

## **The conflict between hole delocalisation and static plus dynamic polarisation in molecular cations: illustration on $Mg_n^+$ clusters\***

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(Received April 27, revised October 19/Accepted December 29, 1987)

In a filled band problem, like an alkaline earth or a rare gas cluster, the positive ion is stabilised by both the hole delocalisation and by polarisation effects. The variational mono-electronic pictures take into account the first factor and the *static* polarisation, disregarding the *dynamic* or instantaneous polarisation, which is a correlation effect. This unbalance of  $\Delta$ SCF treatments underestimates the binding energy and unduly favors the structures in which the hole is concentrated on an atom surrounded by numerous neighbors. Taking into account the dynamic polarisation through CI or effective VB approaches restores the relative stability of structures where the hole is spread over a large number of atoms, as illustrated on the  $Mg_4^+$  problem. This remark is shown to have general implications for covalent molecules.

**Key words:** Hole delocalisation — Dynamic polarisation — Configuration interaction — Effective valence bond —  $Mg_n^+$  clusters

### **1. Introduction**

Even if Koopmans' theorem, and also  $\Delta$ SCF calculations are known to fail frequently for inner valence ionisations, [1] the efficiency of mono-electronic pictures of the molecular electronic wave-function is frequently illustrated through the ionisation problem; the satisfactory agreement between the predictions of Koopmans' theorem and photoelectron spectra is quite general [2] for the lowest

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

energy ionisations, (despite numerous exceptions [3]), and the approximate agreement between the molecular orbital distribution and the observed spin density distribution [2] is frequently considered as a proof of the physical meaning of molecular orbitals and of the prominence of *electronic delocalisation* over all other physical effects in molecules.

The present paper shows first, for the case of positive ions, that delocalisation may be balanced by another important effect, namely polarisation. Hückel-type hamiltonians and Koopmans' theorem applications do not include any polarisation, but only the hole delocalisation, Self-Consistent Hartree-Fock approximations (SCF) for the ion (sometimes labelled  $\Delta$ SCF approximation) include the *static polarisation*; the singly and doubly occupied MOs (molecular orbitals) are recalculated in the field of the ion, and it will be shown that these polarisation effects may favor structures where the hole is rather localised on a central atom, surrounded by numerous polarised atoms.

However the static polarisation is only a small part of polarisation effects; correlated treatments include *dynamic polarisation* effects, i.e. the instantaneous repolarisation of the surrounding atoms when the hole is located on a given atom, before jumping on a neighboring atom and inducing a new instantaneous field. This effect is better understood when working in a localised (VB type) picture, as in Sect. 3.1, but its status in delocalised MOs CI calculations is easy to establish as shown in Sect. 3.2. It is shown that dynamic polarisation effects are very important for the binding energy of the cluster, especially when the static polarisation is weak, and that it may reverse the conclusions of  $\Delta$ SCF calculations concerning the stable conformations of the positive ion.

The numerical illustration<sup>1</sup> concerns the  $Mg_4^+$  ion for which a competition exists between two isomers [4], differing strongly by the extent of the hole (or charge) delocalisation. The clusters of heavy alkaline earth atoms represent an ideal case since the valence band is essentially a filled *s* band (this is not true for Be clusters) with one dominant AO (atomic orbital) per atom. This peculiarity makes possible simple localised and delocalised approaches which are directly related. Section 4 shows that the main conclusions obtained from our analysis of  $Mg_n^+$  clusters are valid for covalent molecules.

## 2. The various energy components illustrated by the $Mg_4^+$ problem

Let us consider two stable conformations of the  $Mg_4^+$  clusters, one being a planar square (a) the other a regular planar centered triangle (b). The equilibrium interatomic distances between nearest neighbor atoms appear to be in the range









(a)



(b)

<sup>1</sup> The calculations are performed in a valence ( $3s+2p+1d$ ) basis set (see [4] for further details)

**Table 1.** Components of the binding energy (BE) of  $Mg_4^+$  at the Koopmans' theorem level (in eV) for various bond lengths  $R$  (in bohr)

$R$	Neutral cluster repulsion <sup>a</sup>		Hole delocalisation <sup>b</sup>		(KT) BE <sup>c</sup>		$\Delta^d$
							
