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"THEORETICAL STUDY OF THE F<sub>2</sub> MOLECULE USING  
THE VARIATIONAL CELLULAR METHOD" (+)

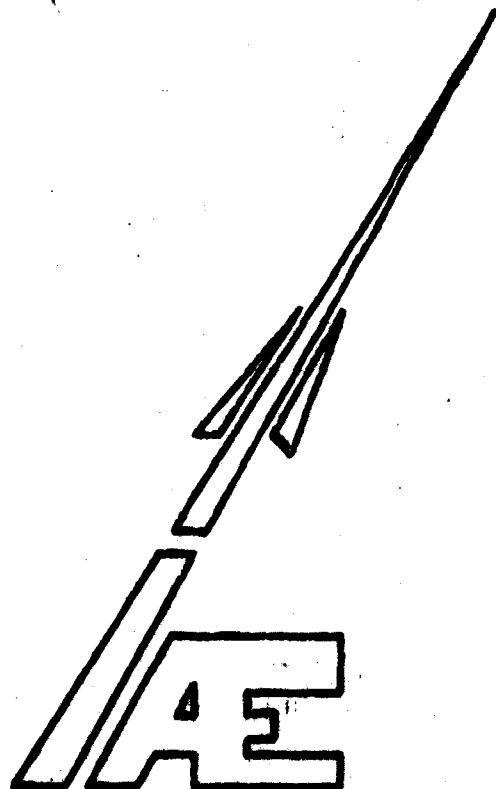
by

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(+) To be submitted to "Journal Physics B"

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THE VARIATIONAL CELLULAR METHOD"<sup>(†)</sup>

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ABSTRACT

Variational Cellular Method calculations for F<sub>2</sub> have been carried out at several internuclear distances. The ground and excited state potential curves are presented. The overall agreement between the VCM results and ab initio calculations is fairly good. (author)

RESUMO

O Método Celular Variacional foi aplicado à molécula F<sub>2</sub> para diversas distâncias interatômicas. As curvas de potencial para os estados fundamental e excitado são apresentadas. De uma maneira geral o acordo entre os resultados dos cálculos do MCV e do "ab initio" é razoavelmente bom. (autor)

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The  ${}^1\Sigma_g^+$  ground state and first excited states,  ${}^1\Pi_u$  and  ${}^1\Pi_g$ , of  $F_2$  have been investigated as a function of the internuclear distance by the recently developed Variational Cellular Method (VCM) (Ferreira and Leite 1978a). Self-consistent potential energy curve for the  ${}^1\Sigma_g^+$  excited state arising from the  $F^+({}^1S) + F^-({}^1S)$  ionic dissociation limit is also presented.

The theoretical formulation of VCM is already well established in the literature (Ferreira and Leite 1978b, 1979, Leite et al 1979). The method is based on the original Wigner-Seitz-Slater cellular theory (Wigner and Seitz 1933, Slater 1934, Leite et al 1975) where the boundary condition problem is reformulated through a variational principle. According to the VCM, the molecular space is partitioned into cells, and the wave function within each cell is expanded in terms of spherical harmonics,  $Y_{\ell m}$ , and solutions of the radial Schrödinger equation,  $R_{\ell}(r)$ , for a spherical cellular potential and energy eigenvalue  $\epsilon_0$ . Therefore, within the cell  $i$ , one has

$$\psi_i(\vec{r}) = \sum_{\lambda} A_{i\lambda} f_{i\lambda}(\vec{r}) = \sum_{\ell m} A_{i,\ell m} R_{\ell}^{i,0}(r) Y_{\ell m}(\vec{r}_i) \quad (1)$$

The VCM secular equation can be written as

$$\sum_{i'\lambda'} \langle i\lambda | H | i'\lambda' \rangle A_{i'\lambda'} = 0 \quad (2)$$

where the matrix  $H$  is obtained by performing surface integrations on the cell boundaries,

$$\langle i\lambda | H | i'\lambda' \rangle = (1 - \delta_{ii'}) \int dS_{ii'} (\partial n_{i\lambda}^* f_{i'\lambda'} + f_{i\lambda}^* \partial n_{i'\lambda'}) \quad (3)$$

The one electron energies are found by searching the values of  $\epsilon_0$  for which the secular equation has nontrivial solutions. The one-electron exchange correlation interactions are treated within the framework of the  $X_{\alpha}$  approximation (Slater 1974). We adopt here the same procedure to divide the molecular space into cells that has been used in the previous applications of VCM (Brescansin et al 1979). The cellular expansions had enough spherical harmonic components to ensure the convergence of the energy eigenvalues. Due to its variational character the method shows very fast convergence.

