Theor Chim Acta (1992) 82: 309–319

Theoretica Chimica Acta

Second-order Green's function calculations of the ionization potential of a $(H_2)_7$ chain embedded in a homogeneous electric field

Michaël Deleuze[1], Joseph Delhalle[1], and Barry T. Pickup[2]

[1] Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix, 61, rue de Bruxelles, B-5000 Namur, Belgium

[2] Department of Chemistry, The University, Sheffield S3 7HF, UK

Received June 3, 1991/Accepted October 11, 1991

Summary. The vertical ionization potential and the related pole strength of a model alternant chain of 14 hydrogen atoms subject to a homogeneous electric field, parallel to the chain and of increasing intensity are calculated, in the framework of a 6-31G** basis set, at the second-order level of the many-body Green's function theory. Trends observed with orbital relaxation, pair removal and pair relaxation effects are interpreted in terms of deformations of the electron density.

Key words: Green's function – Ionization potential – Orbital relaxation – Electron correlation – Polarization

1. Introduction

The study of the electronic structure of polymers is basic to the understanding of many of their properties (electrical, structural, optical, ...). Photoemission techniques are particularly well suited to probe experimentally this structure but they need theoretical supports for accurate interpretation. The vertical ionization potentials (VIP) I_c can be often approximated, after inversion of sign, as the Hartree–Fock energy orbitals, $I_c = -\varepsilon_c$, in the neutral system. This approach does not take into account electron correlation and relaxation effects resulting from the ionization process. Such effects can be so important that the Koopmans approximation [1] becomes qualitatively deficient. More elaborate techniques have then to be used to correct for such deficiencies.

The Hartree–Fock Many-Body Green's Function theory (HF-MBGF) developed [2–7] over many years, has been shown to yield accurate results for a large variety of molecules [8]. In a previous paper [9], this method has been applied to increasing-size model hydrogen chains to follow the size-dependence of the orbital relaxation, pair removal and pair relaxation effects, at the second-order level of the perturbation expansion of the self-energy.

Electronic structure of molecules and polymers is usually computed for isolated systems. In most cases, however, the experimental spectra are recorded in condensed phase, and the electric field effects of the neighbouring molecules are disregarded. As a preliminary attempt to include such effects, we consider in this contribution the changes on the first ionization potential of a finite $(H_2)_7$ chain embedded in a homogeneous electric field.

2. Methodology

2.1. Model system

Hypothetical hydrogen chains have quite often been used as very simple models of oligomeric systems, particularly polyenes, with which they present many similar electronic properties (as, for example, the electron density alternation). In this paper, the VIP of a linear alternating chain of 14 hydrogen atoms embedded in an electric field of variable intensity and directed along the chain axis, has been calculated at the second-order level of the HF-MBGF theory. Bond lengths of 1.40 and 1.80 a.u. have been used to obtain in a neutral environment a simple model of a typical insulator. Despite the large applied electric fields, no relaxation of the geometry has been considered. The aim of this investigation is to study the effects on the relaxation and correlation contributions to the VIP of a slight perturbation in the electron structure of an oligomeric system. The electric field and the main axis of rotation of the chain are oriented along the z-axis, the origin of the reference frame being located at the centre of gravity of the system.

Hartree–Fock calculations are performed using a standard extended polarized (6)-31G** basis set [10]; the $2p_z$ polarization functions are expected to accommodate the influence of the electric field on the electron density in the chain. Orbital exponents are not optimized with respect to the field intensity, and the (6)-31G** basis set used might have a variational flexibility too limited to reproduce accurately the deformation of the electron density under the more extreme fields applied. To assess the influence of the lack in the variational flexibility of the wavefunction, we have also considered calculations with the minimal STO-3G basis set. As it will be noted, both basis sets provide similar trends.

In a way, the basis set limitation confines the polarized electron in a finite box. Because of this important constraint, neither direct field ionization nor tunneling effects can be reproduced. Despite these important restrictions, the $(H_2)_7$ chain is an interesting first model to study before more realistic, but also more complicated insulating or semi-conducting oligomers, such as polyenes. Finally, the actual developments of laser field techniques provide motivation for calculations of ionization potentials of systems embedded in electric fields of high intensity.

