Electron correlation: MBPT2, CASPT2, CC, CPF.

- Electron correlation is often divided into static vs. dynamic.
- The MRPT2 program computes dynamic correlation energy by the Møller-Plessett theory as a second-order perturbation correction to the Hartree-Fock energy.
- The CASPT2 program also computes dynamic correlation energy, but the dynamic correlation is a small perturbation of a CASSCF approximation, which includes the static correlation and allows general electron structure.
- The CC program computes dynamic correlation energy to be added to Hartree-Fock, but is more accurate than MRPT2, and also more forgiving if the electronic structure deviates from Hartree-Fock.
- The MRCI – Multireference CI – program has no limitations imposed by approximations to the Schrödinger equation, but of course there are more or less serious limitations due to basis set, internal data representation and demand of computer resources.
- The CPF program is a modified single-reference CI program. It can compute the so-called CPF (Coupled Pair Functional) and MCPF (Modified CPF) dynamic correlaion energy on top of Hartree-Fock.

Dynamic *vs.* static correlation.

The multiplet splitting of states that are degenerate by symmetry equivalence in the one-electron approximation is an archaetypical example of static correlation:

- Highly variable.
- Well described by a few configuration functions or determinants.
- Configuration coefficients are large. They are sometimes determined already from symmetry requirements. They cannot be obtained from perturbation theory.

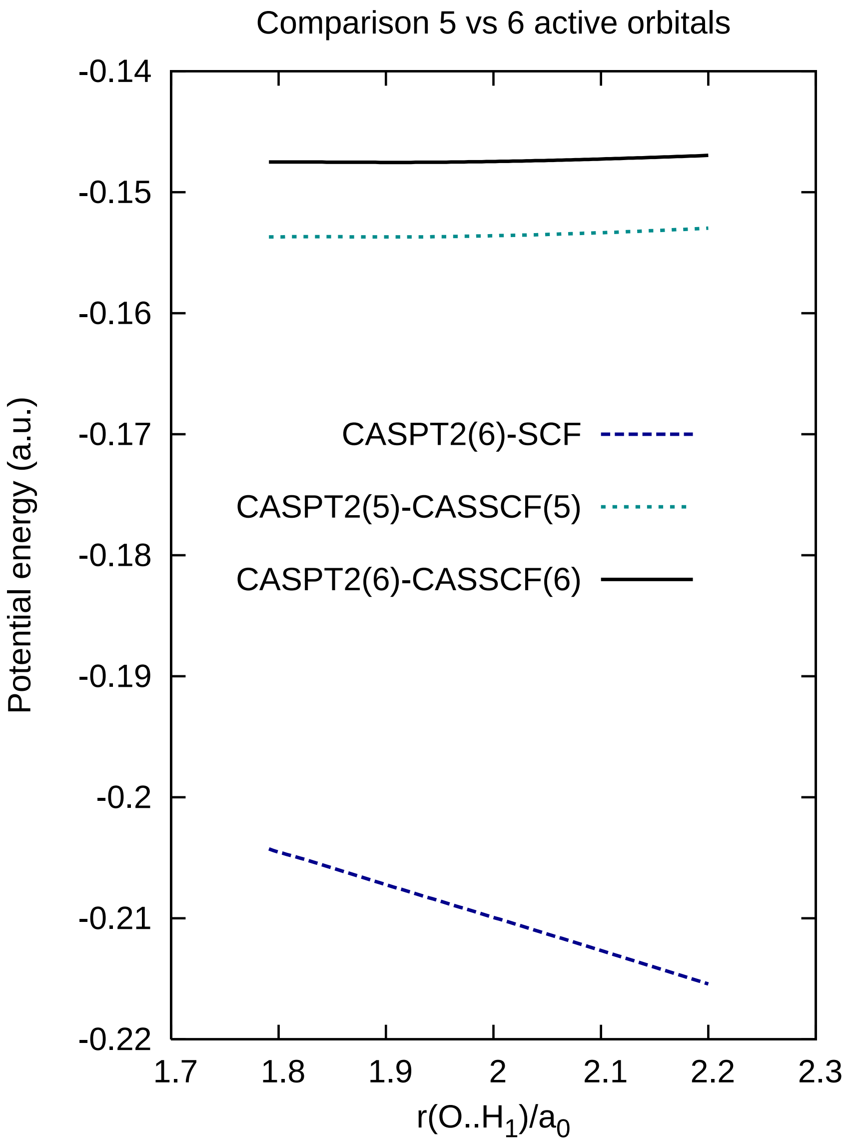
By contrast, when static correlation has been accounted for, the remainder is dynamic correlation:

- Quite predictable, the major contribution is ≈ 1 eV for each closed shell pair, well accounted for by DFT functionals, perturbation theory and Coupled Cluster.
- Requires a large number of determinants in CI approaches.

