Theoret. Chim. Acta (Berl.) 64, 13–19 (1983)

THEORETICA CHIMICA ACTA

Theoretical Study of the Potential Energy Curves of the Diatomic Radicals $Me_{II}X$. III. Application to MgCl, CaF and CaCl Radicals and Some Preliminary Remarks

Rafaele Montagnani, Pierluigi Riani and Oriano Salvetti

Istituto di Chimica Quantistica ed Energetica Molecolare del C.N.R., Via Risorgimento 35, I-56100 Pisa, Italy

The series of calculations of the potential energy curves of the diatomic radicals $Me_{II}X$ (Me_{II} = second group metal, X = halogen), has been extended to MgCl, CaF and CaCl. The calculations have been performed according to a stepwise procedure, outlined in previous works. The presently available results allow comparisons for the first members of the series.

Key words: Electronic transition lasers—MgCl, potential energy curves of~ —CaF, potential energy curves of~— CaCl, potential energy curves of~.

1. Introduction

In two preceding papers [1, 2] (hereafter referred to as I and II) we have outlined a scheme for calculating, by means of independent SCF procedures, the potential energy curves of some low-lying electronic states of the $Me_{II}X$ radicals, where Me_{II} is a metal of group II, *A* or *B*, and X is a halogen. This method has been applied to the BeF, MgF and BeCl radicals. These calculations have been undertaken because of the occurrence of the mercury halide radicals HgCl, HgBr and HgI in the series. They show electronic transitions which can be used for efficient visible and near UV lasers. Actually, the potential energy curves of the mercury halide radicals, reported by Wadt, Hay and Dunning [3], show a close resemblance to those we have calculated for the first members of the series.

In this work we present calculations relative to the isoelectronic radicals MgCl and CaF, and to the CaCl radical. Thus the treatment of all Me_{II} (= Be, Mg, Ca) X (= F, Cl) radicals is completed. For these radicals, an *ab initio* complete study is reasonably possible, while for the other radicals the use of effective core potentials for the heavy atoms will be needed.

For the first three members of the series the calculations have been performed by using very large basis sets without any contraction [I, II]. In the present work, the use of basis sets of such a flexibility dictated a contraction of the basis functions with large orbital exponents. The calculation scheme, with a division of the procedure into successive steps, has been described in I.

2. Basis Functions

Our calculation programs utilize the Modified Gaussian Functions [4, 5]. As in I and II, for the choice of the orbital exponents (α), we have considered the various electronic states originating from the dissociation of the molecules. From the spectroscopic data [6] it is known that there are many dissociated states within the ionic dissociation limit $\mathrm{Me}_{\mathrm{II}}^{+}\,{}^2S + \mathrm{X}^{-}\,{}^1S$. Nevertheless, only the state $\mathrm{Ca}^*\,{}^3P + \mathrm{F}\,{}^2P$ has been taken into account; the calculations of all other states has been omitted because the crossings with the potential energy curves of the $B\,{}^2\Sigma^+$ states occur at very large internuclear distances, beyond the interesting zone.

No change of the basis sets used in *I* and *II* (Huzinaga [7]+very expanded functions) for F, Mg and Cl is needed. For the description of the Ca atom, we have employed the basis set of Wachters [8]. Further, to this basis set one s-type function ($\alpha = 0.009$), 3 p-type functions ($\alpha = 0.1$, 0.03, 0.01), and 7 d_{z^2}-type functions, useful for the description of the excited state ($\alpha = 20.0$, 5.0, 1.25, 0.4, 0.12, 0.04, 0.012) have been added. Contraction has been limited to the functions with higher orbital exponent, as their coefficients in the various orbitals have nearly constant ratios, namely 4 s-type and 2 p-type functions for F and Cl, 3 s and 2 p for Mg, 5 s, 4 p and 2d_{z^2} for Ca. The contraction coefficients are those of Refs. 7 and 8, after normalization; the coefficients of the d_{z^2} functions of Ca have been obtained from an SCF calculation for the $\mathrm{Ca}^{*3}\mathrm{D}$ atom, and are 0.13159 and 0.99131. Fig. 1 shows the curves of the coefficients versus Log α for the Ca atom. These curves allow to qualitatively evaluate the goodness of the basis set (see also I and II).