5.8	1.65	1.06	-2.42	-2.23	0.77	1.17	0.40
6.0	1.32	0.87	-2.28	-2.10	0.96	1.23	0.27
6.2	1.07	0.71	-2.13	-1.97	1.06	<u>1.26</u>	0.20
6.4	0.87	0.58	-1.99	-1.83	1.12	1.25	0.13
6.6	0.71	0.49	-1.85	-1.70	<u>1.14</u>	1.22	0.08

<sup>a</sup>  $E(Mg_4)RHF - 4E(Mg)RHF$ <sup>b</sup>  $E_{Mg_4^+} - E_{Mg_4}$ <sup>c</sup> Binding energy<sup>d</sup> Energy difference  $\Delta = E(Mg_4^+, \text{square}) - E(Mg_4^+, \text{triangle})$ 

of 6 to 6.5 bohrs; for these interatomic distances the interaction between ground state neutral atoms is strongly repulsive and it is clear that the Hartree-Fock ground state ( $\phi_0$ ) energy of  $Mg_4$  will be repulsive with respect to  $4Mg$  atoms, and that structure (b) will be favored (cf. Table 1, first columns). If the repulsion energies were strictly additive and the interaction between non-nearest neighbors were neglected, one might expect that the repulsion energy

$$E_0^{Rep} = E(Mg_4)RHF - 4E(Mg)RHF$$

would be (RHF denotes restricted Hartree-Fock) about 1.33 (i.e.  $4/3$ ) larger in (a) than in (b), which appears to be approximately correct.

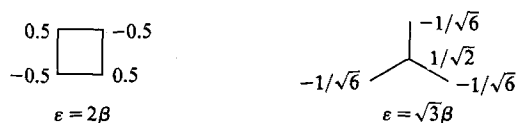
Going to the positive ion, Koopmans' theorem says

$$E^+ = \langle \phi_0 | H | \phi_0 \rangle - \epsilon_n$$

where  $E^+$  is the energy of the positive ion and  $\epsilon_n$  is the highest occupied MO energy. With respect to the  $(3Mg + Mg^+)$  asymptote at the same level of description

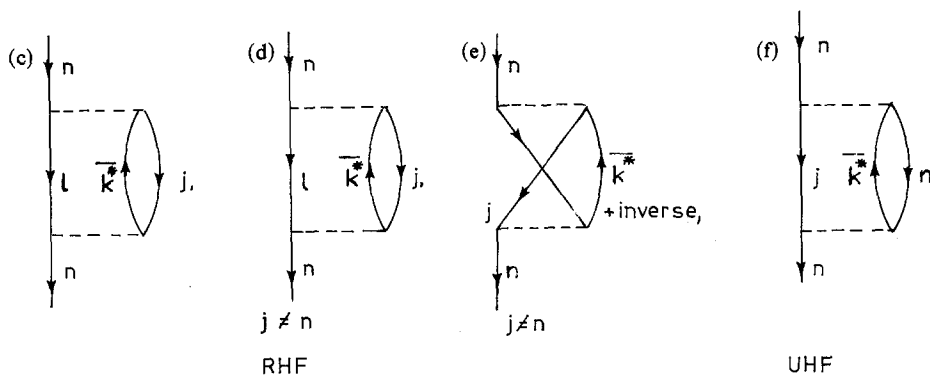
$$\Delta E^+ = E_0^{Rep} - \epsilon_n + \epsilon_s$$

where  $\epsilon_s$  is the energy of the  $3s$  AO in the atom in its  $(3s)^2$  ground state. The hole delocalisation, which is the difference between the molecular and atomic ionisation potentials, is larger in the square structure than in the centered triangle, as immediately seen from the Hückel topologic matrices; for symmetry reasons the hole is equally spread on the four atoms in (a) ( $q_i = 1/4$ ), while largely concentrated ( $q_c = 1/2$ ) on the central atom in (b). The delocalisation is larger in (a) than in (b), (with a ratio  $\cong 2/\sqrt{3}$ ) as confirmed by the *ab initio* calculation