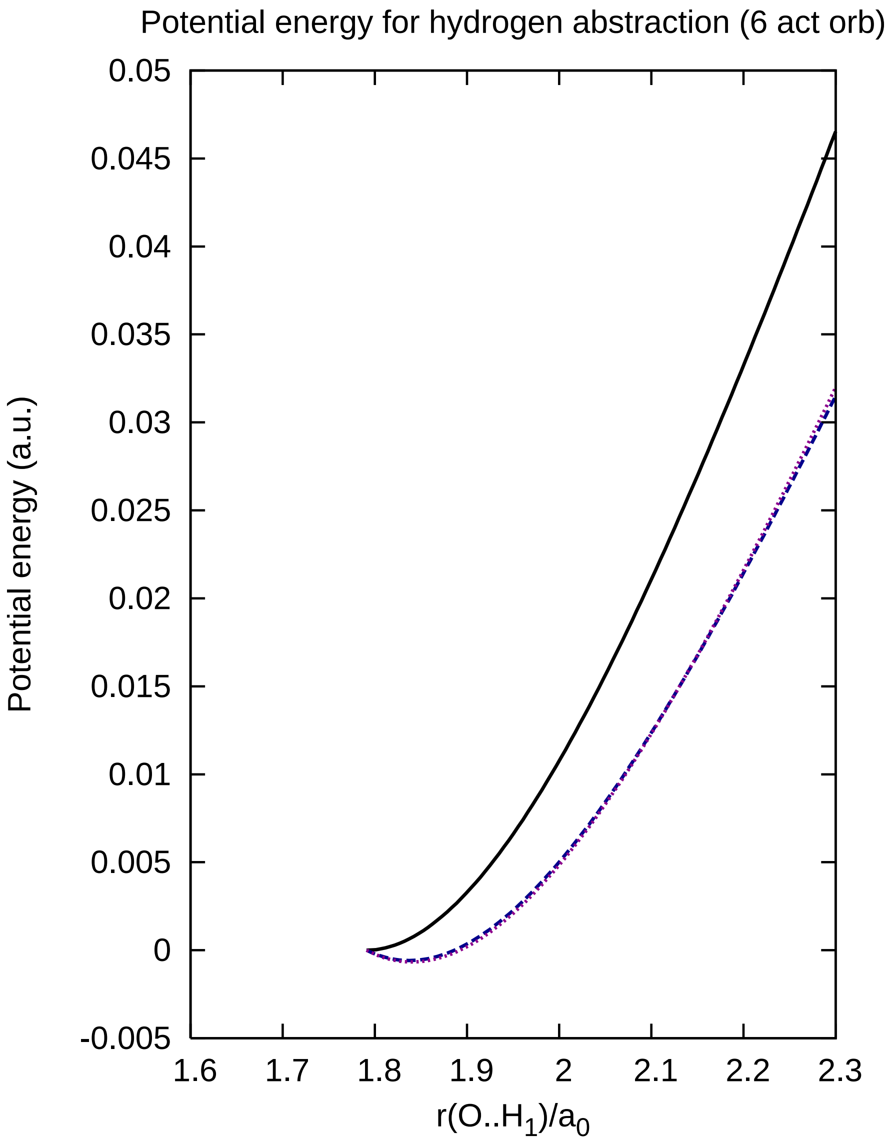
However, the situation is often not clear cut. The distinction is of practical importance for choice of methods, but is also usually done on basis of calculations, i.e., the definition is operational and not theoretical.

Example: Hydrogen abstraction from H2O.

One bond length (OH_1) is varied, and for each bond distance the rest of the molecular structure of H_2O is optimized. The correlation energy ($\approx$ CASPT2 - SCF) is varying. The dynamic correlation energy ($\approx$ CASPT2 - CASSCF) is nearly constant. Note that the CASSCF correlation energy is just a fraction of the full correlation energy, and that it does not increase much with an extra active orbital. The point in getting static correlation right is not to get a large part of the correlation energy, but to make the remaining correlation effects simple and preferably constant.



