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Calculations of molecular polarizabilities using the Valence Effective Hamiltonian (VEH) method*

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In this paper, we investigate the applicability of the Valence Effective Hamiltonian (VEH) method to calculations of theoretical molecular linear polarizabilities by the Sum-Over-States (SOS) methodology. Test calculations are presented on the polyene series. They indicate that the method gives qualitatively the same trends as *ab initio* small basis sets calculations.

Key words: Valence Effective Hamiltonian method — Sum-Over-States methodology — Molecular linear polarizability - Polyenes

1. Introduction

The potentialities of organic compounds for electrooptic and nonlinear optical applications have stimulated intense efforts in the theoretical prediction of linear polarizabilities (α) and first (β) and second (γ) hyperpolarizabilities [1-3]. A first and minimal condition for organic molecules to be of potential interest for nonlinear optics and electrooptics is certainly to have high microscopic electric responses. In a non resonant regime, these are characterized by their static polarizability and first and second hyperpolarizability tensors. There is thus a practical interest for starting a systematic study of structures which could be characterized by high intrinsic polarizability and hyperpolarizability values. Flytzanis rules [4] provide possible correlation between the linear and second-order nonlinear hyperpolarizability γ; they show, for example, that α scales with the length of the conjugation channel to third power while γ scales to the fifth

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

power of that length. Thus information on linear polarizabilities is a first and important step to the molecular design of new materials with high nonlinear hyperpolarizabilities.

Although this information can, in principle, be obtained with current *ab initio* computer programs, even minimal basis sets calculations become prohibitive when applied to large systems of practical interest owing to the huge number of two-electron integrals to be calculated and stored. Thus, there is an imperative need for simplified methods that could more economically produce results of *ab initio* quality. The Valence Effective Hamiltonian, the so-called VEH method, originally developed for molecules by Nicolas and Durand [5, 6] and extended to polymers by André [7], has turned to be a good tool for describing valence electronic structures of hydrocarbons with the same type of accuracy as double-zeta *ab initio* SCF calculations.

Another question of importance is that quantitative estimates of polarizabilities require large basis sets which also makes accurate calculations rapidly untractable. To overcome this limitation, Chablo and Hinchcliffe [8] have chosen to scale *ab initio* minimal basis set results in order to produce values comparable to the experimental ones or to those obtained in larger basis sets. This procedure has by now been successfully tested in our laboratory by applications to several types of conjugated oligomers: polyenes and polydiacetylenes [9–11], polyallenes [12] and polycumulenes [13], octatetraene and its isoelectronic O=CH, HN=CH, O=N, N=N and HN=N substituted conjugated chains [14]. Although it might look questionable at first sight to elaborate a method that mimics *ab initio* calculations in small basis sets, those recent studies have demonstrated the feasibility of using predictively *scaled* minimal basis set results for getting useful trends in homogeneous series.

The method proposed here is a combined methodology of the VEH technique and of the Sum-Over-States (SOS) perturbative scheme. The basic principles of the method are summarized in Sect. 2. In Sect. 3 we investigate its capabilities for doing low-cost reliable polarizability calculations. Model calculations on the polyene series of oligomers are presented and compared with *ab initio* results. More subtle effects like geometrical ones on the molecular polarizability are addressed in Sect. 4 by the example of the influence of C–C/C=C bond alternation. Finally, Sect. 5 displays our conclusions.

2. Methodology

In the VEH method [5, 6, 7], one simulates the Fock Hamiltonian of an *ab initio* valence pseudopotential calculation. The trial one-electron Hamiltonian is taken as the sum of the kinetic energy and a sum of effective atomic potentials of the atoms within their specific chemical environment

$$H_{\mathrm{eff}} = -\tfrac{1}{2}\nabla^2 + \sum_{\mathrm{A}} V_{\mathrm{A}}. \tag{1}$$

For computational reasons, the atomic potentials are chosen as Gaussian projectors

$$V_A = \sum_{i,j} \sum_{l,m} C_{ij,lm;A} |\chi_{i,lm;A}\rangle\langle\chi_{j,lm;A}|. \tag{2}$$

The summations over l, m define the angular dependence of the projector ($l=0$, s-type; $l=1$, p-type). The $\chi_{i,lm}$ are normalized Gaussians:

$$\chi_{i,lm} = N_i r^l \exp(-\alpha_i r^2) Y_{lm}(\theta, \phi). \tag{3}$$

The parameters of the method are therefore the Gaussian coefficients ($C_{ij,lm;A}$) and exponents (α_i). They are determined by a least-square fitting on a series of well-chosen pattern molecules (ethane, butadiene, ...).

