LETTER TO THE EDITOR

Theoretical study of the F₂ molecule using the variational cellular method

Marco A P Lima†, Jose R Leite‡ and Adalberto Fazzio‡
† Divisão de Estudos Avançados, Instituto de Atividades Espaciais, Centro Técnico
Aerospacial, 12200 São José dos Campos, SP, Brasil
‡ Instituto de Física, Universidade de São Paulo, CP 20516, São Paulo, SP, Brasil

Received 9 April 1981

Abstract. Variational cellular method (VCM) calculations for F₂ 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.

Theoretical formulation of the VCM is already well established in the literature
(Ferreira and Leite 1978a). The self-consistent potential energy curve
for the 1Σ⁺ excited state arising from the F⁺(1S) + F⁻(1S) ionic dissociation limit is also
presented.

The theoretical formulation of the 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
wavefunction within each cell is expanded in terms of spherical harmonics, \( Y_{lm} \),
and solutions of the radial Schrödinger equation, \( R_{l}(r) \), for a spherical cellular potential and
energy eigenvalue \( \varepsilon_{0} \). Therefore, within the cell \( i \), one has

\[
\psi_{i}(r) = \sum_{\lambda} A_{i\lambda} f_{i\lambda}(r) = \sum_{lm} A_{i,lm} R_{l}(r) Y_{lm}(\hat{r}).
\]

The VCM secular equation can be written as

\[
\sum_{i'\lambda'} \langle i\lambda | H | i'\lambda' \rangle A_{i',\lambda'} = 0
\]

where the matrix \( H \) is obtained by performing surface integrations on the cell
boundaries,

\[
\langle i\lambda | H | i'\lambda' \rangle = (1 - \delta_{ii'}) \int dS_{il} (\partial_{n} f_{il} \partial_{n} f_{i'\lambda'} + f_{i\lambda} \partial_{n} f_{il} \partial_{n} f_{i'\lambda'}).
\]
divide the molecular space into cells (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 for F_2 are shown.

![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 normalised to the experimental dissociation limit. The arrows show the equilibrium internuclear distance. ---, VCM; ----, experiment.](image)

The $^1\Sigma_g^+$ ground state corresponds to a closed-shell molecular configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(3\sigma_u)^4(1\pi_u)^4$. The $^1\Pi_u$ and $^1\Pi_g$ states were obtained by transferring one electron from the $1\pi_u$ states to the $3\sigma_u$ state. The 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, $R_e = 1.41$ Å (1.41193 Å); dissociation energy, $D_e = 2.90$ eV (1.66 eV) and vibrational frequency, $\omega_e = 906$ cm$^{-1}$ (916.64 cm$^{-1}$) (Huber and Herzberg 1979). The $^1\Pi_u$ and $^1\Pi_g$ excited singlet states both correspond 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 $^1\Pi_u \rightarrow ^1\Sigma_g^+$ and $^1\Pi_g \rightarrow ^1\Sigma_g^+$, according to the VCM, are 4.02 and 7.14 eV, respectively. The first value corresponds to the only dipole-allowed transition, responsible for the observed maximum at 4.80 eV in the F_2 absorption spectrum (Colbourn et al 1976). The ab initio results are 4.64 and 7.56 eV, respectively (Cartwright and Hay 1979).

In order to construct the cells to analyse the $^1\Sigma_g^+$ ionic excited state, we take into account the different size of the ions. In other words, the plane which delimits the two atomic cells is placed in such a way that it divides the internuclear distance in proportional to the ionic radii (Brescansin et al 1979).

In table 1 the calculated total energy, $E$, for the $^1\Sigma_g^+$ ionic singlet state is shown as a function of the internuclear distance. The $^1\Sigma_g^+$ state exhibits an attractive $1/R$ interaction for large $R$ with a minimum at 2.11 Å. This value is in agreement with the ab
Table 1. Calculated VCM energies, $E$, of the $^1\Sigma_g^+$ 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, $-397.6371$ Ryd (Clementi 1965).

<table>
<thead>
<tr>
<th>$R$(Å)</th>
<th>$E$(eV)</th>
<th>$R$(Å)</th>
<th>$E$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.060</td>
<td>12.5891</td>
<td>2.500</td>
<td>15.4361</td>
</tr>
<tr>
<td>2.164</td>
<td>12.5106</td>
<td>2.750</td>
<td>15.9599</td>
</tr>
<tr>
<td>2.169</td>
<td>12.5882</td>
<td>3.000</td>
<td>16.3962</td>
</tr>
<tr>
<td>2.179</td>
<td>12.6766</td>
<td>3.500</td>
<td>17.0819</td>
</tr>
<tr>
<td>2.201</td>
<td>12.9091</td>
<td>4.000</td>
<td>17.5962</td>
</tr>
<tr>
<td>2.254</td>
<td>13.0846</td>
<td>5.000</td>
<td>18.3162</td>
</tr>
</tbody>
</table>

The calculated energy at 2.11 Å is 15.05 eV relative to the ground state energy minimum. This value is also in excellent agreement with the result obtained from ab initio calculations, about 15 eV.

The calculations reported in this letter were undertaken in order to detect, for the first time, the potential and limitations of the VCM in describing 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).

We would like to thank Professor Abel Rosato for helpful discussions and a critical reading of the manuscript.

References

Clementi E 1965 Table of Atomic Functions (IBM J. Res. Dev. Suppl. 9 1–6)
Slater J C 1934 Phys. Rev. 45 794–801
Wigner E and Seitz F 1933 Phys. Rev. 43 804–10