In Figure 1 the potential energy curves

Insert Figure 1

for  $F_2$  are shown. The  ${}^1\Sigma_g^+$  ground state corresponds to a closed shell molecular configuration  $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g)^4$ . The  ${}^1\Pi_u$  and  ${}^1\Pi_g$  states were obtained by transferring one electron from the  $\pi$  states to the  $3\sigma_u$  state. VCM leads to an attractive potential curve for the  ${}^1\Sigma_g^+$  ground state with the following values for the spectroscopic constants (experimental values in parentheses): Equilibrium distance,  $R_e = 1.41\text{\AA}$  (1.41193\AA); dissociation energy,  $D_e = 2.90\text{eV}$  (1.66eV) and vibrational frequency,  $\omega_e = 906\text{cm}^{-1}$  (916.64 $\text{cm}^{-1}$ ) (Huber and Herzberg 1979). The  ${}^1\Pi_u$  and  ${}^1\Pi_g$  excited singlet states correspond both to repulsive potential curves, with the  ${}^1\Pi_u$  curve lying below the  ${}^1\Pi_g$  curve, in agreement with ab initio calculations. The vertical excitation energies  ${}^1\Pi_u \cdot {}^1\Sigma_g^+$  and  ${}^1\Pi_g \cdot {}^1\Sigma_g^+$ , according to VCM, are 4.02eV and 7.14eV, respectively. The first value corresponds to the only dipole-allowed transition, responsible for the observed maximum at 4.80eV in the  $F_2$  absorption spectrum (Colbourn et al 1976). The ab initio results are 4.64eV and 7.56eV, respectively (Cartwright and Hay 1979).

In order to construct the cells to analyse the  ${}^1\Sigma_g^+$  ionic excited state, we are taking into account the different size of the ions. In words, the plane which delimitates the two atomic cells is placed in such away that divides the internuclear distance proportionally to the ionic radii (Brescansin et al 1979).

In Table 1 the calculated total energy, E, for the  ${}^1\Sigma_g^+$  ionic singlet state, as a function of the internuclear distance is shown. The  ${}^1\Sigma_g^+$  state

Insert Table 1

exhibits an attractive  $1/R$  interaction for large R with a minimum at 2.11\AA. This value is in agreement with the ab initio value,  $\sim 2.1\text{\AA}$  (Hay and Cartwright 1976). The calculated energy at 2.11\AA is 15.05eV relative to the ground state energy minimum. This value is also in excellent agreement with the result obtained from ab initio calculations,  $\sim 15\text{eV}$ .

The calculations reported in this letter were undertaken in order to detect, for the just time, the potential and limitations of the VCM to describe

the electronic structure of molecular excited states. Although the overall agreement of the results with ab initio calculations seems to be good, it is worth mentioning that the application of VCM to ionic bonding at small internuclear distances met with some difficulties. The discrepancies between the results presented here for the ground state  $F_2$  and our previous values are due to the more complete basis set used in this calculation (Brescansin et al 1979).