2.2. Theoretical calculations

In a Finite-Field scheme [11], a zeroth-order solution is obtained by solving the one-particle Hartree–Fock equation:

$$f(\boldsymbol{x}_i)\chi_i(\boldsymbol{x}_i) = \varepsilon_i\chi_i(\boldsymbol{x}_i) \tag{1}$$

with the one-particle Fock-operator $f(\boldsymbol{x}_i)$ including the effect of the external homogeneous electric field F. It is written as:

$$f(\boldsymbol{x}_i) = -\tfrac{1}{2}\Delta_i + \sum_a \frac{Z_A}{R_{iA}} + V^{\mathrm{H.F.}}(\boldsymbol{x}_i) + Fz_i \tag{2}$$

$V^{\mathrm{H.F.}}(\boldsymbol{x}_i)$ is the resulting Coulomb and exchange potential due to an average static electron distribution acting on the i-th particle whose space-spin coordinates are denoted $\boldsymbol{x}_i$.

To correct the Koopmans result, one can consider the one-particle many-body Green's function or one-particle propagator for the electron in spin-orbital χ_c. For a time-independent Hartree–Fock operator, the Green's function is solution of the integro-differential equation:

$$[\omega - f(\boldsymbol{x}_i)]G(\boldsymbol{x}_i, \boldsymbol{x}_j, \omega) = \delta(\boldsymbol{x}_i - \boldsymbol{x}_j) + \int \Sigma(\boldsymbol{x}_i, \boldsymbol{x}_k, \omega)(\boldsymbol{x}_k, \boldsymbol{x}_j, \omega)\, d\boldsymbol{x}_k \tag{3}$$

The interactions of the electron in spin-orbital χ_c with the other electrons are introduced through a non-local effective energy-dependent perturbation potential: the self-energy $\Sigma(\omega)$ [12, 13]. It can be written as an infinite perturbation expansion which in the matrix representation within the basis of the HF spin-orbitals is given as:

$$\mathbf{G}(\omega) = [\omega \mathbf{1} - \boldsymbol{\varepsilon} - \boldsymbol{\Sigma}(\omega)]^{-1} \tag{4}$$

with

$$\boldsymbol{\Sigma}(\omega) = \boldsymbol{\Sigma}^{(2)}(\omega) + \boldsymbol{\Sigma}^{(3)}(\omega) + \boldsymbol{\Sigma}^{(4)}(\omega) + \cdots \tag{5}$$

The poles of the Green's function matrix $\mathbf{G}(\omega)$ for the infinite expansion are, after change of sign, the exact Vertical Ionization Potentials and the Vertical Electron Affinities. They can be obtained by solving iteratively the equation:

$$\det[\omega \mathbf{1} - \boldsymbol{\varepsilon} - \boldsymbol{\Sigma}(\omega)] = 0 \tag{6}$$

Pole strength [2, 7], related to the ionization of the spin-orbital χ_c can be calculated, in the approximation of a diagonal self-energy matrix, as:

$$\Gamma_c = \left[1 - \left(\frac{d\Sigma_{cc}(\omega)}{d\omega}\right)_{\omega = \omega_c}\right]^{-1} \tag{7}$$

Γ_c, defined as the residue of $1/(\omega - \Sigma_{cc}(\omega))$ taken at the pole ω_c, can be equated [14, 15] in the diagonal approximation, to the squared overlap $|\langle \Psi_c^{N-1} | a_c | \Psi_0^N \rangle|^2$ between the ionized state calculated within Koopmans approximation and the exact state obtained in the framework of the MBGF theory. Hence, Γ_c is also the fraction of the photoemission intensity associated with a monoelectronic process, the remaining fraction $[1 - \Gamma_c]$ being the intensity borrowed in shake-up or scattering processes resulting from correlation and relaxation effects.

In a one-electron description, the self-energy would have no energy dependence, and the pole strength would be 1 for all VIP's. In a real interacting system, pole strengths larger than 0.9 are usually referred to quasi-monoelectronic processes, while pole strengths smaller than 0.9 are indicative of a breakdown of the molecular orbital picture [16–20].

