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## Singly and doubly charged clusters of ( $S^2$ ) metals. *Ab initio* and model calculations on $Mg_n^+$ and $Mg_n^{++}$ ( $n \leq 5$ )

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**Résumé.** — Des calculs *ab initio* précis incluant la corrélation électronique ont été effectués pour  $Mg_2^+$  et  $Mg_2^{++}$ . Le deuxième système présente un minimum local. A l'aide d'un procédé de diabatisation, on a pu définir un hamiltonien modèle simple porté par les produits des configurations atomiques  $s^2$ ,  $s^1$  et  $s^0$ . L'hamiltonien modèle inclut les effets de polarisation instantanée (ainsi que les effets à trois corps) et la répulsion coulombienne des charges positives pour les agrégats doublement chargés. Il peut être considéré comme une représentation de un ou deux trous actifs dans une bande  $s$  polarisable. Le modèle prédit que la structure la plus stable de  $Mg_3^+$  et  $Mg_3^{++}$  est linéaire, que les structures carrées et triangulaires centrées sont pratiquement équivalentes pour  $Mg_4^+$  et  $Mg_4^{++}$ . Pour  $Mg_5^+$  et  $Mg_5^{++}$  existent également deux minima quasiment dégénérés : le tétraèdre centré et le carré centré. L'existence de telles structures a été confirmée par des calculs Hartree-Fock, par minimisation directe de l'énergie et calcul de la matrice des constantes de force pour la conformation optimale, mais on démontre que dans l'approche du modèle à particules indépendantes les longueurs de liaisons sont trop longues et les structures centrées sont trop stables. L'énergie du minimum de  $Mg_5^{++}$  est située à 1,71 eV au-dessus de la somme des énergies des systèmes  $Mg_3^+$  et  $Mg_2^+$ . Les potentiels d'ionisation verticaux ont été calculés et on démontre que  $Mg_4^+$ ,  $Mg_5^+$  et  $Mg_5^{++}$  peuvent évaporer un atome neutre.

**Abstract.** — Accurate *ab initio* CI calculations on  $Mg_2^+$  and  $Mg_2^{++}$  have been performed. The second appears to have a local minimum. Through a diabatisation procedure, it was possible to define a simple model Hamiltonian spanned by products of atomic  $s^2$ ,  $s^1$  and  $s^0$  configurations. The model Hamiltonian includes instantaneous polarization energies (and three-body effects) and Coulombic repulsion of the holes in doubly charged clusters, and may be considered as treating one or two active holes in the polarizable  $s$  band. The model predicts linear  $Mg_3^+$  and  $Mg_3^{++}$  structures and nearly degenerate square and centred equilateral triangular structures for  $Mg_4^+$  and  $Mg_4^{++}$ ;  $Mg_5^+$  and  $Mg_5^{++}$  both present nearly degenerate minima of centred tetrahedron and centred square structures. The existence of such structures has been confirmed by UHF *ab initio* (gradient + force) calculations; it is shown however that single-determinantal approaches overestimate the bond lengths and unduly favour the centred structures; the  $Mg_5^{++}$  minimum is 1.71 eV above the  $(Mg_3^+ + Mg_2^+)$  dissociation limit and 1.41 eV under the  $(3 Mg + 2 Mg^+)$  dissociation limit. The vertical Ionisation Potentials (IP) have been calculated and it is shown that  $Mg_4^+$ ,  $Mg_5^+$  and  $Mg_5^{++}$  may evaporate a neutral atom.

### 1. Introduction.

The atoms of column II of the periodic table have ground state  $s^2(^1S)$  configurations. The atoms may be considered to keep essentially this ground state structure in small clusters, despite some weak hybridization with the  $sp^{(3,1)P}$  configuration. The electronic population of a neutral cluster of such elements may thus be seen as an ( $s$ ) full band. The positive ion may consequently be treated as a single hole problem,

delocalized on the different sites of the cluster through a single-hole operator. A doubly charged cluster may be considered as a two-hole system in the  $s$  band, and treated like a two-electron problem, including correlation. The present paper proposes such simplified models for singly and doubly charged clusters of ( $s^2$ ) atoms. For Mg clusters the diagonal effective energies and interactions are extracted from accurate MO-CI calculations on  $Mg_n^+$  ( $n = 1, 2$ ) and from the experimental  $Mg_2$  potential curve.

The problem received an increased interest from the recent observation of an  $\text{Hg}_5^{++}$  doubly charged cluster [1], from electron impact on a beam of mercury clusters. The appearance at 22 eV of such a peak in the mass spectrometer analysis was quite surprising since the Coulombic repulsion between the two holes should compel such a small cluster to explode into two singly charged fragments. Brechignac *et al.* [1] suggested that the positive charge in this cluster might be concentrated on the central atom of a compact cluster, the  $\text{Hg}^{++}$  atom (the ionization potential of which is 29 eV) inducing stabilizing polarization forces on the surrounding neutral atoms.

The present work does not concern Hg clusters since the correct treatment of such a heavy atom requires the inclusion of relativistic effects; their treatment is in progress in our laboratory through relativistic pseudopotentials [2, 3], which will be applied further to this precise problem through calculations of  $\text{Hg}_2$ ,  $\text{Hg}_2^+$ ,  $\text{Hg}_2^{2+}$  potential curves. The present paper is limited to the isoelectronic problem of Mg clusters, in order to see whether an  $\text{Mg}_5^{++}$  cluster may exist at least as a stable local minimum. The question is treated through both model and *ab initio* MO calculations, which compare fairly well.

## 2. A simplified model Hamiltonian for $\text{Mg}_n^+$ and $\text{Mg}_n^{++}$ clusters.

**2.1 NEUTRAL INTERACTIONS.** — Let us assume that in the neutral ground state, each atom essentially keeps an  $(s^2)$  configuration. This means that the cluster is essentially held by dispersion forces. This also means that the cluster should have a compact form, maximising the number of nearest neighbours through a packing of tetrahedra. The dissociation energy of  $\text{Mg}_n$  into  $n$  Mg atoms should be directly related to the number  $p$  of nearest neighbours. Assuming an additivity of repulsion energies and dispersion forces (i.e. cancellation between three-body repulsions and three-body dispersive energies) the dissociation energy per atom  $D_e^{(n)}$  of the cluster should be

$$D_e^{(n)} = pD_e/2 \quad (1)$$

where  $D_e$  is the dissociation energy of the dimer. This quantity is rather weak for  $\text{Mg}_2$  ( $D_e = 0.05$  eV) and equation (1) certainly underestimates the dissociation energy of the cluster since the cohesive energy of the metal is 1.1 eV, much larger than  $(12/2)D_e/2$ , which would be the asymptotic limit of equation (1). This may be due to the involvement of the p band, to attractive interaction with second neighbours and/or an attractive balance between many-body forces. It is clear however that the dissociation energy of  $\text{Mg}_n$  is much smaller than that of the corresponding positive cluster  $\text{Mg}_n^+$ , which involves delocalization and polarization energies. The precise research of the geometry and energy of the weak  $\text{Mg}_n$

neutral cluster is not in the scope of our model, and we simply assume that its wave function is dominated by products of  $(s^2)$  atomic configurations

$$\psi_0 = \mathcal{A} \prod_{i=1}^n \varphi_i(2i-1, 2i) + \dots \quad (2)$$

where  $\mathcal{A}$  is an antisymmetrizer,  $\varphi_i$  is either an  $s_i \bar{s}_i$  product of 3s atomic orbitals, or an angularly correlated function

$$\varphi_i = \lambda \cdot |s_i \bar{s}_i| + \mu \cdot (|x_i \bar{x}_i| + |y_i \bar{y}_i| + |z_i \bar{z}_i|).$$

