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Theoretical Study of the Potential Energy Curves of the Series of Diatomic Radicals $\mathrm{Me_{II}X}$. I. Method and its Application to BeF Radical

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A method for calculating potential energy curves of some low lying states of the diatomic radicals $\mathrm{Me_{II}X}$ ($\mathrm{Me_{II}}$ = second group metal, X = halogen) is outlined. Because of the electronic structure of these compounds, applications to electronic transition lasers can be made. The first calculation regards the most simple example of this series, i.e. the BeF radical. The division of the procedure into separated steps allows a sure control of the quality of the results.

Key words: Electronic transition lasers – BeF, potential energy curves of ∼.

1. Introduction

The mercury halide radicals (HgCl, HgBr, HgI) show electronic states which can be used for efficient laser apparatus operating in the visible and in the near U.V. Some low lying states of HgCl and HgBr have been studied by Wadt, Hay and Dunning [1, 2], using a relativistic effective core potential for Hg and nonrelativistic potentials for Cl and Br; potential energy curves elucidate a behaviour which qualitatively justifies the laser action.

It is evident that, because of their electronic structure, molecules like $\mathrm{M_{II}X}$ (where $\mathrm{M_{II}}$ is a metal of the II group, A or B, and X is an halogen) should present very similar potential energy curves. Therefore we think that it is useful to study this series of diatomic radicals, in a more detailed way than the above mentioned calculations for HgCl and HgBr, especially in the regions of crossing between the diabatic potential curves.

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We have taken into account the most simple example, BeF, studying the potential energy curves for some low lying electronic excited states. The calculation scheme is the following:

(a) Determination of the basis functions which are necessary for an accurate description of the various electronic states of the atoms and ions arising from the dissociation of the molecule;

(b) Calculation of the diabatic potential energy curves by means of separate SCF processes, with the lowest number of determinants which give the correct dissociation;

(c) Removal of the crossings between the diabatic potential energy curves by means of configuration interaction near the crossing points;

(d) Calculation of the correlation energy utilizing the method of the density matrix functional [3, 4, 5].

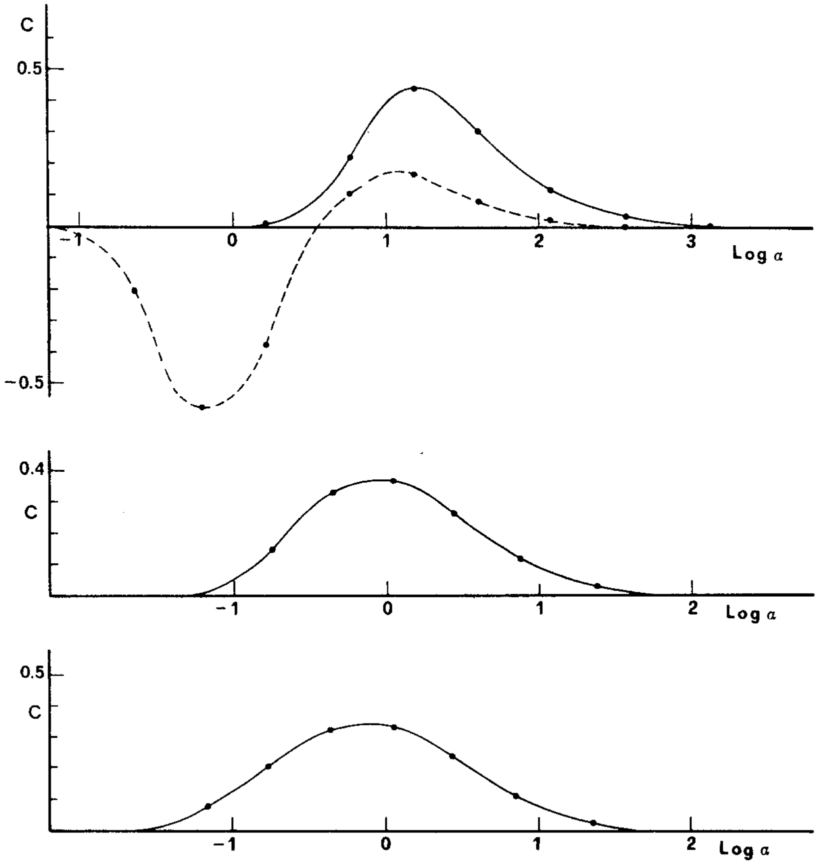

Fig. 1. Behaviour of the coefficients as a function of Log α (α = orbital exponent). (a) F, s-type orbitals; (b) F, p-type orbital; (c) F^-, p-type orbital

