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Resolution of alkane molecular polarizabilities into atomic terms

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Two additive schemes for resolving average molecular electric dipole polarizabilities into atomic contributions, based on the acceleration gauge for the electric dipole, are outlined. Extended calculations have been carried out for a few terms of the alkane series to test the reliability of the partition method. Gross atomic isotropic contributions evaluated for carbon, $\alpha_{Av}^C \approx 5.7$ a.u., and hydrogen, $\alpha_{Av}^H \approx 2.7$ a.u., are actually transferable from molecule to molecule, and can be used to predict fairly accurate average polarizabilities of higher homologous molecules in the alkane series.

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I. INTRODUCTION

The idea that molecular magnetic susceptibilities can be rationalized in terms of atomic contributions transferable from one molecule to another is due to Pascal.¹ A wide series of experimental results proves the reliability of Pascal's hypothesis for a given set of structurally and chemically related homologous molecules.^{2,3}

Attempts have also been made to define a resolution of electric dipole polarizability into atomic terms. Denbigh⁴ and Vogel⁵ succeeded in determining some sets of transferable contributions.

Alternative partitions have been proposed, adopting simple quantum mechanical methods based on molecular orbital localization procedures.^{6,7} Although atomic and bond contributions to average electric dipole polarizabilities can be reasonably defined in this way, the theoretical values depend on the molecular orbital (MO) localization scheme adopted in the calculation. Moreover, due to the fact that complete orbital localization is not actually feasible, small discrepancies are to be expected between total theoretical polarizability and corresponding sums of atomic and bond contributions.^{6,7}

Several molecular orbital approaches for the multicenter distribution of molecular polarization have been proposed, see a recent article by Nakagawa⁸ for extended bibliography. A general formalism has been established by Stone.⁹ Bader and co-workers¹⁰ used the theory-of-atoms-in-molecules to demonstrate the additivity of group polarizabilities.

Quite different partitioning schemes have been made available to define atomic and bond contributions to the total average dipole polarizabilities in molecules, based on rigorous definitions of the quantum mechanical operators suitable to estimate these quantities.^{11,12} Related theoretical procedures and algorithms have been implemented within the SYMO suite of computer programs,¹³ but so far they have not been applied to rationalize molecular polarizabilities in terms of transferable contributions.

The present article sets out to investigate the reliability

of methods discussed in Refs. 11 and 12. A wide numerical test has been performed, in order to document the transferability of (i) gross atomic, (ii) net atomic, and bond polarizabilities. Section II contains a brief outline of the theoretical methods employed in the calculation. Numerical results are presented in Sec. III for a few molecules belonging to the alkane series.

II. THEORETICAL PROCEDURE

Static electric dipole polarizability of a molecule in its electronic reference state (singlet $|\Psi_a^{(0)}\rangle \equiv |a\rangle$) is defined, within the length gauge,

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

in the notation of Ref. 12. Alternative definitions can be obtained using dipole velocity and/or dipole acceleration gauges. From off-diagonal hypervirial relationships,

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

it is easily shown that the electric polarizability can be written in a number of different ways, e.g., in the velocity formalism,

$$\alpha_{\alpha\beta}^{(P,P)} = \frac{e^2}{m_e^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^3} \Re(\langle a | P_{\alpha} | j \rangle \langle j | P_{\beta} | a \rangle), \quad (3)$$

in the mixed length-acceleration formalism,

$$\alpha_{\alpha\beta}^{(R,F)} = -\frac{e^2}{m_e \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^3} \Re(\langle a | R_{\alpha} | j \rangle \langle j | F_{n\beta}^N | a \rangle), \quad (4)$$

in the full acceleration formalism,

$$\alpha_{\alpha\beta}^{(F,F)} = \frac{e^2}{m_e^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^5} \Re(\langle a | F_{n\alpha}^N | j \rangle \langle j | F_{n\beta}^N | a \rangle), \quad (5)$$

where the operators P_α (canonical momentum) and $F_{n\alpha}^N$ (total force of N nuclei acting on n electrons) replace the position operator R_α .

Since the hypervirial theorem is only satisfied if the electronic wave functions are exact eigenstates of a model Hamiltonian,¹⁴ relationship (2) implies that the alternative definitions of Eqs. (1), and (3)–(5) of a given tensor component provide the same numerical value in a restricted number of ideal cases, e.g., within the “exact” Hartree–Fock method, or the multiconfiguration self-consistent field (SCF) scheme allowing for a complete basis set.