In the second-order expansion [5, 6] considered in this work, the matrix elements of the self-energy are defined as:

$$\Sigma_{ij}^{(2)}(\omega) = \tfrac{1}{2} \sum_{ars} \frac{\langle rs || ia \rangle \langle ja || rs \rangle}{\omega + \varepsilon_a - \varepsilon_r - \varepsilon_s} + \tfrac{1}{2} \sum_{abr} \frac{\langle ab || ir \rangle \langle jr || ab \rangle}{\omega + \varepsilon_r - \varepsilon_a - \varepsilon_b} \tag{8}$$

where the sums over a and b run over all the occupied HF spin-orbitals while the sums over r and s run over all the unoccupied HF spin-orbitals of the N-particle system; $\langle ij||kl\rangle$, in this expression, represent the antisymmetrized two-electron integrals:

$$\langle ij||kl\rangle = \int\int dx_1\, dx_2\, \chi_i^*(x_1)\chi_j^*(x_2) r_{12}^{-1}[1 - P_{12}]\chi_k(x_1)\chi_l(x_2) \tag{9}$$

If one neglects the off-diagonal elements of the self-energy in a quasi-particle scheme, one removes, as in Many-Body Perturbation Theory [21–23], the coupling between the ionization (hole) and attachment (particle) sectors of the Green's function. Then considering $\omega = \varepsilon_c$, the correction provided at the second-order of the Green's function theory is strictly equivalent to that one obtained using second-order MBPT, which can be sorted out in three components [6]: the Orbital Relaxation (ORX), the Pair Removal (PRM) and the Pair Relaxation (PRX) contributions to the ionization potential of the electron in spin-orbital χ_c:

$$\mathrm{VIP}_c(\mathrm{MBPT}^{(2)}) = -\varepsilon_c - \Sigma_{cc}^{(2)}(\varepsilon_c) = -\varepsilon_c + \mathrm{ORX} + \mathrm{PRM} + \mathrm{PRX} \tag{10}$$

The ORX term accounts for the energy associated with relaxation of the electron cloud during ionization:

$$\mathrm{ORX} = -\sum_{ar} \frac{|\langle ac||cr\rangle|^{(2)}}{\varepsilon_r - \varepsilon_a} \tag{11}$$

The PRM contribution represents the ground-state correlation which disappears upon removal of the electron in spin-orbital χ_c:

$$\mathrm{PRM} = \tfrac{1}{2}\sum_{ars} \frac{|\langle rs||ca\rangle|^{(2)}}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_c} \tag{12}$$

The PRX contribution accounts for the increase of the remaining correlation in the ionized system because of the presence of the additional virtual spin-orbital χ_c:

$$\mathrm{PRX} = -\tfrac{1}{2} \sum_{ab \neq c,r} \frac{|\langle ab||cr\rangle|^{(2)}}{\varepsilon_c + \varepsilon_r - \varepsilon_a - \varepsilon_b} \tag{13}$$

3. Results and discussion

3.1. Polarization of the electron density

A study of the deformation of the electron density in the $(H_2)_7$ chain embedded in a homogeneous electric field is quite useful to understand the variation of the ionization potential (and related properties such as orbital relaxation and electron correlation effects) of an electron belonging to the highest occupied molecular orbital (HOMO).

Under a weak electric field, the polarization of the electron density in an insulating system results in a succession of electric dipoles [24, 25]. Such an ionic structure can be observed from the evolution with increasing field of the net electric charge on each atom. These charges, obtained within a Mulliken population analysis, are shown in Fig. 1, the electric field being oriented here and henceforth from the left to the right.

Except for the atoms at the ends of the $(H_2)_7$ chain, these charges are the largest for a field intensity of about 0.04 atomic units (1 a.u. = 5.1423 ×

