Ab initio Electronic Structure Calculations of O_2 Using Coupled Cluster Approaches and Many-Body Perturbation Theory

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The ground state of the oxygen molecule is calculated by various methods of coupled cluster approaches and many body perturbation theory using a double zeta plus polarization basis set and the UHF reference state. All the methods employed are capable of describing the oxygen molecule near the equilibrium bond length and the separated atom, but do not correctly depict the breaking of the multiple bond. For this basis set, including more correlations does not necessarily improve the agreement with experiment for molecular properties such as bond lengths and dissociation energies.

Introduction

The electron correlation plays an important role in any quantitative electronic structure calculations and the many-body perturbation theory (MBPT) is one of the popular methods to treat the problem of electron correlations. Although the perturbation method do not yield the upper bound energy, the lower order perturbational methods have significant computational advantages over the variational methods and have some theoretical advantages as well. The MBPT method can be formulated to have size-extensive properties while this cannot be done for the truncated configuration interaction (CI) methods.[1]

The conventional application of the MBPT method is the order by order expansion in the perturbation sequence. The straightforward order by order expansion is now possible up to the fourth order when the single determinental state is used as the reference state.[2-8] The full fifth order MBPT calculation is very formidable task and not likely to be used in any practical application. When the perturbation treatment is desired to infinite order for a certain class of excitations, coupled-cluster (CC) approaches are available. The CC methods are beginning to gain considerable attentions in recent years.[1,9-15] Both CC and MBPT methods as well as the truncated CI methods encounter convergence problems when the single determinental reference state is not adequate to describe the state in question. Therefore, considerable amount of efforts is devoted in developing multireference version of both methods and there have been reports of successful attempts.[1] Since the routine application of the multireference CC and MBPT methods is not yet available, it is important to understand the limitation of the single reference methods. For this reason, comparison of many perturbational methods are performed for the ground state of O_2 molecule.

The oxygen molecule is one of the most widely calculated and still one of the most difficult diatomic molecules to obtain correct dissociation behaviors due to the multiple bonding. Even the UHF methods cannot describe the bond breaking. In this study, we will try to show that O_2 molecule and the atom are reasonably described by including electron correlations using CC and MBPT methods but the dissociation process is not. The present study utilizes the UHF reference state

and the double zeta plus polarization (DZP) basis set of Dunning.[16]

Computational Methods

All calculations are performed with one basis set. The Dunning's basis set[16] used in the present study has been used in other calculations of O_2 and thus provides useful comparisons with other methods.[17,18] The UHF calculations are performed at several internuclear distances for $S_z = 1$ and $S_z = 0$ states. The $S_z = 1$ state has the configuration which yields the $^3\Sigma_g^-$ ground state, but the $S_z = 0$ state is not a pure spin state. Most correlation calculations are for the $S_z = 0$ state.

MBPT calculations have been carried out at the second, third and the fourth order of the perturbation expansions. Coupled cluster approaches used in the study is a coupled-cluster singles and double (CCSD) model developed by Bartlett and coworkers.[14] The coupled cluster approaches for solving the Schrodinger equation are first developed for nuclear structure studies and later adopted in electronic structure calculations by various workers.[1] At present, the CC methods which include all the effects of triple excitations are available.[1] But the programs performing full triple calculations are still being refined and not readily available for the general use. The coupled-cluster single, double, and triple (CCSDT) method employed in this study treats only part of the triple excitations. Because of this truncation, the method is called CCSDT1.[15]

Details of the formalism for all methods used here are available in the literature and not presented here. In fact, all the methods with the possible exception of CCSDT1 are included in some standard molecular calculation packages. Most results of the present study has been computed with the CCSDT1 program developed by Bartlett and corworkers. This program is capable of doing MBPT calculations in addition to CC calculations and a precussor of ACES program by Bartlett and coworkers.[1]

Results and Discussion

Results of UHF calculations for $S_z = 1$ and $S_z = 0$ states are summarized in Table 1. Since O_2 contains multiple bond and the molecular state is a triplet, the usual UHF wavefunction,

Table 1. Energies (in a.u.) from UHF Calculations for O_2

| R (bohr) | $S_z=1$ state | | $S_z=0$ state |
	Sym.	No Sym.	No. Sym
2.2	−149.6594	−149.6594	−149.6305
2.28562	−149.6564	−149.6564	−149.6273
2.32	−149.6532	−149.6532	
2.4	−149.6423	−149.6432	−149.6129
3.0	−149.4956	−149.5693	−149.5788
10.0	−149.9552		−149.6115
O atoms	−149.6115		