The interaction energy between neutral atoms  $i, j$  at distance  $r_{ij}$  is supposed to be equal to the interaction energy of the dimer  $R(r_{ij}) = R_{ij}$  and the total cohesive energy would be

$$E^n = \sum_{i>j} R(r_{ij}) = \sum_{i>j} R_{ij}. \quad (3)$$

**2.2 MODEL HAMILTONIAN FOR THE SINGLY POSITIVE CLUSTER.** — For the positive cluster  $\text{Mg}_n^+$  one may consider, according to the Valence Bond (VB) description, a series of  $n$  localized functions, where the hole concerns the various atoms. If the hole is on the  $i$ th atom

$$\begin{aligned} \phi_i^+ &= \mathcal{A} \left[ \prod_{j<i} \varphi_j(2j-1, 2j) \right] \times \\ &\times s_i(2i-1) \cdot \left[ \prod_{k>i} \varphi_k(2k-2, 2k-1) \right] = a_i^- \psi_0 \quad (4) \end{aligned}$$

where  $a_i^-$  is an annihilation operator of a  $\beta$  spin electron on the site  $i$ . Then the wave function of the cluster is a linear combination of the  $\phi_i^+$ 's

$$\psi_\lambda^+ = \sum_i c_{i\lambda} \phi_i^+ \quad (5)$$

$$\bar{H}\psi_\lambda^+ = E_\lambda^+ \psi_\lambda^+.$$

The matrix elements of the  $n \times n$  model Hamiltonian  $\bar{H}$  are easily obtained as follows. For the diagonal elements, one may write

$$\langle \phi_i^+ | \bar{H} | \phi_i^+ \rangle = \sum_{(j>k)\neq i} R_{jk} + \sum_{j\neq i} R_{ij}^+ + IP_1. \quad (6)$$

$R_{jk}$  represents the instantaneous interaction between neutral centres, supposed to be equal to that in the corresponding neutral systems.  $R_{ij}^+$  is the interaction between the positive atom  $i$  and the neutral atom  $j$ . Its determination will be given below, and  $IP_1$  is the lowest ionization potential of the atom.

The off-diagonal element

$$\langle \phi_i^+ | \bar{H} | \phi_j^+ \rangle = -F_{ij}^+ \quad (7)$$

represents the hopping integral between atoms  $i$  and  $j$ . If  $\varphi_i$  is reduced to  $s_i \bar{s}_i$ , then

$$\langle \phi_i^+ | \bar{H} | \phi_j^+ \rangle = \langle a_i^- \psi_0 | \bar{H} | a_j^- \psi_0 \rangle = -F_{ij} \quad (8)$$

where  $F$  is the Fock operator of the ground state. In fact (see below) we have used effective  $F_{ij}^+$  integrals which introduce some reorganization effects.

For  $Mg_2^+$  the problem reduces to a  $2 \times 2$  matrix

$$\begin{pmatrix} R_{12}^+ & -F_{12}^+ \\ & R_{12}^+ \end{pmatrix} \text{ which generates two roots } {}^2\Sigma_u^+, {}^2\Sigma_g^+$$

$$E({}^2\Sigma_u^+) = R_{12}^+ + F_{12}^+$$

$$E({}^2\Sigma_g^+) = R_{12}^+ - F_{12}^+$$

and thus the functions  $R_{12}^+$  and  $F_{12}^+$  are immediately extracted from the knowledge of the exact potential curves of the diatomic cation

$$R_{12}^+ = (E({}^2\Sigma_u^+) + E({}^2\Sigma_g^+))/2. \quad (9)$$

$$F_{12}^+ = (E({}^2\Sigma_u^+) - E({}^2\Sigma_g^+))/2. \quad (10)$$

Two things should be noticed :

i) the method is identical, at this step, to a Diatom in Molecules (DIM) procedure [4];

ii) it includes polarization forces since  $R_{12}^+$  involves both a purely repulsive part and an  $\alpha_1/2 r^4$  polarization energy of the adjacent atom by the positive charge. Since the singly ionic cluster only bears one positive charge the polarization energy keeps an additive form.

### 2.3 MODEL HAMILTONIAN FOR THE DOUBLY CHARGED CLUSTERS. — For a two-hole cluster, one may imagine two types of elementary VB situations.

— The two holes may be on different atoms, generating a function  $\phi_{ij}^{++}$ . For  $S_z = 0$  one must introduce two determinants :

$$\phi_{ij}^{++} = \mathcal{A} \left( \prod_{k \neq i,j} \varphi_k \times s_i \cdot \bar{s}_j \right) = a_i a_j \psi_0. \quad (11)$$

$$\phi_{ij}^{++} = \mathcal{A} \left( \prod_{k \neq i,j} \varphi_k \times \bar{s}_i \cdot s_j \right) = a_i a_j \psi_0. \quad (12)$$

Their number is thus  $n(n - 1)$ . Their effective energy

$$\begin{aligned} \langle \phi_{ij}^{++} | \bar{H} | \phi_{ij}^{++} \rangle &= 2 IP_1 + \sum_{(k>l) \neq i,j} R_{kl} + \\ &+ \sum_{k \neq i,j} (R_{ki}^+ + R_{kj}^+) + R_{ij}^{++} + \delta_{pol} \end{aligned} \quad (13)$$

involves, besides the energy  $2 IP_1$  needed to ionize two atoms, the interactions between the instantaneously neutral atoms, the interactions between the positive and the neutral atoms, and the Coulombic repulsion between the holes,  $R_{ij}^{++}$  which weakly deviates from  $r_{ij}^{-1}$ . The last term  $\delta_{pol}$  is a correction to the polarization energy which is not additive, since the field created by the two holes on the neutral polarizable atom  $k$  must be combined vectorially. Let us call  $\mathbf{E}_{ki} = \mathbf{r}_{ki}/r_{ki}^2$  the field created by the hole  $i$  on the neutral atom  $k$ .