In actual calculations employing the algebraic approximation, the off-diagonal hypervirial conditions (2) are only approximately fulfilled. Consequently, the numerical estimates of electric dipole polarizability provided by length, velocity, and accelerations gauges are, usually, not identical.

At any rate, whenever corresponding values furnished by different formalisms are sufficiently close one to another, it can be reasonably concluded that the basis set is fairly complete (at least as far as the problem of accurate representation of the set of R_α , P_α , and $F_{n\alpha}^N$ operators is concerned), and the degree of accuracy of theoretical polarizabilities can therefore be assessed.

Other auxiliary theoretical quantities useful to test the quality of a given calculation of electric polarizabilities are the Thomas–Reiche–Khun (TRK) sum rules in different gauges,¹² e.g.,

$$\frac{m_e}{\hbar} \sum_{j \neq a} 2\omega_{ja} \Re(\langle a | R_\alpha | j \rangle \langle j | R_\beta | a \rangle) = n \delta_{\alpha\beta}, \quad (6)$$

$$-\frac{1}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \Re(\langle a | R_\alpha | j \rangle \langle j | F_{n\beta}^N | a \rangle) = n \delta_{\alpha\beta}, \quad (7)$$

$$\frac{1}{m_e \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^3} \Re(\langle a | F_{n\alpha}^N | j \rangle \langle j | F_{n\beta}^N | a \rangle) = n \delta_{\alpha\beta}. \quad (8)$$

The interesting property of the dipole acceleration gauge is due to the fact that the operator $F_{n\alpha}^N$ for the total force of N nuclei on n electrons can obviously be written as a sum over nuclei, i.e.,

$$F_{n\alpha}^N = \sum_{I=1}^N F_{n\alpha}^I, \quad (9)$$

which leads to a clear-cut definition of gross “atomic terms”, via Eq. (4),

$$\alpha_{\alpha\beta}^I = -\frac{e^2}{m_e \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^3} \Re(\langle a | R_\alpha | j \rangle \langle j | F_{n\beta}^N | a \rangle). \quad (10)$$

Owing to the $|\mathbf{r} - \mathbf{R}_I|^{-2}$ dependence of the operator for the I -atomic force term, which actually samples the charge distributions in the domain close to the I nucleus, one can reasonably expect that the resolution $\alpha_{Av} = \sum_{I=1}^n \alpha_{Av}^I$ is meaningful.

An alternative partition in terms of “net atomic” α^{II} , and “bond” α^{IJ} contributions is provided by Eq. (5), i.e.,

$$\alpha_{\alpha\beta}^{II} = \frac{e^2}{m_e^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}^5} \Re(\langle a | F_{n\alpha}^I | j \rangle \langle j | F_{n\beta}^J | a \rangle). \quad (11)$$

It should be observed that the extra-diagonal tensor components defined within mixed gauges do not generally satisfy the symmetry constraint $\alpha_{\alpha\beta} = \alpha_{\beta\alpha}$, compare relationships (4) and (10), unless they are calculated via the exact eigenfunctions to a model Hamiltonian. Therefore, it could sometimes be necessary to introduce properly symmetrized definitions, e.g., for the gross atomic polarizabilities, in the form $\bar{\alpha}_{\alpha\beta}^I = (1/2)(\alpha_{\alpha\beta}^I + \alpha_{\beta\alpha}^I)$. As we are essentially interested in average polarizability values, this task is not pursued in the present work.

It is worth noticing that the atomic contributions in Eq. (10) closely resemble the analytic expression for the dipole electric shielding¹² of nucleus I ,

$$\gamma_{\alpha\beta}^I = \frac{e}{\hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \Re(\langle a | E_{I\alpha}^n | j \rangle \langle j | R_\beta | a \rangle), \quad (12)$$

where the operator for the electric field of n electrons on nucleus I is related to the force terms in Eq. (11),

$$F_{n\alpha}^I = -F_{I\alpha}^n = -Z_I E_{I\alpha}^n. \quad (13)$$

It can be reasonably argued that transferability of atomic and bond polarizabilities defined via Eqs. (10) and (11) is actually expected in a limited number of cases, i.e., an additive scheme should probably work only within a restricted set of molecules characterized by similar structural and chemical properties.

As in the case of magnetic susceptibilities,² strain effects, delocalized electrons, functional groups inducing charge polarization, etc., can cause large perturbations, and would imply the need for “constitutive corrections,” “excitations contributions,” etc.

