

Theoretical Investigation of Oxygen Molecule Excited States

Seifollah Jalili and Leila Jamishidi

Department of Chemistry, K. N. Toosi University of Technology, P.O. Box 15875-4416, Tehran, Iran

Introduction

In recent years, we have seen an impressive development of ab initio quantum chemical methods to study molecules in their ground electronic state, but development of such methods for the excited states is not so extensive. The reason is the large complexity of excited state wave functions. To explain the electronic spectra of molecular systems, knowledge about the energetic position of electronically excited states relative to the ground state, as well as information about geometric and electronic properties of excited states, is necessary. Today, several quantum chemical approaches for the calculation of excited states are available which yield energies and oscillator strengths of several excited states in one single calculation. In analogy to ground state methods, excited-state methods can also be divided into wave-function-based methods and electron-density-based methods. Typical wave-function based methods are CI, Multi Reference CI (MRCI), or Multi- Reference Moller-Plesset approaches, Complete Active Space SCF (CASSCF), and complete active space perturbation theory of second order (CASPT2) [1,2,3]. In this paper five low-lying excited states of oxygen molecule were investigated by CIS(D) and CASSCF methods and the excitation energies were obtained.

Keywords: Oxygen molecule, Excited state, Excitation energy, CASSCF, CIS(D)

Computational Details

In this work, we have studied oxygen molecule excited states using CIS(D) and CASSCF methods. In the CASSCF method, the active space consisted of 8 electrons (2p electrons of oxygen atoms), and 6 orbitals. The orbitals included in the active space are arised from the 2s and 2p atomic orbitals of oxygen. These orbitals are 3 doubly occupied orbitals (o_g , n_u , n_u), 2 singly occupied orbitals (n^*_g , n^*_g), and one virtual orbital (o^*_u). The excitation energies were obtained as the difference of ground and

excited state total energies. Calculations in the excited states were performed in the experimental bond length of oxygen, 1.21 Å. All calculations have been performed with the Gaussian03 suite of programs. We have chosen the 6-31+G* basis set for our calculations.

Results and Discussion

Excitation energies calculated from CASSCF(8,6) and CIS(D) methods are presented in Table 1. $E_{\text{ex},1}$ is the first excitation energy and so on.

Table 1: Oxygen molecule excitation energies (eV)

| method | $E_{\text{ex},1}$ | $E_{\text{ex},2}$ | $E_{\text{ex},3}$ | $E_{\text{ex},4}$ | $E_{\text{ex},5}$ |
|--------|-------------------|-------------------|-------------------|-------------------|-------------------|
| CASSCF | 6.01 | 6.01 | 6.16 | 10.22 | 9.29 |
| CIS(D) | 6.82 | 6.82 | 6.99 | 8.54 | 8.52 |

Due to high symmetry in the oxygen molecule, there are many degenerated excited states in this molecule. As seen in Table 1, the two first excited states are degenerated in both methods, and the excitation energy of them is 6.01 and 6.82 eV in the CASSCF and CIS(D) methods, respectively. The third excited state is slightly higher than the first and second excited states by 0.15 eV and 0.17 eV in the CASSCF and CIS(D) methods, respectively. The fourth and fifth excited states are degenerated in the CIS(D) method. This degeneracy is absent in CASSCF method and the energy difference of two states is 0.93 eV.

References

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