# MCQDPT vs. XMCQDPT: low-lying excited states of $O_3$ molecule

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# Introduction: A brief overview of MCQDPT theory

- Reliable, cost-effective alternative to other multi-reference (MR) approaches, such as MR-CI(+Q), *ic*-MRCI, MR-AQCC and MR-ACPF.
- It is a multistate, van-Vleck-based perturbation theory (PT) with one-particle zero-order Hamiltonian and "perturb-then-diagonalize" ideology, thus well-suited for treatment of several "difficult" situations, such as conical intersection or avoided-crossing states of interest.
- Intruder States Avoidance (ISA) technique can be applied to get rid of intruder states problem, which is common for many PT theories.
- State-specific formulation of MCQDPT is known as MR-MP2 theory.

# Introduction: Low-lying states of $O_3$

$O_3$ molecule is a famous example of a "difficult" molecule. Due to complex electronic structure, to obtain accurate and reliable result one has to use high-level electronic structure methods. Clearly, MCQDPT is among them.

This presentation is mainly devoted to the difficulties with the original MCQDPT theory treatment encountered in a study of 1D-sections of selected low-lying states of the ozone molecule.

# Low-lying states of $O_3$: MCQDPT picture

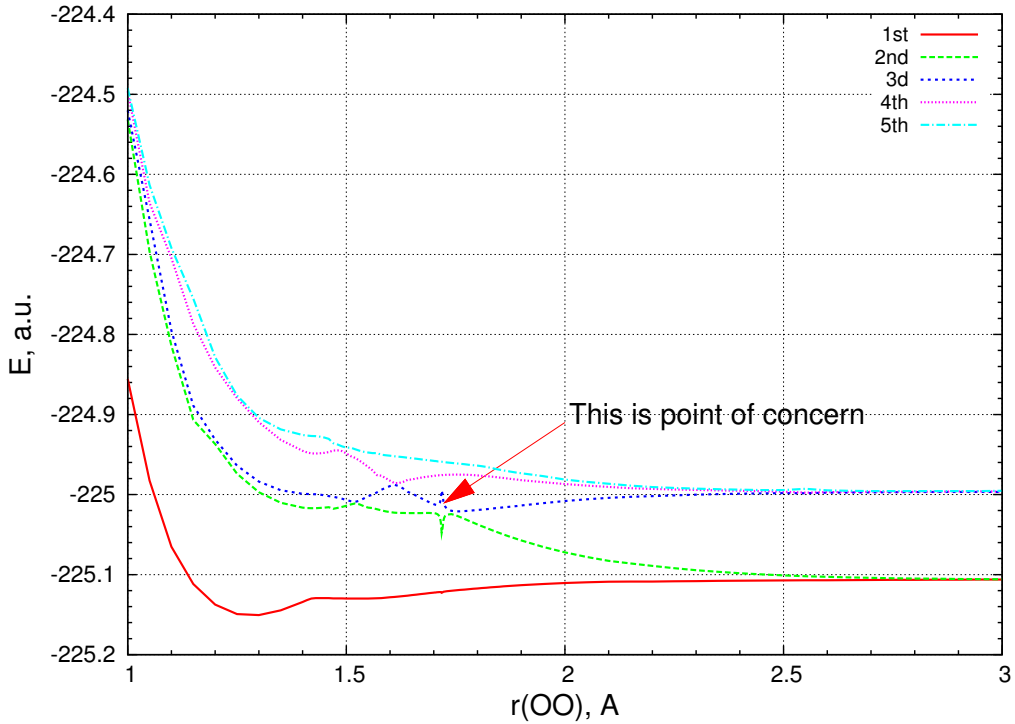


Figure: The overall shape of the 1D-sections of potential energy surfaces of several low-lying singlet electronic states along antisymmetric dissociation pathway calculated using original MCQDPT theory.