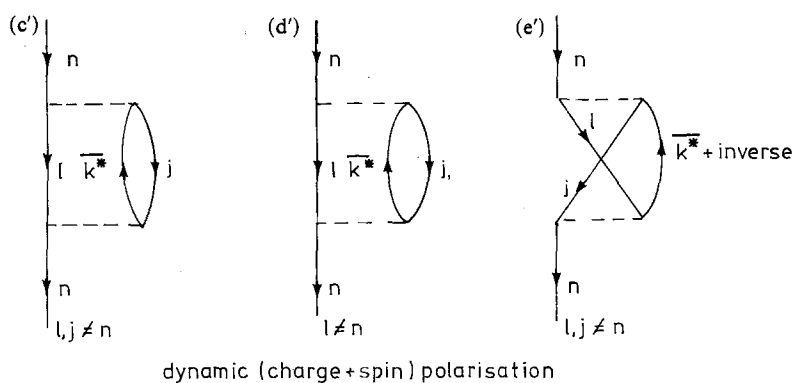
(cf. Table 1, columns 2 and 3). Koopmans' theorem should therefore indicate a balance between the repulsion and hole delocalisation effects as confirmed by the last columns of Table 1; both structures appear to have stable minima, with a 1.1 to 1.3 eV binding energy; the centered triangle is more stable than the square, but only by 0.12 eV (2.8 kcal/mole). The two isomers are nearly degenerate at this level of description.





Going from Koopmans' theorem level to variational RHF or UHF descriptions of the ion will introduce successively static charge- and spin-polarisation effects. The following diagrammatic second order contributions are included where  $k^*$  is an empty MO, and  $j$  an occupied MO. Notice that in (c)  $\bar{j}$  may be equal to  $\bar{n}$ , the highest occupied MO; the corresponding correction is the repolarisation of the singly occupied MO, which is important in the atom (0.293 eV). This correction is not identical for the molecule where the hole  $n$  is delocalised. The remainder of the RHF stabilisation (d) is the static charge polarisation effect. The spin polarisation vanishes on the atom in the frozen core approximation, while it may become significant in the cluster.



The overall (charge+spin) static polarisation is given by the UHF calculation. The UHF binding energy of the cluster is 1.38 eV for the square, 1.73 eV for the centered triangle; the latter appears significantly more stable by 0.35 eV (i.e. 8 kcal/mole), in contradiction with the predictions of a model valence-bond-hamiltonian [4].





Starting from this single determinantal description the various second order contributions to the ionisation potential have been derived in [5] and one may find in [6] illustrations of their balance in many molecular systems. Dynamic charge- and spin-polarisation effects are included by the second order diagrams (c'), (d') and (e') or by the (two-hole)-(one-particle) ( $2h-1p$ ) Configuration Interaction (CI). Notice that when the interatomic distances increase and when the hole localises on *one* atom, these contributions vanish; the corresponding CI may therefore be compared to the RHF( $3Mg+Mg^+$ ) asymptote. As seen from Table 2, this correction is large (0.4 eV in (a), 0.25 eV in (b)) and pushes the


**Table 2.** Components of the binding energy, BE (eV) from variational calculations of  $Mg_4^+$  for various bond length (in bohr)

UHF level					$\Delta^a$
<i>R</i>	Static (charge + spin) polarisation effect		(UHF)-BE		
5.8	-0.592	-0.759	1.07	1.64	0.57
6.0	-0.576	-0.757	1.24	1.70	0.46
6.2	-0.559	-0.757	1.32	<u>1.73</u>	0.40
6.4	-0.543	-0.756	1.37	1.73	0.36
6.6			<u>1.38</u>		
$\infty$	-0.293				
<i>(2h + 1p)CI level</i>					
<i>R</i>	Dynamic (charge + spin) polarisation effect		((2h - 1p)CI) - BE		
5.8	-0.397	-0.256	1.47	1.90	0.43
6.0	-0.408	-0.256	1.65	1.95	0.30
6.2	-0.419	-0.253	1.74	<u>1.98</u>	0.24
6.4	-0.430	-0.250	1.80	1.98	0.18
6.6			<u>1.81</u>		
<i>Best-CI</i>					
<i>R</i>	Other interatomic correlation effects		(Best-CI)-BE		
5.8	-0.45	-0.19	1.92	2.09	0.17
6.0	-0.37	-0.16	2.02	<u>2.11</u>	0.09
6.2	-0.31	-0.10	<u>2.05</u>	2.08	0.03
6.4	-0.24	-0.03	2.04	2.01	-0.03

