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Resolution of molecular polarizabilities of CH_3-X and CH_3-CH_2-X derivatives into atomic terms

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An additive scheme for resolving average molecular electric dipole polarizabilities into atomic contributions, based on the acceleration gauge for the electric dipole, has been applied to a series of methyl and ethyl derivatives, CH_3-X and CH_3-CH_2-X. Extended calculations have been carried out to test the reliability of the partition method. Gross atomic isotropic contributions have been evaluated for carbon, hydrogen, and heteroatoms, showing a good degree of transferability from molecule to molecule. The theoretical values of atomic polarizabilities can be used to predict fairly accurate average polarizabilities of higher homologous molecules in the series of X-substituted alkanes. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1343902]

I. INTRODUCTION

If molecules are made up of atoms, as we can concisely state relying on a widespread reductionist attitude of chemists, then a global molecular property can be thought of as a sum of corresponding atomic contributions. This idea was found empirically correct in a few cases, involving series of homologous molecules characterized by similar structure, e.g., geometrical parameters such as bond distances and bond angles, chemical and physical properties, etc. The systematic work of Pascal on magnetic susceptibilities,[1–3] preceding the quantum era, provides a paradigma that paved the way to many aspects of modern chemical thinking.[4]

A number of efforts have been reported later on to assess the reliability of a resolution of total quantities into group contributions possibly transferable from molecule to molecule. Besides its theoretical interest, the importance of this work in practical applications is evident, as it can enable researchers to estimate relevant features of big systems *a priori* with some degree of confidence.

A sophisticated and aesthetically appealing formulation of the hypothesis of ''atoms-in-molecules'' has been proposed by Bader and co-workers within the framework of a topological analysis of the vector field representing the gradient of electronic charge distribution.[5–9] Attempts have successfully been made to interpret some quantities, e.g., magnetic susceptibilities, electric polarizabilities, and so on, as a sum of atomic terms. Extension to other properties, for instance, optical rotatory power, is in principle straightforward. Accordingly, we could decide that a global molecular property can be basically resolved into contributions arising from different basins that can be expected to define atoms-in-molecules *à la* Bader.

However, other procedures have been proposed to investigate the legitimacy of partitioning schemes allowing for *ad hoc* quantum chemical tools. They rely on different assumptions, and throw light on particular aspects related to the quantum mechanical representation adopted to rationalize observed properties, which may help to understand the reasons why the reductionist approach is justifiable in a very general perspective.[10–16]

II. BASINS OF ATOMIC OPERATOR AS ''ATOMS-IN-MOLECULES''

Whereas a ''Bader atom-in-molecule'' is geometrically and topologically defined by asymptotic lines of the gradient field, we could alternatively suppose that an ''atom'' within a given molecule is a region of space which defines the actual domain of a certain ''atomic'' operator. Such a domain is not necessarily closed and is not uniquely defined, depending on the form of the operator itself. At any rate, the reliability of partitioning methods based on this definition can only be established via empirical criteria and numerical tests. Some examples may help us understand its evident limits and its possible merits.

Static electric dipole polarizability is customarily defined within the dipole length representation (R,R) via the equation

$$\alpha_{\alpha\beta}^{(R,R)} = \frac{e^2}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \Re(\langle a|R_\alpha|j\rangle\langle j|R_\beta|a\rangle) \qquad (1)$$

for a molecule in the singlet electronic reference state $|\Psi_a^{(0)}\rangle \equiv |a\rangle$. Such an expression, obtained allowing for the Goeppert–Mayer form of the interaction Hamiltonian[17,18] within Rayleigh–Schrödinger perturbation theory, is not suitable to provide a rationalization of a global molecular property in terms of atomic contributions. However, a different definition of electric dipole polarizability can be arrived at

allowing for the interaction Hamiltonian in the dipole acceleration picture, or (which is fully equivalent) using off-diagonal Ehrenfest relations.[18] Thus we replace matrix elements of the position operator in Eq. (1) by those of the operator for the force of N nuclei on n electrons,

$$\langle a|R_\alpha|j\rangle = -\frac{1}{m_e}\omega_{ja}^{-2}\langle a|F_{n\alpha}^N|j\rangle, \tag{2}$$

to define electric polarizability in mixed length-acceleration formalism,

$$\alpha_{\alpha\beta}^{(R,F)} = -\frac{e^2}{m_e\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}^3}\Re(\langle a|R_\alpha|j\rangle\langle j|F_{n\beta}^N|a\rangle). \tag{3}$$

