Revista Brasileira de Física, Vol. 14, nº 1, 1984

Study of the Cl_2 Molecule by the Variational Cellular Method

ABEL ROSATO*

Departamento de Física do ITA, Instituto de Estudos Avançados, CTA, 12200, São José dos Campos, SP, Brasil

and

MARCO A.P. LIMA

Instituto de Estudos Avançados, CTA, 12200, São José dos Campos, SP, Brasil

Recebido em 18 de abril de 1984

Abstract A self-consistent calculation based on the Variational Cellular Method is performed on the Cl_2 molecule. The results obtained for the ground state potential curve and the first excited state, the dissociation energy, the molecular orbital energies and other related parameters are compared with other methods of calculations and with available data and the agreement is satisfatory.

1. INTRODUCTION

Once the Variational Cellular Method (VCM)[1,2] has proved to be a satisfactory method for calculating potential curves for the ground state and excited states of diatomic molecules, it began to be used in two different lines of calculation - the halogen and the ven der Waals diatomic molecules. The excellent results obtained for the first elements of each family, namely F_2[3] and Ne_2[4], prompt us to continue the work toward heavier elements in these families. Chlorine molecule was the natural choice for the next application of the VCM, and it seems to us an important one, due to the scarcity of calculations in the literature envolving this molecule.

Some advantage of the method, namely the removal of the constant part of the muffin-tin region, and the freedom to divide the space into cells of arbitrary shape, makes it particularly suited for calcuilations envolving diatomic molecules. Self consistency in the one-electron potential is reached with relative facility and the amount of computer time needed to establish the potential curve for several internuclear distances as is explained later, is not so big.

Some efforts have been made on the study of the Cl_2 molecule. Douglas *et al*[5] have obtained experimental values for some spectroscopic constants; a molecular orbital self-consistent-field calculation

---

*Work partially supported by FINEP (Brazilian Government Agency).

determined, among other things, the potential curves for the ground state[6], and for some excited states[7] and orbital energies[8]; a total energy calculation at the equilibrium separation and related one electron properties were performed by Williams and Amos[6] using a 922-term valence shell configuration interaction. Using this same procedure, Heil et al[9] calculated the valence bond potential energy as a function of the internuclear separation and the spectroscopic constants of the Cl_2 molecule.

2. BASIC THEORY

Details of the Variational Cellular Method are presented in References 1,2,10. The basic idea of the method consists on dividing the molecular space into cells of arbitrary shape, one cell for each atom of the molecule, for convenience taken as spheres centered at the nuclei, with radius that should be chosen as proportional to the covalent radius of the atoms. An outer cell, encircling the atomic cells, extends from these cells to infinite. The cells so defined fill all space and there is no overlap between the atomic cells because theyhave a plane surface of contact. For homonuclear molecules the cells are constructed like in Fig. 1 where $a_1 = a_2 = a$ and $\rho = 2a$.

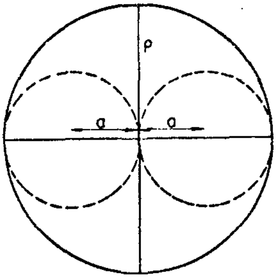

Fig.1 - The cells used for the Cl_2 molecule are the half spheres drawn in hard lines. The spheres drawn In dashed lines are the inscribed spheres.

Within each atomic cell an inscribed sphere is drawn and the region inside it is the region where the charge density is considered as spherically symmetric. In the region between the Inscribed sphere and the corresponding atomic cell the averaged charge density is made constant. The value of this constant depends on the cell.

To begin the calculation, an expression for the electronic charge density in the form of a sum of Yukawa terms is assumed[12]. Then the exchange-correlation contribution to the energy of the system is calculated according to the scheme of the Slater $X\alpha$ approximation[13].

The Coulomb potential, which satisfies Poisson's equation and consequently mekes the electrostatic energy functional an extreme, can be calculated[10]. With the starting charge density and the Coulomb potential, the electrostatic energy of the system is calculated, and the one-electron potential can be obtained. Next, the matrix elements $H_{i\lambda,r3\lambda'}$ of Reference 1 are constructed, since the radial Schrödinger equation can be formed and its solution, the radial wave function, can be obtained by numerical methods. The energy eigenvalues ε_i, or molecular orbital energies, are the values of ε for which the secular equation, deduced from the matrix H has a nontrivial solution. In this way, all terms necessary to calculate the total electronic energy of the system are known and it can be determined for each value of the internuclear distance R, in a self-consistent way.