We think that this procedure is competitive not only because of its calculation simplicity and the reliability of the results, but also because the separated steps of the procedure allow a more immediate and intuitive vision of the results themselves.

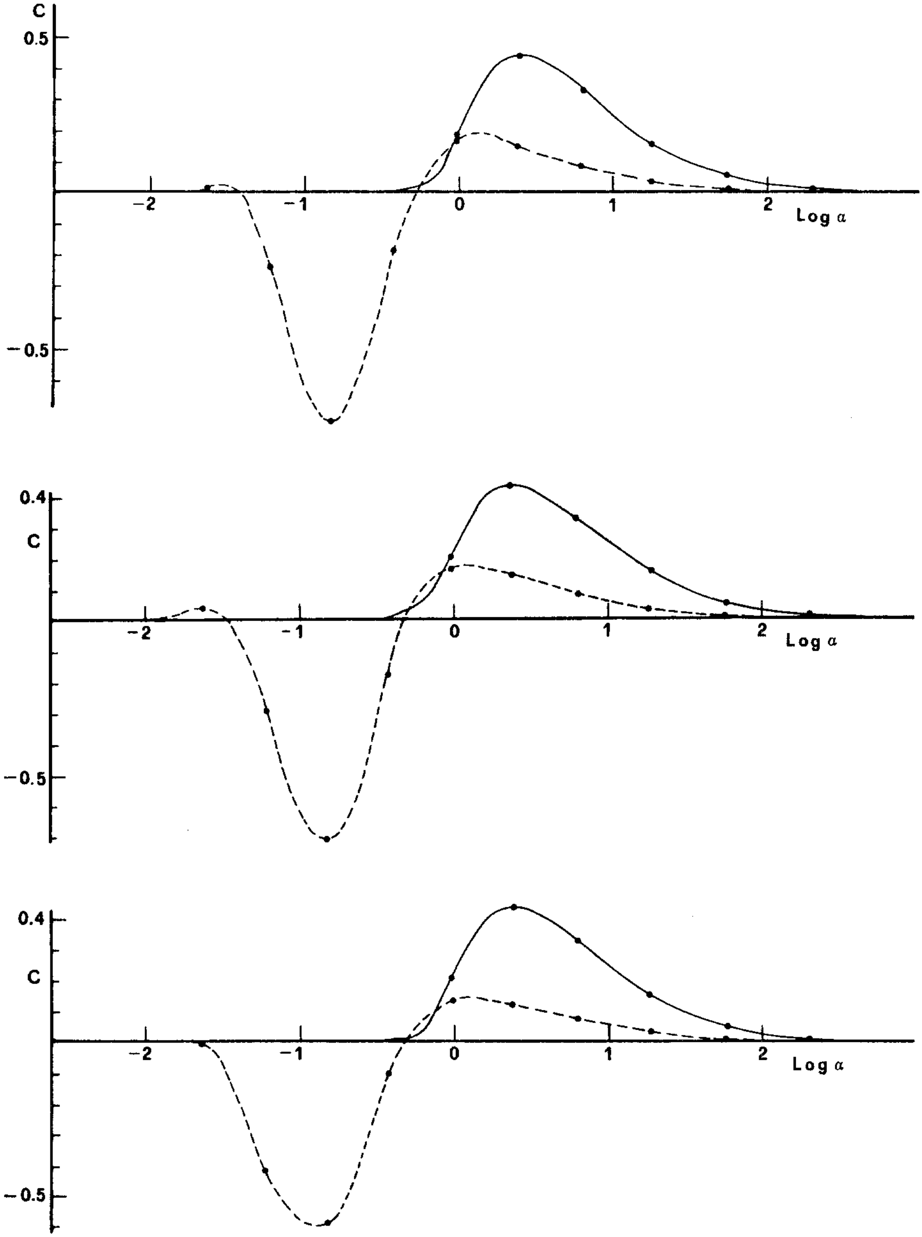

Fig. 2. As in Fig. 1. (a) Be^+, *s*-type orbitals; (b) $Be^{*1}P$, *s*-type orbitals; (c) $Be^{*3}P$, *s*-type orbitals

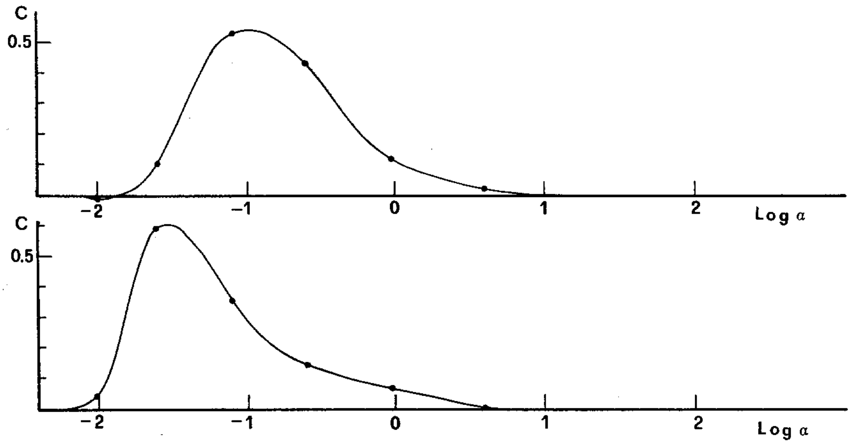

Fig. 3. As in Fig. 1. (a) $\mathrm{Be}^{*3}P$, p-type orbital; (b) $\mathrm{Be}^{*1}P$, p-type orbital

2. Basis Functions

Our calculation programs utilize the Modified Gaussian Functions [6, 7]. For the choice of the orbital exponents (α), we consider the various electronic states coming from the dissociation of the molecule. These states, ordered according to increasing energy, are the following:

(1) $\mathrm{Be}(1s^2 2s^2)^1S + \mathrm{F}(1s^2 2s^2 2p^5)^2P$
(2) $\mathrm{Be}^*(1s^2 2s^1 2p^1)^3P + \mathrm{F}(1s^2 2s^2 2p^5)^2P$
(3) $\mathrm{Be}^*(1s^2 2s^1 2p^1)^1P + \mathrm{F}(1s^2 2s^2 2p^5)^2P$
(4) $\mathrm{Be}^+(1s^2 2s^1)^2S + \mathrm{F}^-(1s^2 2s^2 2p^6)^1S$.

As a qualitative criterion of judgement of the goodness of the basis set, we plot the coefficients of the basis functions in the various orbitals as a function of $\log \alpha$. The curves obtained for the F atom with the basis set of Huzinaga [8] show clearly the goodness of the basis set itself, while for the F^- ion the addition of an expanded p-type function is necessary (Fig. 1). For the Be atom, the s-type basis set of Huzinaga has been expanded to describe accurately also the excited states. For the ^3P and ^1P states, a p-type basis set of 7 functions has been employed. Figs. 2 and 3 show the curves for $\mathrm{Be}^+\ {}^2S$, $\mathrm{Be}^*\ {}^1P$ and $\mathrm{Be}^*\ {}^3P$. Table 1 shows our basis sets.