The nice feature of the dipole acceleration picture is that the $F_{n\alpha}^N$ operator can readily be written as a sum over nuclei, i.e.,

$$F_{n\alpha}^N = \sum_{I=1}^N F_{n\alpha}^I. \tag{4}$$

The operators for the force of nucleus I on n electrons,

$$F_{n\alpha}^I = -e^2\sum_{i=1}^n Z_I\frac{\mathbf{r}_i-\mathbf{R}_I}{|\mathbf{r}_i-\mathbf{R}_I|^3}, \tag{5}$$

where $\mathbf{r}_i$ and $\mathbf{R}_I$ denote electronic and nuclear coordinates, possess the peculiar ''atomic'' form that we have in mind: due to its overall dependence on $|\mathbf{r}-\mathbf{R}_I|^{-2}$, each operator actually samples the charge distributions in a domain in the environment of the I-nucleus. Accordingly, it leads to a precise definition of gross ''atomic polarizabilities,'' via Eq. (3),

$$\alpha_{\alpha\beta}^I = -\frac{e^2}{m_e\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}^3}\Re(\langle a|R_\alpha|j\rangle\langle j|F_{n\beta}^I|a\rangle). \tag{6}$$

Total average molecular polarizability can now be resolved as

$$\alpha_{\mathrm{Av}} = \sum_{I=1}^N \alpha_{\mathrm{Av}}^I. \tag{7}$$

Such a resolution is physically sound, as it is based on the rigorous definition of the total force, Eq. (4). It was also found reliable in some numerical tests on the electric polarizabilities of the alkane series, where it provides values of hydrogen and carbon atomic polarizabilities that are transferable from molecule to molecule with good accuracy.[13] It should be noticed that the (R,R) polarizability, Eq. (1), is a tensor characterized by symmetry in the exchange of $\alpha-\beta$ indices, and can therefore be reduced to the principal axis system in any case. Tensors like those defined via Eqs. (3) and (6) are not in general symmetric, unless certain hypervirial theorems[19] are identically fulfilled. If necessary, symmetrized properties could be defined in numerical calculations, e.g.,

$$\tilde{\alpha}_{\alpha\beta}^{(R,F)} = \tfrac{1}{2}(\alpha_{\alpha\beta}^{(R,F)} + \alpha_{\beta\alpha}^{(R,F)}). \tag{8}$$

At any rate, as we are essentially interested in the diagonal components and trace of the polarizability tensor, this aspect will not be further investigated here.

We could consequently attempt to yield a definition of the Ith atom in a molecule as that region which essentially coincides with the domain weighed by the $\mathbf{F}_n^I$ operator. At first sight, such a definition may seem quite loose for evident reasons. The main objection is that it depends on the type of operator, that for the atomic force in the present case, which implies that other operators, e.g., the atomic torque[20,18,14] $\mathbf{K}_n^I = \mathbf{R}_I\times\mathbf{F}_n^I$, might actually gauge slightly different domains of the electronic charge. In any event, both show the same dependence on $|\mathbf{r}-\mathbf{R}_I|^{-2}$. As a piece of evidence assessing the practicality of the definition of atomic basin proposed above, we observe that the definition of Thomas–Reiche–Kuhn (TRK) atomic populations provided by an analogous partition of oscillator strengths in mixed length-acceleration picture via Eq. (5) seems quite reliable on empirical grounds. In fact, the TRK populations are to a good extent transferable within a set of homologous molecules, and are related to measurable quantities, i.e., infrared intensities.[21,15,16]