To simplify the problem, in this work we limited ourselves to investigate the electric dipole polarizability of some lower homologous terms of the alkane series, namely methane, ethane, propane, and butane, which meet the aforementioned requirements.

III. RESULTS AND DISCUSSION

The random-phase approximation (RPA) to the electronic polarization propagator¹⁵ has been adopted in the calculation.

Zero-order molecular orbitals are expanded over atomic gaussian functions. Three different basis sets have been employed. The first one, hereafter referred to as I , is an *ad hoc* basis set, developed by Sadlej to evaluate near Hartree–Fock electric dipole polarizabilities within the length gauge.¹⁶ Basis set II, also developed by Sadlej *et al.*^{17,18} to yield accurate representation of the force operator in Eq. (9), has been successfully used to predict near Hartree–Fock estimates of nuclear electric shieldings^{19,20} and infrared (IR) intensities.^{21,22} Owing to the similarity between relations (10) and (12), both involving transition matrix elements within the mixed length-force gauge, as underlined above, we expect basis II to be suitable also in the prediction of gross atomic polarizabilities. The reasons of our choice of basis sets are therefore evident: as the theoretical determinations of $\alpha_{Av}^{(R,R)}$ via basis set I are expected to be of near Hartree–Fock quality, a resolution of $\alpha_{Av}^{(R,F)}$ evaluated by

TABLE I. Specification of basis sets and SCF energies (in Hartree).

Basis set	Contraction scheme		Number of GTOs	Number of CGTOs	Energy (a.u.)
	GTO	CGTO			
CH₄					
I	(10s 6p 4d/6s 4p)	[5s 3p 2d/3s 2p]	124	62	-40.203 439 8
II	(14s 14p 5d/5s 5p)	[6s 6p 2d/2s 2p]	166	68	-40.195 680 4
III	(13s 8p 4d/8s 3p)	[8s 6p 4d/6s 3p]	129	110	-40.215 757 9
C₂H₆-E					
I	(10s 6p 4d/6s 4p)	[5s 3p 2d/3s 2p]	212	106	-79.239 953 5
II	(14s 14p 5d/5s 5p)	[6s 6p 2d/2s 2p]	292	120	-79.225 191 5
III	(13s 8p 4d/8s 3p)	[8s 6p 4d/6s 3p]	224	190	-79.259 173 7
C₂H₆-S					
I	(10s 6p 4d/6s 4p)	[5s 3p 2d/3s 2p]	212	106	-79.244 727 2
II	(14s 14p 5d/5s 5p)	[6s 6p 2d/2s 2p]	292	120	-79.230 009 8
III	(13s 8p 4d/8s 3p)	[8s 6p 4d/6s 3p]	224	190	-79.264 142 3
C₃H₈					
I	(10s 6p 4d/6s 4p)	[5s 3p 2d/3s 2p]	300	150	-118.288 443 4
II	(14s 14p 5d/5s 5p)	[6s 6p 2d/2s 2p]	418	172	-118.265 988 3
III	(13s 8p 4d/8s 3p)	[8s 6p 4d/6s 3p]	319	270	-118.313 914 6
C₄H₁₀					
I	(10s 6p 4d/6s 4p)	[5s 3p 2d/3s 2p]	388	194	-157.331 879 3
II	(14s 14p 5d/5s 5p)	[6s 6p 2d/2s 2p]	544	224	-157.301 944 2

basis set II into transferable atomic contributions of Eq. (10) should furnish a reliable partition of total electric polarizabilities of alkanes, provided that the identity

$$\alpha_{Av}^{(R,R)} \approx \alpha_{Av}^{(R,F)} \quad (14)$$

holds. In other words, even if relationship (14) would be exactly fulfilled only in a complete basis set calculation, it should be met with sufficient accuracy throughout the calculations, when the left-hand side (lhs) [right-hand side (rhs)] has been obtained via *ad hoc* basis set I (II), proving *a posteriori* the near Hartree-Fock (HF) quality of theoretical polarizabilities.