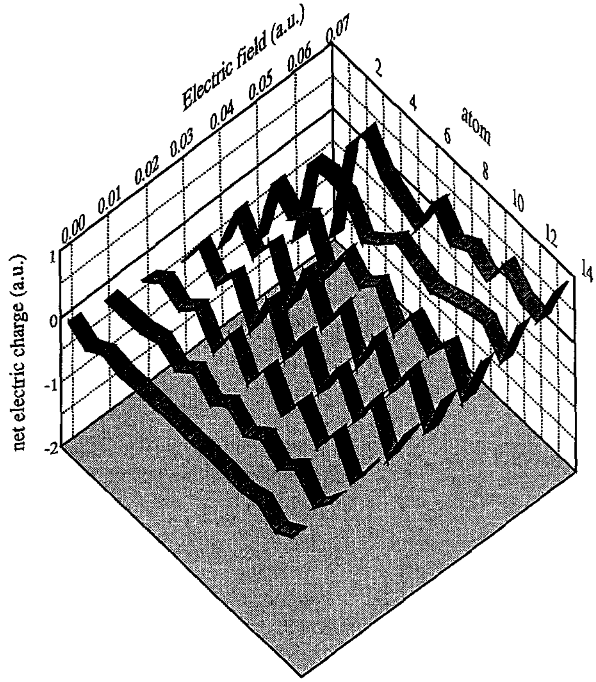

Fig. 1. Variation of the net electric charges in the $(H_2)_7$ model chain embedded in increasing electric fields (6-31G** basis set)

10^{11} V m^{-1}). The large variations and inversion of sign observed at higher fields are indicative of a sudden collapse of the ionic structure at about 0.06 a.u.

The absolute values of all the net electric charges in the $(H_2)_7$ chain can also be summed, leading to an estimate value of the degree of ionicity in the oligomer. The variation of this quantity is provided in Fig. 2. It shows a maximum at $F \cong 0.04$ a.u., and a minimum at $F \cong 0.06$ a.u. In the same way, the degree of ionicity of 7 isolated hydrogen molecules with the same orientation in the electric field have also been estimated. This time, it increases almost linearly with respect to the field intensity. Deviation to linearity observed with the $(H_2)_7$ chain are due to transfer of charge between the interacting (H_2) monomer subunits. This electron transfer can be estimated by subtracting the estimated degree of ionicity in the set of 7 isolated (H_2) molecules from the degree ionicity of the $(H_2)_7$ chain. A maximum occurs at $F \cong 0.065$ a.u., and two minima at $F \cong 0.035$ a.u.

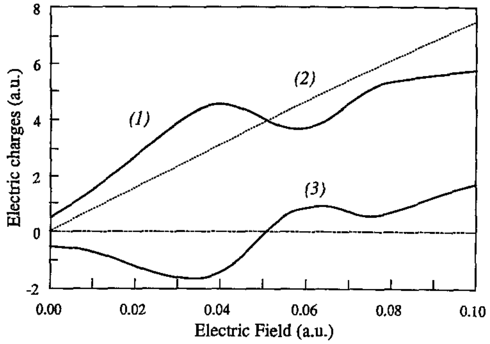

Fig. 2. Variation with increasing electric fields, of the: (1) ionicity degree in the model $(H_2)_7$ chain, (2) ionicity degree in a set of 7 non-interacting H_2 molecules, (3) = (2) − (1) estimated electron transfer (6-31G** basis set)