Resolutions of molecular properties allowing for similar mathematical procedures may also serve to exclude some possibilities, e.g., that of resolving the total electric dipole moment as a sum of bond moment vectors. As a matter of fact, the rotational constraint for nuclear electric shieldings clearly shows that the molecular property which can actually be written as a sum of atomic terms is instead a dipole moment tensor.[18,21]

III. DISCUSSION OF RESULTS

Attempting to extend the investigations of Ref. 13 on alkanes, a larger series of molecules has been considered in the present study. Two high-quality Gaussian basis sets, referred to as I and II, were used to obtain numerical estimates for gross atomic polarizabilities in methyl and ethyl derivatives, CH_3-X and CH_3-CH_2-X, with $X=F$, OH, NH_2, within the coupled Hartree–Fock (HF) level of accuracy. They are constructed according to the contraction schemes $(14s14p5d/5s5p)\rightarrow[6s6p2d/2s2p]$ and $(13s8p4d/8s2p)\rightarrow[8s6p4d/6s2p]$, respectively, where functions on heavy atoms and hydrogens are separated by a slash as usual. The detailed description of these basis sets, as well as the molecular geometries adopted in the calculations, can be found in Ref. 16, where Thomas–Reiche–Kuhn atomic populations have been evaluated via nuclear electric shieldings.

The conclusions arrived at by inspection of the results reported in Tables I–VI are as follows.

(i)   Basis sets I and II provide two alternative sets of gross atomic polarizabilities. The internal consistency and homogeneity of data from basis set I is guaranteed by the accurate values of the TRK sum rule within the mixed length-acceleration and length-velocity gauges.[15,16] Analogous features of consistency and homogeneity characterize theoretical atomic polarizabilities from basis set II, whereby TRK sum rules of near-Hartree–Fock quality are obtained (almost the same values for all formalisms). We recall that the closeness or otherwise of the results arrived at in different pictures gives a measure of ba-

TABLE I. Atomic contributions to electric polarizability (a.u.) for the CH_3NH_2 molecule.

Basis set	Formalism	I	α_{xx}	α_{yy}	α_{zz}	α_{Av}
	$(F(I),R)$	C_1	4.008	4.800	3.909	4.239
		H_1	4.100	2.028	1.369	2.499
I		H_2	1.681	2.707	3.373	2.587
		N_1	7.750	6.839	5.234	6.607
		H_3	2.251	0.948	2.016	1.738
	(F,R)		23.722	20.977	21.288	21.996
	(R,R)		24.783	21.730	22.111	22.875
	(F,F)		22.799	20.358	20.585	21.247
	(R,P)		23.809	21.136	21.311	22.086
	(P,P)		22.990	20.694	20.650	21.445
	(P,F)		22.890	20.521	20.614	21.342
	$(F(I),R)$	C_1	4.514	5.378	4.360	4.751
		H_1	4.213	2.017	1.449	2.560
II		H_2	1.797	2.849	3.490	2.712
		N_1	8.399	8.363	5.704	7.488
		H_3	2.320	1.107	2.018	1.815
	(F,R)		25.360	23.670	22.527	23.852
	(R,R)		25.296	23.088	22.428	23.604
	(F,F)		25.466	24.457	22.677	24.200
	(R,P)		25.240	23.020	22.376	23.545
	(P,P)		25.188	22.955	22.328	23.491
	(P,F)		25.307	23.609	22.479	23.798

TABLE III. Atomic contributions to electric polarizability (a.u.) for the CH_3F molecule.