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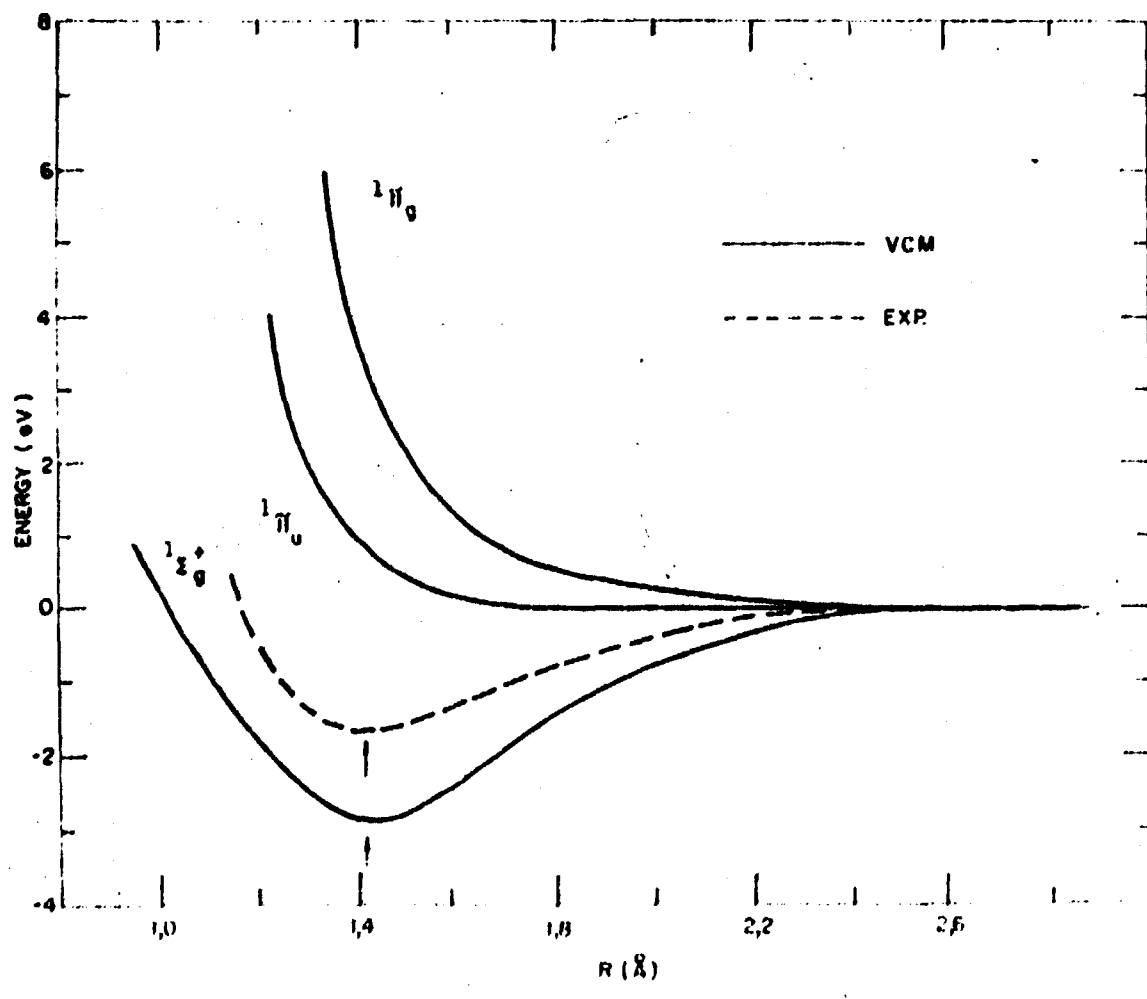
FIGURE CAPTION

FIGURE 1 - Potential energy curves for the  ${}^1\Sigma_g^+$  ground state and the  ${}^1\Pi_u$  and  ${}^1\Pi_g$  electronic excited states of  $F_2$ . The experimental ground state curve was obtained by Colbourn et al (1976). The theoretical curves have been normalized to the experimental dissociation limit.

TABLE 1

Calculated VCM energies,  $E$ , of the  ${}^1\Sigma_R^+$  ionic state of  $F_2$  as a function of the internuclear distance,  $R$ . All energies are relative to the Hartree-Fock ground state dissociation limit,  $-397.6371\text{Ry}$  (Clementi 1965)

$R(\text{\AA})$	$E(\text{ev})$	$R(\text{\AA})$	$E(\text{ev})$
2.060	12.5891	2.500	15.4361
2.164	12.5106	2.750	15.9599
2.169	12.5882	3.000	16.3962
2.179	12.6766	3.500	17.0819
2.201	12.9091	4.000	17.5962
2.254	13.0846	5.000	18.3162





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