3. Potential Energy Curves

We have taken into account the diabatic states $X\,{}^2\Sigma^+$, $A\,{}^2\Pi$, $B\,{}^2\Sigma^+$ for all molecules; for the CaF the $C\,{}^2\Sigma^+$ state also has been considered. The fillings are analogous to those of the corresponding states of BeF, BeCl and MgF in I and II. The orthogonality of the B and C states with the ground state has been obtained by limiting the space of variability of one orbital, according to our SCF procedure for the excited states [9, 10]. As regards the CaF molecule, the orthogonality between the B and C states has not been imposed, because of

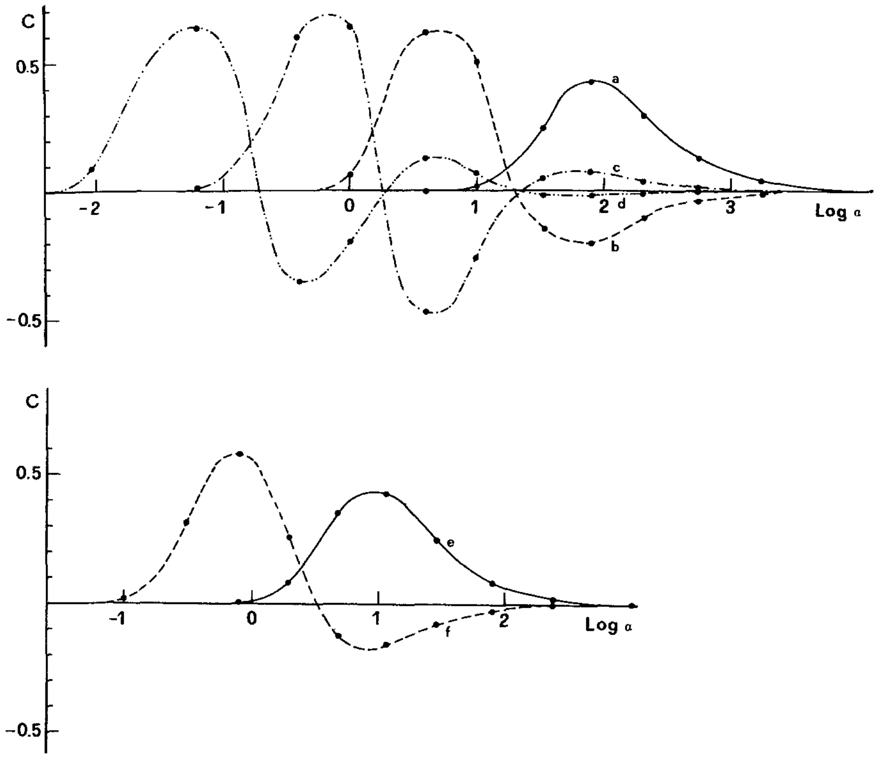

Fig. 1. Behavior of the coefficients as a function of Log α (α = orbital exponent) for the Ca atom. *a*: 1*s*; *b*: 2*s*; *c*: 3*s*; *d*: 4*s*; *e*: 2*p*; *f*: 3*p*

the excessive limitation of the space of variability. On the other hand, the overlap is very small [I, II].

The SCF energies are reported in Tables 1, 2 and 3. The values of the total energy have been obtained adding the correlation energy, calculated separately

Table 1. Energy values (a.u.) of the MgCl radical in the various states

R	$X\,^2\Sigma^+$	$A\,^2\Pi$	$B\,^2\Sigma^+$
3.0	−658.9228	−658.9652	−658.6472
3.5	−659.1150		−658.8407
4.0	−659.1708		−658.9227
4.5	−659.1763		
5.0	−659.1641	−659.0135	−658.9915
6.0	−659.1283		−659.0258
8.0	−659.0864	−659.0663	−659.0570
10.0	−659.0863		−659.0377
12.0	−659.0863		−659.0215
15.0	−659.0863	−659.0862	−659.0046
20.0	−659.0863		−658.9868

Table 2. Energy values (a.u.) of the CaF radical in the various states

R	$X\,^2\Sigma^+$	$A\,^2\Pi$	$B\,^2\Sigma^+$	$C\,^2\Sigma^+$
3.0	−776.1858			
3.5	−776.2974			
4.0	−776.3122	−776.1309	−776.0949	
5.0	−776.2726	−776.1588	−776.1235	
6.0	−776.2284	−776.1666	−776.1385	
7.0	−776.1946	−776.1706		
8.0	−776.1728		−776.1589	
10.0	−776.1734		−776.1361	−776.0895
12.0	−776.1734	−776.1734	−776.1179	
15.0	−776.1734		−776.1004	−776.1090
20.0	−776.1734		−776.0833	−776.0979