Example: Hydrogen abstraction from H2O.

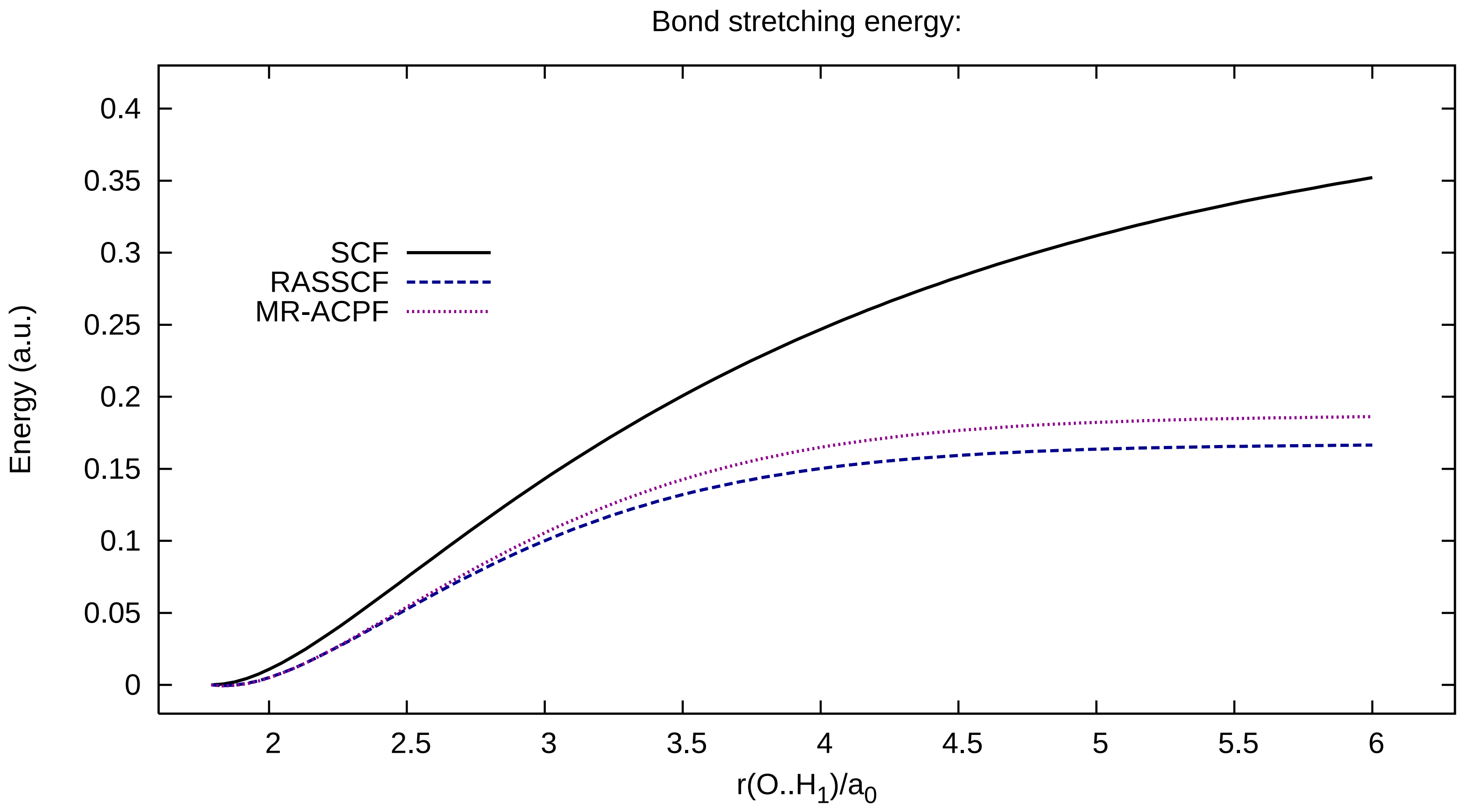


The potential energy curve computed by SCF is too high (in fact, SCF will not be able to dissociate correctly) and the bonds are too short. Already the CASSCF curve is quite accurate, in spite of the rather large dynamic correlation energy.

