

Semiempirical calculation of N₂ molecule structure

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SUMMARY

This work presents a semiempirical calculation of the electronic structure for the ground state of the N₂ molecule, to study an interesting case of Koopman's theorem application to ionization potential determination for this molecule. Valence orbital energies, force constant and vibration frequency are also determinate. It is an exercise to the implementation and tests of MOPAC package.

KEY WORDS: N₂, Semiempirical, Ionization Potential. MOPAC.

Cálculo semiempírico da estrutura da molécula N₂

RESUMO

Este trabalho apresenta um cálculo semiempírico da estrutura eletrônica do estado fundamental da molécula N₂, para o estudo de um caso interessante da aplicação do teorema de Koopman na determinação do potencial de ionização para esta molécula. As energias dos orbitais de valência, constante de força e frequência de vibração também foram determinados. Isto é um exercício para a implementação e testes do programa MOPAC.

DESCRITORES: N₂, Semiempírico, Potencial de Ionização, MOPAC.

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1. INTRODUCTION

It is well known (SZABO, A. and OSTLUND, N. S.,1982) an interesting case about the use of the Koopmans' theorem for evaluation of the ionization potential for N₂ molecule: when the Hartree-Fock calculation is performed with STO-3G basis, it predicts the 3σ_g orbital to be higher than 1π_u orbital, whereas the Hartree-Fock calculation with the better basis set for this molecule Near-HF-limit(CADE P. E. et al., 1966), it predicts 1π_u orbital to be the highest energy. Curiously, STO-3G calculation is in agreement with the experiment, but not the Near-HF-limit calculation.

Since semiempirical methods are parametrized for valence electrons descriptions, a semiempirical method is used to study this case.

2. HARTREE-FOCK REVIEW

The Hartree-Fock (LEVINE, I. N., 1975) method for atomic and molecular calculations is the best possible wave function calculation for one electron into spatial spin-orbital. The fundamental equations for a closed shell state of a n-electron system are:

$$F(1)\phi_i(1) = \varepsilon_i\phi_i(1) \quad , \text{ where} \quad (1)$$

$$F(1) = H_o(1) + \sum_j [2J_j(1) - K_j(1)] \quad , \text{ and} \quad (2)$$

$$H_o(1) = -(\hbar^2 / 2m)\nabla_1^2 - \sum_n Z_n e^2 / r_{1n} \quad (3)$$

$$J_j(1)\phi_i(1) = \phi_i(1) \int |\phi_j(2)|^2 e^2 / r_{12} dv_2 \quad (4)$$

$$K_j(1)\phi_i(1) = \phi_j(1) \int \phi_j^*(2)\phi_i(2)e^2 / r_{12} dv_2 \quad (5)$$

$F(1)$ is the Hartree-Fock operator for one-electron. $F(1)$ include $H_o(1)$ (core Hamiltonian), $J_j(1)$ (Coulomb repulsion) and $K_j(1)$ (Exchange interaction). The constant ε_i is the energy of the orbital $\phi_i(1)$. By the Koopmans' theorem, ε_i for the highest energy orbital of the system is the Ionization Potential. *Ab initio* calculation uses correct Fock operator whereas a semiempirical calculation uses parameters for the evaluations of the integrals (4) and (5), obtained from experimental data.

Several semiempirical methods, for example, PPP (Parise-Parr-Pople), CNDO(Complete Neglect Differential Overlap), MINDO (Modified Intermediate Neglect Differential Overlap), use a Hamiltonian that includes some repulsion terms. All these methods assume that valence electrons may be treated separately from the core electrons. Then, these methods are parametrized for valence electrons and may be accurate for valence orbital energies, dipole moments, ionization potentials, but not accurate for core energies.

3. CALCULATION REPORTS

All the calculations are performed using MOPAC (LOBANOV, V., 1996;DEWAR, M. J. S. and THIEL, W. J., 1977; STEWART, J. J. P., 1990) package, version 6.0 for Win95, after installation and test with the *formaldehyde* molecule, using MNDO calculation, as in TESTDATA section of the MOPAC Manual (STEWART, J. J. P., 1990).