Basis set	Formalism	I	α_{xx}	α_{yy}	α_{zz}	α_{Av}
	$(F(I),R)$	C_1	4.107	4.107	3.165	3.793
		H_1	1.456	3.994	1.630	2.360
I		F_1	1.991	1.999	6.464	3.487
	(F,R)		14.281	14.281	15.517	14.360
	(R,R)		14.767	14.767	15.272	14.935
	(F,F)		13.882	13.882	13.886	13.883
	(R,P)		14.278	14.278	14.696	14.418
	(P,P)		13.895	13.895	14.252	14.014
	(P,F)		13.886	13.886	14.064	13.946
	$(F(I),R)$	C_1	4.586	4.586	3.431	4.201
		H_1	1.559	4.102	1.787	2.483
II		F_1	2.216	2.216	6.626	3.686
	(F,R)		15.294	15.294	15.417	15.335
	(R,R)		15.284	15.284	16.161	15.576
	(F,F)		15.761	15.761	14.769	15.430
	(R,P)		15.234	15.234	16.097	15.521
	(P,P)		15.186	15.186	16.034	15.469
	(P,F)		15.249	15.249	15.357	15.285

to a well-known analysis of ''quadratic'' second-order properties presented by Moccia,[22] which can be empirically formulated by the statement ''the larger, the better.'' At any rate, basis set I, owing to its reduced size, can be adopted in calculations on bigger molecules attempting to build up a larger set of transferable atomic polarizabilities which include, for in-

sis set quality.[19] Thus basis set I is suitable to represent the force operator, and basis set II is flexible enough to guarantee accurate predictions of a number of second-order properties in different ''pictures.''

(ii)   Atomic, group, and total polarizabilities from basis set II are larger than corresponding values from basis set I. The former are expected to be more accurate owing

TABLE II. Atomic contributions to electric polarizability (a.u.) for the CH_3OH molecule.

Basis set	Formalism	I	α_{xx}	α_{yy}	α_{zz}	α_{Av}
	$(F(I),R)$	C_1	3.881	3.872	3.872	3.875
		H_1	2.419	3.217	1.424	2.353
I		H_2	2.642	1.624	3.700	2.655
		O_1	4.742	7.049	3.639	5.143
		H_3	1.105	2.101	0.544	1.250
	(F,R)		17.431	19.486	16.880	17.932
	(R,R)		18.060	20.361	17.446	18.622
	(F,F)		16.917	18.732	16.430	17.360
	(R,P)		17.536	19.569	16.885	17.997
	(P,P)		17.148	18.913	16.466	17.509
	(P,F)		17.027	18.819	16.445	17.430
	$(F(I),R)$	C_1	4.272	4.313	4.328	4.304
		H_1	2.525	3.332	1.529	2.462
II		H_2	2.780	1.738	3.814	2.777
		O_1	5.075	7.184	3.812	5.357
		H_3	1.160	2.077	0.595	1.277
	(F,R)		18.593	20.381	17.891	18.955
	(R,R)		18.873	20.657	18.098	19.210
	(F,F)		18.423	20.171	18.024	18.873
	(R,P)		18.777	20.564	18.000	19.114
	(P,P)		18.685	20.475	17.909	19.023
	(P,F)		18.501	20.293	17.793	18.862

TABLE IV. Atomic contributions to electric polarizability (a.u.) for the $C_2H_5NH_2$ molecule.

Basis set	Formalism	I	α_{xx}	α_{yy}	α_{zz}	α_{Av}
	$(F(I),R)$	C_1	4.837	5.417	3.503	4.586
		H_2	2.686	2.230	3.067	2.661
I		N_1	8.799	6.157	4.996	6.651
		H_3	0.979	2.347	2.005	1.777
		C_2	4.264	7.662	4.168	5.365
		H_4	3.514	2.211	1.314	2.346
		H_5	1.997	2.343	3.352	2.564
	(F,R)		32.741	35.285	30.827	32.951
	(R,R)		34.020	36.799	32.000	34.273
	(F,F)		31.635	33.968	29.812	31.805
	(R,P)		32.973	35.441	30.864	33.093
	(P,P)		32.120	34.294	29.910	32.108
	(P,F)		31.871	34.126	29.858	31.952
	$(F(I),R)$	C_1	5.436	6.103	3.923	5.154
		H_2	2.864	2.342	3.165	2.791
II		N_1	9.980	6.892	5.436	7.436
		H_3	1.048	2.464	2.008	1.840
		C_2	4.664	8.451	4.601	5.905
		H_4	3.585	2.309	1.400	2.431
		H_5	2.076	2.462	3.436	2.658
	(F,R)		35.641	38.291	32.579	35.504
	(R,R)		35.273	37.687	32.411	35.124
	(F,F)		36.146	39.024	32.820	36.000
	(R,P)		35.181	37.610	32.351	35.047
	(P,P)		35.092	37.538	32.294	34.975
	(P,F)		35.554	38.220	32.522	35.432

TABLE V. Atomic contributions to electric polarizability (a.u.) for the C_2H_5OH molecule.