3. Potential Energy Curves

We have taken into account the following diabatic states:

(1) $X\ {}^2\Sigma^+$, with electronic structure $\sigma_1^2\sigma_2^2\sigma_3^2\sigma_4^2\sigma_5^1\pi^4$

(2) $A\ {}^2\Pi$, with electronic structure $\sigma_1'^2\sigma_2'^2\sigma_3'^2\sigma_4'^2\sigma_5'^2\pi'^3$.
The orthogonality to the ground state is given in this case by the symmetry; the dissociation limit of both of them is $\mathrm{Be}\ {}^1\mathrm{S} + \mathrm{F}\ {}^2\mathrm{P}$.

(3) At short internuclear distances, the third state is $B\ {}^2\Sigma^+$, with electronic structure $\sigma_1''^2\sigma_2''^2\sigma_3''^2\sigma_4''^1\sigma_5''^2\pi''^4$. This state has substantially an ionic character

Table 1. Basis functions

α	Center	Type
6224.0	Be	*s*
929.6	Be	*s*
209.2	Be	*s*
58.1	Be	*s*
18.5	Be	*s*
6.44	Be	*s*
2.41	Be	*s*
0.955	Be	*s*
0.38	Be	*s*
0.151	Be	*s*
0.060	Be	*s*
0.025	Be	*s*
18.0	Be	*p*
4.0	Be	*p*
0.96	Be	*p*
0.25	Be	*p*
0.08	Be	*p*
0.025	Be	*p*
0.01	Be	*p*
37736.0	F	*s*
5867.1	F	*s*
1332.5	F	*s*
369.44	F	*s*
116.84	F	*s*
40.349	F	*s*
40.349	F	*s*
14.966	F	*s*
5.876	F	*s*
1.653	F	*s*
0.6108	F	*s*
0.2333	F	*s*
102.26	F	*p*
23.94	F	*p*
7.521	F	*p*
2.772	F	*p*
1.10	F	*p*
0.4468	F	*p*
0.1719	F	*p*
0.065	F	*p*

and dissociates into the two ions $\mathrm{Be}^+\ {}^2S + \mathrm{F}^-\ {}^1S$. In our SCF procedure [9, 10] all the orbitals can vary in the space spanned by the basis functions, with the exception of σ_5'' which is confined to space orthogonal to σ_1, σ_2, σ_3 and σ_4. This limitation guarantees the orthogonality with the ground state. The modifications of the σ_4 and σ_5 orbitals, which change their occupation number going from one state to another, are very relevant, unlike those of the σ_1, σ_2 and σ_3 orbitals. The effect of these variations is shown in Fig. 4.

(4) The filling $\sigma_1^2\sigma_2^2\sigma_3^2\sigma_4^1\sigma_5^1\sigma_6^1\pi^4$ gives two doublets, $C\ {}^2\Sigma^+$ and $D\ {}^2\Sigma^+$, by means of the appropriate spin combinations. At short internuclear distance, the energies

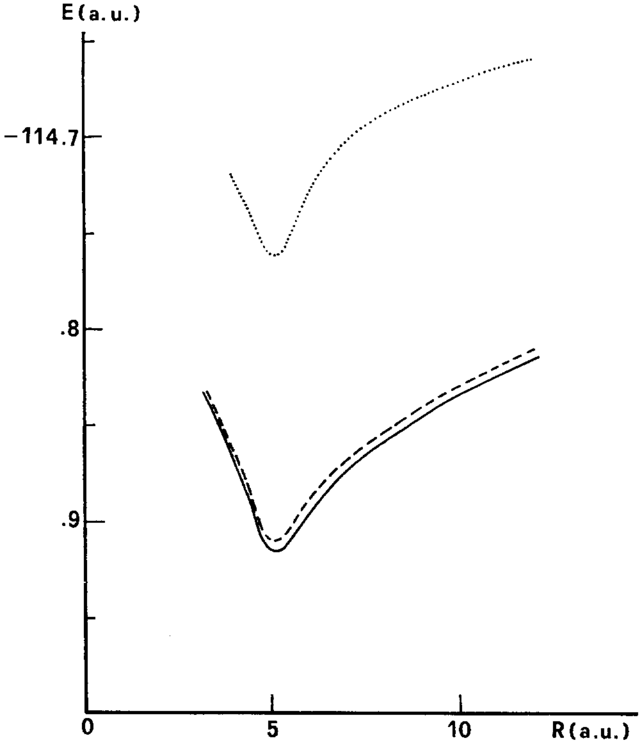

Fig. 4. Effect of the frozening of the orbitals on the $B\,^2\Sigma^+$ state energy. Dotted curve: orbitals of the ground state. Dashed curve: only variation of σ_4 and σ_5 orbitals. Solid curve: variation of all the orbitals