In the first calculation, for ground $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 - ^1\Sigma_g^+$ state of molecule, a MNDO Hamiltonian was used, as implemented in MOPAC.

Table 1 sums up the results for valence orbital energies and other results for comparison. The Heat of Formation of molecule obtained in this calculation is 8.27666 Kcal/mol for interatomic equilibrium distance 1.103802 angstroms.

Table 1. Valence orbital energies (eV) for N₂ ground state molecule. R is the interatomic distance.

Orbital	MOPAC ^a R=2.082 au	MS ^b R=2.068 au	RHF ^c R=2.068 au	RHF ^d	VCM ^e R=2.1 au	Exp. ^f
$2\sigma_u$		-18.3	-21.2		-18.6	-18.6
$1\pi_u$	-16.2	-18.2	-16.8	-16.7	-16.7	-16.8
$3\sigma_g$	-14.9	-14.1	-17.3	-17.3	-13.0	-15.5

a) This work. MOPAC with MNDO calculation.

b) WEINBERGER, P. and KONOWALOW, D. (1973).

c) CADE, P. E. et al. (1966).

d) ERMLER, W. C. and McLEAN, A. D. (1980).

e) FERREIRA, L. G. and LEITE, J. R. (1979).

f) SIEGBAHN, K. et al. (1969).

Table 2 contains the results for Ionization Potential (I.P.).

Tabel 2. Koopmans' Ionization Potential (I.P.) for N₂ ground state molecule.

	MOPAC ^a	MS ^b	RHF ^c	RHF ^d	VCM ^e	Exp. ^f
I. P. (eV)	14.9	14.1	17.3	17.3	13.0	15.5

a) This work. MOPAC with MNDO calculation.

b) WEINBERGER, P. and KONOWALOW, D. (1973).

c) CADE, P. E. et al. (1966).

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In second calculation for the same configuration of the molecule, the input data file has been prepared with the specific format for thermometric calculations.

```
GEO-OK MINDO/3 FORCE SYMMETRY EIGINV PI +
MECI BONDS CHARGE=0 ROT=8 THERMO LARGE PRECISE
```

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N
N      1.103802
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Table 3 shows the results for some spectroscopy constants obtained and experimental values for comparison. In this calculation, the Zero-point energy ($h\nu_0/2$) given by MOPAC-MINDO/3 calculation is 3.53 Kcal/mol, whereas experimental value is 3.35 Kcal/mol (SZABO, A. and OSTLUND, N. S., 1982). In MOPAC calculations, Heat of Formation, force constant and vibration frequency are related to the values at 25 degree C. Generally in *ab initio* methods, energy calculations are related to the molecule in vacuum, without vibration at 0 Kelvin.

Table 3. Spectroscopy Constants for N₂ ground state molecule.

	K_e (mdyn/Å)	ν_e (cm ⁻¹)
MOPAC ^a	24.20	2421.9
Exp. ^b	22.94	2358.0

a) This work. MOPAC with MINDO/3 calculation.

b) BOURCIER, S. (1970).

4. FINAL REMARKS

The valence orbital energies obtained with MOPAC are in good agreement with the experimental values and show $3\sigma_g$ orbital as the highest energy, in opposite to the Near-HF-limit, that shows the $1\pi_u$ as the highest energy orbital.

Koopmans' Ionization Potential obtained with MOPAC for $3\sigma_g$ orbital is in agreement with the experimental value. Than the subject of this work was reached and showed a good performance of MOPAC program to valence electronic structure descriptions.

Two spectroscopy constants determinate with MOPAC, force constant k_e and vibration frequency ν_e are in agreement with the experiment with differences less than 0.1 %.

The utilization of the MOPAC program is easy and it is faster. The result obtained to Ionization Potential, related to the experimental value, is better than *ab initio* results. MINDO Hamiltonian privilege the binding energies calculation, where *ab initio* methods can fail. This version of MOPAC program installed, have not implemented the routine to potential curves calculation and the binding energy not might be obtained.

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