On the other hand both basis sets I and II are presumably unsuitable to give accurate values of $\alpha_{Av}^{(F,F)}$, the average polarizability in the full acceleration gauge. As a matter of fact, one should apply Sadlej's "polarization" recipe^{17,18} one more time to account for the second force operator appearing in definitions of Eqs. (5) and (8), in order to develop doubly polarized basis sets for carbon and hydrogen, which lies beyond the aims of the present article. In any event, attempts have been made to evaluate α_{Av}^{IJ} via relationship (11) by means of basis sets I, II, and III. The extended basis set III is similar to the one previously employed for a large number of molecular properties and related sum rules.^{13,23} Its (*s/p*) substratum has been taken from van Duijneveldt tables,²⁴ the exponents of 3*d* functions on carbon are 1.61, 0.43, 0.15, and 0.062. The exponents for 2*p* functions on hydrogen are 4.02, 0.952, and 0.294. Owing to its size and flexibility, the corresponding theoretical estimates of several response properties are expected to be close to the Hartree-Fock limit.

The molecular geometries of ethane, propane, and butane molecules used in the present study have been opti-

mized by means of the GAMESS program²⁵ using the 6-31G** basis set.²⁶ The geometry of methane is the same as in previous articles.¹³

The results of our calculations are reported in Tables I to XI. Basis sets are described in Table I, where SCF energies are also given. Incidentally, it can be observed that total energies from basis sets I and II are poor in comparison with those obtained via basis sets of the same (or smaller) size using energy-optimized exponents: it is worth recalling that

TABLE II. TRK sum rules from RPA for the CH₄^a molecule.

Basis set	Formalism	N_x
I	(R,R)	8.537
	(R,P)	8.496
	(P,P)	8.489
	(R,F)	8.347
	(P,F)	8.300
	(F,F)	11.004
II	(R,R)	13.103
	(R,P)	10.008
	(P,P)	8.726
	(R,F)	10.089
	(P,F)	8.758
	(F,F)	8.797
III	(R,R)	9.940
	(R,P)	9.931
	(P,P)	9.928
	(R,F)	10.074
	(P,F)	10.079
	(F,F)	10.286

^aThe exact value is 10; $N_x=N_y=N_z$. The coordinates in bohr are C₁=(0,0,0), H₁=(0,-1.683 396,1.190 341), H₂=(0,1.683 396,1.190 341), H₃=(−1.683 396,0,−1.190 341), H₄=(1.683 396,0,−1.190 341).

TABLE III. Atomic contributions to electric polarizability (a.u.) of methane.^a

Basis set	Formalism	<i>I</i>	α_{xx}	α_{yy}	α_{zz}	α_{Av}
I	$(F(I),R)$	C ₁	1.619	1.619	1.619	1.619
		H ₁	1.566	3.583	2.575	2.575
	(F,R)		11.919	11.919	11.919	11.919
	(R,R)		16.038	16.038	16.038	16.038
	(F,F)		17.297	17.297	17.297	17.297
II	$(F(I),R)$	C ₁	5.253	5.253	5.253	5.253
		H ₁	1.461	3.489	2.475	2.475
	(F,R)		15.155	15.155	15.155	15.155
	(R,R)		15.693	15.693	15.693	15.693
	(F,F)		14.697	14.697	14.697	14.697
III	$(F(I),R)$	C ₁	5.780	5.780	5.780	5.780
		H ₁	1.597	3.631	2.614	2.614
	(F,R)		16.237	16.237	16.237	16.237
	(R,R)		16.052	16.052	16.052	16.052
	(F,F)		16.453	16.453	16.453	16.453
	(R,P)		16.011	16.011	16.011	16.011
	(P,P)		15.972	15.972	15.972	15.972
(P,F)		16.198	16.198	16.198	16.198	

^aHere, and in the following tables, the conversion factor to SI units per molecule is 1 a.u. $\approx 0.164\,877\,8 \times 10^{-40}$ Fm². The molecular geometry has been specified in Table II.

basis sets I and II are especially meant for electric polarizabilities in different gauges. In fact, the nice features of basis set II can be judged from inspection of Table II, reporting TRK sum rules in the mixed length-acceleration gauge for methane. The results obtained for the other alkane molecules have not been shown for the sake of space. In any event, for all the molecules studied here the (R,F) values are virtually equal to the number n of electrons (a little bit larger in every case). It is also evident that the same basis set is usually unsuitable to predict accurate TRK sum rules in other formalisms, which, on the other hand, are nicely satisfied by basis set III. In addition, basis set I, for all of the molecular systems investigated here, provides insufficiently accurate TRK constraints also within the full length gauge, although corresponding estimates for $\alpha_{Av}^{(R,R)}$ in Tables III–VII are close to the HF limit,¹⁶ as it can be verified by a comparison with corresponding values from basis set III for methane, ethane in eclipsed and staggered conformations, propane, and butane.

