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A STUDY OF THE GROUND STATES OF Be_2, Mg_2 AND Ca_2 BY THE MULTIPLE SCATTERING Xα METHOD

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The paper presents the MSXα total and orbital energies for the lowest states of Be_2, Mg_2 and Ca_2 according to non-spin-polarized calculations with exchange parameter $\alpha = 2/3$ in the so-called atomic regions of molecules. The calculated potential curves for Mg_2 and Ca_2 correspond to dissociation energies D_e and equilibrium separations R_e which are too large compared to the experimental values: that is, D_e are too large by factors between 1.59 and 8.94, while R_e are too large by factors 1.03 and 1.11, respectively.

1. *Introduction*

Since its introduction a decade ago [1, 2] the multiple scattering Xα(MSXα) approximation (sometimes called SCF-SW-Xα for self-consistent field scattered wave Xα) has been used extensively for calculations of electronic states of molecules and complexes. The method has been the subject of recent review articles [3–5] and a book [6]. It is sufficient to note that the method Xα promises to be superior to the Hartree–Fock (HF) scheme. First of all, the total energy for a molecule or cluster automatically goes to the proper separated atom limit as the internuclear distances are increased to infinity, i.e. as the system dissociates. This is not true of the HF total energy. Second, the SCF-SW-Xα theory rigorously satisfies Fermi statistics, thereby ensuring the proper ordering and occupation of electronic energy levels [6], whereas the HF theory does not. Finally, Slater [7] has proved that the total energy rigorously satisfies both the virial and Hellmann–Feynman theorems, which facilitates the calculation of equilibrium cohesive properties of molecules and solids.

As initially formulated, the MSXα method depends on two main approximations: the α modulated statistical exchanges and the "muffin-tin" form of the potential which are discussed elsewhere [8–10]. Molecular space is partitioned into three mutually exclusive regions of potential as shown in Fig. 1. A sphere surrounding each atom comprises

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region I. A single outer sphere surrounds the cluster of atomic spheres. Region III lies outside the outer sphere. The remainder of space comprises region II, the intersphere region. Inside a sphere of region I and region III, the molecular potential is averaged over angles to produce an approximate potential which is spherically symmetrical with respect to the center of the sphere under consideration. The molecular potential is averaged over the volume of region II to produce an approximate potential which is constant [1, 2, 11]. These combined processes yield a muffin-tin potential.

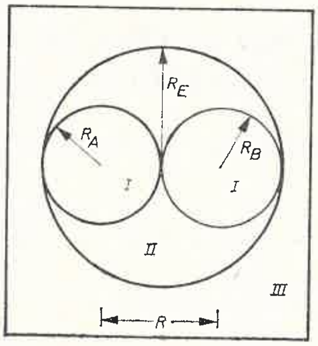

Fig. 1. Division of molecule space for two atoms interacting, at a distance R, into I — atomic, II — interatomic and III — extramolecular regions

The MSXα method has been applied, in the muffin-tin formulation, to a variety of diatomic molecules, including for example: H_2^+ [12], H_2, Li_2 [3], C_2 [12], N_2[9], O_2 [9], F_2 [9], Ne_2 [8], Cl_2 [13]. This paper presents MSXα calculations for the lowest states of Be_2, Mg_2 and Ca_2. We use the values of $\alpha = 2/3$ [14, 15] in atomic regions I and $\alpha = 1$ in regions II and III. The atomic sphere radii are chosen to be half of the internuclear separation. The expansion of the wave function in l–m-like partial waves is carried out to $l = 2$. Orbitals arising from the atomic $1s$ levels for Be_2, $1s2s\,2p$ ones for Mg_2 and $1s2s2p3s3p$ levels for Ca_2 were treated as "core" levels. (It means, for example, that in the case of Be_2, we have treated the $1\delta_g$ and $1\delta_u$ orbitals as a single orbital with an occupancy of 4.) The orbital energies were determined with the accuracy $1 \cdot 10^{-5}$ Ry and the molecular potential was considered to be self-consistent when it changed by no more than $10^{-2}\%$ in successive iterations. All molecules were treated as non-spin-polarized systems.