Then the polarization energy is

$$E_{pol} = \sum_{k \neq i,j} \left[ -\frac{\alpha_1}{2} (\mathbf{E}_{ki} + \mathbf{E}_{kj})^2 \right]. \quad (14)$$

Since  $R_{ki}^+$  involved a term  $-\frac{\alpha_1}{2} E_{ki}^2$ ,  $\delta_{pol}$  is given by

$$\delta_{pol} = \sum_{k \neq i,j} [-\alpha_1 \mathbf{E}_{ki} \cdot \mathbf{E}_{kj}]. \quad (15)$$

It gives the three-body correction to the polarization energy.

— The two holes may be on the same atom, which is now  $s^0$ , while the others are neutral ( $s^2$ ). The corresponding VB function is

$$\phi_{ii}^{++} = \mathcal{A} \prod_{k \neq i} (\varphi_k) = a_i a_i \psi_0. \quad (16)$$

The diagonal energy associated with this function is

$$\langle \phi_{ii}^{++} | \bar{H} | \phi_{ii}^{++} \rangle = IP_2 + \sum_{(k>l) \neq i} R_{kl} + \sum_{k \neq i} R_{ki}^{2+}. \quad (17)$$

$IP_2$  is the double-ionization potential

$$IP_2 = E(Mg^{++}(3s^0)) - E(Mg(3s^2)).$$

$R_{ki}^{2+}$  is an effective interaction between Mg and  $Mg^{++}$ , and its practical extraction will be given below.

One may conceive two main types of off-diagonal interactions :

$$i) \quad \langle \phi_{ij}^{++} | \bar{H} | \phi_{ik}^{++} \rangle = F_{(ij)k}^{++} \cong F_{jk}^+. \quad (18)$$

The hopping integral corresponding to the jump of a hole from the site  $j$  to the site  $k$  may be taken equal to its value for the singly positive cluster. Actually

$$F_{(ij)k}^{++} = F_{jk}^+ - \langle j | J_i | k \rangle$$

where  $J_i$  is the Coulombic operator relative to the ( $3s$ ) atomic orbital of the atom  $i$ ; the three-centre integral should be small compared to the mono-electronic (essentially kinetic) integral.

One may neglect the bielectronic integrals (corresponding to  $2e^-$  jump) such as

$$\langle \phi_{ik}^{++} | H | \phi_{pq}^{++} \rangle = 0 \quad \text{if } i \neq p \text{ and } k \neq q$$

(even when  $i = q$  and  $p = k$ ); this approximation is usual in chemistry, in the various Zero Differential Overlap (ZDO) systematics [5, 6], and in Solid State Physics in the Hubbard Hamiltonian [7] which is the crudest version of this approximation; the ZDO approximation consists in neglecting the bielectronic interaction involving overlap distributions.

$$ii) \quad \langle \phi_{jj}^{++} | \bar{H} | \phi_{ii}^{++} \rangle = -F_{ij}^{2+}, \quad (19)$$

represents the hopping integral for the jump of a hole

from a doubly charged atom to an (adjacent) neutral atom, this jump creating a pair of positively charged atoms. In a simple model one may write

$$F_{ij}^{2+} = - \langle a_{\bar{j}} a_j \psi_0 | \bar{H} | a_{\bar{i}} a_i \psi_0 \rangle = - \langle i | F - J_i | j \rangle. \quad (20)$$

In that precise case the integral  $\langle i | J_i | j \rangle$  cannot be neglected, since it only involves two centres, and  $F_{ij}^{2+} \neq F_{ij}^+$ .

$$\begin{array}{cc|cc} & |a\bar{b}| & |b\bar{a}| & & |a\bar{a}| & |b\bar{b}| \\ \left[ \begin{array}{cc} 2 IP_1 + R_{ab}^{++} & K_{ab} \\ & 2 IP_1 + R_{ab}^{++} \end{array} \right. & & \left. \begin{array}{cc} F_{ab}^{2+} & F_{ab}^{2+} \\ F_{ab}^{2+} & F_{ab}^{2+} \\ IP_2 + R_{ab}^{2+} & K_{ab} \\ & IP_2 + R_{ab}^{2+} \end{array} \right] \end{array}$$

The bicentric exchange integrals  $K_{ab}$  may be neglected.

The triplet state  $(|a\bar{b}| - |b\bar{a}|)/\sqrt{2}$ , of  ${}^3\Sigma_u^+$  symmetry has an energy

$$E({}^3\Sigma_u^+) = 2 IP_1 + R_{ab}^{++} \quad (21)$$

which determines  $R_{ab}^{++}$  (or the deviation of the repulsion from its coulombic part). The singlet  ${}^1\Sigma_u^+$  state  $(|a\bar{a}| - |b\bar{b}|)/\sqrt{2}$  has an energy

$$E({}^1\Sigma_u^+) = IP_2 + R_{ab}^{2+} \quad (22)$$

which determines the function  $R^{2+}$ .

The  $({}^1\Sigma_g^+)$  ground state energy is given by a second degree equation

$$\begin{array}{cc|c} |a\bar{b}| + |b\bar{a}|/\sqrt{2} & |a\bar{a}| + |b\bar{b}|/\sqrt{2} & \\ \hline E({}^3\Sigma_u^+) - x & 2 F_{ab}^{2+} & \\ & E({}^1\Sigma_u^+) - x & \end{array} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

and the knowledge of the  ${}^1\Sigma_g^+$  ground state energy  $E({}^1\Sigma_g^+)$  will determine the value of  $F_{ab}^{2+}$  as a function of the interatomic distance

$$F_{ab}^{2+} = - \frac{1}{2} [E({}^3\Sigma_u^+) - E({}^1\Sigma_g^+)]^{1/2} \times [E({}^1\Sigma_u^+) - E({}^1\Sigma_g^+)]^{1/2}. \quad (23)$$

**2.4 DIATOMIC POTENTIAL CURVES OF  $Mg_2$ ,  $Mg_2^+$  AND  $Mg_2^{2+}$  AND  $r$  DEPENDENCE OF THE 6 PARAMETERS OF THE MODEL HAMILTONIAN.** — The model involves 6 parameters  $R$ ,  $R^+$ ,  $F^+$ ,  $R^{++}$ ,  $R^{2+}$ ,  $F^{2+}$ . The first is identical to the ground state potential energy of the neutral dimer and rather than calculating it, a function fitted to the experimental spectroscopic parameters [8-9] has been used

$$R = \mathcal{M}(r) \exp[a_4 \exp(a_1 - r)] \quad (24)$$

The two-hole model requires the knowledge of three supplementary functions,  $R_{ij}^{++}$ ,  $R_{ij}^{2+}$  and  $F_{ij}^{2+}$ . This information may be obtained from the potential curves of the doubly charged diatom  $Mg_2^{2+}$ . In that case one has two electrons in two orbitals, and the problem is isomorphic to the  $H_2$  problem. There are four determinants  $|a\bar{b}|$ ,  $|b\bar{a}|$ ,  $|a\bar{a}|$  and  $|b\bar{b}|$  where  $a$  and  $b$  are the two 3s AO's of the two atoms A and B. The matrix takes the form