<sup>a</sup> Difference between the  and  energies

**Table 3.** Comparison of the static and dynamic polarisation effects (in eV) for various bond lengths  $R$  (in bohr)

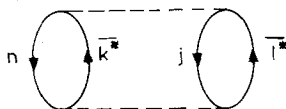
$R$	Static polarisation effects			Static and dynamic polarisation effects		
			$\Delta^b$			$\Delta^b$
5.8	0.592	0.759	0.167	0.987	1.015	0.028
6.0	0.576	0.757	0.181	0.984	1.013	0.029
6.2	0.559	0.757	0.198	0.978	1.010	0.032
6.4	0.543	0.756	0.213	0.973	1.006	0.033
$\infty$	0.293 <sup>a</sup>					

<sup>a</sup> Singly occupied AO repolarisation

<sup>b</sup> Difference between square and centered triangle

binding energy of the cluster to 1.8 or 2.0 eV. Table 3 gathers the static + dynamic polarisation effects and one may notice that they are almost the same for both structures (0.98 eV for the square, 1.01 eV for the centered triangle), in great contrast with the RHF and UHF predictions, which favored the centered structure. At this  $(2h - 1p)$  level of description the difference between (a) and (b) is only 0.16 eV (3.5 kcal/mole).

An important contribution to the molecular ionisation potential is the loss of electronic correlation due to the electron removal which corresponds to ground state second order diagrams, where  $n$  is the molecular orbital from which ionisation takes place. It is easy to show that for Mg clusters this correction is essentially



shape independent and equal to the valence correlation energy of an Mg atom. The ground state correlation is primarily due to the local  $(s\bar{s} \rightarrow p\bar{p})$  double excitations and is introduced by local bielectronic integrals  $(s_r p_r, \bar{s}_r \bar{p}_r)$  on the atoms  $r$ ; one may localise the virtual  $p$  MOs on the various atoms and the desired contribution to the second order ( $\epsilon_n^{(2)}$ ) is then



$$\epsilon_n^{(2)} = \sum_{j=1,n} \sum_r \frac{(np_r, jp_r)^2}{\epsilon_n + \epsilon_j - 2\epsilon_p}$$

A closure approximation gives

$$\epsilon_n^{(2)} = \frac{1}{\Delta E} \sum_{j=1,n} \sum_r C_{nr}^2 C_{jr}^2 (s_r p_r, s_r p_r)^2$$

where  $C_{jr}$  is the coefficient of the MO  $j$  on the AO  $s_r$ . Since  $\sum_j C_{jr}^2 = 1$  (full occupation of the  $s$  band) and  $\sum_r C_{nr}^2 = 1$  (normalisation) and assuming that the



$(s_r p_r, s_r p_r)$  integral between localized MOs is identical to the  $(sp, sp)$  atomic integral  $\varepsilon_n^{(2)} = (sp, sp)^2 / \Delta E$  i.e. the typical atomic correlation energy.

The full CI result has been approached through a multi-reference CI scheme (the improved-CIPSI algorithm [7]). One includes there both intraatomic correlation effects and dispersion interactions between the atoms; the latter result in a weak energy stabilisation of the cluster (0.3 eV for the square, 0.15 eV for the centered triangle). The fact that this correction is larger in the square structure is easily understood if one remembers that the polarisability is much larger for the neutral atom than for the ionised atom  $\alpha = \alpha(\text{Mg}) \gg \alpha(\text{Mg}^+) = \alpha^+$ . Therefore in the square <sup>+</sup> one has necessarily always two neutral-neutral interactions in  $\alpha^2/R^6$ , and two  $\alpha\alpha^+/R^6$  interactions, while in <sup>+</sup> the centered structure one has essentially three  $\alpha\alpha^+/R^6$  interactions.

