1.088
H_3								
(R)	0.939	0.774	0.911	0.875	0.917	0.769	0.886	0.857
(P)	0.860	0.670	0.865	0.798	0.914	0.761	0.884	0.853
(F)	0.865	0.670	0.869	0.801	0.927	0.767	0.899	0.864

[a] Proton H_3 belongs to NH_2 group. The coordinates in bohr are C1: (1.1829403, −0.7419205, 0); H1: (2.8680957, 0.4343929, 0); H2: (1.2766342, −1.9575021, 1.6549169); N1: (−1.0926431, 0.8224321, 0) and H3: (−2.1598048, 0.4348032, 1.5075363).

Table 3
Nuclear electric shielding tensors for the CH_3OH[a] molecule

Formalism	Basis I				Basis II			
	γ_{xx}	γ_{yy}	γ_{zz}	γ_{Av}	γ_{xx}	γ_{yy}	γ_{zz}	γ_{Av}
C_1								
(R)	0.920	0.883	0.929	0.911	0.927	0.890	0.940	0.919
(P)	0.785	0.754	0.790	0.776	0.929	0.893	0.941	0.921
(F)	0.788	0.756	0.794	0.780	0.955	0.918	0.964	0.946
H_1								
(R)	1.048	1.116	0.949	1.038	1.035	1.094	0.926	1.018
(P)	0.950	1.031	0.800	0.927	1.031	1.092	0.916	1.013
(F)	0.957	1.036	0.805	0.933	1.068	1.095	0.910	1.024
H_2								
(R)	1.073	1.016	1.148	1.079	1.051	0.996	1.129	1.059
(P)	0.955	0.869	1.073	0.966	1.043	0.987	1.126	1.052
(F)	0.959	0.870	1.078	0.969	1.045	0.973	1.185	1.068
O_1								
(R)	1.064	1.106	1.080	1.084	1.037	1.077	1.049	1.055
(P)	0.883	0.938	0.874	0.898	1.035	1.079	1.035	1.049
(F)	0.882	0.938	0.880	0.900	1.028	1.077	1.034	1.047
H_3								
(R)	0.809	0.755	0.642	0.736	0.790	0.723	0.636	0.716
(P)	0.741	0.731	0.545	0.672	0.786	0.721	0.625	0.711
(F)	0.741	0.734	0.545	0.673	0.760	0.707	0.591	0.686

[a] Proton H_3 belongs to OH group. The coordinates in bohr are C1: (−0.747551, 1.301051, 0); H1: (0.488930, 2.763199, 0); H2: (−1.943457, 1.224462, 1.673803); O1: (0.788194, −1.018990, 0) and H3: (−0.242505, −2.469551, 0).

Table 4
Nuclear electric shielding tensors for the CH_3F^a molecule

Formalism	Basis I				Basis II			
	γ_{xx}	γ_{yy}	γ_{zz}	γ_{Av}	γ_{xx}	γ_{yy}	γ_{zz}	γ_{Av}
C_1								
(R)	0.930	0.930	0.830	0.897	0.940	0.940	0.827	0.903
(P)	0.795	0.795	0.699	0.763	0.942	0.942	0.831	0.905
(F)	0.799	0.799	0.703	0.767	0.968	0.968	0.853	0.930
H_1								
(R)	0.950	1.160	1.020	1.043	0.924	1.141	0.999	1.022
(P)	0.797	1.107	0.868	0.924	0.915	1.141	0.993	1.016
(F)	0.804	1.112	0.870	0.929	0.915	1.226	0.954	1.032
F_1								
(R)	1.039	1.039	1.106	1.061	0.993	0.993	1.054	1.013
(P)	0.827	0.827	0.924	0.860	0.983	0.983	1.055	1.007
(F)	0.831	0.831	0.918	0.860	0.963	0.963	1.030	0.985

[a] The coordinates in bohr are C1: (0, 0.0000019, −1.3776700); H1: (0, 1.9354625, −2.0499179); H2: (−1.6761726, −0.9677327, −2.0499175) and F1: (0, −0.0000011, 1.1937800).