Table 2. Total and Core Electron(1s) Contributions (in a.u.) to Total Energies of O_2 at $R=2.28562$ bohr and Two Atoms Using MBPT Methods with DZP Basis Set.

| | Total | | Core | |
	O_2	O atoms	O_2	O atoms
$\Delta E(2)$	−0.35623	−0.21626	−0.02768	−0.02754
$\Delta E(3)$	0.00170	−0.01362	−0.00102	−0.00116
$\Delta E(4)$	−0.01962	−0.00557	−0.00013	−0.00005

where real spinorbitals are assumed, cannot dissociate into two equivalent O atoms for $S_z=1$ state. In addition, the inversion symmetry is broken at some internuclear distance due to the so called UHF instability.[19] This bifurcation of the symmetry-conserved (Sym. in Table 1) and the symmetry-broken (No Sym. in Table 1) solutions occurs near the distance of 2.4 bohr. If complex molecular orbitals are used, spinorbitals with a spin will begin to mix with those with β spin at the longer distances and produce another bifurcation point in the UHF potential curve of O_2. In the present case, this should happen at the distance shorter than 3.0 bohr since the UHF energy at 3.0 bohr is already higher thant the sum of the atomic energies. The present calculation do not consider complex molecular spinors and does not attempt to describe regions of large atomic separations. The atomic limits are calculated by performing UHF calculations for the oxygen atom with the $S_z=1$ configuration.

The $S_z=0$ state can dissociate into two O atoms with $S_z=1$ and $S_z=-1$ configurations as shown in Table 1 for $R=10$ bohr. But this state near the equilibrium bond length is expected to have some contributions from the triplet state and not the pure $^1\Delta_g$ state. The potential curve for the $S_z=0$ state has a large barrier near $R=3.0$ bohr. This barrier is an artifact of the UHF calculation and not present in CI calculations by Saxon and Liu.[20]

Electron correlations are treated with MBPT second, third and fourth calculations and with CCSD and CCSDT1 using the single references state from the UHF calculations. The σ orbitals from the 1s atomic orbitals are not included in most calculations since the contribution from the 1s core orbitals are found to be negligible in the test calculations in which molecular calculations at $R=2.28562$ bohr and atomic calculations are performed with and without frozen core assumptions. From these test calculations, it is possible to obtain correlation energies due to 1s core orbitals at each level of the perturbation as shown in Table 2. Electron correlation energies due to the 1s core orbitals which are given under the column denoted

Table 3. Correlation Energy Contributions in MBPT and CC Calculations for the $S_z=1$ State of O_2 at Several Intrnuclear Distances Near Equilibrium Bond Lengths. 1s Core Orbitals are Treated as Frozen Core Orbitals and All Units are Atomic Units.

R(bohr)	2.28562	2.32	2.35	3.0
UHF	−149.65643	−149.65322	−149.64965	−149.49556
$\Delta E(2)$	−0.32830	−0.33282	−0.33684	−0.44164
$\Delta E(3)$	0.00264	0.00423	0.00571	0.06540
$\Delta E(4)$				
SDQ (4)	−0.00906	−0.00975	−0.01039	−0.03904
$T(4)$	−0.01037	−0.01101	−0.01160	−0.03468
$\Delta E(1-4)$	−0.34508	−0.34934	−0.35312	−0.44996
ΔE(CCSD)	−0.33423	−0.33767	−0.34067	−0.40460
ΔE(CCSDT1)	−0.34365	−0.34753	−0.35095	−0.42674

Table 4. R_e and D_e for the Ground State of O_2 Calculated with DZP Basis Set Using Various Methods

Methods	R_e (bohr)	D_e (eV)
UHF	2.212	1.31
MBPT(2)	2.36	5.08
MBPT(3)	2.30	4.25
MBPT(4) SDQ	2.31	4.38
MBPT(4) SDTQ	2.32	4.60
CCSD	2.31	4.33
CCSDT1	2.31	4.53
MR-MBPT(2)^a	2.305	5.67
GVB-CI^b	2.339	4.88
FCI^c	2.318	4.637
Experiment	2.2818	5.213

^{a} Quasidegenerate MBPT calculations from Ref. 17. ^{b} From Ref. 18. ^{c} Full CI on smaller orbital space from Ref. 21.

as Core in Table 2 are not very large to begin with, amounting to about 10% of the total correlation energy at the second order. At higher orders, the ratio of the core contribution to the total fluctuates, but the magnitude is very small. What is customarily important in determining molecular properties are relative changes from atom to molecules. In this respect, the errors due to the frozen core approximation, which is the difference between energies at $R=2.28562$ and atoms in Table 2, is about 0.0001 a.u. at all levels of the perturbation theory. This result is what is expected but reported here since an example of the frozen core test is not readily available.