As long as the matrix elements of the effective Hamiltonian are evaluated in a Gaussian basis set (whose Gaussians should not be confused with those of Eqs. (2)-(3) defining the atomic potentials), this VEH technique does reduce the integral evaluation to the calculation of kinetic and overlap between Gaussian functions only. Since it further avoids the iterative cycles inherent to all SCF calculations, the method is very fast and economic in computing time. It is completely theoretical, in the sense that the potentials do not contain any experimental data and are determined from first principles, and, by its very principle, does give valence orbital energies of *ab initio* quality.

Static dipole polarizabilities were calculated using the Sum-Over-States (SOS) method [15] which makes use of time-independent perturbation theory. Resulting expressions for the components of the ground state polarizability tensor are

$$\alpha_{ij} = -4 \sum_{a,r} \langle a|\mu_i|r\rangle\langle r|\mu_j|a\rangle / (\varepsilon_a - \varepsilon_r) \qquad i, j = x, y, z, \tag{4}$$

where $\langle a|\mu_i|r\rangle$, $\langle r|\mu_j|a\rangle$ are dipole matrix elements between occupied (index a) and virtual (index r) molecular orbitals, and ε_a, ε_r are one-electron orbital energies. Only closed-shell structures are considered. The "brute force" implementation is not always a trivial task if nonlinear terms are required; efficient algorithms have been developped for such calculations using a fast recurrent SOS method [16] and allow for an efficient evaluation of (hyper)polarizability terms. They are an integral part of the present SOS-VEH scheme.

3. Static longitudinal polarizabilities of H-(CH=CH)$_n$-H oligomers

For sake of comparison, the SOS-VEH method was first tested on the series of H-(CH=CH)$_n$-H oligomers for which many *ab initio* calculations of the static polarizability were done in this Laboratory, using both the Sum-Over-States (SOS) [15] and the Finite-Field (FF) [9, 10] methods in various basis sets. The FF methodology corresponds to a direct minimization procedure of the Hamiltonian including the electric field interaction effect. It is thus a coupled Hartree-Fock scheme which takes into account part of the electronic rearrangement. The SOS technique, on the other hand, tries to get the seond-order perturbation effect due to the external field from unperturbed orbitals. Due to Brillouin theorem, it does not imply electron rearrangements and is equivalent to an uncoupled Hartree–Fock scheme. This lack of reorganizational effect makes that SOS values of electrical polarizabilities are typically 60–80% of the FF ones.

Within the VEH method, the calculations presented here have been made using the following effective potentials:

(i) Effective potentials optimized for alkenes [5]. The first one, identified as VEH-I, reproduces the valence orbital spectrum given by an *ab initio* pseudopotential calculation in a minimal basis set. The second one, denoted by VEH-II, reproduces the valence spectrum of a double-zeta quality.

(ii) A universal potential, denoted by VEH-U, which mimics double-zeta pseudopotential calculations for all hydrocarbons (both saturated and unsaturated) [17].

The SOS-VEH results are reported in Table 1 for the polarizability components. They should be compared with *ab initio* results summarized in the same table [9, 15]. The experimental geometries were used in the cases of ethylene [18], butadiene [19] and hexatriene [20], while the geometry of octatetraene was extrapolated from that of hexatriene. The x and y axes were chosen in the molecular plane, the C=C bond being inclined by ca. 30 deg with respect to the "longitudinal" y axis (see Fig. 1).

It is verified from the results that the standard *ab initio* SOS values underestimate by 16–19% the corresponding values obtained by the FF methodology. This arises as already mentioned because the SOS method corresponds to an uncoupled Hartree–Fock scheme and does not include important hole-electron correlations [3]. On the other hand, the flexibility of the basis set has a strong effect on the actual values of the components. As expected, the change is larger for the direction where the electrons are poorly described by minimal basis sets (e.g. α_{zz} corresponds to π-electrons which are only described by carbon $2p_z$ orbitals in a minimal basis set calculation. A more extensive analysis on the ethylene molecule in the SOS scheme is also given in Table 1 which includes results of minimal (STO-3G), extended split-valence (4-31G and 6-31G) and polarized (6-31G**) basis sets. A change from minimal to polarized basis sets yields an improvement by a factor 1.86 in the total polarizability, the effect being more marked for the α_{zz} component which improves by a factor of 4.53. It is important to note however that the "best" strictly *ab initio* SOS calculated value (17.45 a.u.) is still only 61% of the "experimental" values (28.48 a.u.). A better description of the carbon 1s inner shell has only a minor effect (which is however more marked in the z-direction). The inclusion of polarized orbitals has little effect on the molecular in-plane components but markedly modifies the perpendicular α_{zz} component.