2. Total energy and orbital energies

In Tables I–III the total energies are listed for $Be_2(1\delta_g^2 1\delta_u^2 2\delta_g^2 2\delta_u^2)$, $Mg_2(1\delta_g^2 1\delta_u^2 2\delta_g^2 2\delta_u^2 3\delta_g^2 1\pi_u^4 1\pi_g^4 3\delta_u^2 4\delta_g^2 4\delta_u^2)$ and $Ca_2(1\delta_g^2 1\delta_u^2 2\delta_g^2 2\delta_u^2 3\delta_g^2 3\delta_u^2 1\pi_g^4 1\pi_u^4 4\delta_g^2 4\delta_u^2 5\delta_g^2 5\delta_u^2 2\pi_g^4 2\pi_u^4 6\delta_g^2 6\delta_u^2)$ as a function of the internuclear separation R. These energies were calculated according to the scheme outlined by Connolly [16]. We used standard MSXα computer programs developed by Olson, Konowalow and Rosenkrantz [17]. The R dependence of the orbital energies for the above diatomic molecules are given in Figs. 3 and 4. Spectroscopic constants

TABLE I

MSXα total energies for Be_2 in the configuration $1\delta_g^2 1\delta_u^2 2\delta_g^2 2\delta_u^2$ according to non-spin-polarized calculations with exchange parameter $\alpha = 0.66667$

R [a_0]	$-E_{\mathrm{total}}$[Ry]	R [a_0]	$-E_{\mathrm{total}}$[Ry]
3.00	56.75681	8.00	56.89821
3.50	56.84399	8.50	56.89671
4.00	56.88478	9.00	56.89559
4.50	56.90314	9.50	56.89479
5.00	56.90960	10.00	56.89424
5.05	56.90986	10.50	56.89386
5.10	56.91005	11.00	56.89361
5.15	56.91018	12.00	56.89336
5.20	56.91026	13.00	56.89327
5.25	56.91030	14.00	56.89323
5.30	56.91029	15.00	56.89322
5.35	56.91026	16.00	56.89311
5.40	56.91019	17.00	56.89317
5.50	56.90997	18.00	56.89320
6.00	56.90788	19.00	56.89321
6.25	56.90657	20.00	56.89322
6.50	56.90520	21.00	56.89322
6.75	56.90384	22.00	56.89322
7.00	56.90252	24.00	56.89323
7.50	56.90016	∞	56.89232

TABLE II

MSXα total energies for Mg_2 in the configuration $1\delta_g^2\ 1\delta_u^2\ 2\delta_g^2\ 2\delta_u^2\ 3\delta_g^2\ 1\pi_u^4\ 1\pi_g^4\ 3\delta_u^2\ 4\delta_g^2\ 4\delta_u^2$ according to non-spin-polarized calculations with exchange parameter $\alpha = 0.66667$

R [a_0]	$-E_{\mathrm{total}}$[Ry]	R [a_0]	$-E_{\mathrm{total}}$[Ry]
4.00	792.85263	7.55	793.00111
4.50	792.91013	7.60	793.00114
5.00	792.95058	7.65	793.00112
5.50	792.97604	7.67	793.00113
6.00	792.98951	7.70	793.00113
6.50	792.99671	7.75	793.00113
6.75	792.99868	7.80	793.00112
7.25	793.00084	7.90	793.00107
7.35	793.00089	8.00	793.00102
7.40	793.00097	9.00	792.39952
7.50	793.00108	∞	792.99500