Basis set	Formalism	I	α_{xx}	α_{yy}	α_{zz}	α_{Av}
	$(F(I),R)$	C_1	3.559	5.362	3.395	4.105
		H_2	2.420	2.347	3.396	2.721
I		O_1	7.320	4.763	3.598	5.227
		H_3	0.671	2.687	0.520	1.293
		C_2	4.452	7.266	4.401	5.373
		H_4	3.593	2.193	1.292	2.359
		H_5	1.887	2.244	3.223	2.451
	(F,R)		28.211	31.452	26.445	28.703
	(R,R)		29.346	32.823	27.384	29.851
	(F,F)		27.244	30.255	25.667	27.722
	(R,P)		28.393	31.557	26.459	28.803
	(P,P)		27.628	30.486	25.727	27.947
	(P,F)		27.430	30.366	25.694	27.830
	$(F(I),R)$	C_1	3.920	6.005	3.818	4.581
		H_2	2.555	2.490	3.479	2.841
II		O_1	7.589	4.922	3.798	5.436
		H_3	0.711	2.668	0.566	1.315
		C_2	4.885	7.980	4.864	5.910
		H_4	3.675	2.314	1.369	2.452
		H_5	1.966	2.364	3.302	2.544
	(F,R)		29.821	33.595	27.977	30.464
	(R,R)		30.223	33.332	28.059	30.538
	(F,F)		29.545	33.949	28.243	30.579
	(R,P)		30.090	33.257	27.968	30.438
	(P,P)		29.963	33.185	27.884	30.344
	(P,F)		29.695	33.524	27.888	30.369

TABLE VI. Atomic contributions to electric polarizability (a.u.) for the C_2H_5F molecule.

Basis set	Formalism	I	α_{xx}	α_{yy}	α_{zz}	α_{Av}
	$(F(I),R)$	C_1	3.224	5.161	3.582	3.989
		H_2	1.811	2.374	3.118	2.434
I		F_1	5.619	3.006	1.956	3.527
		C_2	4.561	7.223	4.538	5.440
		H_4	3.608	2.145	1.293	2.349
		H_5	1.882	2.116	3.172	2.390
	(F,R)		24.398	26.516	23.948	24.954
	(R,R)		25.464	27.634	24.817	25.972
	(F,F)		23.492	25.549	23.211	24.084
	(R,P)		24.548	26.650	23.935	25.045
	(P,P)		23.807	25.837	23.214	24.286
	(P,F)		23.646	25.688	23.209	24.181
	$(F(I),R)$	C_1	3.520	5.769	4.010	4.433
		H_2	1.950	2.507	3.208	2.555
II		F_1	5.800	3.120	2.203	3.707
		C_2	5.012	7.925	5.000	5.979
		H_4	3.684	2.262	1.376	2.441
		H_5	1.967	2.243	3.256	2.489
	(F,R)		25.850	28.573	25.517	26.647
	(R,R)		26.296	28.514	25.369	26.726
	(F,F)		25.560	29.032	26.123	26.905
	(R,P)		26.217	28.446	25.304	26.656
	(P,P)		26.141	28.381	25.243	26.588
	(P,F)		25.886	28.566	25.508	26.653
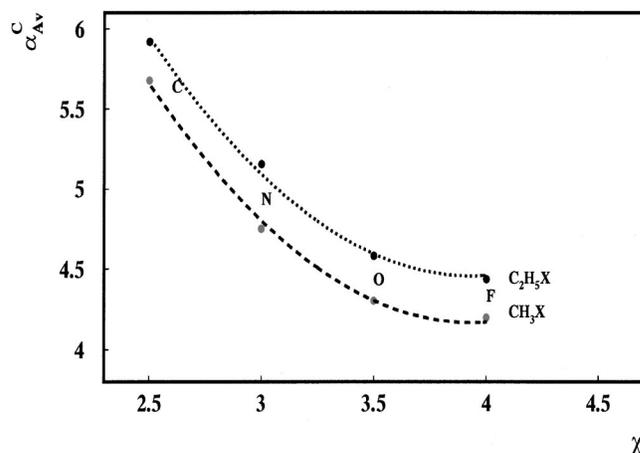
FIG. 1. Average atomic polarizability, α_{Av}^C, of methyl carbon in CH_3-X and C_2H_5-X molecules as a function of Pauling electronegativity χ of the heavy atom Y.