where  $\mathcal{M}$  is a Morse function involving three parameters  $a_1$ ,  $a_2$ ,  $a_3$  (see Table I). The second ( $R^+$ ) and third ( $F^+$ ) functions were determined from accurate MO-CI calculations on  $Mg_2^+$ , using a [3s 2p 1d] basis set. The  ${}^2\Sigma_g^+$  and  ${}^2\Sigma_u^+$  potential curves were in agreement with a previous calculation by Stevens and Krauss [10]. The resulting functions have been fitted as follows :

$$F^+ = - (a_1 + a_2 r) \exp(- a_3 r) \quad (25)$$

$$R^+ = \mathcal{M}^+(r) - 0.5 \alpha_1 (r^{-4}) f_1(r) \quad (26)$$

where  $\mathcal{M}^+$  is a Morse function,  $\alpha_1$  the polarizability of neutral atoms and  $f_1(r)$  a short range screening of the electric field. The three last parameters come from calculations on  $Mg_2^{2+}$ , which were achieved in the same basis set (and complete CI). The main problem concerned the definition of  $R^{2+}$ , the energy of the  $(|a\bar{a}| - |b\bar{b}|)/\sqrt{2}$  state, dissociating into  $Mg^{2+} + Mg(3s^2)$  ( $IP_2 = 22.67$  eV), due to a curve crossing with a state dissociating into  $Mg^+(3p) + Mg^+(3s)$ , at 19.72 eV above  $Mg(3s^2) + Mg(3s^2)$ , i.e. 2.9 eV below the preceding dissociation limit ( $IP_2$ ). An *ab initio* diabaticization procedure [11] has been applied to that problem in order to define nearly diabatic  ${}^1\Sigma_u^+$  and  ${}^1\Sigma_g^+$  excited states keeping the  $Mg(3s^2) + Mg^{++}(3s^0)$  character from infinite distances to the relevant short range region [12]. The resulting parameters have been fitted as follows

$$R^{++} = r^{-1} + \mathcal{M}^{++}(r) - \alpha_2 r^{-4} f_2(r) \quad (27)$$

$$R^{2+} = \mathcal{M}^{2+}(r) \quad (28)$$

$$F^{2+} = - (a'_1 + a'_2 r) \exp(- a'_3 r) \quad (29)$$

where  $R^{++}$  involves a Coulombic  $r^{-1}$  repulsion, a Morse potential and a (screened) polarizability part,  $\alpha_2$  being the polarizability of  $Mg^+$  atoms.  $R^{2+}$  has been fitted by a simple Morse function.

Table Ia. —  $R$  parameters of the model.  $\mathcal{M}$  are Morse functions :  $a_2[(1 - \exp(-a_3(r - a_1)))^2 - 1]$  and  $f$  are screening functions :  $1 - a_4 \exp[-a_5(r - a_6)^2]$ .

Parameter	Analytical function	$a_1$ (au)	$a_2$ (hartree)	$a_3$ ( $\text{au}^{-1}$ )	$a_4$	$a_5$ ( $\text{au}^{-1}$ )	$a_6$ (au)
$R$	$\mathcal{M}(r) \exp(a_4 \exp(a_1 - r))$	7.35198	0.001923	0.57233	0.0337597	—	—
$R^+$	$\mathcal{M}^+(r) - 0.5 \alpha_1 r^{-4} f_1(r)$	7.57822	0.002333	0.586467	0.619702	0.120311	3.78258
$R^{++}$	$\mathcal{M}^{++}(r) + r^{-1} - \alpha_2 r^{-4} f_2(r)$	7.34894	0.004322	0.505123	0.894654	0.092967	3.03449
$R^{2+}$	$\mathcal{M}^{2+}(r)$	7.46170	0.050549	0.317424	—	—	—

Table Ib. —  $F$  parameters of the model.

Parameter	Analytical function	$a_1$ (au)	$a_2$ (hartree $\text{au}^{-1}$ )	$a_3$ ( $\text{au}^{-1}$ )
$F^+$	$(a_1 + a_2 r) \exp(-a_3 r)$	0.646202	0.269301	0.571140
$F^{2+}$		2.44539	0.998238	0.722744

The explicit representation of the polarization energy in equation (26) is not compulsory for singly charged clusters. The determination of a screening function for the electric field was required for a correct estimate of the three-body term in equation (15). The screening function has been determined by comparing the energies of  $\text{Mg}_A + \text{Mg}_B^+$  (3s frozen) in minimal and extended basis sets for  $\text{Mg}_A$ . An analogous procedure has been used for  $\text{Mg}_A^+ + [\text{Mg}_B^{(+)}$  (3s frozen)]. The potential curves used for the parametrization have been plotted in figure 1a, c). The ground state potential curve of  $\text{Mg}^{++}$  is repulsive with  $r_{ab}^{-1}$  behaviour, but it presents a local minimum for  $r = 2.93 \text{ \AA}$  which is due to the mixing between the « pseudo-neutral » ( $|a\bar{b}| + |b\bar{a}|\rangle/\sqrt{2}$  configuration with the doubly ionic ( $|aa| + |bb|\rangle/\sqrt{2}$  configuration (as in  $\text{H}_2$ ), through the hopping integral  $F^{2+}$ . The

parameters have been plotted as functions of the interatomic distance in figure 2. They have the expected  $r$ -dependence. One should notice however that for short  $r$  values, the  $F^{2+}$  integral has a larger amplitude than  $F^+$ ; this increase may be due either to the effect of the hole (cf. Eq. (20)) or to the indirect role of the  $\text{Mg}(3p) + \text{Mg}(3s)$  state which belongs to the same range of energy. Standard deviation from experimental data for the  $R$  parameter of  $\text{Mg}_2$  and from *ab initio* calculations for the  $R^{k+}$  and  $F^{k+}$  parameters of  $\text{Mg}_2^+$  and  $\text{Mg}_2^{2+}$  is less than  $10^{-3}$  hartrees.

### 3. Results.

3.1 VERTICAL IONIZATION POTENTIALS. — Assuming compact structures for the neutral clusters (i.e. equilateral triangle for  $\text{Mg}_3$ , tetrahedron for  $\text{Mg}_4$  and regular trigonal bipyramid for  $\text{Mg}_5$  with  $r = r_e(\text{Mg}_2) = 7.35$  a.u. interatomic distances), the vertical ionization potentials have been calculated and they appear in table II for both single and double ionizations. Notice the rapid decrease of the ionization potentials; for a regular linear chain or cycle of  $n$  atoms the ionization potential would decrease as  $n^{-1}$  (as shown from Huckel type analytic derivations [13]). If, for a given value of  $n$ , the cluster becomes more compact, the increasing number of nearest neighbours, and consequently of hopping integrals, results in a lowering of the ionization potential. This increased compactness explains the rapid decrease of the calculated ionization potentials.

It may be interesting to analyse the space and spin symmetries of the lowest states of the ion, as predicted by our model, and compared to the mono-electronic picture, which suggests to empty the highest occupied MO (or MO's if a degeneracy occurs).