As a matter of fact, the diagonal components of the polarizability tensor in the length gauge, $\alpha_{xx}^{(R,R)}$, etc., are “quadratic” properties, which tend to the HF limit from below (see, in any event, an article by Moccia).²⁷ Therefore, in any calculation adopting the algebraic approximation, it can be usually expected that the criterion “the larger, the better” holds for these theoretical quantities.^{13,28,29} Accordingly, owing to the special features of Sadlej’s basis set,¹⁶ one can reasonably argue that, in many cases, the theoretical $\alpha_{Av}^{(R,R)}$ values arrived at in this study furnish accurate lower bounds to the corresponding HF values.

It is surprising to observe that also basis II is capable of predicting quite precise $\alpha_{\alpha\beta}^{(R,R)}$ values (usually slightly smaller than corresponding ones evaluated via basis set I),

TABLE IV. Atomic contributions to electric polarizability (a.u.) of ethane in the eclipsed conformation.^a

Basis set	Formalism	<i>I</i>	α_{xx}	α_{yy}	α_{zz}	α_{Av}
I	$(F(I),R)$	C ₁	2.888	1.738	1.738	2.121
		H ₁	2.428	1.400	3.986	2.605
	(F,R)		20.345	19.634	19.634	19.871
	(R,R)		29.286	25.848	25.848	26.994
	(F,F)		26.317	31.092	31.092	29.500
II	$(F(I),R)$	C ₁	6.749	4.407	4.407	5.188
		H ₁	2.329	3.270	1.967	2.522
	(F,R)		27.473	24.522	24.522	25.506
	(R,R)		28.563	25.411	25.411	26.412
	(F,F)		26.518	23.754	23.754	24.675
III	$(F(I),R)$	C ₁	7.474	4.879	4.879	5.744
		H ₁	2.492	1.421	4.037	2.650
	(F,R)		29.897	26.132	26.132	27.387
	(R,R)		29.380	25.844	25.844	27.023
	(F,F)		30.465	26.474	26.474	27.805
	(R,P)		29.349	25.780	25.780	26.970
	(P,P)		29.319	25.718	25.718	26.918
(P,F)		29.868	26.070	26.070	27.336	

^aThe coordinates in bohr of the eclipsed conformer are C₁:(1.441 861 2, 0,0); H₁:(2.194 412 5,0,1.913 346 3); H₃:(2.194 412 5, 1.657 006 5, -0.956 673 15).

although it has been specifically designed for nuclear electric shieldings.^{17,18} At any rate, the theoretical predictions yielded by basis sets I and II fulfill the condition (14) quite satisfactorily.

Accordingly, it can be expected that the quantities calculated from relationship (10) via basis set II provide reliable numerical values for the “gross atomic contributions” defined in this way. The degree of transferability of these

TABLE V. Atomic contributions to electric polarizability (a.u.) of ethane in the staggered conformation.^a

Basis set	Formalism	<i>I</i>	α_{xx}	α_{yy}	α_{zz}	α_{Av}
I	$(F(I),R)$	C ₁	3.012	1.610	1.610	2.078
		H ₁	2.450	4.105	1.406	2.653
	(F,R)		20.719	19.753	19.753	20.075
	(R,R)		29.396	26.050	26.050	27.165
	(F,F)		26.968	31.015	31.015	29.666
II	$(F(I),R)$	C ₁	6.780	4.300	4.300	5.126
		H ₁	2.335	4.032	1.334	2.566
	(F,R)		27.572	24.697	24.697	25.656
	(R,R)		28.700	25.574	25.574	26.698
	(F,F)		26.593	23.942	23.942	24.826
III	$(F(I),R)$	C ₁	7.501	4.773	4.773	5.682
		H ₁	2.496	4.161	1.436	2.697
	(F,R)		29.979	26.335	26.335	27.550
	(R,R)		29.478	26.043	26.403	27.188
	(F,F)		30.531	26.683	26.683	27.966
	(R,P)		29.443	25.978	25.978	27.133
	(P,P)		29.410	25.915	25.915	27.080
(P,F)		29.947	26.273	26.273	27.498	

^aThe coordinates in bohr of the staggered conformer are C₁:(1.441 861 2, 0,0); H₁:(2.194 412 5, -1.913 346 3,0); H₃:(2.194 412 5, 0.956 673 15, 1.657 006 5).