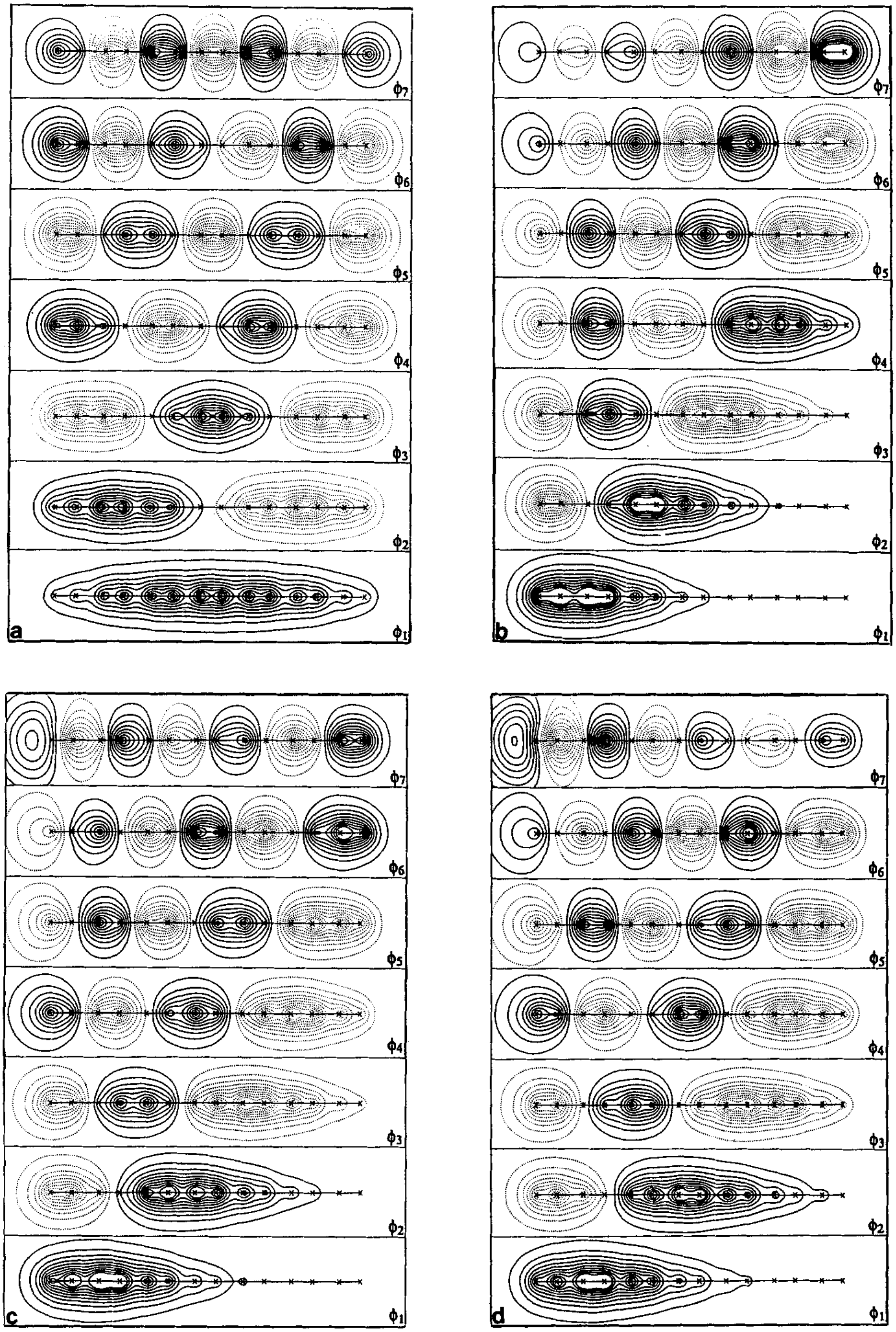

Fig. 3a–d. Occupied molecular orbitals of the model $(H_2)_7$ chain embedded in increasing electric fields, this fields being applied from the left to the right: **a** $F = 0.00$ a.u., **b** $F = 0.04$ a.u., **c** $F = 0.06$ a.u., **d** $F = 0.075$ a.u.

and $F \cong 0.075$ a.u., respectively. For fields smaller than 0.05 a.u., the electron transfer has a negative value. To explain this, one has to consider a back polarization of one or several molecular orbitals in this oligomeric system.

In Fig. 3, the shape of the occupied orbitals is shown at zero field, and in electric fields of increasing intensity. At $F = 0.04$ a.u., the polarization of the electron density toward the electric field is mainly due to the low lying (inner) occupied orbitals $\phi_1\phi_2\phi_3$ characterized by the more bonding contributions. On the other hand, the more antibonding (outer) occupied orbitals $\phi_4\phi_5\phi_6$ and ϕ_7 account for the back polarization previously pointed out. At first glance, this seems counterintuitive and in contrast with the trends observed in conjugated systems e.g. polyenes. To explain this behaviour, one must refer to the σ-symmetry of the molecular orbitals of the hydrogen chain. In this particular case, the polarization of the outer molecular orbitals results in changes of the nodal characteristics along the molecular axis, each time requiring energy and leading to a strong destabilization. Hence, on the basis of the number of nodes, inner molecular orbitals are more easily polarized than the outer ones. The back-polarization observed in the highest occupied orbitals results from a delicate balance between increasing electron repulsion and the effect of the electric field.

The collapse of ionicity is revealed at $F \cong 0.06$ a.u. by a large increase in the electron transfer between the (H_2) subunits. It is mainly due to the HOMO, as it is easily observed from the shape of molecular orbitals.