3. RESULTS

In this section we present the results of the VCM calculation for the Cl_2 molecule.

A. Ground State

The electron configuration of Cl_2 in its ground state is

$$KKLL(4\sigma_g)^2(4\sigma_u)^2(5\sigma_g)^2(2\pi_u)^4(2\pi_g)^4 - {}^1\Sigma_g^+$$

In the calculation of the potential curve the molecular orbitals coming from the atomic states ls, 2s and $2p$ were considered as frozen during the iterative process. Only those molecular states coming from the valence orbitals $3s$ and $3p$ were allowed to vary during the self-consistent process. This approximation, the frozen core approximation, saves a lot of computer time and its effect on the molecular orbital energies is very small, as can be seen through Table 1. This Table also presents the results of an "*ab initio*" effective core potential calculation[14] for comparison.

The calculated potential curve for the ground state of the Cl_2 molecule is given in Figure 1 and in Table 2 the numerical results are presented.

The bases set used for expansion of the molecular orbitals was the same for all values of the internuclear distance R, and for the

Table 1 - Comparison of the molecular orbital energies at the equilibrium separation for valence-electron and all-electron calculations. All energies are in Ry. [a]For R_e = 3.90 a,; [b]Reference 14.

	VCM[a]		AB INITIO[b]	
	valence-electron	all-electron	valence-electron	all-electron
$4\sigma_g$	- 1.60330	- 1.60395	- 2.40152	- 2.45310
$4\sigma_u$	- 1.42209	- 1.42277	- 2.05804	- 2.04434
$5\sigma_g$	- .74672	- .74705	- 1.25410	- 1.24292
$2\pi_u$	- .74385	- .74408	- 1.13634	- 1.14994
$2\pi_g$	- .63067	- .63087	- .90436	- .90780

Table 2 - Calculated points of the potential curve for thegroundstate of the Cl_2 molecule (valence-electron calçulation)

$R(a_0)$	E(Ry)	R(a,)	E(Ry)
2.90	- 59.18546	4.00	- 59.96335
3.40	- 59.89245	4.20	- 59.95808
3.45	- 59.90447	4.50	- 59.93788
3.50	- 59.91858	5.00	- 59.88054
3.60	- 59.94223	5.50	- 59.83269
3.70	- 59.95986	6.40	- 59.78134
3.80	- 59.96232	7.00	- 59.76331
3.90	- 59.96446		

five valence molecular orbitals of interest, ν_{max} did not exceed the value 3 in each cell. To get a convergente of the order of 10^{-5} in the one-electron potential a number of approximately 20 iterations was necessary for any value of R. The computer time needed to perform one iteration is about 70 sec in a Cyber 170/730. The internucleardistance R_e at which the potential curve is a minimum occurs at R_e = 3.90 a,. For this distance we also performed the calculation taking intoaccount all electrons of the system, and the result obtained for the total energy was - 1 838.159 Ry. The largest internuclear distance considered was R = 7.0 a_0, and for this value of R the total energy in a all-electron calculation was - 1 837.958 Ry. It is interesting to compare this value of the energy with the Hartree-Fock calculation, as performed by Clementi[15], which showed that the Cl_2 molecule dissociates into two neutral ^2P etoms at infinite separation with total energy equal to - 1 837.927 Ry.

The dissociation energy D_e, which is defined as the difference between the total VCM energy of the molecule and that of the separated atoms, has the value 3.15 eV in our calculation, while the experimental result is 2.51 eV[7].

Once one has the potential curve, one can determine the vibrational frequency ω_e of the molecule by fitting a parabola to the calculated points nearest to the minimum of the potential curve. The result obtained using this procedure is shown in Table 3.

Table 3 -- Characteristics constants of the Cl_2 molecule in the ground state. [a]Reference 5. [b]Reference 7. [c]Reference 8. [d]Reference 14. [e]Reference 16. [f]Reference 6.