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

R	$X\,^2\Sigma^+$	$A\,^2\Pi$	$B\,^2\Sigma^+$	$C\,^2\Sigma^+$	$D\,^2\Sigma^+$
2.0	−113.9612	−113.6278			
2.5	−114.1171	−113.8507			
2.7	−114.1243				
3.0	−114.1141	−113.9117	−113.8258		
3.5	−114.0756	−113.9375	−113.8511		
4.0	−114.0331	−113.9541	−113.8691		
4.5	−113.9951		−113.8863	−113.7612	
5.0	−113.9775	−113.9726	−113.9139	−113.8296	−113.7648
6.0	−113.9803		−113.8939	−113.8612	−113.7724
7.0	−113.9812	−113.9809	−113.8733	−113.8864	−113.7795
8.0	−113.9815		−113.8560	−113.9030	−113.7813
9.0	−113.9815		−113.8421	−113.9142	−113.7824
10.0	−113.9816		−113.8308	−113.9141	−113.7846
15.0	−113.9816		−113.7965	−113.9138	−113.7986
50.0	−113.9816	−113.9816	−113.7495		−113.8076

of these doublet states are higher than the energy of the ionic one, but their dissociation limits (Be^{*3}P+F^{2}P, Be^{*1}P+F^{2}P) are lower. This fact elucidates a crossing between the diabatic potential curves. The energy of the state which dissociates as triplet plus doublet is always lower than that of the state which dissociates as singlet plus doublet; the crossings with the ionic state are at about 7 and 14 a.u., respectively. The orthogonality of these states to the ground state has been taken into account by confining the σ_6 orbital to a space orthogonal to σ_1, σ_2, σ_3, σ_4 and σ_5: the problem of orthogonality to the $B\ ^2\Sigma^+$ state and of orthogonality between the two doublets is more complex. This last problem could be solved building up the two doublets by means of the same spatial orbitals: orthogonality is guaranteed by the spin functions. On the other hand, even if we remove this constraint calculating the two states by separate SCF