The lowest state of the triangular  $\text{Mg}_3^+$  is of course degenerate, according to the mono-electronic picture (to which our model Hamiltonian is here identical).

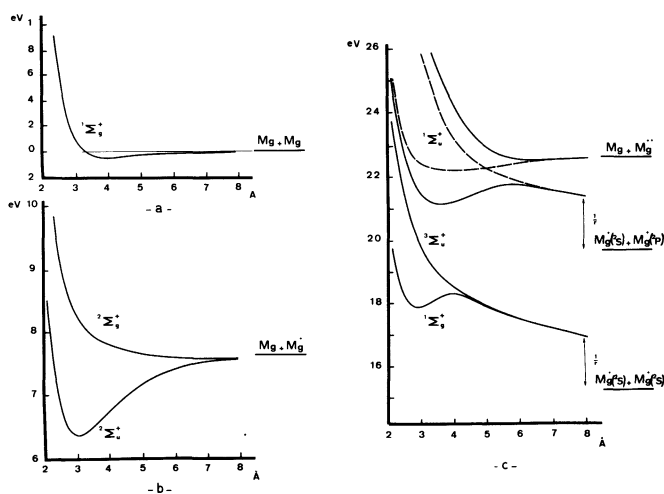


Fig. 1. — a) Experimental  $\text{Mg}_2$  potential curve. b) *Ab initio*  $\text{Mg}_2^+$  ( $^2\Sigma_u^+$  and  $^2\Sigma_g^+$ ) potential curves. c) *Ab initio* adiabatic (—) and diabatic (-----)  $\text{Mg}_2^{2+}$  potential curves.



3.2 RELAXED GEOMETRIES AND ADIABATIC IONIZATION POTENTIALS. — The results appear in table III, figures 3-4.

The  $Mg_2^+$  and  $Mg_2^{++}$  structures have already been given, and one may see (Fig. 1c) that the latter is a local minimum in the repulsive ground state potential curve; this local minimum might accept up to 6 vibrational levels, the barrier being 0.35 eV.

The ground state geometries of  $Mg_3^+$  and  $Mg_3^{++}$  are both linear with longer distances (3.1 Å) in  $Mg_3^+$  than in  $Mg_3^{++}$  (3.0 Å); this is a general trend in the series. The states are of  $^2\Sigma_g^+$  and  $^1\Sigma_g^+$  symmetry in agreement with the orbital model (ionizations from the highest occupied MO).

For both  $Mg_4^+$  and  $Mg_4^{++}$  two geometries are in competition, namely the square and the centred triangle. Both are real minima on the potential surfaces, the former being 0.6 eV below for  $Mg_4^+$ , 0.07 eV below for  $Mg_4^{++}$ . The nearest neighbour distances are shorter in the centred triangle than in the square, especially for the doubly charged species ( $\Delta r = 0.2$  Å). The states are of  $^2A_1$  and  $^1A_1$  symmetries for the centred triangle,  $^2B_{2g}$  and  $^1A_{1g}$  for the square, in agreement with the MO picture.

For  $Mg_5^+$  and  $Mg_5^{++}$  two nearly degenerate minima were found, corresponding to the centred tetrahedron (more stable by 0.02 eV in  $Mg_5^+$ ) and centred square (preferred in  $Mg_5^{++}$  by 0.09 eV). They all are fully symmetric, and correspond to ionizations of the highest valence MO in the delocalized MO picture.

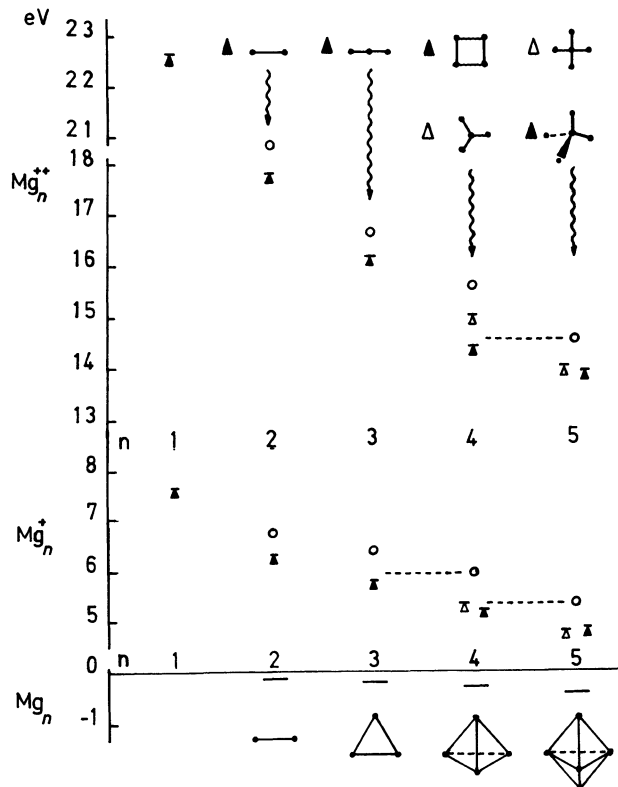


Fig. 3. — Intrinsic energies of  $Mg_n$ ,  $Mg_n^+$  and  $Mg_n^{++}$  clusters (model Hamiltonian), relative to  $n$  separated Mg atoms for  $\circ$  neutral ground state conformation.  $\Delta$  and  $\blacktriangle$ , relaxed conformations of the ions.

Table III. — Energies  $E$  (eV) and nearest neighbour distances  $a$  (Å) of  $Mg_n^+$  and  $Mg_n^{++}$  clusters (the zero of energy is  $n$  Mg atoms).

Structure	$n$	Charge	Symmetry	$a$		$E$	
				UHF	Model	UHF	Model
linear	2	+	$^2\Sigma_u^+$	3.17	2.99	5.52	6.35
		++	$^1\Sigma_g^+$	2.93	2.93	16.71	17.82
linear	3	+	$^2\Sigma_g^+$	3.23	3.10	5.01	5.81
		++	$^1\Sigma_g^+$	3.00	2.99	14.42	16.21
square	4	+	$^2B_2$	3.51	3.20	5.18	5.23
		++	$^1A_1$	3.22	3.12	14.13	14.39
centred triangle	4	+	$^2A_1$	3.33	3.15	4.83	5.30
		++	$^1A_1$	3.06	2.94	13.45	14.99
centred tetrahedron	5	+	$^2A_1$	3.39	3.16	4.71	4.77
		++	$^1A_1$	3.13	2.93	12.84	13.87
centred square	5	+	$^2A_1$	3.49	3.15	4.96	4.75
		++	$^1A_1$	3.23	2.95	13.38	13.96