As a final result, one sees in Table 2 that

- (i) the binding energy of the positive cluster is slightly larger than 2 eV, i.e. approximately twice larger than at the Koopmans' theorem level,
- (ii) the two structures are nearly degenerate, the centered structure is only more stable by 0.07 eV (i.e. 1.4 kcal/mole); this result is in rather good agreement with both the Koopmans' result (0.12 eV) and the previously published result of a model VB (valence bond) hamiltonian which gave  $\Delta E = -0.06$  eV in favor of the square. The overall stability of the  $\text{Mg}_4^+$  clusters predicted by this simple model (2.412 eV) was in much better agreement than all the variational single-deter-

**Table 4.** Binding energies, BE, (eV) and interatomic distances ( $r_e$ ) (bohrs) of  $\text{Mg}_4^+$  clusters at various levels of description

				$\Delta$
KT	BE	1.14	1.26	0.12
	$r_e$	6.63	6.25	
UHF	BE	1.38	1.73	0.35
	$r_e$	6.63	6.30	
$(2h-1p)$ CI	BE	1.81	1.97	0.16
	$r_e$	6.55	6.20	
Best CI	BE	2.05	2.11	0.06
	$r_e$	6.25	5.97	
Model <sup>a</sup> Hamiltonian	BE	2.41	2.34	-0.07
	$r_e$	6.05	5.95	
Model <sup>b</sup> Hamiltonian	BE	2.11	2.23	0.12
	$r_e$	6.25	5.98	

<sup>a</sup> [4]

<sup>b</sup> Including induced dipole-induced dipole third order effects (G. Durand, unpublished results)

minantal results (cf. Table 4). Notice in Table 4 that, as expected, the dispersion contributions besides the  $(2h-1p)$  CI, which are taken into account, shorten the bond lengths by 0.3 to 0.2 bohrs.

The artefacts of the variational single-determinantal descriptions are explained in the next section.

### 3. Qualitative distortions of the variational single determinantal pictures of the ion, due to the maximisation of static polarisation effects

#### 3.1. The localised approach

In this section we introduce a VB effective hamiltonian, treating the problem as the interaction between local ionized structures. Referring to the excitonic treatment of electronic excitations, one may call this approach an excitonic treatment. If one refers to a VB model, the hole may be on one of the four atoms: a natural model space is spanned by the four localised determinants  $a_p\phi_0$  where

$$\phi_0 = |\bar{1}\bar{1} \quad \bar{2}\bar{2} \quad \bar{3}\bar{3} \quad \bar{4}\bar{4}|$$

$p = 1, 2, 3$  or  $4$  is a localised MO of  $\text{Mg}_4$  and  $a_p$  is the associated annihilation operator. Then the zeroth order hamiltonian is of dimension four, and the delocalisation hopping operators

$$\langle a_p\phi_0 | H | a_q\phi_0 \rangle a_p^+ a_q = -F_{pq} a_p^+ a_q$$

couple the four determinants. The diagonal terms are

$$\langle a_p\phi_0 | H | a_p\phi_0 \rangle = \langle \phi_0 | H | \phi_0 \rangle - \langle p | F | p \rangle$$

and the CI matrix is identical to the Fock operator of the Ground state (with changed signs). At this level the model is identical to Koopmans' theorem. However if one applies the quasi degenerate perturbation theory to take into account further effects, the diagonal terms will be lowered by *instantaneous localised* polarisation effects and by intra and inter atomic correlation effects. Notice that this problem defines a so-called complete model space and that a linked cluster diagrammatic expansion is then possible [8]. The diagrams are identical to those of the preceding section except for the fact that the hole is now localised.