Table 5
Nuclear electric shielding tensors for the $C_2H_5NH_2{}^a$ molecule

Formalism	Basis I				Basis II			
	γ_{xx}	γ_{yy}	γ_{zz}	γ_{Av}	γ_{xx}	γ_{yy}	γ_{zz}	γ_{Av}
C_1								
(R)	0.921	0.919	0.955	0.932	0.932	0.939	0.965	0.945
(P)	0.791	0.794	0.814	0.800	0.935	0.941	0.968	0.948
(F)	0.792	0.794	0.817	0.801	0.968	0.978	0.992	0.979
H_2								
(R)	1.081	1.055	1.118	1.085	1.066	1.043	1.102	1.070
(P)	0.975	0.945	1.054	0.991	1.062	1.038	1.099	1.066
(F)	0.975	0.947	1.056	0.993	1.072	1.040	1.125	1.079
N_1								
(R)	1.104	1.074	1.039	1.072	1.108	1.074	1.040	1.074
(P)	0.952	0.906	0.886	0.914	1.107	1.072	1.041	1.073
(F)	0.950	0.910	0.888	0.916	1.128	1.086	1.052	1.088
H_3								
(R)	0.805	0.921	0.914	0.880	0.799	0.898	0.892	0.863
(P)	0.711	0.836	0.872	0.806	0.793	0.893	0.890	0.857
(F)	0.712	0.840	0.875	0.809	0.793	0.913	0.904	0.870
C_2								
(R)	0.989	1.005	0.976	0.990	0.996	1.022	0.983	1.000
(P)	0.845	0.873	0.832	0.850	0.998	1.025	0.986	1.003
(F)	0.848	0.874	0.835	0.852	1.020	1.062	1.010	1.031
H_4								
(R)	1.108	1.005	0.949	1.021	1.097	0.987	0.932	1.005
(P)	1.080	0.888	0.813	0.927	1.096	0.983	0.925	1.001
(F)	1.081	0.893	0.817	0.930	1.132	0.985	0.912	1.010
H_5								
(R)	1.004	1.040	1.122	1.055	0.985	1.024	1.105	1.038
(P)	0.891	0.920	1.063	0.958	0.978	1.019	1.102	1.033
(F)	0.894	0.922	1.066	0.961	0.977	1.025	1.129	1.044

[a] The coordinates in bohr are C1: (−0.870844, 0.569649, 0); H2: (−1.901613, 1.262838, 1.637693); N1: (1.696210, 1.613135, 0); H3: (1.962108, 2.717921, 1.507645); C2: (−0.895367, −2.345812, 0); H4: (1.027292, −3.055701, 0) and H5: (−1.850346, −3.101258, 1.355242).

Table 6
Nuclear electric shielding tensors for the $C_2H_5OH^a$ molecule

Formalism	Basis I				Basis II			
	γ_{xx}	γ_{yy}	γ_{zz}	γ_{Av}	γ_{xx}	γ_{yy}	γ_{zz}	γ_{Av}
C_1								
(R)	0.871	0.917	0.925	0.904	0.877	0.935	0.937	0.916
(P)	0.743	0.794	0.788	0.775	0.880	0.938	0.939	0.919
(F)	0.745	0.794	0.791	0.777	0.903	0.974	0.960	0.946
H_2								
(R)	1.089	1.060	1.142	1.097	1.072	1.047	1.125	1.081
(P)	0.970	0.944	1.073	0.996	1.065	1.041	1.123	1.076
(F)	0.970	0.948	1.078	0.999	1.046	1.058	1.181	1.095
O_1								
(R)	1.111	1.069	1.077	1.086	1.080	1.042	1.048	1.057
(P)	0.942	0.891	0.873	0.902	1.080	1.042	1.035	1.052
(F)	0.938	0.894	0.879	0.904	1.075	1.039	1.033	1.049
H_3								
(R)	0.716	0.849	0.647	0.737	0.714	0.801	0.640	0.718
(P)	0.643	0.835	0.550	0.676	0.710	0.799	0.630	0.713
(F)	0.642	0.841	0.550	0.678	0.695	0.775	0.598	0.689
C_2								
(R)	0.990	1.002	0.979	0.990	0.997	1.018	0.986	1.000
(P)	0.845	0.870	0.834	0.850	0.999	1.021	0.989	1.003
(F)	0.849	0.870	0.837	0.852	1.024	1.054	1.014	1.031
H_4								
(R)	1.104	0.998	0.939	1.014	1.094	0.982	0.992	0.999
(P)	1.079	0.879	0.803	0.920	1.093	0.978	0.914	0.995
(F)	1.081	0.884	0.807	0.924	1.144	0.978	0.906	1.009
H_5								
(R)	0.992	1.029	1.108	1.043	0.973	1.012	1.090	1.025
(P)	0.878	0.909	1.048	0.945	0.966	1.007	1.088	1.020
(F)	0.881	0.912	1.050	0.948	0.967	1.009	1.115	1.030