stance, second-row substituents as $-PH_2$, $-SH$, and $-Cl$. In such a case, accuracy and consistency of atomic polarizabilities should be sought within that set.

(iii) Let us denote by Y the heavy atom entering the substituent group X in the series CH_3-X and CH_3-CH_2-X, then $Y=$F, O, N, C for $X=$F, OH, NH_2, CH_3. The (average) gross atomic polarizabilities of a given Y atom, characterized by electronegativity higher than that of carbon, estimated via each basis set, are virtually transferable from CH_3-X to CH_3-CH_2-X compounds. Tiny differences between α_{Av}^Y from basis set I in ethyl and methyl derivatives can be entirely explained in terms of the inductive effect of the aliphatic chain always acting upon X in the same direction. In fact, for $Y=$F, O, N, C (see also Tables V and VI of Ref. 13) the values $3.49\leftrightarrow3.53$, $5.14\leftrightarrow5.23$, $6.61\leftrightarrow6.65$, and $5.13\leftrightarrow5.17$ a.u. were obtained for α_{Av}^Y respectively in CH_3-X and CH_3-CH_2-X.

The corresponding estimates from basis set II are comparatively more accurate, and can be interpreted as near-HF gross atomic polarizabilities. From the tables in this work, and Tables V and VI of Ref. 13, $\alpha_{Av}^F = 3.69\leftrightarrow3.71$, $\alpha_{Av}^O=5.36\leftrightarrow5.44$, $\alpha_{Av}^N=7.49\leftrightarrow7.44$, $\alpha_{Av}^C = 5.68\leftrightarrow5.72$ a.u., respectively for $CH_3-X\leftrightarrow CH_3-CH_2-X$. Whereas theoretical atomic polarizabilities of Y slightly increase for both basis sets on passing from CH_3-X to CH_3-CH_2-X, the opposite trend observed for α_{Av}^N from basis set II is not easy to explain. It might depend on a number of reasons, e.g., geometrical parameters. In any event, the numerical difference, roughly 0.05 a.u., is quite small.

(iv) In the CH_3-CH_2-X series, for $Y=$F, O, N, C, α_{Av}^C of the methyl group from basis set I vary within the interval $5.35\leftrightarrow5.44$ a.u. The corresponding values from basis set II range within $5.91\leftrightarrow5.99$ a.u. We can see

that the effect of the perturbation introduced in the molecule by the Y heteroatom is strongly attenuated, or virtually lost, after two bonds. Similar trends are observed for the atomic polarizabilities of hydrogens belonging to the methyl group of CH_3-CH_2-X. Therefore, the group polarizability of CH_3 is fairly transferable in this series. The largest deviations from full transferability were found for $Y=C$ of a methyl group of propane (see Table VI of Ref. 13).

(v)   The atomic polarizabilities of methylic carbon in CH_3 and methylenic carbon in CH_3-CH_2-X are clearly correlated with the electronegativity[23] of X (see Fig. 1). Therefore, allowing for (iv) it can be argued that X produces essentially a nearest-neighbor effect in the CH_3-CH_2-X series.

ACKNOWLEDGMENTS

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