Table 3. Energy values (a.u.) of the CaCl radical in the various states

R	$X\,^2\Sigma^+$	$A\,^2\Pi$	$B\,^2\Sigma^+$
3.5	−1136.1593		
4.0	−1136.3002		−1136.1040
4.5	−1136.3539	−1136.1729	
5.0	−1136.3633		−1136.1610
6.0	−1136.3416	−1136.2265	−1136.1879
7.0	−1136.3113	−1136.2043	
8.0	−1136.2861	−1136.2380	−1136.2165
9.0	−1136.2671	−1136.2395	−1136.2250
10.0	−1136.2528	−1136.2305	
12.0	−1136.2405		−1136.2311
15.0	−1136.2405	−1136.2404	−1136.2140
20.0	−1136.2404		−1136.1967
30.0	−1136.2404		−1136.1797

[11, 12], to the SCF energy. The crossing between the diabatic states $B\,^2\Sigma^+$ and $C\,^2\Sigma^+$ of the CaF molecule has been eliminated by means of a CI process. This CI process has been performed only between the configurations of the crossing states. The potential energy curves are plotted in Figs. 2, 3 and 4.

4. Some Preliminary Remarks

A first certain datum, already observed by Wadt et al. (mercury halides) and by Klinning et al. (CaCl) [13–16] is related to the type of the wavefunctions for the X and B states of all radicals we have studied. At large internuclear distances, the X states are covalent; in the attractive region, their characters become strongly ionic. On the contrary, the B states are purely ionic from large internuclear distances to the minimum, and assume a prevalent covalent character at shorter separations. Every radical has its own value of interatomic distance

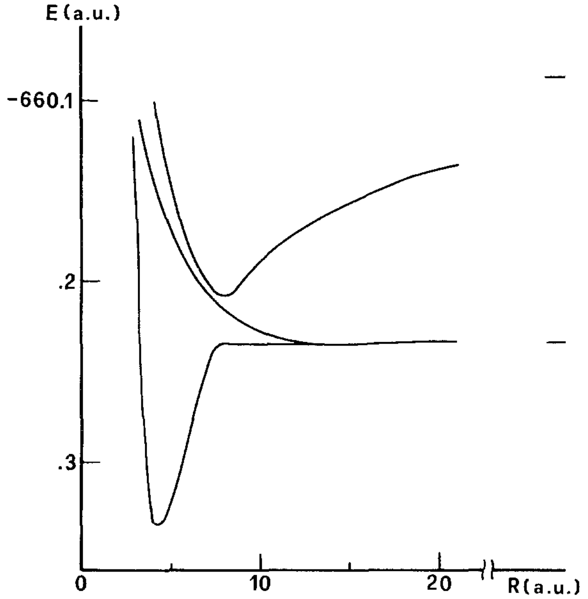

Fig. 2. Potential energy curves of the MgCl radical, including the correlation energy

