Calculation of the Ground and Excited States of the Ne_2 Molecule by the Variational Cellular Method

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The potential curves for the ground $^1\Sigma_g^+$ and for the first singlet excited state $^1\Sigma_u^+$ of the Ne_2 molecule are determined by the Variational Cellular Method. From these curves some spectroscopical constants are obtained. Ionization energies of the excited state $^1C_u^+$ are calculated.

As curvas de potencial para o estado fundamental $^1\Sigma_g^+$ e para o primeiro estado excitado $^1\Sigma_u^+$ da molécula do Ne, foram determinadas pelo Método Celular Variacional. A partir destas curvas algumas constantes espectroscópicas foram obtidas. As energias de ionização do estado excitado $^1\Sigma_u^+$ foram calculadas.

1. INTRODUCTION

The recently proposed Variational Cellular Method (VCM)[1,2] has been shown to be an efficient method for the description of the electro-

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nic structure of covalent diatomic molecules[3,4]. The purpose of this paper is to examine how this method works for diatomic molecule formed from the noble gases, where the interaction is weak and of the van der Waals type. Initially, the potential curves for the ground state $^1\Sigma_g^+$ and for the first singlet excited state $^1\Sigma_u^+$ of the Ne, rnolecule were calculated. Then the results obtained for these curves and the spectroscopical constants derived from them were compared witli the available experimental results and with other theoretical methods such as MS-$X\alpha$, Hartree-Fock and "ab initio" methods.

Some preliminary results of this calculation were presented before[5].

2. DETAILS OF THE CALCULATION

The VCM is a variational version of the Cellular Method originally proposed by Wigner-Seitz-Slater[6,8] For crystals. It is bases on the partition of the molecular space into no-overlapping cells which surround the atoms of the molecule. The cells in principle can have any shape, but to facilitate the calculations, they are taken as spheres. Inside the cells the one-electron potential is constructed as a spherical symmetric one from a muffin-tin charge density. Figure 1 shows the partition of the molecular space used in this work.

Fig.1 - Partition of the molecular space. Points denote the nuclei sites. R is the internuclear distance. Heavy drawn circunferences are the inscribed spheres.
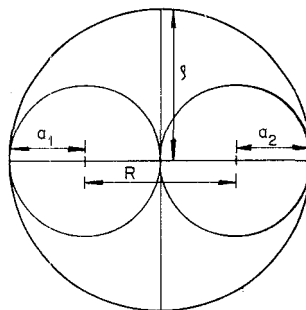
According to the general formulation of the VCM[2] the position of the plane surface that separates the cells and the parameter ρ in Fig.1, can be chosen at will. Since it was showed[3] that for homonuclear molecule the

dissociation energy is a minimum when $\rho \approx R$, where R is the internuclear distance, that is, $R = a_1 + a_2$ and a_i is proportional to the covalent radius of the atom i, in this work we took $\rho = R$.

Inside the cell i, the electronic wave function is expanded in spherical harmonics

$$\psi_i(\vec{r}) = \sum_\lambda A_{i\lambda} f_{i\lambda}(\vec{r}) \tag{1}$$

where

$$f_{i\lambda}(\vec{r}) = R_\ell^{\varepsilon_0}(\vec{r}_i) Y_\lambda(\hat{r}_i) \tag{2}$$

and λ denotes the angular momentum pair (ℓ, m) and $R_R^{\varepsilon_0}$ is the solution of the radial Schrödinger equation for the energy ε_0. From the well known variational expression for the energy[1,2]

$$\varepsilon \sum_i \int d\Omega \psi_i^* \psi_i = \sum_i \int d\Omega \psi_i^* (-\nabla^2 + V)\psi_i + \frac{1}{2} \sum_{S_{ij}} \int dS (\psi_i - \psi_j) \cdot$$

$$\cdot (\partial_n \psi_j^* - \partial_n \psi_i^*) + \frac{1}{2} \sum_{S_{ij}} \int dS (\psi_i^* + \psi_j^*)(\partial_n \psi_j + \partial_n \psi_i) \tag{3}$$

one obtains the secular equation

$$\sum_{i'\lambda'} <i\lambda|H|i'\lambda'> A_{i'\lambda'} = 0 \tag{4}$$

where the matrix elements of the Hermitian matrix H are given by

$$<i\lambda|H|i'\lambda'> \equiv (1-\delta_{ii'}) \int dS_{ii'} (f_{i'\lambda'} \partial_n f_{i\lambda}^* + f_{i\lambda}^* \partial_n f_{i'\lambda'}) \tag{5}$$

The integral is performed on the surfaces separating the cells and ∂_n denotes the outward normal derivative. The variational expression adopted for the electronic energy is of the form

$$E|\psi_i^*, \psi_i, n, v, c| = \sum_i K|\psi_i^*, \psi_i| + U|n-p, c| - S|p| + E_x|n| + \int v(p-n) \tag{6}$$

where a detailed explanation of each term is presented in Reference 9.