In fact, for a simple closed shell close to an equilibrium structure, most methods (including DFT) will do nicely.

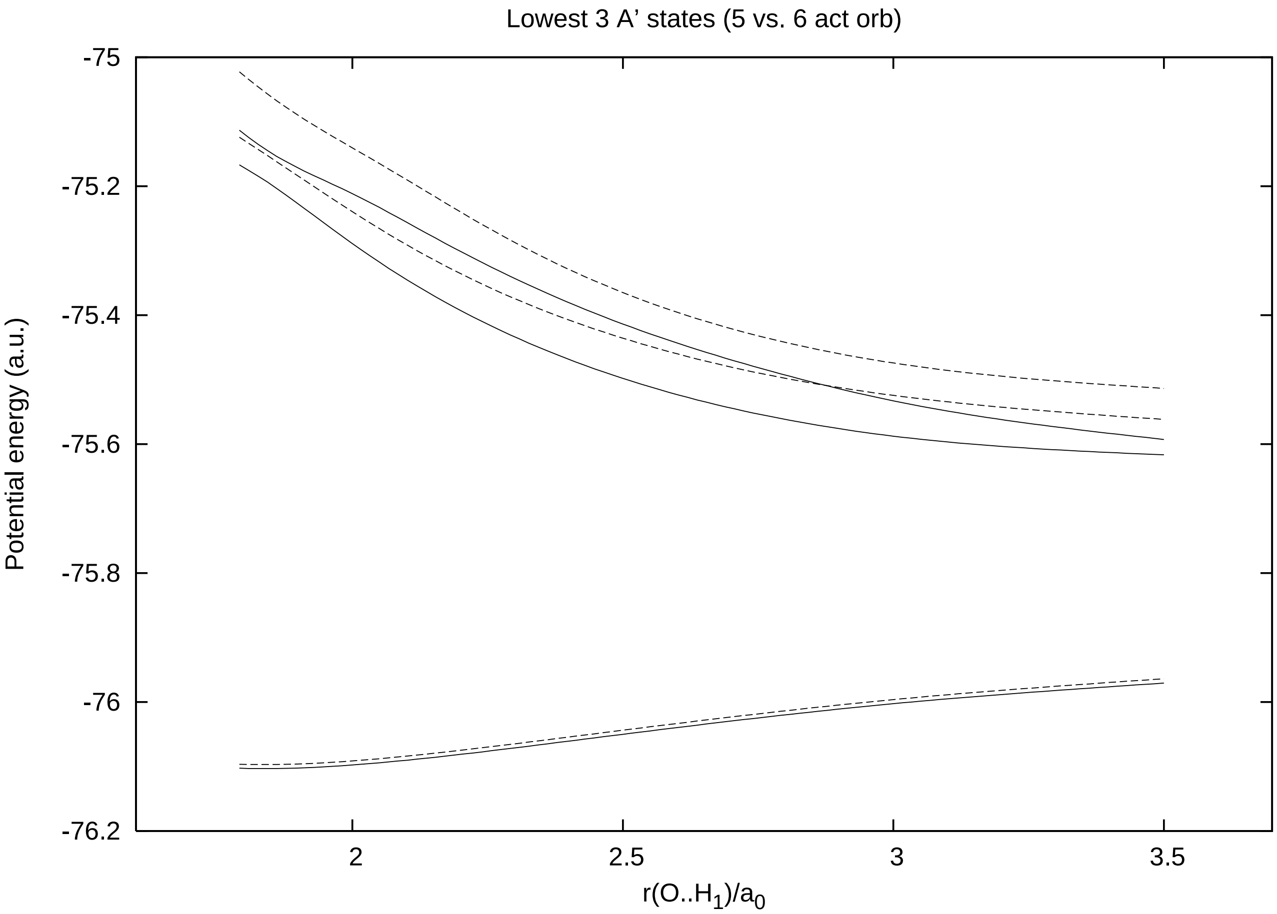
Example: Hydrogen abstraction from H2O.

Over a larger range of distances, the picture is slightly different:



Example: Hydrogen abstraction from H2O. Excited states.

Even if the dynamic correlation may be fairly constant along a potential curve, it usually differs for different electronic states. Generally speaking, excited states require more active orbitals.



The CASSCF/RASSCF is often insufficient.