Correlation contributions in MBPT and coupled cluster calculations are shown in Table 3 for several internuclear distances near calculated equilibrium bond lengths. All calculations in Table 3 utilize the symmetry enforced UHF state as the reference state. At this region of the potential energy curve, total energies from the UHF calculations monotonically increase, but correlation energies have different behaviros depending on the order. In the MBPT calculations, the third order contributions, $\Delta E(3)$, are the smallest, positive and increasing with the internuclear distance. Other MBPT contributions are all negative and decrease with the internuclear distance. As a result, calculated equilibrium bond lengths are different

as shown in Table 4. As in any other reasonable perturbation calculations, the second order, $\Delta E(2)$, has the largest contribution for the ground state of O_2 as shown in Table 3. Among the shown correlation contributions, $\Delta E(2)$ and the fourth order triple contribution, $\Delta E(4)$, are always negative, but the sign of other contributions may vary depending upon the choice of the reference state. When the sign of the contributions vary from one order to another and the magnitude of the perturbation expansion alternates as here, one should be careful in assessing the convergence of the perturbation calculations. Although the second order result is acceptable for many applications, we may say that O_2 is an example where the low order perturbation treatment is rather inadequate. This effect is shown in the equibrium bond length and the dissociation energy of O_2 summarized in Table 4.

Results from CCSD and CCSDT1 calculations are also shown in Table 3 and 4. Contributions from the triple excitations, the difference between CCSD and CCSDT1, are not too different from $T(4)$ although CCSDT1 includes triple contributions in an iterative manner. For the molecular properties in Table 4, triple excitations have little effect on the bond length, but are responsible for about 5% change (0.2 eV) in dissociation energy in MBPT fourth order and coupled cluster calculations. Since the coupled cluster method includes correlation contributions that goes beyond the fourth order MBPT, the good agreement between the fourth order MBPT and CCSDT1 results is a good indication that these results are close to the exact full CI limit for the present basis set. In fact, R_e and D_e are in good agreement with the full CI calculation performed with the same basis set but with more frozen core orbitals.[21]

The results are qualitatively different for the calculations at $R = 3.0$ bohr where symmetry enforced UHF calculation yields higher energies than the sum of the atomic energies. All correlation contributions become substantially larger than those near the equilibrium bond lengths although internuclear separation has been increased only by 0.65 bohr. Clearly MBPT calculations do not converge even at the fourth order. The third and fourth order contributions in Table 3 are large. In addition, the energy from the fourth order calculation differs from that of CCSDT1 by 0.02 a.u. compared with 0.01 a.u. at $R = 2.35$ bohr. It is also natural to suspect even CCSD and CCSDT1 calculations at $R = 3.0$ bohr. In the CCSD calculations with the symmetry broken UHF reference state, the CCSD energy is converged to the same energy as that in Table 3 while all MBPT energies are quite different. This is not a proof but a strong support to a claim that the CC method is reliable. CCSD and CCSDT1, however, fail to converge at larger internuclear distances because connected quadruples, which are totally omitted in CCSD and CSDT1 methods, become essential in the correct description at these larger distances.

In summary, we have shown that MBPT and CC methods based upon UHF reference state can be used to estimate the molecular properties by taking the difference between the stable molecular state and the atom even for molecules like O_2. The discrepencies between the lower order and higher order values are substantial in MBPT calculations for the present basis set, and the same is expected for the extended basis sets. Coupled cluster approaches are applicable in broader region

of the potential energy curve than MBPT methods, but still not adequate for the whole potential curve. Results from the present study will be useful in selecting computational procedures suitable for the degree of accuracy desired for a given problem in the molecular electronic structure calculations.

An extensive study on CCSDT method for other diatomic molecules can be found in the recent article by Scuseria *et al.*[22]

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