	VCM	EXP.	PREVIOUS WORK		
$R_e(a_0)$	3.90	3.757[a]	3.8[b]	3.7619[c]	3.81[d]
D_e(eV)	3.15	2.5139[a]	0.87[b]	2.475[e]	1.918[d]
ω_e(cm^{-1})	490	559.71[a]	577[b]	564.9[e]	603.7[c]
E(Ry)	-1838.159	-1837.960[b]	-1837.980[c]	-1965.659[d]	-1838.228[f]

This table also presents the characteristic constants of the Cln molecule as provided by the VCM and by other methods, where R_e is the equilibrium internuclear separation, D_e is the dissociation energy, ω_e the vibrational frequency and E the total energy at the equilibrium sepuration.

B. Excited State

The excited state of the Cl_2 molecule that we have studied in this paper is the state ${}^1\Pi_u$. Table 1 indicates that this state can be simply obtained by transferring one electron from the $2\pi_g$ orbital to the $5\sigma_u$ orbital, and it corresponds to the following valence electron configuration.

$$(4\sigma_g)^2(4\sigma_u)^2(2\pi_u)^4(5\sigma_g)^2(2\pi_g)^3(5\sigma_u) \; - \; {}^1\Pi_u$$

The basis set used for expansion of the molecular orbitals was the same as used for the ground state and the convergence in the one-electron potential was approximately the same. The frozen-core approximation was used for all values of R (except for $R = R_e$ where we performed an all-electron calculation) and only the six valence orbitals above were calculated. The numerical results are presented in Table 4 and Figure 2 shows these results.

Table 4 - Celculated points of the potential curve for the excited state ${}^1\Pi_u$ of the Cl_2 molecule.

$R(a_0)$	E(Ry)	$R(a_0)$	E(Ry)
3.40	- 59.68761	4.20	- 59.87683
3.50	- 59.73831	4.50	- 59.88416
3.60	- 59.78696	4.70	- 59.87157
3.70	- 59.81650	5.00	- 59.84517
3.90	- 59.85618		
4.00	- 59.87048		

The internuclear distance at the equilibrium position is $R_e = 4.50$ a, which is in good agreement with other previous work as can be seen in the Table 5. The vibrational frequency was determined by a parabolic fit to the calculated points near the minimum of the potential curve, in a way analogous to the ground state case. The result obtained for this quantity was 382 m-.'.

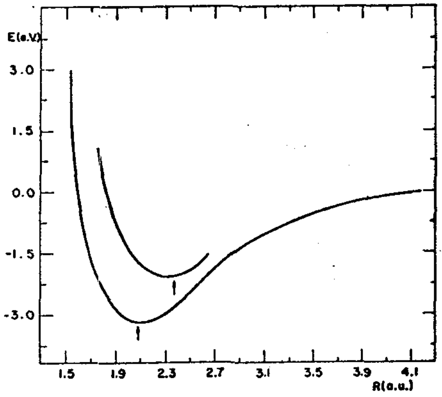

Fig.2 - Potential energy curves of the ground state and first excited state of Cl_2. The arrows indicate the equilibrium positions.

Table 5 - Characteristic constants of the Cl_2 molecule In the excited state. [a]Reference 5. [b]Reference 16. [c]Reference 17.

	VCM	EXP.	PREVIOUS WORK	
$R_e(a_0)$	4.50	4.52[a]	4.67[b]	
ω (cm^{-1})	382	261.9[a]	239.4[a]	258.0[c]
E(Ry)	- 1838.078	-	-	-

Table 5 presents some characteristic constants of the excited state $^1\Pi_u$ of the Cl_2 molecule and compares them with other results. Since our calculation does not involve spin-polarizãtion nor the coupling of spin with the orbital motion, our result should be compared to the Π_{0+u} state whlch is the excited state studled in the previous works mentioned in Table 5. The last line of that Table is the total energy of the molecular excited state at the equilibrium separatlon, obtained when one performs an all-electron calculation. Our exclted state curve, besides belng a little bit too curved near the equilibrium positlon overestimates the molecular attractlon. Our calculatlon gives the value 8888 cm^{-1} for the dlstance between the minimum of the two curves $^1\Sigma_g^+$ and $^1\Pi_u$ while the experimental result Is 18310.5 cm^{-1} [18]. One possible cause of thls discrepancy could be the basis set used to represent the molecular orbitals of the excited state. While this set gives satisfactory results for the ground state curve it may not be the more adequated one for state $^1\Pi_u$.

C. Ionization Energies

One way to obtain the ionization energy of a given state is to consider it as the difference between the total energies of the system in the ground state and in the ionic state with one electron removed from the state in consideration. Another way of doing it is to consider the Slater transition-state concept[18].