3.2. HF *orbital energies*

The variation of the HF orbital energies with respect to the field intensity can be directly correlated with the electron cloud deformation in the corresponding molecular orbital. In Fig. 4, all the occupied and the lowest unoccupied (LUMO) molecular orbital levels are plotted. For fields increasing from 0.00 to 0.04 a.u., inner orbitals, polarized in the electric field, are stabilized, while back-polarized outer orbitals are destabilized.

On the other hand, the LUMO, the unoccupied orbital with the more bonding contributions, is strongly stabilized under polarization, leading to a low minimum in the HF HOMO-LUMO energy separation at $F \cong 0.060$ a.u. The sudden electron transfer through the HOMO observed at that field value is the direct outcome of an avoided crossing of the HOMO and the LUMO.

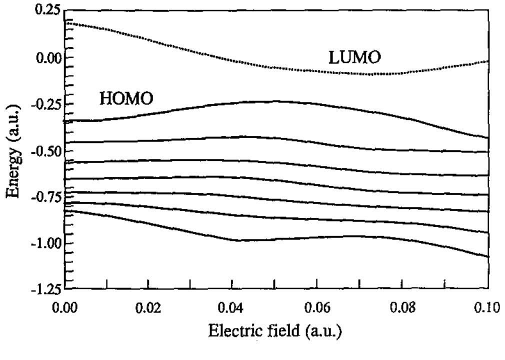

Fig. 4. Variation of the HF molecular orbital energies in the $(H_2)_7$ model chain embedded in increasing electric fields (6-31G** basis set)

It is obvious, when considering the shape of the HOMO after the electron transfer and its energy at $F \cong 0.07$ a.u., that an electron belonging to it would be directly field ionized, at such a field. The electron density being confined in a finite box, we observe a slight stabilization of the HOMO after the electron transfer, but this is of more formal interest.

3.3. HOMO *second-order* MBGF *and* MBPT *calculations*

In Fig. 5a, the evolution of the second-order Green's function ionization potential of an electron belonging to the HOMO is compared to the Koopmans result.

At the lower fields, the relaxation contributions have a larger magnitude than the pair removal contribution, leading to a negative second-order correction. The sudden inversion of sign observed with this correction can be related to the electron transfer through the HOMO at $F \cong 0.060$ a.u., resulting in very strong correlation effects. At that value of field, the HOMO-LUMO energy separation is smallest, and hence, excitation process can occur very easily: the drop in the HOMO pole strength below the threshold value 0.9 reveals a complete breakdown of the molecular orbital picture (Fig. 5b) for the ionization of the other molecular orbitals.

The second-order MBGF correction to the HOMO VIP can also be interpreted in perturbation theory (Fig. 6), leading to very similar trends with increasing electric fields. The variation of the second-order MBPT correction is also analysed in terms of its three components: ORX, PRM, PRX.

The maximum in the amplitude of the ORX effect at $F \cong 0.045$ a.u. is related to the largest accumulation of the electron density revealed by the maximum in the estimated degree of ionicity (Fig. 2), and also to the high localization of the HOMO at the right-hand side of the oligomer (Fig. 3b). On the other hand, the energy separation between the HOMO-1 and the HOMO increases smoothly for fields ranging from 0.00 to 0.04 a.u., leading to a decreasing relaxation of the remaining electron pairs after the ionization process (PRX).

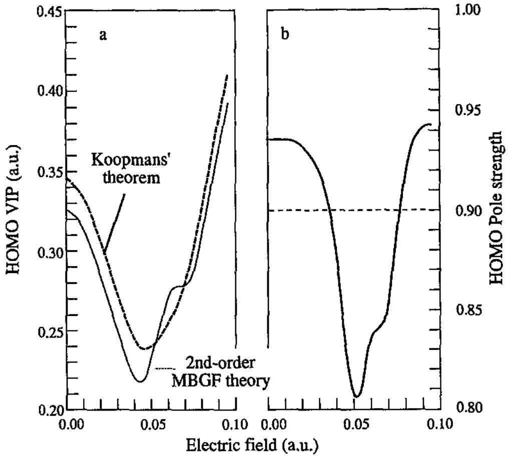

Fig. 5. Variation of the HOMO ionization potential of the model hydrogen chain (*a*) and its related pole strength (*b*) with increasing intensities of the electric field