# Low-lying states of $O_3$: MCQDPT picture

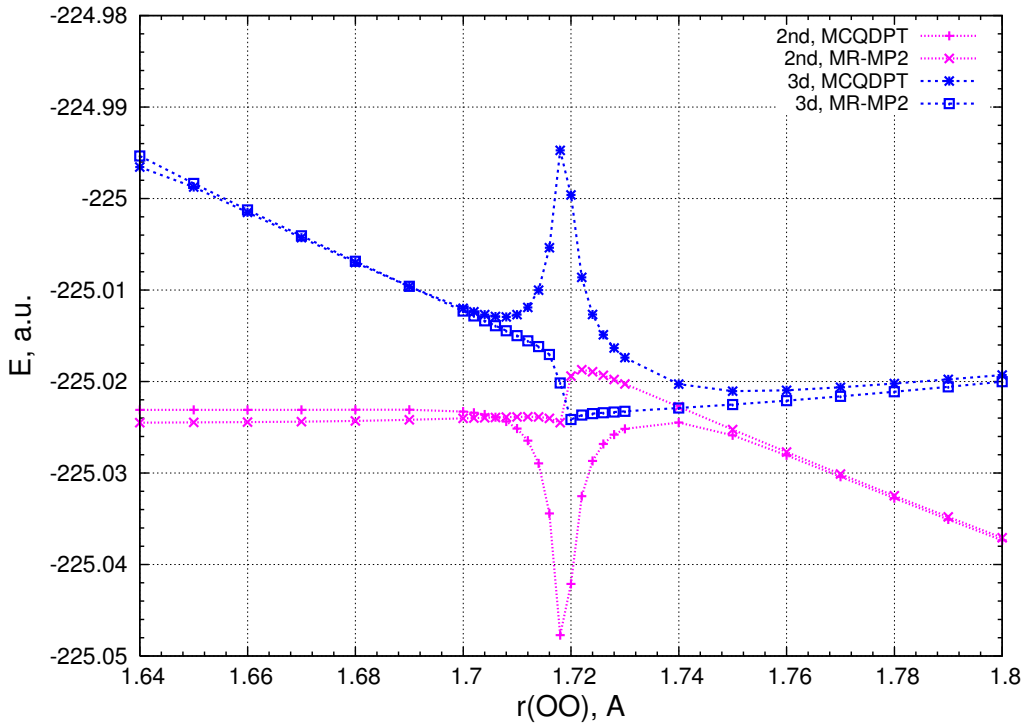


Figure: A detailed view of the problem region. Both MCQDPT and diagonal elements of the effective Hamiltonian (a.k.a MR-MP2 energies) are shown for the second and the third electronic states.

# Low-lying states of $O_3$: MCQDPT picture

Lets consider the geometry, which corresponds to the extreme point $R(OO_1) = 1.718$ Å, $R(OO_2) = 1.207$ Å, $\angle OOO = 116.8^\circ$ .
It is clear, that the problem might be with off-diagonal ($H_{23}$) term of the Hamiltonian, which is way too large.

```
 *** EFFECTIVE HAMILTONIAN (0-2) ***
-----------------------------------
           2                3
-2.250245D+02
-2.794081D-02 -2.250202D+02
```

# Low-lying states of $O_3$: MCQDPT picture

Two states are very close to each other at CASSCF level, the spacing between them is merely $5.54 \cdot 10^{-4}$ a.u. (0.015 eV). Diagonal elements of MCQDPT Hamiltonian are also close to each other ($4.4 \cdot 10^{-3}$ a.u., see above).

```
-------------------------------
*** MC-QDPT2 ENERGIES ***
-------------------------------
STATE                    1ST ORDER
  2   E(MCSCF)= -224.4438070199
  3   E(MCSCF)= -224.4432527323
-------------------------------
```

# Low-lying states of $O_3$: MCQDPT picture

The mixing between states is strong[2] and spacing between them at MCQDPT level ($\Delta_{MCQDPT}$) is of $2H_{23}$ in magnitude (1.44 eV!).

| | 2 | 3 |
|---|---|---|
| | -225.047725 | -224.994736 |
| 1 | 0.206175 | 0.013639 |
| 2 | 0.710624 | 0.669561 |
| 3 | 0.664293 | -0.729956 |
| 4 | -0.013854 | -0.124203 |
| 5 | 0.014246 | -0.030514 |
| 6 | 0.104046 | 0.048057 |

[2] Expansion coefficients of the eigenvectors of the effective Hamiltonian over a basis of model space (CASSCF vectors) are given in a table.

# Summary: MCQDPT issues

- Off-diagonal matrix elements of the effective Hamiltonian seems to be incorrect.
- It is very likely, that the original MCQDPT theory would fail in the proximity of a not-symmetry-related[3] conical crossing seam.
- Diagonal elements of the effective Hamiltonian (MR-MP2 energies), however, could be use in computing energy deltas between states, though their reliability and accuracy are questioned.

