Semiempirical calculation of $\text{N}_2$ molecule structure

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SUMMARY

This work presents a semiempirical calculation of the electronic structure for the ground state of the $\text{N}_2$ 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: $\text{N}_2$, Semiempirical, Ionization Potential. MOPAC.

Cálculo semiempírico da estrutura da molécula $\text{N}_2$

RESUMO

Este trabalho apresenta um cálculo semiempírico da estrutura eletrônica do estado fundamental da molécula $\text{N}_2$, 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: $\text{N}_2$, Semiempírico, Potencial de Ionização, MOPAC.
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 N$_2$ molecule: when the Hartree-Fock calculation is performed with STO-3G basis, it predicts the $\hat{\sigma}_g$ orbital to be higher than $1\pi_u$ 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 $1\pi_u$ 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:

$$ F(1)\phi_1(1) = \varepsilon_1 \phi_1(1), \text{ where} $$

$$ F(1) = H_o(1) + \sum_J [2J_J(1) - K_J(1)] \text{, and} $$

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

$$ J_J(1)\phi_1(1) = \phi_1(1)\int [\phi_J(2)]^2 e^2 / r_{12} \, dv_2 $$

$$ K_J(1)\phi_1(1) = \phi_J(1)\int \phi_J(2)\phi_1(2)e^2 / r_{12} \, dv_2 $$

$F(1)$ 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 $\varepsilon_1$ is the energy of the orbital $\phi_1(1)$. By the Koopmans’ theorem, $\varepsilon_1$ 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 \(1\sigma_u^2 \ 2\sigma_g^2 \ 2\pi_u^2 \ 1\pi_u^2 \ 3\sigma_g^2 \ 1\Sigma_g^+\) 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 \(N_2\) ground state molecule. R is the interatomic distance.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>MOPAC(^a) R=2.082 au</th>
<th>MS(^b) R=2.068 au</th>
<th>RHF(^c) R=2.068 au</th>
<th>RHF(^d) R=2.1 au</th>
<th>VCM(^e)</th>
<th>Exp.(^f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2\sigma_u)</td>
<td>-18.3</td>
<td>-18.2</td>
<td>-16.8</td>
<td>-16.7</td>
<td>-16.7</td>
<td>-16.8</td>
</tr>
<tr>
<td>(1\pi_u)</td>
<td>-14.9</td>
<td>-14.1</td>
<td>-17.3</td>
<td>-17.3</td>
<td>-13.0</td>
<td>-15.5</td>
</tr>
<tr>
<td>(3\sigma_g)</td>
<td>-19.3</td>
<td>-18.2</td>
<td>-16.8</td>
<td>-16.7</td>
<td>-16.7</td>
<td>-16.8</td>
</tr>
</tbody>
</table>

\(^a\) This work. MOPAC with MNDO calculation.
\(^c\) 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 N$_2$ ground state molecule.

<table>
<thead>
<tr>
<th></th>
<th>MOPAC$^a$</th>
<th>MS$^b$</th>
<th>RHF$^c$</th>
<th>RHF$^d$</th>
<th>VCM$^e$</th>
<th>Exp.$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. P. (eV)</td>
<td>14.9</td>
<td>14.1</td>
<td>17.3</td>
<td>17.3</td>
<td>13.0</td>
<td>15.5</td>
</tr>
</tbody>
</table>

a) This work. MOPAC with MNDO calculation.
c) CADE, P. E. et al. (1966).
f) SIEGBAHN, K. et al. (1969).

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

N
N 1.103802

Table 3 shows the results for some spectroscopic 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 \textit{ab initio} methods, energy calculations are related to the molecule in vacuum, without vibration at 0 Kelvin.
Table 3. Spectroscopy Constants for N\textsubscript{2} ground state molecule.

<table>
<thead>
<tr>
<th></th>
<th>$K_e$ (mdyn/Å)</th>
<th>$\nu_e$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOPAC$^a$</td>
<td>24.20</td>
<td>2421.9</td>
</tr>
<tr>
<td>Exp.$^b$</td>
<td>22.94</td>
<td>2358.0</td>
</tr>
</tbody>
</table>

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


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 $\nu_e$ 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 \textit{ab initio} results. MINDO Hamiltonian privilege the binding energies calculation, where \textit{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.
5. REFERENCES