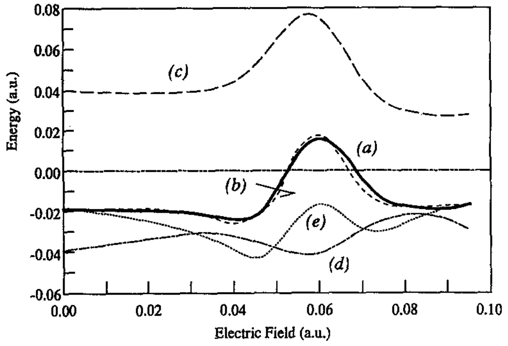

Fig. 6. Variation of the second-order MBGF correction (*a*) with increasing electric fields. The related second-order MBPT correction (*b*) is sorted out in its three components: the pair removal (*c*), the pair relaxation (*d*), and the orbital relaxation (*e*) contributions (6-31G** basis set)

The collapse of the electron density alternation for values of field intensity around 0.06 a.u. is revealed by a very strong exacerbation of the correlation effects (PRM, PRX). In contrast, at such fields, the HOMO is delocalized homogeneously over the whole chain. Hence, the resulting delocalization of the positive hole created during the ionization of an electron in the HOMO, leads, as it has been already reported [9], to a strong limitation in the magnitude of the orbital relaxation effect.

At $F \cong 0.075$ a.u., another maximum in the magnitude of the ORX effect can also be related to the localization of the HOMO on the left-hand side of the $(H_2)_7$ chain this time (Fig. 3d). The resulting electron density accumulation is revealed by a small limitation in the electron transfer between neighbouring (H_2) subunits (Fig. 2).

3.4. *Influence of the basis set*

To estimate the basis set dependence of the results obtained, trends calculated using 6-31G** and STO-3G basis set are compared. Both basis sets provide similar variation for all the properties considered in this work, as the variation with increasing field intensities of the second-order MBGF/MBPT correction to the HOMO VIP and its three components ORX, PRM, PRX obtained using a minimal STO-3G basis set (Fig. 7). The same sequence of maxima and minima is obtained as when using a 6-31G** basis set (Fig. 6), this sequence being simply

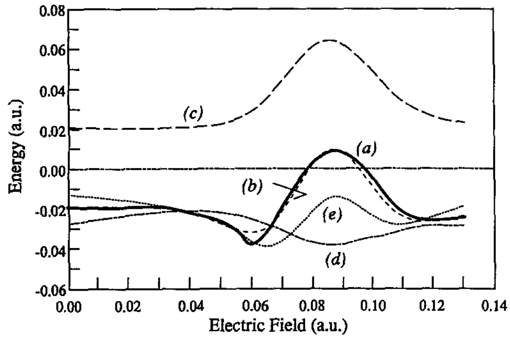

Fig. 7. Variation of the second-order MBGF correction (*a*) with increasing electric fields. The related second-order MBPT correction (*b*) is sorted out in its three components: the pair removal (*c*), the pair relaxation (*d*), and the orbital relaxation (*e*) contributions (STO-3G basis set)

spread out on a larger range of electric fields. Due to the lower variational flexibility of the STO-3G basis set, the electron transfer through the HOMO and the resulting collapse in the electron density alternation has to occur at larger electric fields.

On the other hand, using larger basis set than the 6-31G** basis set would allow such a collapse at lower fields. Here again, the collapse being ruled by the particular symmetry of the molecular orbitals of the hydrogen chain, it occurs irrespective of the size of the basis set used.

4. Conclusions

The polarization under an electric field of the electron density in an insulating oligomeric system leads to a complicated evolution of the correlation and relaxation effects that affect the ionization potential of such a system. In this paper, this evolution, which has been calculated for a small alternant hydrogen chain, can be qualitatively explained using such simple criteria as the first HOMO-LUMO energy separation and the degree of accumulation of the electron density in the model oligomer.