[3] In the case of symmetry-related conical intersections off-diagonal elements could be close to zero due to symmetry.

# Low-lying states of $O_3$: XMCQDPT picture

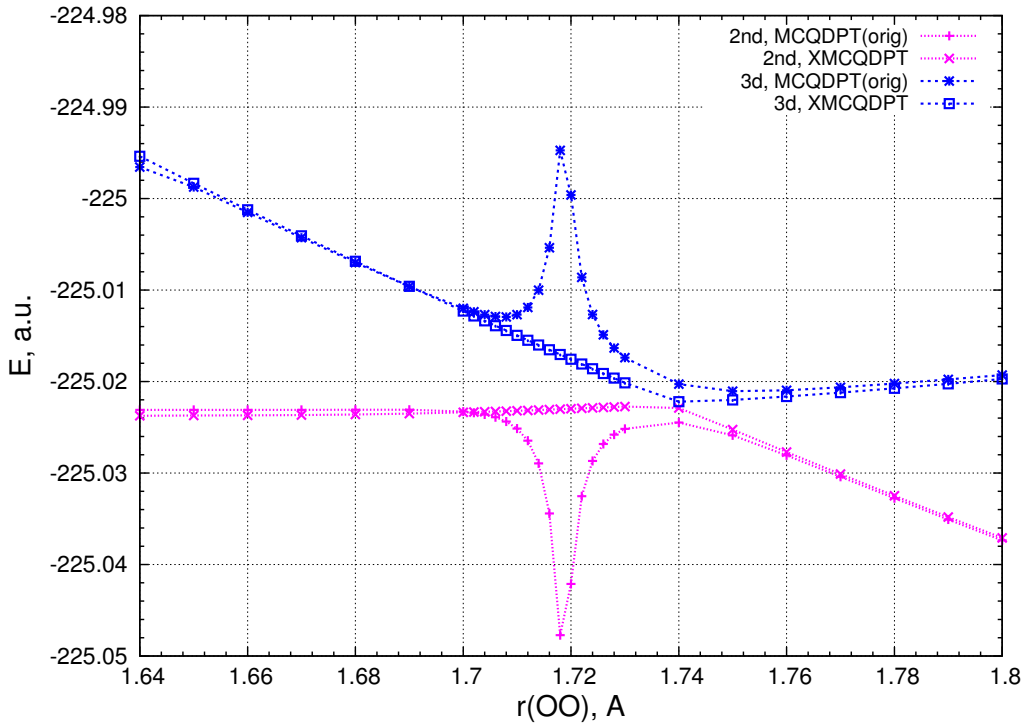


Figure: MCQDPT vs. XMCQDPT cuts. XMCQDPT treatment completely removes artificial repulsion between potential energy curves. It is very likely that the current picture is correct, since these electronic states of $O_3$ are known to exhibit conical intersection.

# Low-lying states of $O_3$: XMCQDPT picture

Off-diagonal term of the effective Hamiltonian $H_{23}$ is less than its counterpart in original MCQDPT theory by an order of magnitude, while the difference between diagonal ones ($2.79 \cdot 10^{-3}$ a.u.) is comparable.

```
*** EFFECTIVE HAMILTONIAN (0-2) ***
-----------------------------------
              2                   3
-2.250214D+02
-2.577257D-03-2.250186D+02
```

# Conclusions

- Original MCQDPT theory suffers from incorrect treatment of off-diagonal matrix elements of the effective Hamiltonian. Under several circumstances it could become important and quantitatively or ever qualitatively incorrect results could be obtained. This problem has nothing to do with the intruder states problem.
- XMCQDPT treatment completely removes any difficulties with electronic states of ozone; the curves are smooth, nice looking, and presumably correct; one might expect that the major issues with original MCQDPT seem to be removed.
- Clearly, XMCQDPT theory should be preferred over original MCQDPT theory in any further studies.

# Technical details

- **Basis set:** aug-cc-pVTZ.
- **Active space:** full-valence complete active space – 18 electrons over 12 orbitals.
- State-averaged over 6 lowest singlet states CASSCF procedure with a subsequent MCQDPT treatment. ISA denominator shift is equal to 0.01 a.u.