From previous simple example, we already learn that

- The dynamic correlation is *not quite* constant, when a bond is broken. CASSCF is not sufficient to obtain accurate relative energies.
- The dynamic correlation is *not quite* the same, for different excited states.
- For breaking a bond, CASSCF usually overshoots somewhat, as compared to SCF.

Increasing the active space until the results settle within required accuracy is possible only for two or three electrons. Usually, we use maybe twelve active orbitals. That is why we can say that CASSCF gives only static correlation (in practice, and usually, not as a theoretical dictate). RASSCF offers larger active space, but often with troublesome convergence.

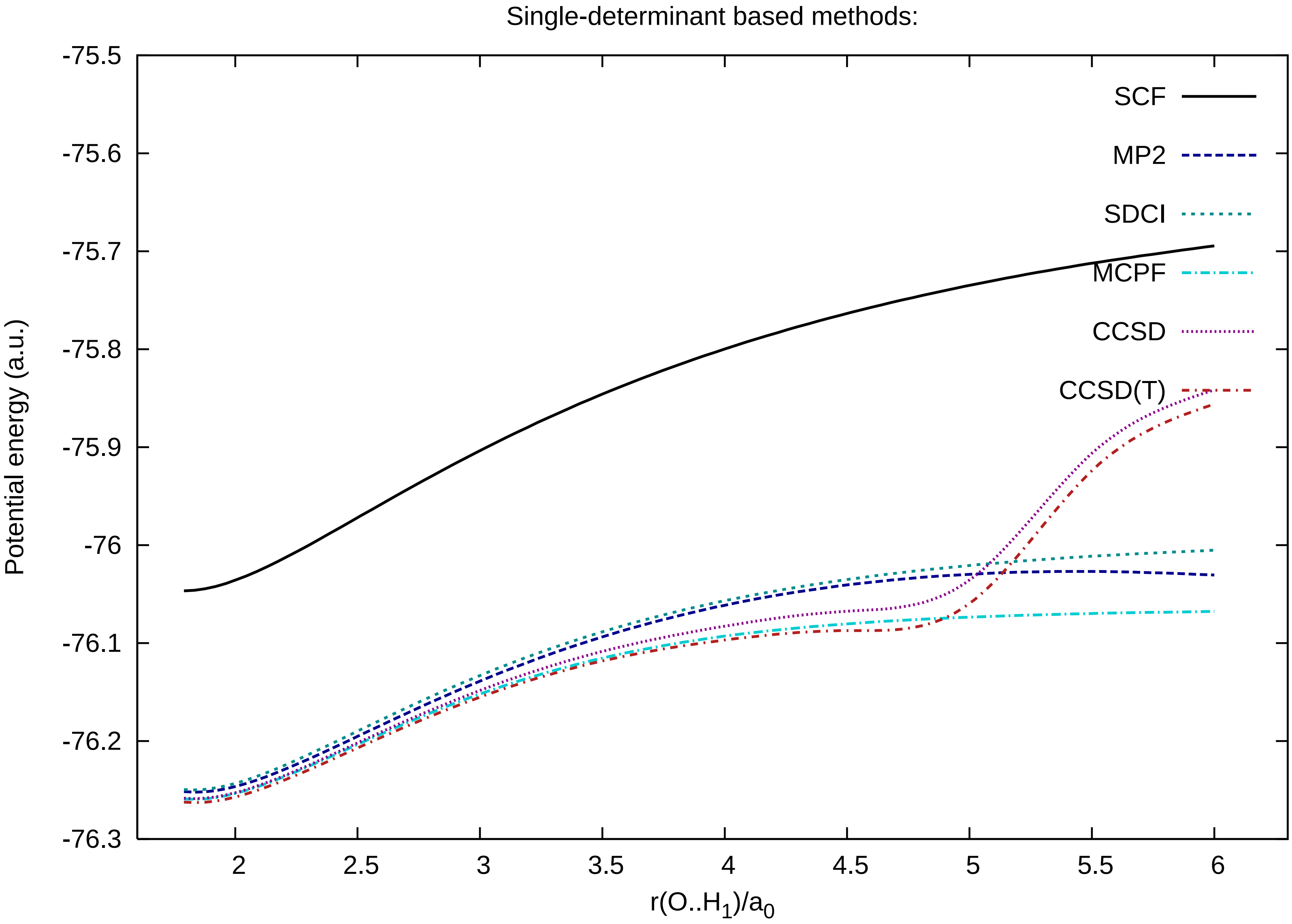
Examples of active spaces.