We performed the calculation of the ionízation energy taking into consideration these two possibilities. The results are shown in the first two columns of Table 6.

Table 6 - Ionization energies of the ground stete of Cl_2 molecule in eV.

[a] Ionization energies calculated according to the difference between total energies. The internuclear distance is R_e = 3.90 a_o.

[b] Ionization energies calculated according to Slater transition-state concept.

[c] See Ref. 19.

[d] See Ref. 8. The internuclear distance is R_e = 3.7619 a_o

	VCM[a]	VCM[b]	EXP[c]	HF[d]
$5\sigma_g$	12.92	14.16	15.94	16.15
$2\pi_u$	12.92	14.10	14.11	15.39
$2\pi_g$	11.42	12.65	11.50	11.87

The last column of Table 6 shows the dissociation energy calculated according to Koopman's theorem. Except for the $2\pi_u$ state the transition-state $X\alpha$ method is not more accurate than the Koopman's theorem results, as for as Cl_2 molecule is concerned. However it leads to a better result than the calculation based on the difference between total energies. The two methods give results which differ by 8 to 9% and this could be a measure of the neglected terms of third and higherorder derivatives which appear in eq. (7.4) of Reference 18.

We would like to thank Dr. José R. Leite for supplyingus with the computer programs necessary for the calculation and for many helpful discussions. Also our thanks to Dr. A. Fazzio and Dr. Fernando R. Ornellas for the critical reading of the manuscript.

REFERENCIES

1. Luiz G. Ferreira and José R. Leite, Phys.Rev.Lett. 40, 49 (1978).

2. Luiz G. Ferreira and José R. Leite, Phys.Rev. A 18, 335 (1978).

3. Marco A.P.Lima, José R.Leite and A.Fazzio, Rev.Bras.Fís.*12*,315(1982).

4. Alexandre D.Martins, MSc Thesis, ITA, 1981, unpublished.

5. A.E.Douglas, C.K.Moller and B.P.Stoicheff, Can.J.Phys. *41*, 1174 (1963).

6. J.H.Williams and R.D.Amos, Chem.Phys.Letters 70, 162 (1980).

7. T.L.Gilbert and Arnold C.Wahl, J.Chem.Phys.55, 5247 (1971).

8. Peter A.Straub, A.D. McLean, Theoret.Chim.Acta 32, 227 (1974). S. D.Peyerimhoff and R.J.Buenkee, Chem.Phys. *57*, 279 (1981).

9. Thimothy G. Heil, Stephen V. O'Neil and Henry F. Schaefer III.Chem. Phys.Letters 5, 253 (1970).

10. Luiz G. Ferreira and José R. Leite Phys. Rev. A 20, 689 (1979).

11. Luiz M. Brescansin, José R. Leite and Luiz G. Ferreira, J. Chem. Phys. 71, 4923 (1979).

12. Marco A.P. Lima and Luiz G. Ferreira, Phys. Rev. 22, 343 (1980).

13. J.C.Slater, *Quantum Theory* of *Molecules and Solids*, vol. 4 (McGraw--Hill, New York, 1974).

14. Luis R. Kahn, Paul Baybutt and Donald G. Truhlar, J.Chem. Phys. 65, 3826 (1976).

15. E.Clementi, IBM J.Res.Dev. 9, 2 (1965).

16. G. Herrberg, *Molecular Spectra and Molecular Structure*, vol. 1. *Spectra of Diatomic Molecules* (Van Nostrand, Princeton 1950).

17. P.Venkateswarlu and B.N.Khanna, Proc.Indian Acad. Sci. A 49, 117 (1959).

18. J.C.Slater, The *Calculation* of *Molecular Orbitals*, (John Wiley and Sons. Inc., 1979) p. 49.

19. D.C. Frost, C.A.McDowell and D.A.Vroon, J.Chem.Phys.*46*, 4255 (1967).

Resumo

Um cálculo autoconsciente baseado no Método Celular Variacional foi feito para a molécula Cl_2. Os resultados obtidos para a curva de potencial do estado fundamental e do primeiro estado excitado, a energia de dissociação, as energias dos orbitais moleculares, e outros parâmetros correlatos são comparados com outros métodos de cálculo e com dados experimentais disponíveis e o acordo é satisfatório.