TABLE VI. Atomic contributions to electric polarizability (a.u.) of propane.^a

Basis set	Formalism	<i>I</i>	α_{xx}	α_{yy}	α_{zz}	α_{Av}	
I	$(F(I),R)$	C ₁	2.037	3.713	2.643	2.798	
		C ₂	1.816	3.182	2.414	2.471	
		H ₁	3.226	1.954	3.063	2.747	
		H ₃	3.364	1.802	2.646	2.604	
		H ₇	1.379	4.361	2.338	2.693	
	(F,R)			28.334	29.915	28.856	29.035
				35.725	41.992	37.524	38.410
				44.262	39.690	41.842	41.931
II	$(F(I),R)$	C ₁	3.849	6.907	5.291	5.349	
		C ₂	3.983	6.808	4.725	5.172	
		H ₁	3.147	1.861	2.956	2.655	
		H ₃	3.295	1.701	2.557	2.518	
		H ₇	1.300	4.259	2.274	2.611	
	(F,R)			33.892	39.565	35.430	36.295
				35.106	41.132	36.784	37.674
				32.835	38.192	34.536	35.093
III	$(F(I),R)$	C ₁	4.282	7.594	5.872	5.916	
		C ₂	4.415	7.515	5.222	5.717	
		H ₁	3.248	1.984	3.109	2.781	
		H ₃	3.412	1.834	2.679	2.642	
		H ₇	1.401	4.412	2.380	2.731	
	(F,R)			36.059	42.752	38.012	38.941
				35.697	42.073	37.533	38.434
				36.493	43.501	38.564	39.519
				35.624	42.015	37.469	38.369
				35.552	41.958	37.407	38.306
		35.987	42.695	37.951	38.878		

^aThe coordinates in bohr are C₁:(0.0, -1.090 132 8); C₂:(0.2, 405 497 0, 0.508 165 65); H₁:(1.644 023 01, 0, -2.322 339 6); H₃:(1.657 100 9, 2.488 777 8, 1.717 629 0); H₇:(0, 4.085 2091 4, -0.670 106 9). Coordinate system was chosen so that the theoretical dipole moment (≈ 0.48 a.u. from basis sets I, II, and III), is always oriented along the *z* axis.

atomic polarizabilities from molecule to molecule within the alkane series can be assessed by inspecting Tables III–VII.

Average carbon contributions α_{Av}^C seem to depend very slightly on molecular conformation, compare, in Tables IV and V, $\alpha_{Av}^C \approx 5.2$ a.u. and $\alpha_{Av}^C \approx 5.1$ a.u. from basis set II, respectively, for eclipsed and staggered conformers. The results for hydrogen are fairly close one another, basis set II yields the value $\alpha_{Av}^H \approx 2.5$ a.u.

Very similar values have been obtained, via basis set II, for the other alkane molecules examined here. Therefore their transferability from molecule to molecule is excellent, as it can be observed in Tables III–VII. The estimates arrived at via basis set III are slightly higher, i.e., $\alpha_{Av}^C \approx 5.7$ a.u. and $\alpha_{Av}^H \approx 2.7$ a.u.

Three main conclusions emerge from these findings: (i) the electric dipole polarizability of alkanes can actually be rationalized in terms of gross atomic contributions; (ii) the values $\alpha_{Av}^C \approx 5.7$ a.u. and $\alpha_{Av}^H \approx 2.7$ a.u. for methyl groups, and $\alpha_{Av}^C \approx 5.9$ a.u. and $\alpha_{Av}^H \approx 2.8$ a.u. for methylene groups, can be used to predict average electric polarizabilities of higher homologous terms in the alkane series; (iii) basis set II provides good approximations to near Hartree–Fock values from basis set III: the discrepancies are about 10%. From