8 correlated electrons in	6	10	16	24	orbital
gives:	225	44100	3.3M	113M	determinant
16 correlated electrons in	10	12	14	16	orbital
gives:	2025	245025	9M	165M	determinant
24 correlated electrons in	20	22	24		orbital
gives:	16G	418G	7.3T		determinant

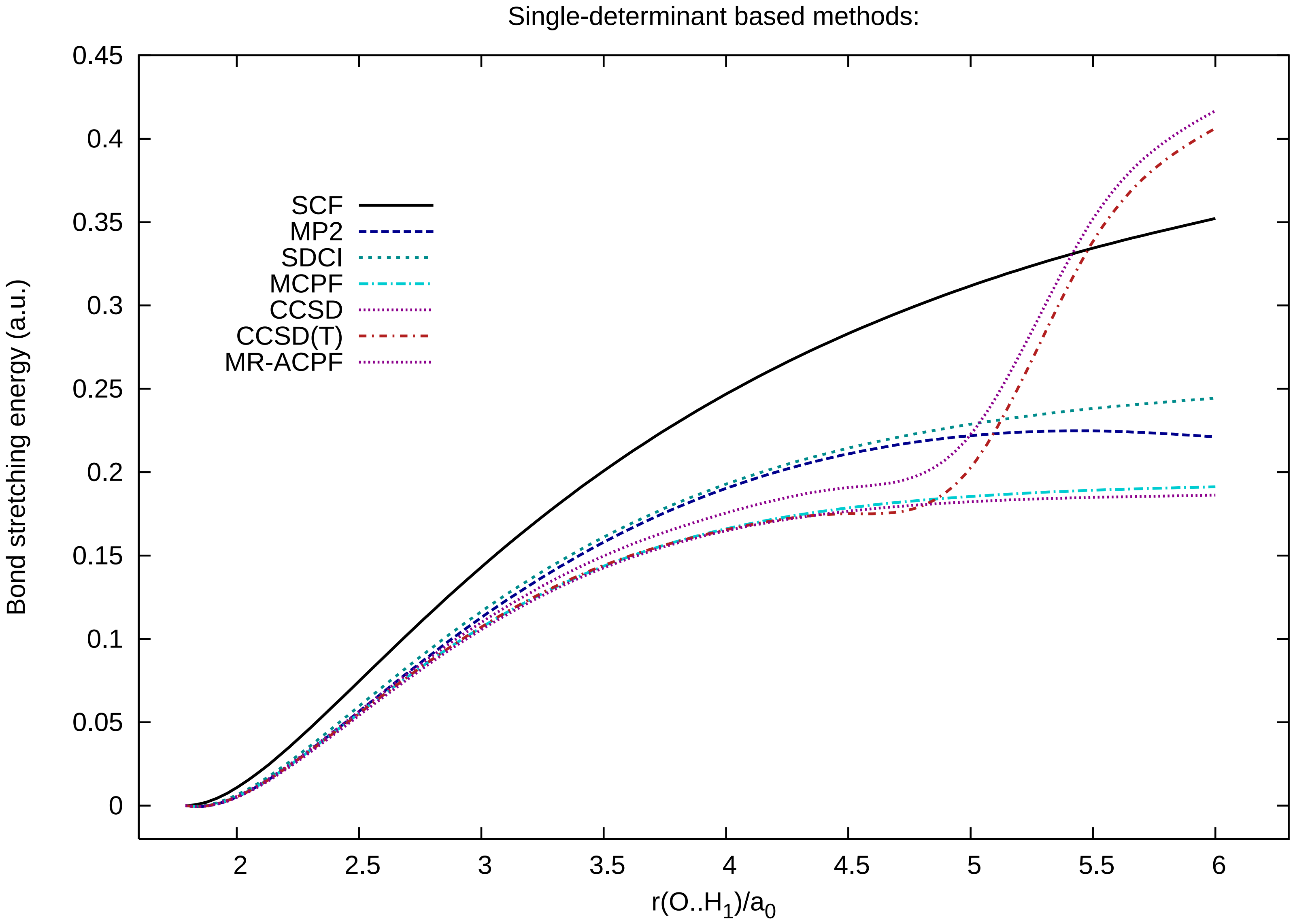
At the same time, if the wave function is predominantly closed-shell, MP2 could do a very good job att correlating 24 electrons in 24 orbitals using roughly 10000 determinants. . .