TABLE III

MSXα total energies for Ca_2 in the configurations $1\delta_g^2\,1\delta_u^2\,2\delta_g^2\,2\delta_u^2\,3\delta_g^2\,3\delta_u^2\,1\pi_g^4\,1\pi_u^4\,4\delta_g^2\,4\delta_u^2\,5\delta_g^2\,5\delta_u^2\,2\pi_g^4\,2\pi_u^4\,6\delta_g^2\,6\delta_u^2$ according to non-spin-polarized calculations with exchange parameter $\alpha = 0.66667$

R [a_0]	$-E_{\text{total}}$[Ry]	R [a_0]	$-E_{\text{total}}$[Ry]
6.00	2695.99501	9.30	2696.64722
6.50	2696.06813	9.40	2696.64721
8.50	2696.64641	9.50	2696.64713
8.60	2696.64673	10.00	2696.64656
8.70	2696.64682	11.00	2696.64504
8.80	2696.64689	12.00	2696.64368
8.90	2696.64692	13.00	2696.64276
8.95	2696.64729	14.00	2696.64218
9.00	2696.64738	15.00	2696.64187
9.05	2696.64731	16.00	2696.64171
9.10	2696.64731	17.00	2696.64164
9.20	2696.64727	∞	2696.57076

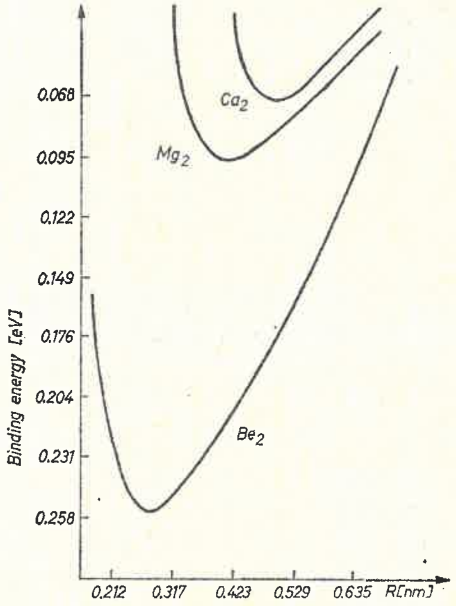

Fig. 2. Binding energy curves for Be_2, Mg_2 and Ca_2

for the ground $^1\Sigma_g^+$ states of Be_2, Mg_2 and Ca_2 found from various calculations [18, 19] are listed together with the present determinations in Tables IV–VI. In these tables the experimental data [20, 21] are given for comparison.