TABLE VII. Atomic contributions to electric polarizability (a.u.) of butane.^a

Basis set	Formalism	<i>I</i>	α_{xx}	α_{yy}	α_{zz}	α_{Av}	
I	$(F(I),R)$	C ₁	4.296	3.033	2.230	3.186	
		C ₃	3.170	2.090	1.809	2.356	
		H ₁	2.113	2.858	3.158	2.710	
		H ₅	2.097	2.395	3.333	2.609	
		H ₉	3.829	3.039	1.384	2.751	
	(F,R)			39.430	37.336	36.810	37.859
				56.992	47.445	45.223	49.887
				51.413	54.723	57.527	54.554
				56.979	47.534	45.274	49.929
				57.102	47.755	45.488	50.115
II	$(F(I),R)$	C ₁	7.653	5.117	3.573	5.448	
		C ₃	7.459	4.198	3.910	5.189	
		H ₁	2.011	2.761	3.086	2.619	
		H ₅	1.982	2.318	3.268	2.523	
		H ₉	3.720	2.985	1.304	2.670	
	(F,R)			53.636	44.917	42.992	47.182
				55.829	46.623	44.536	48.996
				51.692	43.427	41.641	45.587
				53.840	45.005	43.038	47.295
				52.133	43.639	41.761	45.844
		51.906	43.528	41.698	45.711		

^aThe coordinates in bohr are C₁:(0.988 800 0, -1.054 242 0, 0); C₃:(3.700 988 6, -0.062 560 5, 0); H₁:(0.700 501 0, -2.254 143 3, 1.644 802 3); H₅:(-4.067 223 6, -1.092 737 0, 1.657 195 8); H₉:(-5.057 117 8, 1.602 071 4, 0).

the data obtained for propane one can suggest that the values 13.7 and 11.5 a.u., respectively, for the CH₃- and CH₂-groups, can be used to obtain average polarizabilities of alkane molecules of near HF quality.

Owing to its reduced size, basis set II is useful to obtain reliable gross atomic polarizabilities in larger molecular systems.

The gross isotropic atom polarizabilities arrived at via the theoretical approaches described in the present article are numerically different from those reported by Nakagawa, see Table II of Ref. 8, $\alpha_{Av}^C \approx 4.27$ a.u. and $\alpha_{Av}^H \approx 3.16$ a.u. In addition, correlation effects and vibrational contributions were not taken into account in our study. Accordingly, it can probably be argued that different calculation methods only prove the reliability of additive schemes for electric dipole polarizability, as they seem to sample different features and domains of a given molecular wave-function. In other terms, the definitions of “atomic” contributions to molecular properties are apparently not univocal, they rather depend on the basic assumptions of the localization procedure.

TABLE VIII. Pair polarizabilities α_{Av}^{IJ} of methane molecule from basis sets II and III (a.u.).

<i>IJ</i>	α_{Av}^{IJ} (Basis II)	α_{Av}^{IJ} (Basis III)
C ₁ , C ₁	3.689	3.976
C ₁ , H ₁	0.337	0.434
H ₁ , H ₁	1.838	1.981
H ₁ , H ₂	0.088	0.090

TABLE IX. Pair polarizabilities α_{Av}^{IJ} of ethane molecule from basis sets II and III (a.u.).

<i>IJ</i>	α_{Av}^{IJ} (Basis II)		α_{Av}^{IJ} (Basis III)	
	Staggered	Eclipsed	Staggered	Eclipsed
C ₁ , C ₁	3.828	4.027	4.210	4.418
C ₁ , C ₂	-0.022	-0.251	0.042	-0.182
C ₁ , H ₁	0.445	0.466	0.564	0.584
C ₁ , H ₂	-0.081	-0.071	-0.091	-0.082
H ₁ , H ₁	2.157	2.211	2.322	2.383
H ₁ , H ₂	-0.045	-0.382	-0.057	-0.408
H ₁ , H ₃	0.114	0.113	0.121	0.119
H ₁ , H ₄	-0.010	0.046	-0.105	0.003

The “pair polarizabilities” evaluated in this study via Eq. (11) are reported in Tables VIII–XI. Basis set I, which is obviously unsuitable to represent the force operator, see for instance Table XI, provides very poor results. Accordingly, only theoretical values from basis sets II and III are given in Tables VIII–X. The former is not flexible enough to guarantee accurate estimates of properties in the (F, F) formalism, compare the corresponding TRK sum rules in Table II and polarizabilities in Tables III–VII, as it is especially designed for (R, F) properties only.^{17,18}

The overall performance of basis set III, as far as the (F, F) gauge is concerned, seems to be much better, even if TRK sum rules and polarizabilities are constantly overestimated. For instance, in the case of propane, the value $\alpha_{Av}^{(F,F)} \approx 39.5$ a.u., probably lies beyond the Hartree–Fock limit, close to $\alpha_{Av}^{(R,R)} \approx 38.4$ a.u., predicted via basis sets I and III.

TABLE X. Pair polarizabilities α_{Av}^{IJ} of propane molecule from basis sets II and III (a.u.).