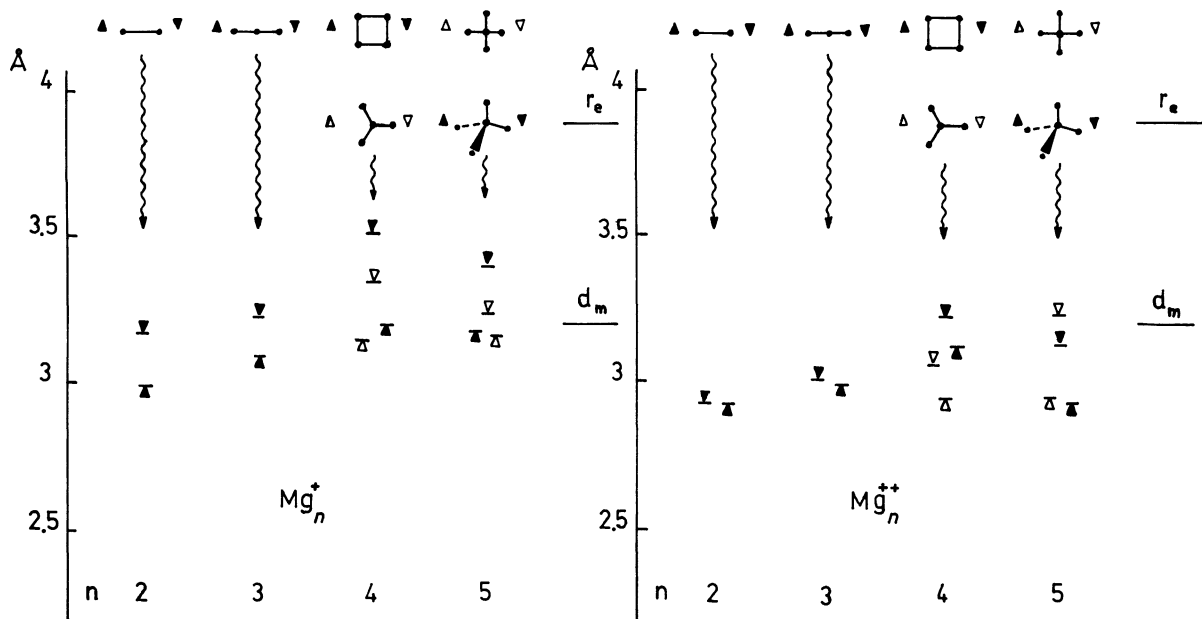


Fig. 4. — Interatomic distances between nearest neighbours in positive ions (relaxed conformations).  $\nabla$ ,  $\blacktriangledown$  UHF *ab initio* calculation.  $\triangle$ ,  $\blacktriangle$  model calculation.  $r_e$   $Mg_2$  experimental  $r_e$ .  $d_m$  metallic nearest neighbour distance.

It seems likely that for larger and larger clusters the number of competing minima will increase and their exhaustive research will become a real problem. In these structures, whose topology is similar, the interatomic distances are almost identical.

For centred structures, the positive charge tends to be concentrated on the central atom; this charge is close to one for doubly charged species; this may be understood by the decrease in electronic repulsions when the central atom has no valence electron, by the polarization of the surrounding neutral electrons and by the role of cross-roads played by the central atom in the hole delocalization.

The relaxation energies (differences between vertical and adiabatic ionization potentials) are quite large :

0.40 eV for  $Mg_2^+$ , 0.54 eV for  $Mg_3^+$ , 0.66 eV for  $Mg_4^+$  and 0.53 eV for  $Mg_5^+$

0.45 eV for  $Mg_2^{++}$ , 0.41 eV for  $Mg_3^{++}$ , 1.19 eV for  $Mg_4^{++}$  and 0.57 eV for  $Mg_5^{++}$ .

There is no clear trend in this series.

The adiabatic ionization potentials appear in table II. They decrease regularly with  $n$ , and it is clear that one is still quite far from the asymptote, which would be the metallic values (one and two extraction potentials of the metal).

**3.3 EVAPORATION, AGGREGATION AND FRAGMENTATION PROCESSES.** — Figure 3 gives the intrinsic energies of  $Mg_n$ ,  $Mg_n^+$  and  $Mg_n^{++}$  taking the energy of  $n$  Mg separated atoms as the zero of energy. This picture makes easy a direct discussion of the enthalpy variations in the processes



(neglecting the zero vibration contributions). The aggregation process (a) occurs from the relaxed structure of  $Mg_{n-1}^{k+}$  ( $k = 1, 2$ ), toward a relaxed geometry of  $Mg_n^{k+}$  ( $k = 1, 2$ ). The decrease of the relaxed geometry energies in figure 3 indicates that the aggregation process is always exoenergetic. We have not analysed the existence of barriers in these processes, but it is quite clear — as summarized in figure 5 — that the aggregation of a neutral atom on the central atom of the centred structure of  $Mg_{n-1}^+$  and  $Mg_{n-1}^{++}$  should proceed without difficulty, i.e. in the same symmetry and with small rearrangements. The processes which change the symmetry, i.e. those involving the square geometries, are more problematic and the research of activation barriers should be performed.

The evaporation processes are only possible from the vertical ionizations. They are only exoenergetic for  $4^+ \rightarrow 3^+ + 1$  and  $5^+ \rightarrow 4^+$  (square) + 1 and for  $5^{++} \rightarrow 4^{++}$  (square) + 1. The energy excess is very low (see Fig. 3) and the existence of barriers is possible in view of the large geometry (and symmetry) changes.

The possible fragmentation of  $Mg_5^{++}$  into  $Mg_2^+ + Mg_3^+$  has been analysed. The exoenergeticity is 1.72 eV when starting from the lowest energy tetrahedral geometry toward the relaxed geometry  $Mg_3^+$  and  $Mg_2^+$  ions. For a fragmentation pathway keeping  $C_{2v}$  symmetry, the intersection between the relevant  ${}^1A_1(Mg_5^{++})$  and  ${}^1B_2(Mg_3^+ + Mg_2^+)$  potential surfaces has its lowest energy 0.21 eV above the tetrahedron  $Mg_5^{++}$  energy minimum. This quantity may be considered as an estimate of the barrier.