[a] The coordinates in bohr are C1: (−0.897349, 0.594346, 0); H2: (−1.896262, 1.299580, 1.657242); O1: (1.604424, 1.481436, 0); H3: (1.589942, 3.261443, 0); C2: (−0.853070, −2.299482, 0); H4: (1.093279, −2.945406, 0) and H5: (−1.778222, −3.078261, 1.659001).

electrons, n, for basis set I. Within (P,F) and (F,F) formalisms, the results are usually less accurate. This behaviour is expected owing to the ad hoc character of basis set I, especially devised for (R) nuclear electric shielding tensors defined via Eq. (3) by Sadlej and coworkers [27,28]. Quite remarkably, also the diagonal components of the TRK tensors arrived at within the (R,P) formalism via basis set I (not reported in Table 8) are very close to the number of electrons, in accordance with Eq. (2). On the other hand, the accuracy of TRK sum rules is approximately 97–103% for basis set II within the various formalisms examined in the present work: the numerical predictions via basis set II are the most accurate ones, but its size would make the calculations very ex-

pensive for molecules larger than those studied here.

Some conclusive statements can be made allowing for the theoretical results achieved in the present study:

(1) The diagonal components of the $\gamma^I_{(R)\alpha\beta}$ and $\gamma^I_{(P)\alpha\beta}$ tensors evaluated via large basis set II are close to one another in general, and virtually the same in many cases (with a small difference in the third decimal place). Owing to the good flexibility of this basis set, we are confident that the estimates of nuclear electric shielding within length and velocity gauges reported in the tables are of near HF quality.

(2) The diagonal components of the $\gamma^I_{(F)\alpha\beta}$ tensors from basis set II are comparatively less ac-

Table 7
Nuclear electric shielding tensors for the $C_2H_5F^a$ molecule

Formalism	Basis I				Basis II			
	γ_{xx}	γ_{yy}	γ_{zz}	γ_{Av}	γ_{xx}	γ_{yy}	γ_{zz}	γ_{Av}
C_1								
(R)	0.847	0.898	0.925	0.890	0.849	0.914	0.936	0.900
(P)	0.718	0.777	0.791	0.762	0.852	0.917	0.938	0.902
(F)	0.720	0.778	0.794	0.764	0.874	0.952	0.964	0.930
H_2								
(R)	1.032	1.045	1.106	1.061	1.015	1.030	1.089	1.045
(P)	0.905	0.928	1.036	0.956	1.009	1.025	1.087	1.040
(F)	0.905	0.932	1.041	0.959	0.966	1.059	1.151	1.059
F_1								
(R)	1.094	1.058	1.038	1.063	1.045	1.007	0.994	1.016
(P)	0.909	0.850	0.827	0.862	1.045	0.998	0.984	1.009
(F)	0.905	0.854	0.831	0.863	1.019	0.979	0.963	1.009
C_2								
(R)	0.992	1.009	0.982	0.995	1.000	1.024	0.989	1.004
(P)	0.847	0.876	0.836	0.853	1.002	1.028	0.992	1.007
(F)	0.850	0.877	0.840	0.855	1.029	1.057	1.018	1.035
H_4								
(R)	1.102	1.000	0.933	1.012	1.090	0.980	0.916	0.997
(P)	1.075	0.881	0.797	0.918	1.090	0.980	0.908	0.993
(F)	1.078	0.886	0.801	0.922	1.148	0.983	0.905	1.012
H_5								
(R)	0.987	1.015	1.098	1.033	0.969	0.999	1.080	1.016
(P)	0.872	0.895	1.037	0.935	0.962	0.995	1.078	1.011
(F)	0.875	0.897	1.040	0.937	0.963	0.989	1.106	1.020