<i>IJ</i>	α_{Av}^{IJ} (Basis II)	α_{Av}^{IJ} (Basis III)
C ₁ , C ₁	3.835	4.287
C ₁ , C ₂	0.118	0.199
C ₂ , C ₂	3.957	4.350
C ₂ , C ₃	-0.117	-0.122
C ₁ , H ₁	0.541	0.669
C ₁ , H ₃	0.004	-0.002
C ₁ , H ₇	-0.021	-0.027
C ₂ , H ₁	-0.047	-0.051
C ₂ , H ₃	0.430	0.543
C ₂ , H ₄	-0.098	-0.109
C ₂ , H ₇	0.427	0.540
C ₂ , H ₈	-0.005	-0.097
H ₁ , H ₁	2.427	2.600
H ₃ , H ₃	2.122	2.278
H ₇ , H ₇	2.125	2.279
H ₁ , H ₂	0.160	0.173
H ₁ , H ₃	-0.108	-0.115
H ₁ , H ₄	-0.029	-0.036
H ₁ , H ₇	-0.089	-0.093
H ₃ , H ₆	0.120	0.127
H ₃ , H ₇	0.106	0.109
H ₃ , H ₈	-0.030	-0.033
H ₇ , H ₈	0.046	0.050

TABLE XI. Pair polarizabilities α_{Av}^{IJ} of butane molecule from basis sets I and II (a.u.).

<i>IJ</i>	α_{Av}^{IJ} (Basis I)	α_{Av}^{IJ} (Basis II)
C ₁ , C ₁	12.439	3.968
C ₃ , C ₃	14.029	3.947
C ₁ , C ₂	-0.810	0.244
C ₁ , C ₃	-1.178	0.102
C ₁ , C ₄	-0.435	-0.052
C ₃ , C ₄	0.252	-0.003
C ₁ , H ₁	-0.654	0.532
C ₁ , H ₂	0.067	0.042
C ₁ , H ₅	0.040	-0.079
C ₁ , H ₆	0.026	-0.011
C ₁ , H ₉	-0.002	0.001
C ₁ , H ₁₀	0.055	-0.021
C ₃ , H ₁	0.011	-0.061
C ₃ , H ₅	-0.014	-0.024
C ₃ , H ₆	-0.777	0.430
C ₃ , H ₉	-0.053	0.038
C ₃ , H ₁₀	-0.791	0.427
C ₄ , H ₁	0.041	-0.090
H ₁ , H ₁	2.519	2.396
H ₅ , H ₅	-0.225	0.212
H ₆ , H ₆	2.246	2.125
H ₉ , H ₉	2.251	2.135
H ₁ , H ₂	-0.117	-0.115
H ₁ , H ₃	0.164	0.168
H ₁ , H ₄	-0.003	-0.002
H ₁ , H ₅	-0.044	-0.045
H ₁ , H ₆	-0.109	-0.108
H ₁ , H ₇	-0.024	-0.023
H ₁ , H ₈	-0.031	-0.024
H ₁ , H ₉	-0.035	-0.034
H ₁ , H ₁₀	-0.086	-0.087
H ₂ , H ₆	-0.437	-0.045
H ₂ , H ₁₀	-0.035	-0.034
H ₅ , H ₆	-0.001	-0.001
H ₅ , H ₇	0.115	0.121
H ₅ , H ₈	-0.055	-0.006
H ₅ , H ₉	0.010	0.107
H ₆ , H ₇	-0.005	-0.006
H ₆ , H ₁₀	0.098	0.107
H ₇ , H ₈	-0.119	-0.001
H ₉ , H ₁₀	0.054	0.052

The partial failure of basis set III to provide more accurate representation of electron distribution around pairs of nuclei is due to the intrinsic inadequacies of gaussian functions.

Accordingly, the attempts made here to evaluate “net atomic” and “bond polarizabilities” give only rough estimates. In any event, the degree of transferability of α_{Av}^{IJ} values does not seem fully satisfactory. It is definitely lower than that of “gross” atomic terms α_{Av}^I . The negative bond contribution $\alpha_{Av}^{(C_1, C_2)} \approx -0.18$ a.u. and $\alpha_{Av}^{(H_1, H_2)} \approx -0.42$ a.u., obtained via basis set III for the eclipsed conformer of ethane, are difficult to justify from the physical point of view. It might well happen that these estimates are heavily affected by basis set deficiencies.

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