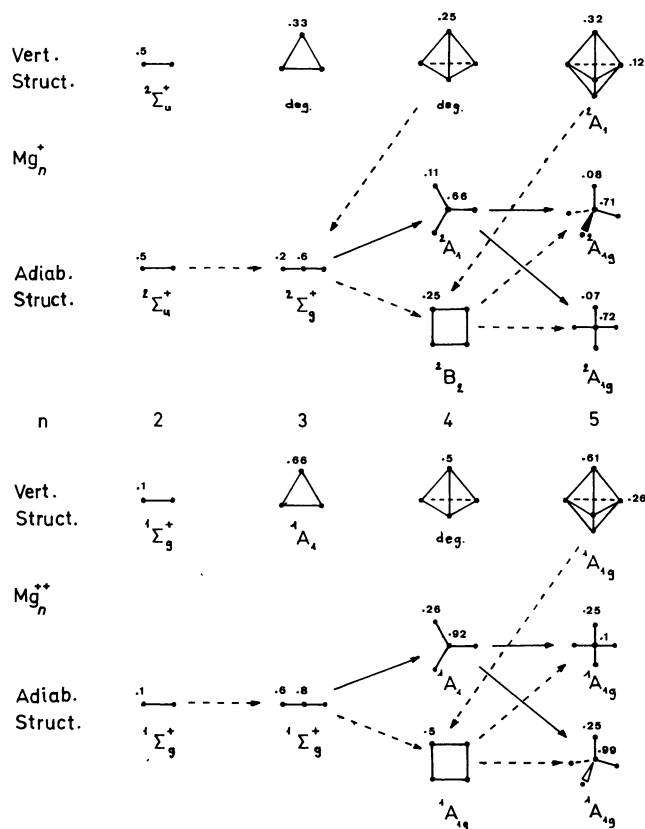
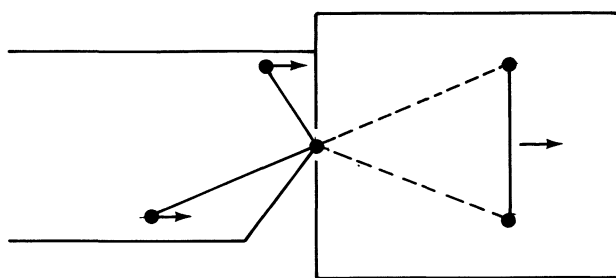
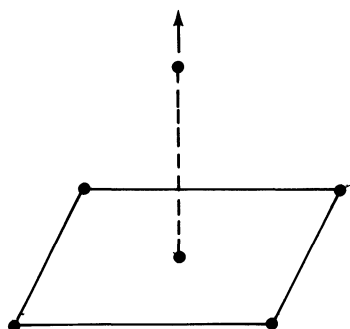
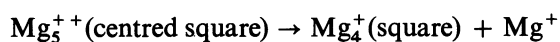


Fig. 5. — Net charges, symmetries of the clusters, and schematic views of possible aggregation and evaporation processes. —→ allowed processes. - - - - - hypothetical processes (exoenergetic but with possible barriers).



Another fragmentation process,



has also been explored. Its exoenergeticity is 1.09 eV, lower than the preceding one. It is quite clear that the doubly charged species tend to explode into equal size fragments, due to the *n* dependence of the stability of Mg<sub>n</sub><sup>+</sup> clusters.

$$\text{Mg}_n^+ + \text{Mg}_n^+ < \text{Mg}_{n+1}^+ + \text{Mg}_{n-1}^+ < \dots < \text{Mg}_{2n-1}^+ + \text{Mg}^+$$

The barrier for the extraction process of the central atom of Mg<sub>5</sub><sup>++</sup> is only 0.14 eV.

### 3.4 OBSERVABILITY OF DOUBLY CHARGED CLUSTERS. —

The existence of local minima in the potential energy hyper-surface of Mg<sub>n</sub><sup>++</sup> is not sufficient to insure the observability of these clusters, since these minima are significantly higher than the result of a fragmentation into Mg<sub>p</sub><sup>+</sup> + Mg<sub>q</sub><sup>+</sup> (*p* + *q* = *n*). Another factor which may prevent the observation of the doubly charged clusters is the great difference between the geometry of the neutral cluster and that of this local minimum. A vertical double ionization would not lead to the doubly charged cluster since it brings an important energy excess and the system could hardly achieve the travel from the original neutral cluster conformation to that of the doubly charged minimum and stay in that region which is only surrounded by weak barriers.

This statement is schematically illustrated in figure 6, representing for instance the Mg<sub>3</sub><sup>(k+)</sup> (*k* = 0, 1, 2) potential curves as functions of two parameters only *r* = *r*<sub>AB</sub> = *r*<sub>BC</sub> and *θ* = *∠*ABC. It is quite clear that the vertical double ionization gives a small probability to stay in the local minimum of the upper surface.

As a very important fact, one should notice that in all the cases studied here, the stable conformations of Mg<sub>n</sub><sup>+</sup> and Mg<sub>n</sub><sup>++</sup> are quite similar. This means that an ionization from Mg<sub>n</sub><sup>+</sup> to Mg<sub>n</sub><sup>++</sup> would be nearly vertical, and would lead close to the bottom of the Mg<sub>n</sub><sup>++</sup> structure, giving an opportunity for this cluster to have a significant lifetime. One must thus assume that the ejections of the two electrons under the electron impact are not simultaneous. During the time separating the first and second electron emission, the cluster Mg<sub>n</sub><sup>+</sup> should rearrange toward the stable Mg<sub>n</sub><sup>+</sup> configuration, which is an absolute minimum, the second emission proceeding without important geometry changes towards the secondary minimum of the Mg<sub>n</sub><sup>++</sup> potential hypersurface which holds the Mg<sub>n</sub><sup>++</sup> cluster (cf. Fig. 6).

These remarks are crucial for small clusters, and for all cases where the charges are quite concentrated, inducing important rearrangements of the positive cluster with respect to the neutral one. For very large clusters the rearrangements might become small (*vide infra*) and creations of doubly charged clusters might proceed in one step.

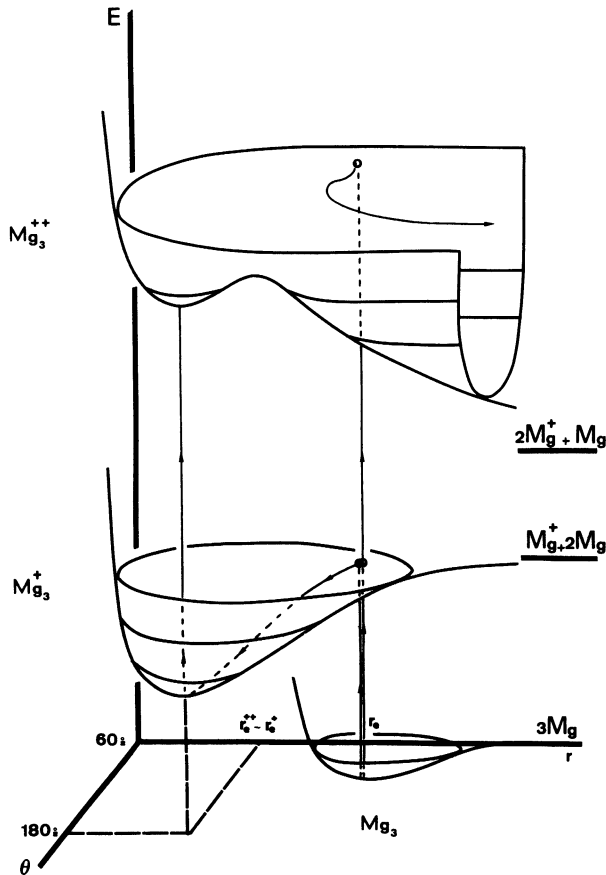


Fig. 6. — Schematic view of the lowest potential surfaces of  $Mg_3^{(k+)}$  ( $k = 0, 1, 2$ ) as functions of  $r = r_{AB} = r_{BC}$  and  $\theta = \widehat{ABC}$ .