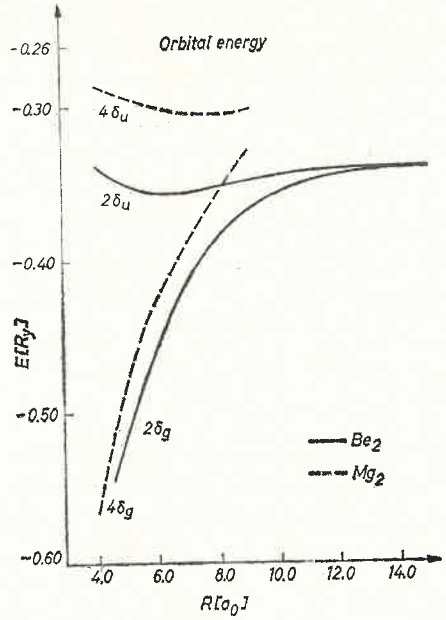

Fig. 3. R dependence of two highest orbital energies for Be_2 and Mg_2

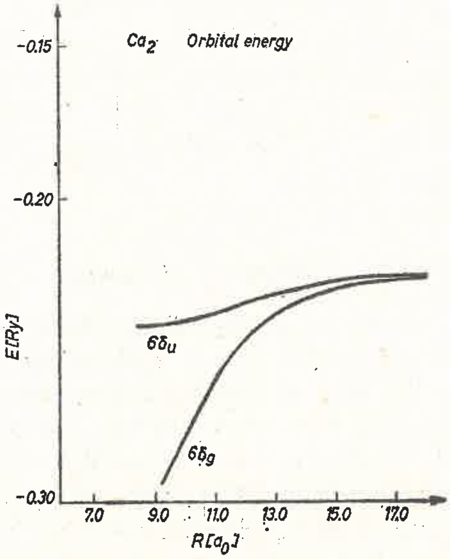

Fig. 4. R dependence of two highest orbital energies for Ca_2

TABLE IV

Spectroscopic constants for the ground $^1\Sigma_g^+$ state of Be_2

Source	R_e [Å]	D_e [cm^{-1}]	ω_e [cm^{-1}]	$\omega_e x_e$ [cm^{-1}]
experiment	—	—	—	—
MS — Xα[a]	2.778	1973.4212	327.3855	13.5781
BLMO SCF[b]	2 000	—	—	—
empirical extrapolation[c]	—	5646.228	—	—

[a] This work. [b] Best limited LCAO MO SCF results, Reference [18]. [c] Reference [19].

TABLE V

Spectroscopic constants for the ground $^1\Sigma_g^+$ state of Mg_2

Source	R_e [Å]	D_e [cm^{-1}]	ω_e [cm^{-1}]	$\omega_e x_e$ [cm^{-1}]
experiment[a]	3.890	424	51.12	1.64
MS-Xα[b]	4.002	673.1824	39.2535	0.5722

[a] Reference [20]. [b] This work.

TABLE VI

Spectroscopic constants for the ground $^1\Sigma_g^+$ state of Ca_2

Source	R_e [Å]	D_e [cm^{-1}]	ω_e [cm^{-1}]	$\omega_e x_e$ [cm^{-1}]
experiment[a]	4.28	940	65.0	1.11
MS-Xα[b]	4.7625	8407.4278	3.1611	0.000297

[a] Reference [21]. [b] This work.

3. *Discussion of results*

The MSXα potential curves for Be_2, Mg_2 and Ca_2 (Tables I–III and Fig. 2) are qualitatively correct. That is, they all exhibit a steep repulsion, pass through a minimum, and approach the large separation limit of dissociated atoms essentially correctly. However, the quantitative shortcomings of these curves are also evident from those tables and the data [18–21] in Tables IV–VI. There it is seen (Tables V, VI) that our calculated potential curves correspond to dissociation energies D_e as well as to equilibrium separation R_e which are too large when compared to the experimental values [20, 21]. Concomitantly, the frequency of the vibrations ω_e and the first anharmonicity constants $\omega_e x_e$ are too small when compared to the experimental results. It is difficult to compare our spectroscopic constants for Be_2 (Table IV) with theoretical data [18, 19] since they are single (on the contrary its spectrum was not measured). For Mg_2 and Ca_2 the MSXα values of the calculated equilibrium separations are respectively a factor of 1.03 and 1.11 times larger than the experimental ones. The calculated D_e values are, respectively, a factor 1.59 and 8.94 times larger than the experimental ones. At the same time, the calculated ω_e values are, respectively, only 76% and 4.85% of the experimental values. Let us remember here that MSXα scheme (with the same atomic exchange parameter α for all three regions (Fig. 1)) has been much less successful in calculating the equilibrium separations of potential energy curves for diatomic molecules of N_2, O_2 and F_2[9] than that with $\alpha = 2/3$ and $\alpha_{II} = \alpha_{III} = 1$ (Fig. 1) applied to Be_2, Mg_2 and Ca_2 in this paper.

The question of why the MSXα results for Mg_2 are more realistic than those for Ca_2 is being investigated in the Laboratory of the Chemistry Department in the State University of New York at Binghamton.

A variety of remedies for the above difficulties has recently been proposed (see Ref. [22]). Among such remedies, Rosenkrantz and Konowalow proposed semiempirical MTX$\bar{\alpha}_R$ method [22]. This method seems to be competitive with other schemes which are designed to improve the original MSXα schemes.

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