[a] The coordinates in bohr are C1: $(-0.922544, -0.564614, 0)$; H2: $(-1.846614, -1.331421, 1.660316)$; F1: $(1.508992, -1.452826, 0)$; C2: $(-0.931529, 2.323121, 0)$; H4: $(1.006345, 2.995412, 0)$ and H5: $(-1.867546, 3.084520, 1.660605)$.

curate (they should coincide with $\gamma^I_{(R)\alpha\beta}$ and $\gamma^I_{(P)\alpha\beta}$ in the HF limit). This is related to the well-known problems concerning reliable description of charge distribution in the region of space close to the nuclei typical of Gaussian functions. This shortcoming is evidenced by the use of force operators which sample the electron distribution locally. The deviations of $\gamma^I_{(F)\alpha\beta}$ from the virtual limit indicated by $\gamma^I_{(R)\alpha\beta} \approx \gamma^I_{(P)\alpha\beta}$ are larger for the heteroatom I = N, O, and F, and for hydrogens directly bonded to N, and O, whereas smaller discrepancies are usually observed for hydrogens in a CH bond.

(3) The diagonal components of theoretical $\gamma^I_{(R)\alpha\beta}$ shielding from basis set I form an internally consistent set of values, as proven by the accurate TRK sum rule in (R, F) formalism. In many cases, they are close to corresponding estimates from basis set II, which suggests that, in larger calculations on big molecules, Sadlej basis set I can be used with confidence. Larger differences between

basis sets I and II occur for $\gamma^I_{(R)\alpha\beta}$ where I = N, O, and F.

(4) The TRK populations of carbon and hydrogen of a methyl group in the CH_3–X series were found to vary almost linearly with the Pauling electronegativity of X, in accordance with chemical intuition.

(5) The TRK populations of carbon and hydrogen in the methylenic group of the CH_3–CH_2–X series are also biased by the group electronegativity of X. A number of semiquantitive relationships between these quantities can be obtained allowing for different definitions of electronegativity available in the literature.

(6) The perturbation due to X is of nearest-neighbour type: it is virtually lost after one bond. In fact, the population of C in the methyl group of the enlarged CH_3–CH_2–X series, for X = CH_3, NH_2, OH, and F, is transferable from molecule to molecule, with tiny differences that can be imputed

Table 8
TRK sum rules, N_{Av}, from RPA for the CH_3X and $C_2H_5X^a$ molecules

Formalism	Basis set I						Basis set II					
	CH_3NH_2	CH_3OH	CH_3F	$C_2H_5NH_2$	C_2H_5OH	C_2H_5F	CH_3NH_2	CH_3OH	CH_3F	$C_2H_5NH_2$	C_2H_5OH	C_2H_5F
(R, R)	23.756	24.368	25.075	34.165	34.804	35.507	17.905	17.888	17.863	25.839	25.820	25.800
(R, P)	17.997	17.989	17.997	25.995	25.986	25.987	17.857	17.806	17.776	25.793	25.741	25.712
(P, P)	15.634	15.343	15.056	22.701	22.402	22.114	17.827	17.744	17.702	25.769	25.687	25.642
(R, F)	18.081	18.066	18.061	26.097	26.084	26.078	18.061	17.803	17.599	26.142	25.887	25.684
(P, F)	15.665	15.376	15.087	22.738	22.441	22.151	18.044	17.752	17.539	26.138	25.851	25.635
(F, F)	15.708	15.420	15.128	22.789	22.495	22.202	18.373	17.893	17.540	26.672	26.198	25.844

[a] The exact number of electrons is 18 for CH_3NH_2, CH_3OH, and CH_3F; and 26 for $C_2H_5NH_2$, C_2H_5OH, and C_2H_5F.

to the inductive effect of X (for X = CH_3, see the results reported in Table 4 of Ref. [1]). The populations of methylic hydrogens (H_3 and H_7 in Table 4 of Ref. [1] for X = CH_3, H_4 and H_5 in the Tables 5–7 here) in the same series seem slightly more affected by the electronegativity of the heteroatom entering the X function. The TRK population of this heteroatom is almost exactly transferable from CH_3–X to CH_3–CH_2–X series for a given basis set.

Eventually, it is worth recalling that the theoretical estimates of nuclear shielding tensors reported in Tables 2–7 could be useful to rationalize experimental values of APT and IR intensities [29] for the series of molecules examined in this study. Theoretical values for nondiagonal components of nuclear electric shielding tensors are available on request.

Acknowledgements

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