According to its second order expansion, the diagonal term of the effective hamiltonian  $H_{pp}^{\text{eff}} = \langle a_p\phi_0 | H | a_p\phi_0 \rangle$  is stabilised by the quantity

$$\varepsilon_{pp}^2 = \sum_I \frac{\langle a_p\phi_0 | H | \phi_I \rangle \langle \phi_I | H | a_p\phi_0 \rangle}{E_p^0 - E_I^0}$$

where  $\phi_I$  is a  $(2n-1)e^-$  determinant which does not belong to the model space and  $E_I^0$  is its zeroth-order energy.  $\phi_I$  can only be simply- or doubly-excited with

<sup>2</sup> It may be proved that the off-diagonal terms  $H_{pq}^{\text{eff}}$  are only changed at third-order by polarisation effects



respect to  $a_p\phi_0$  and one may distinguish the following contributions,

- (i) ( $\bar{p} \rightarrow \bar{p}^*$ ) single excitations of the atom  $p$  which repolarise the singly occupied AO  $\bar{p}$ , as occurs in the  $\text{Mg}^+$  atomic ion
- (ii) ( $q \rightarrow q^*$ ) single excitations on the atom  $q$  in the field of the positive hole on the atom  $p$ , which bring an instantaneous (or dynamic) charge and spin polarisation effect, vanishing for large interatomic distances as  $\alpha_q/R_{pq}^4$  for the charge polarisation and exponentially for the spin polarisation
- (iii) ( $q \rightarrow q^*$ )<sup>2</sup> double excitations on the atom  $q$ , which bring intra-atomic correlation effects, also present in the three neutral Mg atoms at the asymptote
- (iv) ( $q \rightarrow q^*$ ,  $r \rightarrow r^*$ ) ( $q \neq r \neq p$ ) double excitations concerning instantaneously neutral atoms, which bring dispersion energies between them (in  $\alpha^2/R^6$ )
- (v) ( $q \rightarrow q^*$ ,  $\bar{p} \rightarrow \bar{p}^*$ ) double excitations concerning the instantaneously ionised atom and the neutral atoms, and bringing the ion-neutral dispersion energies (in  $\alpha\alpha^+/R^6$ ).

The distance- and shape-dependent corrections to  $\langle a_p\phi_0 | H | a_p\phi_0 \rangle$  are therefore

$$-\frac{1}{2} \sum_{q \neq r} \alpha/R_{pq}^4 - \sum_{q, r \neq p} c\alpha^2/R_{qr}^6 - \sum_{q \neq p} c'\alpha\alpha^+/R_{pq}^6$$

where  $c$  and  $c'$  are constants ( $\sim -\epsilon_s$ ). If the first term is dominant, and non-nearest neighbor interactions are neglected all diagonal energies are shifted by  $-\alpha/R^4$  in the square, while in the centered structure the shift is  $-(\alpha/2)/R^4$  when the hole is on the outer atoms and  $-(\frac{3}{2})\alpha/R^4$  when it is on the central atom. The overall effect of the instantaneous charge-polarisation is therefore practically the same for both structures. If the cluster was larger with  $n$  equivalent centers on a circle or a sphere, the shift of the diagonal would be size-independent.

### 3.2. Delocalised MO treatment

When using the delocalised picture, as was done in the calculations mentioned above, the hole is delocalised on the various centres

$$|n\rangle = \sum_p c_{np} |p\rangle$$

and the static charge polarisation of the doubly occupied MOs by the hole may be obtained to the second order

$$\epsilon_{\text{pol}}^{(2)} = \sum_{jk^*} \frac{2\langle j | -J_n | k^* \rangle^2}{\epsilon_j - \epsilon_{k^*}}$$

The virtual MO  $k^*$  may be localised on atom  $q$  without any loss of generality, let us call that MO (of  $3p$  character)  $q^*$ . To a reasonable approximation

$$\epsilon_{\text{pol}}^{(2)} = \sum_j \sum_{q^*} 2c_{jq}^2 \frac{\langle q | -J_n | q^* \rangle^2}{\epsilon_j - \epsilon_{q^*}}$$

One may consider two extreme cases according to the degree of delocalisation of the hole. If the hole is perfectly localised on the centre  $r$ ,  $\varepsilon^2$  will give the polarisation of the neighbor atoms, since  $\sum_j c_{jq}^2 = 1$

$$\varepsilon_{\text{pol}}^{(2)} = n_v \sum_{q^*} \frac{\langle q | -J_r | q^* \rangle^2}{\varepsilon_q - \varepsilon_{q^*}}.$$

If the hole is equally spread over all the  $n$  atoms of the cluster, the field  $\vec{E}_q$  created on each atom  $q$  by the hole decreases as  $n^{-1}$  and since

$$2 \sum_j c_{jq}^2 = 2 - \frac{1}{n}$$

$$\varepsilon_{\text{pol}}^{(2)} = n \left( 2 + \frac{1}{n} \right) \frac{\alpha}{2} \sum_{q^*} \langle q | \vec{E}_q | q^* \rangle^2$$

and the polarisation energy decreases to zero as  $n^{-1}$  [9] when  $n$  increases. The static polarisation energy, the only one included in a self-consistent energy, decreases as  $1/n$  when the charge is equally spread over  $n$  atoms.