To begin the calculation, one assumes an expression for the electronic charge density in the form of a sum of Yukawa terms[10]. Then, the exchange-correlation contribution to the energy of the system is calculated according to the Slater Xa approximation. The Coulomb potential, which satisfies Poisson's equation, and consequently makes the electrostatic energy functional an extreme, can be calculated. Next the one-electron potential is obtained in all points of the molecular space. The radial Schrödinger equation can be solved numerically, and the matrix elrments $\langle i\lambda|H|i'\lambda'\rangle$ of Eq. (5) can be constructed. The values of the energy for which the secular equation, Eq. (4), has a nontrivial solution are the molecular orbital energies.

3. RESULTS

The ground state of Ne_2 has the following molecular configuration

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(3\sigma_u)^2(1\pi_g)^4(1\pi_u)^4 - {}^1\Sigma_g^+$$

and it dissociates into two ground states $Ne(2p^6)$ atoms with Hartree-Fock total energy - 514.1880 Ry [11]. The first singlet excitate state, ${}^1\Sigma_u^+$, which dissociates into Ne $(2p^5,3s)$ arid Ne $(2p^6)$ in the separated atom limit, can be formed by transfering one electron form the $3\sigma_u$ orbital to the $4\sigma_g$ orbital. The calculated points of the potential curves for these states are given in Table 1, and the corresponding curves are shown in Figure 2.

Table 1, or Figure 2, also present the results obtained by using other methods, such as MS-Xa, LCAO and CI, where the zero value of the energy was set at the energy of the separated atom limit. One interesting feature about Fig. 2 is the almost complete agreement between the results for the VCM and the MS method. In general, there are discrepancies between these two methods mainly due to the well known error introduced in the calculation by adopting the rnuffin-tin approximation for the one-electron potential, which is inherent in the MS method[3]. In the Ne_2 case, our calculations show that most of the molecular charge are con-

Table 1 - Calculated points of the potential curves for the ground state and first excited state of the Ne, molecule. The energies are in Ry and are relative to the separated-atom limit.[a]

$R(a_0)$	$^1\Sigma_g^+$			$^1\Sigma_u^+$	
	VCM[b]	MS-$X\alpha$	LCAO[d]	VCM[b]	CI[e]
3.0	0.660	0.666	0.192		1.23060
3.25					1.19804
3.5	0.290	0.281	0.060		1.19740
3.75					1.20858
4.0	0.144	0.143	0.019		1.22252
4.3				1.147	
4.5	0.076	0.091		1.113	1.23828
4.55				1.110	
4.6				1.110	
4.65				1.111	
4.7				1.111	
4.8				1.112	
5.0	0.044	0.072	0.003	1.113	1.24112
5.2	0.032				
5.5		0.064	0.002	1.114	1.24212
5.8	0.018				
6.0	0.014	0.061	0.002	1.115	1.24134
6.22	0.012				
6.4	0.010				
6.5			0.002	1.115	
6.6	0.008				
6.7	0.007				
6.9	0.006				
7.3	0.004				
7.6	0.004				