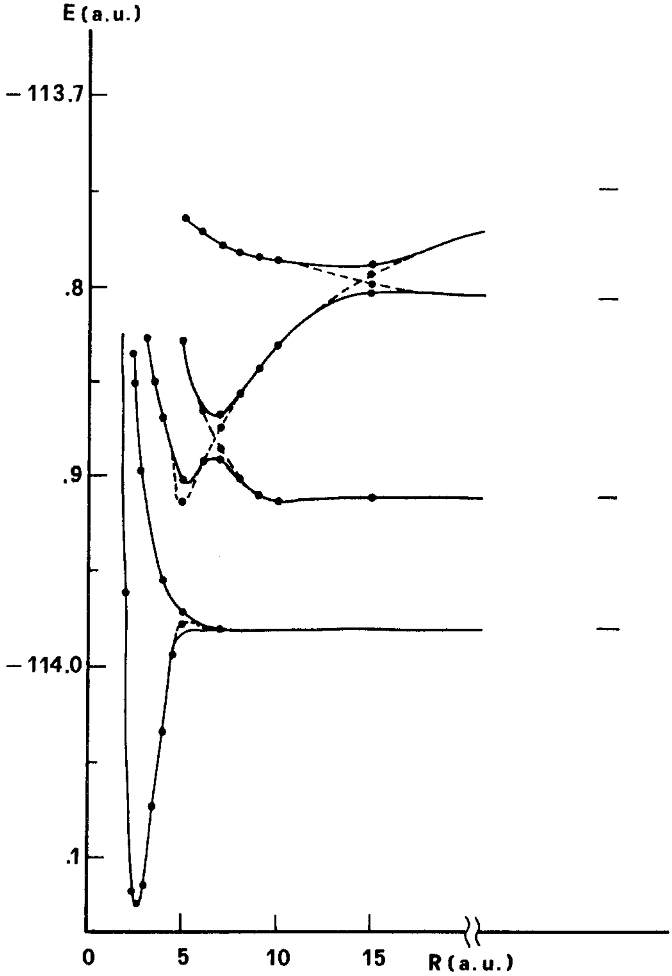

Fig. 5. Potential energy curves of BeF radical. Dashed curve: diabatic. Solid curve: adiabatic. On the right the dissociation limits are shown

procedures, the variation of the orbitals is very small, so that the two states remain orthogonal within a very good approximation. We remember also that the dissociation limit itself guarantees the orthogonality between the two doublets at large internuclear distances. In our scheme, the orthogonality to the $B\ ^2\Sigma^+$ state can be obtained by confining the σ_6 orbital to a space orthogonal not only to $\sigma_1 \cdots \sigma_5$, but also to $\sigma_1'' \cdots \sigma_5''$; this limitation gives, however, an excessive contraction of the space of variability. On the other hand, the σ_6 orbital lies in the space spanned by the virtual orbitals of the ground state; this space coincides, with very good approximation, with the space spanned by the virtual orbitals of the $B\ ^2\Sigma^+$ state. Moreover, in this case also, at large internuclear distances the orthogonality is guaranteed by the dissociation limits. Actually, even if we do not introduce other limitations to the space of σ_6, the overlap between the two doublets and the ionic state remains very small at all internuclear distances. The energy values for the various states are reported in Table 2.

The adiabatic potential curves have been obtained by means of a configuration interaction process; since the mixing of the states is significant only near the

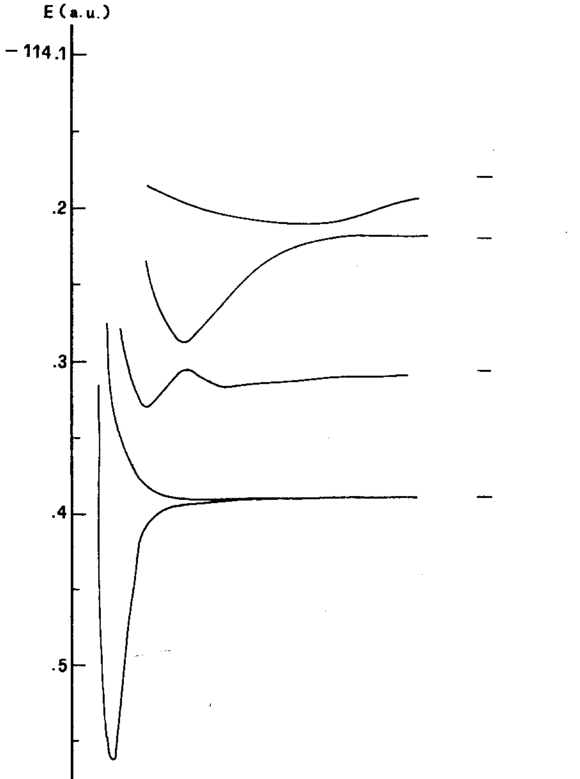

Fig. 6. Adiabatic potential energy curves of BeF radical, including the correlation energy

crossings, the CI procedure has been performed only with the couples of crossing states. Our diabatic and adiabatic potential curves are reported in Fig. 5.

The correlation energy has been calculated by integrating an electronic density functional and it has been added to the SCF–SCF CI energy values. In Fig. 6 the total energy curves are shown. In view of the control worked out on the single steps, we think that our method should be adequate to the calculation of the potential energy curves of the series or diatomic radicals $\mathrm{Me}_{\mathrm{II}}\mathrm{X}$, of which the BeF molecule is the most simple example.

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