It is striking to note that both the SOS-VEH-I and SOS-VEH-II potentials give polarizability values close to the ones obtained by the FF method in a 4.31G basis set and are, in this sense, better than those obtained by the *ab inititio* SOS method in the same basis set. Whatever potential is used, the VEH values are systematically larger than the corresponding *ab initio* ones, the largest increase being observed in the case of the VEH-U potential. That point is to be correlated

Table 1. Influence of basis sets and methodologies on the polarizabilities of polyenes (C_nH_{n+2}). Comparison of *ab initio* and VEH calculated longitudinal polarizabilities of H–(CH=CH)$_n$–H oligomers, $n = 1, 2, 3$, and 4. See Fig. 1 for the definition of cartesian axes. α is the average polarizability $(1/3)\sum_i \alpha_{ii}$. Results in atomic units ($1\ \text{a.u.} = 0.148176 \cdot 10^{-24}\ \text{cm}^3 = 0.164867 \cdot 10^{-40}\ \text{C}^2\,\text{m}^2\,\text{J}^{-1} = 0.296352 \cdot 10^{-24}\ \text{esu}$)

	α_{xx}	α_{yy}	α_{zz}	α
C_2H_4				
FF-STO-3G	13.20	17.48	2.53	11.06
FF-4.31G	22.78	29.19	5.90	19.29
SOS-STO-3G	11.11	15.12	1.93	9.39
SOS-4.31G	18.15	23.78	5.61	15.84
SOS-6.31G	18.43	24.31	6.22	16.34
SOS-6.31G**	19.17	24.42	8.75	17.45
CDNOVSB	17.07	24.98	4.18	14.41
SOS-VEH-I	16.81	24.84	2.60	14.75
SOS-VEH-II	16.32	24.24	2.57	14.38
SOS-VEH-U	22.68	32.88	3.20	19.59
Exp.				28.48
C_4H_6				
FF-STO-3G	24.83	47.85	4.75	25.81
FF-4.31G	40.73	73.40	12.19	42.11
SOS-STO-3G	22.12	38.12	3.77	21.34
SOS-4.31G	34.88	55.91	11.25	34.02
CNDOVSB	21.71	82.98	5.84	36.84
SOS-VEH-I	33.87	69.06	5.18	36.03
SOS-VEH-II	32.86	67.42	5.12	35.13
SOS-VEH-U	47.54	112.92	6.54	55.66
Exp.				56.70
C_6H_8				
FF-STO-3G	37.72	100.50	6.98	48.40
FF-4.31G	Not calc.	152.67	Not calc.	Not calc.
SOS-STO-3G	33.87	73.71	5.64	37.74
SOS-4.31G	52.89	102.58	16.95	57.47
CNDOVSB	21.84	196.38	6.96	75.06
SOS-VEH-I	53.31	159.90	7.84	73.69
SOS-VEH-II	51.69	156.05	7.75	71.83
SOS-VEH-U	76.19	275.79	10.07	120.68
$\mathrm{C8H}_{10}$				
FF-STO-3G	49.58	174.56	9.15	77.76
FF-4.31G	Not calc.	246.10	Not calc.	Not calc.
SOS-STO-3G	44.88	114.75	7.44	55.69
SOS-4.31G	69.84	156.20	22.53	82.85
SOS-VEH-I	71.10	276.58	10.39	119.36
SOS-VEH-II	68.93	269.71	10.26	116.30
SOS-VEH-U	102.00	506.02	13.39	207.14

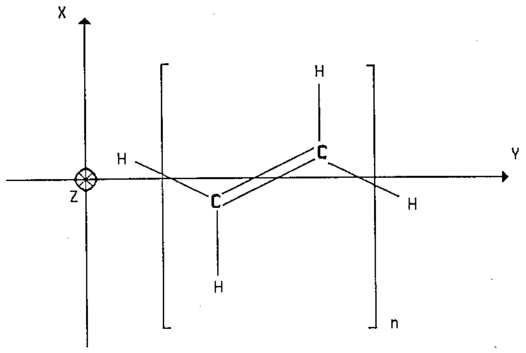

Fig. 1. Orientation of cartesian axes for the polarizability components of H–(CH=CH)$_n$-H oligomers

to the fact that, in polymers, the VEH method has turned to produce energy gaps of excellent quality [21,22]. This is a clear indication that part of the electron-hole correlation is included into the virtual one-electron levels by that methodology. The Koopmans transition energies (denominators of the perturbation expansion (4)) are thus reduced and, consistently, the calculated values of the polarizabilities are larger (in agreement with the experimental trends). The same behaviour has also been observed in semi-empirical polarizability CNDO-type calculations (where the experimental transition energies is a basic ingredient of the parametrization through the correlation decrease of empirically evaluated one-electron integrals) [23].