[a] The energy for the separated atom is - 514.188 Ry.[11]. [b] This work. [c] Reference 12. [d] Reference 13. [e] Reference 14.
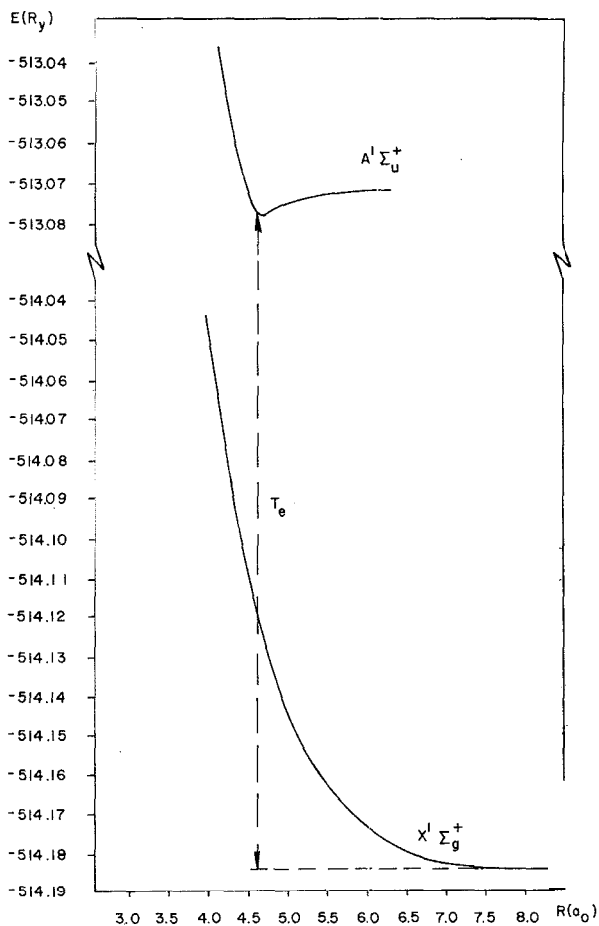
Fig.2 - Potential energy curves for the ground state $^1\Sigma_g^+$ and first sin-glet excited state $^1\Sigma_u^+$ of Ne_2 molecule.

centrated inside the inscribed sphere of Fig. 1, and so this approxima-tion to the potential is not very important.

The spectroscopical constant related to the excited state $^1\Sigma_u^+$ are presented in Table 2. In this table, T_e is the energy of the $^1\Sigma_u^+$ state, at the equilibrium separation, relative to the ground state $^1\Sigma_g^+$ for the separated atom limit.

The repulsive interaction of the type $A\exp(-br)$, which takes place for small internuciear distance, can be uniquelly determined by

Table 2 - Spectroscopic constants of the excited state $^1\Sigma^+$.

	VCM[a]	CI[b]	EXP.[c]
T_e (cm^{-1})	121374	131247	133800
ω_e (cm^{-1})	495[d]	526[d]	176
R_e (Å)	2.4[d]	1.80[d] 1.79[b]	-
D_e (ev)	0.1[d]	0.56[d] 0.57[b]	

a) This work. b) Reference 14. c) Reference 15. d) These results were obtained by a parabolic fit to the calculated points near the minimum of the potential curve.

looking for the Born-Mayer parameters[16] $\acute{A}$ and b which give the best fit of theexporiential curve to the VCM curve for thestate $^1\Sigma_g^+$. Table 3 presents the values of these parameters obtained by a least square fitting to the VCM curve and to other curves obtained by other methods

Table 3 - Born-Mayer parameters for the state $^1\Sigma_g^+$ of the Ne, rnolecule[a].

	VCM[b]	MS-$X\alpha$[c]	LCAO[d]	Statistical[e]	EXP[f]
A(Ry)	47	32.5	198	202.8	337
$b(a_0^{-1})$	1.44	1.33	2.31	2.327	2.44
ΔR[g]	3.0-4.5	3.0-4.5	3.0-4.0	1.0-4.0	3.0-4.5

a) These results were obtained by a least square fitting. b) This work. c) Reference 12. d) Reference 13. e) Reference 17. f) Reference 18. g) Region of R where the fitting is performed.

The theoretical ionization spectrum of the bound excited state $^1\Sigma_u^+$ of the Ne_2 molecule was computed using two different procedures: one of these is by considering the total energy differences between the neutral and ioniied atoms and the other one is by the Slater transition-state concept[19]. Throuhg Table 4 we can see that these two rnethods give almost identical results for the ionization energy, as it should.

Table 4 - Ionization energies of the excited state $^1\Sigma_u^+$ of the rnolecule Ne_n in eV.

	VCM[a]	VCM[b]
$4\sigma_g$	3.36	3.65
$3\sigma_u$	24.74	24.86
$1\pi_g$	24.86	24.94
$1\pi_u$	24.90	24.99
$3\sigma_g$	24.97	24.81

[a] Calculated according to the difference between total energies. The internuclear distance is $R_e = 4.55 \, a,$.

[b] Calculated according to the Slater tranrition-state concept.

To conclude we can say that, even though no attempt was made to describe precisely the binding of the ground state, the VCM worked very well for the Ne_2 molecule. The method is simple, fast and the results are good. We feel that any affort dispensed in the sense of generalizing it to apply for polyatomic systems will be worthwhile.

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