#### 4. Comparison with *ab initio* SCF calculations ; methodological discussion.

**4.1 RESULTS OF SCF CALCULATIONS.** — Valence only [14] SCF calculations have been performed on both singly and doubly charged clusters, using (3s, 2p) AO basis sets (i.e. deleting the 3d AO involved in the MO-CI calculation on  $Mg_2^+$  and  $Mg_2^{++}$ ). A UHF (Unrestricted Hartree Fock) formalism was used with  $S_z = 1/2$  for  $Mg_n^+$  and  $S_z = 0$  for  $Mg_n^{++}$ , but for the latter the solutions were always pure singlets.

These calculations have been performed to check ; i) the occurrence of minima close to the structures predicted by our model ; ii) the possible importance of p AO's which do not appear explicitly in our scheme.

The energies and geometries appear in table III ; they concern real minima obtained from a gradient program and force constants calculations. They confirm that all the predicted minima also appear in a mono-electronic approach. This agreement is not too surprising since, for the studied minima, the model wave-functions were consistent with single and double ionizations from the highest occupied MO. Significant differences appear however :

i) the ionization potentials are always much lower

than in our model. This is already true for  $n = 1$ , since the correlation of the  $s^2$  pair in Mg is very important, increasing the ionization potential by about 1 eV ; this defect is still acting in the cluster UHF calculation ;

ii) the relative energy ordering of the two minima for  $Mg_4^+$ ,  $Mg_4^{++}$  and  $Mg_5^+$  is reversed with respect to our model ; one may notice that for  $Mg_4^+$  and  $Mg_4^{++}$  the mono-electronic calculation favours the centred structure ;

iii) the bond interatomic distances are much larger (see Fig. 4).

These two points of disagreement will be discussed later. The electronic populations calculated according to the Mulliken criterion would indicate a more even net charge distribution ; they also would indicate a significant p population on the central atom. However a careful examination of the MO's shows that  $p_c$  AO's do not appear with coefficients larger than 0.15 ; the hybridization is therefore rather weak and the apparent p population is essentially due to the overlap of the  $p_c$  AO's of the central atom with the s AO's of the surrounding atoms, in a typical artifact of Mulliken's population analysis. This is confirmed by the fact that the  $p_c$  diagonal element of the density matrix is negligible ( $< 0.03$  eV).

#### 4.2 COMPARISON BETWEEN MODEL AND *ab initio* SCF CALCULATIONS.

— The discrepancies between our model and SCF results may be easily understood. It is clear that *ab initio* SCF calculations introduce many-body repulsive effects which are not taken into account in our model. However these many-body effects are not very large and they cannot explain the differences in bond distances and in the relative energy orderings of the  $Mg_4^+$  and  $Mg_4^{++}$  isomers.

i) Regarding the interatomic distances, one should notice that in a cluster the probability for two adjacent atoms to be both neutral is  $1 - \frac{1}{n}$  for singly charged

clusters and  $1 - \frac{2(2n-1)}{n(n+1)}$  for doubly charged clusters.

In both cases this probability goes rapidly to one. One may therefore expect that when  $n$  increases the mean interatomic distances tend toward that of the neutral cluster (i.e. the metal for large  $n$ ). Since the mono-electronic picture does not take into account the dispersion energy between neutral atoms, it will let the cluster explode and the interatomic distances will tend to infinity. This failure will also occur in positive clusters since the delocalization energy of the hole is bound by  $kF^+$  ( $k$  being a scalar, depending on the compactness of the cluster) as are the upper or lower limits of a band. Since the repulsive interactions  $\Sigma R$  increase as  $n$ , the delocalization of the hole, included in the mono-electronic scheme, cannot fight efficiently against the increasing repulsions, and the positive cluster is more and more loosely bound with larger and larger interatomic distances.

This defect, which does not appear in our model, is very difficult to overcome in *ab initio* calculation, since it would require the calculation of dispersion forces — a task which is already difficult for  $Mg_2$  [15].

ii) Regarding the relative energies of centred *versus* square structures in  $Mg^+$  and  $Mg^{++}$ , one should notice that the Hartree-Fock approximation only takes into account the *static* field. In homogeneous structures, as is the square cluster, the charge is equally spread, the static field is weak everywhere; on the contrary if the charge is well concentrated on one atom — as occurs for the central atom of the centred triangle — the static field is important on the surrounding atoms, and the HF approximation is able to take this effect into account.

Our model deals with instantaneous repolarizations in all VB local structures, and therefore takes into account an effect which would only appear through double excitations in the MO scheme (change of the hole from the highest occupied MO to lower MO plus one excitation to the outer polarization space).

These comments — which will be developed in detail in a forthcoming paper [16] — explain the preference of the mono-electronic calculation for centred structures, as due to an unbalanced purely static treatment of polarization effects.

## 5. Conclusion.

A careful extraction of information from the potential curves of the diatoms  $Mg_2$ ,  $Mg_2^+$  and  $Mg_2^{++}$ , corresponding to the states keeping an  $s^p + s^q$  ( $p + q = 4, 3, 2, p, q \leq 2$ ) character, permits to define a simple model Hamiltonian of low size for the study of singly and doubly charged clusters. The Hamiltonian involves only 6 parameters and its size is  $n^2$  for doubly charged

clusters. The parameters being analytic functions of the interatomic distances gradient techniques may be easily applied.

Since the extraction of the parameters has been done from calculations involving basis sets and CI, they should provide some information for large cluster studies, which are unattainable from direct MO-CI calculations since they rapidly require reductions of the basis set and/or severe CI truncations. The superiority of our model over *ab initio* SCF calculations appeared clearly in the preceding discussion on both the internuclear distances (unreliable in SCF calculations) and the energy ordering of various minima (unduly preferred as centred structures in SCF calculations).

The present work has shown stable structures for  $Mg_n^+$  and  $Mg_n^{++}$  for  $n \leq 5$ . It will be interesting to analyse the general topology of the potential energy hypersurface(s), taking benefit of some recent theoretical advances [17]. This would give better insurance regarding the number of minima, a problem which will be of increasing importance for larger clusters. It will also be worthwhile to analyse the existence and heights of barriers for aggregation, evaporation and fragmentation processes.

Extension to larger clusters of Mg atoms is in progress. An isoelectronic series may be treated, namely the  $Hg_n^+$  or  $Hg_n^{++}$  clusters studied in reference [1]. The extraction of the basic parameters for this heavy atom is in progress. Finally one should mention that a direct extension to rare gas clusters is easy to perform, the number of AO being then increased to  $3n$  (and the size of the matrix to  $(3n)^2$  for doubly positive clusters). In that last case the problem of hybridization, which may lead to difficulties for large values of  $n$  in  $s^2$  atoms, would be avoided.

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