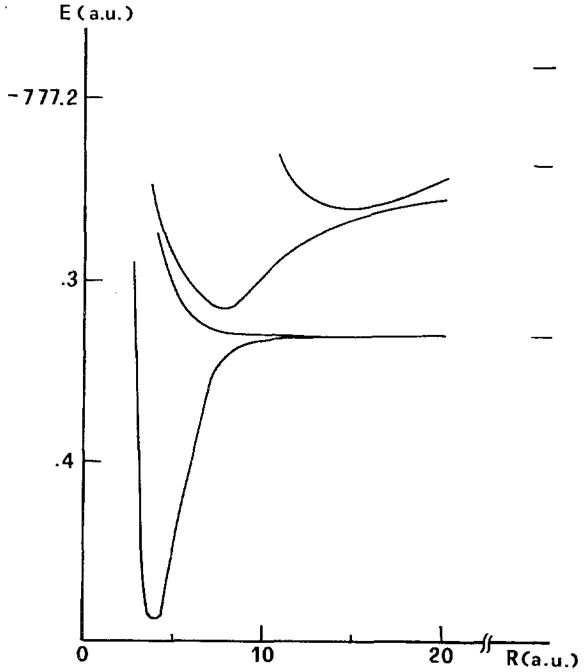

Fig. 3. As in Fig. 2, CaF radical

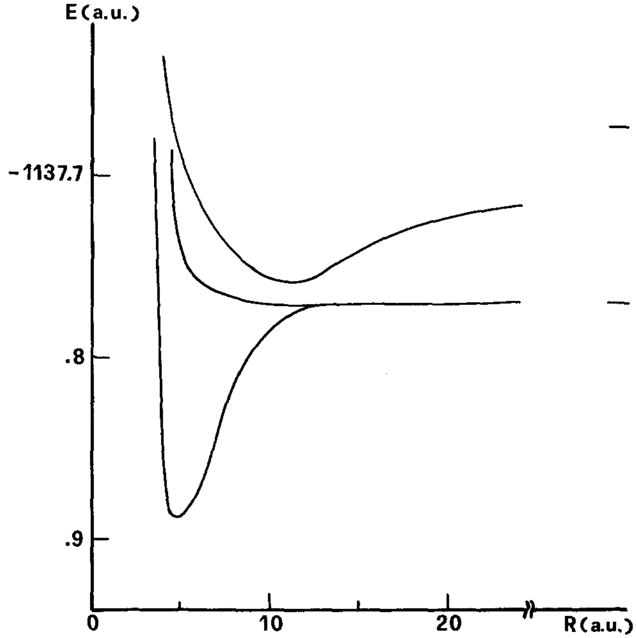

Fig. 4. As in Fig. 2, CaCl radical

at which both changes of the wavefunction character are observed (minimum of the potential energy curve for the *B* state, beginning of the attractive region for the *X* state). These changes give rise to very serious problems of convergence of the SCF processes. It is to be pointed out that the behaviors of the potential energy curves of *B* states in the attractive region is strictly a coulombian one (dissociation limit $-R^{-1}$). On the contrary, the potential value of the *X* state in the ionic region is lower because of a partial covalent character of the bond. The additional contribution to the bond energy can be explained also by a charge polarization [16].

Table 4. Equilibrium interatomic distances for the $\mathrm{Me_{II}X}$ radicals in the $X\,^2\Sigma^+$ state. *A*: Ref 17, sum of the ionic cristal radii; *B*: SCF values, *I*, *II* and this work; *C*: ratio *A*/*B*

Molecule	*A*	*B*	*C*
BeF	3.34	2.8	1.19
MgF	4.06	3.4	1.19
CaF	4.74	3.9	1.22
BeCl	4.25	3.7	1.15
MgCl	4.97	4.2	1.18
CaCl	5.65	4.8	1.18

The equilibrium interatomic distances for the *X* states are compared with those obtained as a sum of the ionic radii [17] in Table 4. Our values are always lower, but the ratio is quite constant. It is necessary to keep in mind that the reference values are the values of ionic cristal radii.

The crossing distances between *B* and *C* states can be evaluated from the spectroscopic data [6], if assumption is made that the potential energy curves of the *C* states are quite flat at large internuclear distances (i.e., $Me^{*}_{II}\,{}^3P$ and $X\,{}^2P$ atoms do not appreciably interact). The crossings occur roughly at 21 a.u. for MgCl and 41 a.u. for CaCl. These values surely justifie the omission of the calculation of the $C\,{}^2\Sigma^+$ potential energy curves.

References

1. Montagnani, R., Riani, P., Salvetti, O.: Theoret. Chim. Acta (Berl.) **60**, 399 (1982)
2. Montagnani, R., Riani, P., Salvetti, O.: Theoret. Chim. Acta (Berl.), **62**, 329 (1983)
3. Hay, P. J., Wadt, W. R., Dunning, T. H. Jr.: Annu. Rev. Phys. Chem. **30**, 311 (1979)
4. Golebiewsky, A., Mrozek, J.: Int. J. Quantum Chem. **7**, 623 (1973)
5. Golebiewsky, A., Mrozek, J.: Int. J. Quantum Chem. **7**, 1021 (1973)
6. Atomic Energy Levels, Circular 467, US Department of Commerce, National Bureau of Standards (1949)
7. Huzinaga, S.: Approximate atomic functions. Div. of Theoretical Chemistry, Dept. of Chemistry, The University of Alberta, Canada (1971)
8. Wachters, A. J. H.: J. Chem. Phys. **52**, 1033 (1970)
9. Colle, R., Montagnani, R., Riani, P., Salvetti, O.: Theoret. Chim. Acta (Berl.) **48**, 251 (1978)
10. Colle, R., Montagnani, R., Riani, P., Salvetti, O.: Theoret. Chim. Acta (Berl.) **48**, 257 (1978)
11. Colle, R., Salvetti, O.: Theoret. Chim. Acta (Berl.) **37**, 329 (1975)
12. Colle, R., Salvetti, O.: Theoret. Chim. Acta (Berl.) **53**, 55 (1979)
13. Berg. L. E., Klynning, L., Martin, H.: Physica Scripta **21**, 173 (1980)
14. Klynning, L., Martin, H.: Physica Scripta **22**, 221 (1980)
15. Klynning, L., Martin, H.: Physica Scripta **24**, 25 (1981)
16. Klynning, L., Martin, H.: Physica Scripta **24**, 33 (1981)
17. Handbook of Chemistry and Physics, Weast, R. C., ed. Cleveland, Ohio: CRC Press, 1977

Received January 19, 1983/May 3, 1983