In the particular case of the hydrogen chain, the σ-symmetry of molecular orbitals has to be considered to understand the back-polarization of the outer orbitals, namely due to the HOMO, at weak electric fields. At higher fields, it results in important charge reorganizations, revealed by a strong alternation of the electron density along the chain. At very high fields, a collapse of the electron density accumulation is observed, leading to an electron transfer between the (H_2) subunits. This collapse can be interpreted as a transition of an insulating state to a quasi-metallic state and related to (a) a minimum one-particle gap due to avoided crossing between the HOMO and LUMO, to (b) a sudden exacerbation of the correlation effects resulting in a breakdown of the molecular picture for the ionization of an electron in the HOMO, and (c) to a strong limitation of the orbital relaxation effect resulting from such an ionization.

At the largest fields considered here, the 6-31G** basis set employed is probably too small to provide an accurate description of the polarization of the electron density. Improvements should be considered.

Moreover, the second-order Green's function method, while qualitatively correct, is quantitatively deficient; to obtain accurate results, one should use a third-order perturbation expansion of the self-energy. However, calculation of the antisymmetrized two-electron integrals over HF spin-orbitals is computationally so demanding that it has prevented us from studying much more complex and realistic systems with our present program. Research is underway to increase the efficiency and accuracy of our calculations.

Acknowledgements. The authors thank Prof. J. M. André for his interest in this work. They acknowledge also the kind help of F. Valette and Dr. J. Fripiat. M. Deleuze is grateful to the FNRS (National Belgian Science Foundation) for his Research Assistant position. All calculations reported here have been made on the Namur-Scientific Computing Facility (Namur-SCF), a result of the cooperation between the Belgian National Fund for Scientific Research (FNRS), IBM-Belgium, and the Facultés Universitaires Notre-Dame de la Paix (FUNDP). The authors acknowledge the support of this project within the framework of the (1990–1991) scientific agreement between United-Kingdom (British Council) and Belgium (CGRI-Communauté Française de Belgique).

References

1. Koopmans TA (1933) Physica 1:104
2. Csanak GS, Taylor HS (1971) Adv Atom Molec Phys 7:287
3. Doll JD, Reinhardt WP (1972) J Chem Phys 57:1169
4. Ecker F, Hohlneicher G (1972) Theoret Chim Acta (Berl) 25:289
5. Cederbaum LS, Hohlneicher G (1973) Mol Phys 26:1405
6. Pickup BT, Goscinski O (1973) Mol Phys 26:1013
7. Cederbaum LS, Domcke W (1977) Adv Chem Phys 36:205
8. Von Niessen W, Schirmer J, Cederbaum LS (1984) Comput Phys Rep 1:57 and references therein
9. Deleuze M, Delhalle J, André JM (1992) Int J Quantum Chem 41:243
10. Hariharan PC, Pople JA (1972) J Chem Phys 56:2257
11. Cohen HD, Roothaan CCJ (1965) J Chem Phys 43:S34
12. Dyson FJ (1949) Phys Rev 75:1736
13. Inkson JC (1984) Many-body theory of solids. Plenum Press, NY
14. Cederbaum LS (1973) Theoret Chim Acta 31:239
15. Cederbaum LS (1974) Mol Phys 28:479
16. Cederbaum LS, Hohlneicher G, Von Niessen W (1973) Chem Phys Lett 18:503
17. Cederbaum LS (1974) Chem Phys Lett 25:562
18. Schirmer J, Domcke W, Cederbaum LS, Von Niessen W (1978) J Phys B 11:1901
19. Domcke W, Cederbaum LS, Schirmer J, Von Niessen W, Brion CE, Tan KH, (1979) Chem Phys 40:171
20. Cederbaum LS, Domcke W, Schirmer J, Von Niessen W (1986) Adv Chem Phys 65:115
21. Brandow BH (1967) Rev Mod Phys 39:771
22. Kvanicka V (1977) Adv Chem Phys 36:345
23. Lindgren I (1974) J Phys B 7:2441
24. Bodart V (1987) PhD Thesis "Calcul de polarisabilités et hyperpolarisabilités de chaînes conjuguées, étude formelle et application en optique linéaire", FUNDP-Namur (Belgium), p 140
25. André JM (1987) in: Jortner J et al (eds) Large finite systems. D Reidel, Dordrecht, p 277