It is easy to demonstrate that, on the contrary, the (static+dynamic) polarisation energy does not decrease with the delocalisation of the hole; it is sufficient to remember that the  $(2h-1p)$  CI is independent of the localisation of the MOs, since the subspace of these determinants is invariant under unitary transformations of the MOs. Since it has been shown in the excitonic VB approach that the  $(2h-1p)$  CI gives an almost size-independent correction through a uniform shift of the diagonal energies of the effective hamiltonian, it is clear that the inclusion of dynamic polarisation effects in delocalised scheme through  $(2h-1p)$  CI must have a non-vanishing effect.

This analysis explains the numerical results mentioned above which showed that

- (i) static polarisation effects were much smaller in the cyclic (i.e. delocalised) conformation than in the centered triangle which essentially concentrates the charge on the central atom,
- (ii) (static+dynamic) polarisation effects are almost identical in the two structures; the dynamic polarisation becomes much smaller in the centered triangle than in the square.

The slight remaining differences between the large CI and the model hamiltonian results may be due to the small underestimation (by  $\sim 12\%$ ) of the finite basis set polarisability in the *ab-initio* calculation and/or the neglect of repulsive induced dipole-induce dipole third-order interactions in the model calculations. For instance, the inclusion of this last contribution in the model hamiltonian largely reduces the differences between its results and the CI results (see bottom of Table 4).

#### 4. Discussion and conclusion

The importance of the dynamic polarisation effects has been clearly demonstrated in the preceding analysis: when the hole is delocalised on a large number of

centres the *static* polarisation tends to *vanish* while the *dynamic* polarisation *increases*. Using a  $\Delta\text{SCF}$  approximation (i.e. independent SCF calculations of neutral and ionised clusters or molecules), one will obtain a vanishing stabilisation of the ion with respect to the Koopmans' description if, for symmetry reasons, the hole is delocalised on a large number of atoms; the actual (dynamic) polarisation effects are to be found in the  $(2h - 1p)$  CI and remain important in a large cluster, whatever the extent of the hole delocalisation.

Another artefact of this  $\Delta\text{SCF}$  description is that it will prefer molecular conformations where the hole is localised (and  $\Delta\text{SCF}$  calculations will overestimate the charge-concentration to maximise the static polarisation energy).

These conclusions are not limited to the case of  $\text{Mg}_n^+$  clusters nor to the problem of a hole in a filled band. All covalent molecules may be considered as interacting ( $2e^-$ ) bonds or lone pairs, i.e. as a filled band. If the lowest excitation energies are large enough, the positive ion problem may be treated in an excitonic approach as the interaction between localised ionisation concerning the various bonds or lone pairs. The same conclusions concerning the vanishing polarisation effects resulting from the  $\Delta\text{SCF}$  calculations in symmetrical delocalised problems and the artefacts in favor of localised ionisations are therefore valid for molecules. The last effect may result in space symmetry breaking if the static polarisation by a local hole becomes larger than the hole delocalisation energy, as occurs in the well-known inner-shell ionisation problem [5]. The present analysis shows that the main conclusions previously obtained in that very special case remain valid for ionisation within the valence shell. The inclusion of dynamic polarisation effects is quantitatively important to obtain a reasonable ionisation potentials and qualitatively important to determine correctly the balance between delocalisation and polarisation effects which is distorted by  $\Delta\text{SCF}$  treatments in favor of hole-concentrating structures.

*Acknowledgments.* This work is dedicated to J. Koutecký and his friends from Praha, for their contribution to the maintenance of the VB point of view in Quantum Chemistry.

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