Assuming as in the literature [24-26] that the behaviour of the longitudinal polarizability as a function of the number n of double bonds in the alkene molecule is analytically represented by equations of the form

$$\alpha_{yy} = Kn^p \tag{5}$$

or, alternatively,

$$\text{Log}\ \alpha_{yy} = C + p\ \text{Log}\ n \tag{6}$$

we present in Table 2 the p-values obtained by least-square fitting for the *ab initio* and VEH calculations. As expected, due to the electron–electron interactions

Table 2. Values of the exponent obtained by fitting *ab initio* and VEH results with an equation of the form $\alpha_{yy} = kn^p$

Method	p
FF-STO-3G	1.663
FF-4.31-G	1.541
SOS-STO-3G	1.464
SOS-4.31-G	1.357
SOS-VEH-I	1.736
SOS-VEH-II	1.730
SOS-VEH-U	1.966

Table 3. Influence of bond alternation $\Delta R = R_{C\text{-}C}\text{-}R_{C=C}$ on the longitudinal polarizability of H-(CH=CH)$_n$-H oligomers. See Fig. 1 for the definition of cartesian axes. Results in atomic units (1 a.u. = $0.148176 \cdot 10^{-24}$ cm^3 = $0.164867 \cdot 10^{-40}$ C^2 m^2 J^{-1} = $0.296352 \cdot 10^{-24}$ esu)

	α_{yy} (a.u.)			
	$\Delta R = 0.1$ Å	$\Delta R = 0.05$ Å	$\Delta R = 0.025$ Å	$\Delta R = 0.0125$ Å
C_2H_4				
FF-STO-3G	17.34	17.91	18.20	18.30
SOS-STO-3G	15.27	15.93	16.28	16.46
SOS-VEH-I	25.61	27.98	29.30	30.00
SOS-VEH-U	33.50	35.37	36.37	36.90
C_4H_6				
FF-STO-3G	47.04	52.68	55.82	57.46
SOS-STO-3G	41.10	45.09	47.36	48.57
SOS-VEH-I	81.53	104.22	119.23	127.87
SOS-VEH-U	124.18	141.58	151.82	157.36
C_6H_8				
FF-STO-3G	92.10	108.99	118.71	124.02
SOS-STO-3G	75.22	86.50	93.35	97.13
SOS-VEH-I	165.68	242.37	300.07	335.66
SOS-VEH-U	280.41	343.75	383.74	406.20
C_8H_{10}				
FF-STO-3G	149.36	186.00	208.12	220.36
SOS-STO-3G	114.44	137.11	151.71	160.05
SOS-VEH-I	270.41	443.69	590.17	686.53
SOS-VEH-U	499.15	655.34	760.73	822.02

and the bond alternation of the carbon–carbon backbone, they differ substantially from the "ideal metallic" value $p = 3$ predicted by the free-electron model [24] and the Hückel method [25, 26] where a regular (non-alternant) skeleton is implicitly assumed.

4. Polarizability versus bond alternation

As a further test, we have also examined the behaviour of the polarizability as a function of *bond alternation* $\Delta R = R_{C\text{-}C}\text{-}R_{C=C}$. That test is of crucial importance since the parameters of the atomic potentials used in the VEH-method were obtained for equilibrium or near-equilibrium geometries and it is thus interesting to see the behaviour of such potentials for calculations of polarizabilities in non-optimized geometries. In this series of tests, the reference polyenic structure (corresponding to $\Delta R = 0.1$ Å) is taken from the unit cell geometry of the infinite polyene theoretically optimized by Karpfen [27]. All changes in ΔR were made keeping the total chain length identical, in order to properly separate length effects from bond alternation effects. The calculations are reported in Table 3. The inclusion of ethylene in the results (although ΔR is not defined in that case) means that the molecule was conventionally considered with the same double C=C bond length as in the other terms of the series. Previous *ab initio* calculations on the polyene series predicted an increase of α_{yy} as ΔR decreases, i.e., the more "homogeneous" or "metallic"' the structure, the more rapidly the polarizability will tend to an infinite limit [10, 15]. As seen in Table 3, this effect is also predicted by SOS-VEH calculations. For all compounds, the values of the longitudinal polarizability are enhanced when the structures become more regular and the effect is more pronounced in the larger compounds although there may be appreciable differences between the predicted values from one method to another. This idea has already suggested the possibility of enhancing (hyper)polarizability through geometry adjustments [9–15].

5. Conclusion

The results we have obtained in the particular case of the polyene series indicate that the VEH method is an excellent candidate for doing low-cost reliable polarizability calculations in homogeneous series. Of course, no miracle could be expected from such a simple method to make accurate theoretical predictions of molecular polarizabilities which would in all cases require extensive *ab initio* calculations in large basis sets (including correlation effects). We consider the VEH method as a potential substituent to *ab initio* or semi-empirical SCF methods for situations involving such large molecular sizes and number of electrons that, for computational reasons, one cannot do better than order-of-magnitude predictions in small basis sets.

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