So why not use single-determinant based methods like MP2 then?

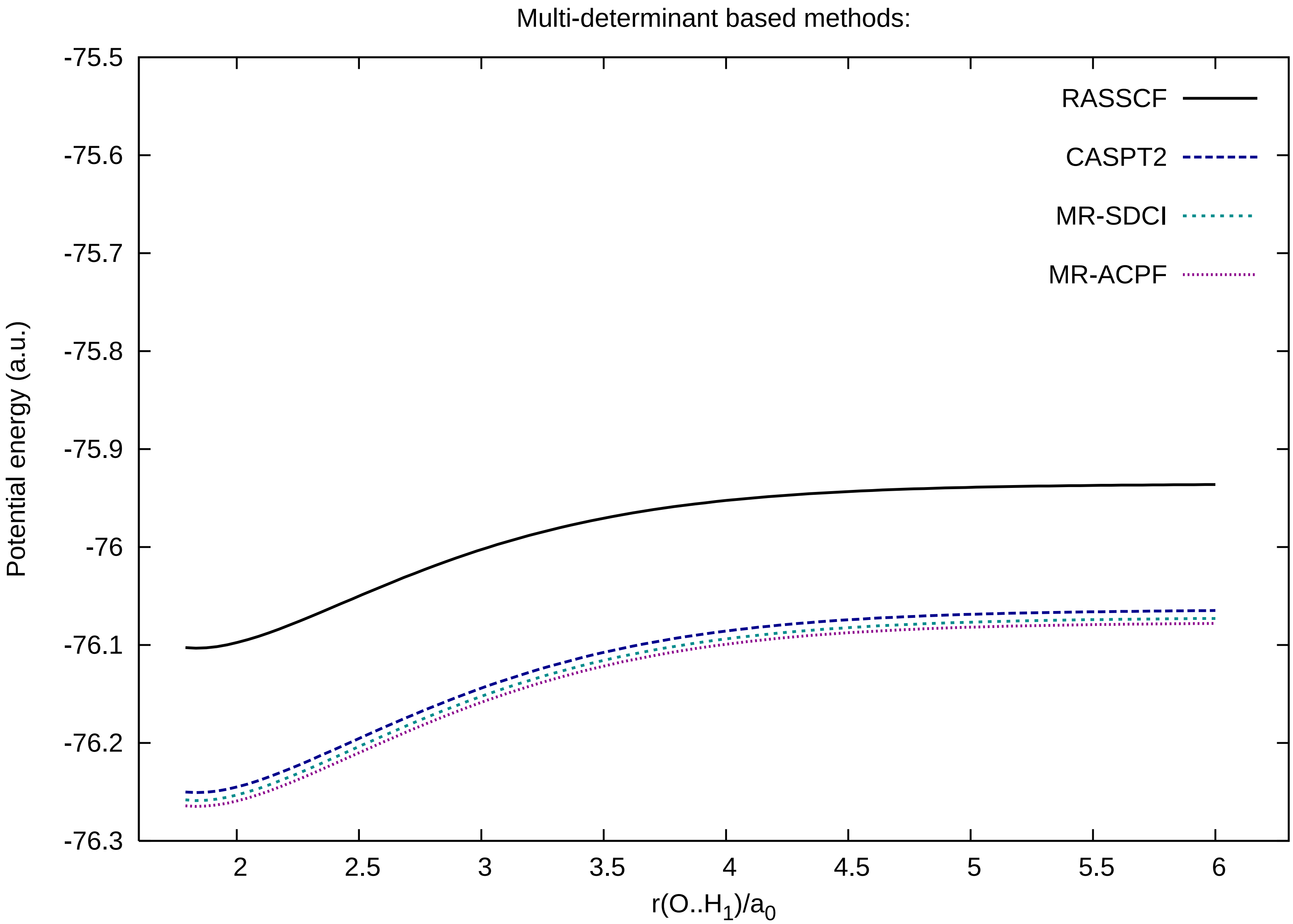
Single-determinant (-based) methods.



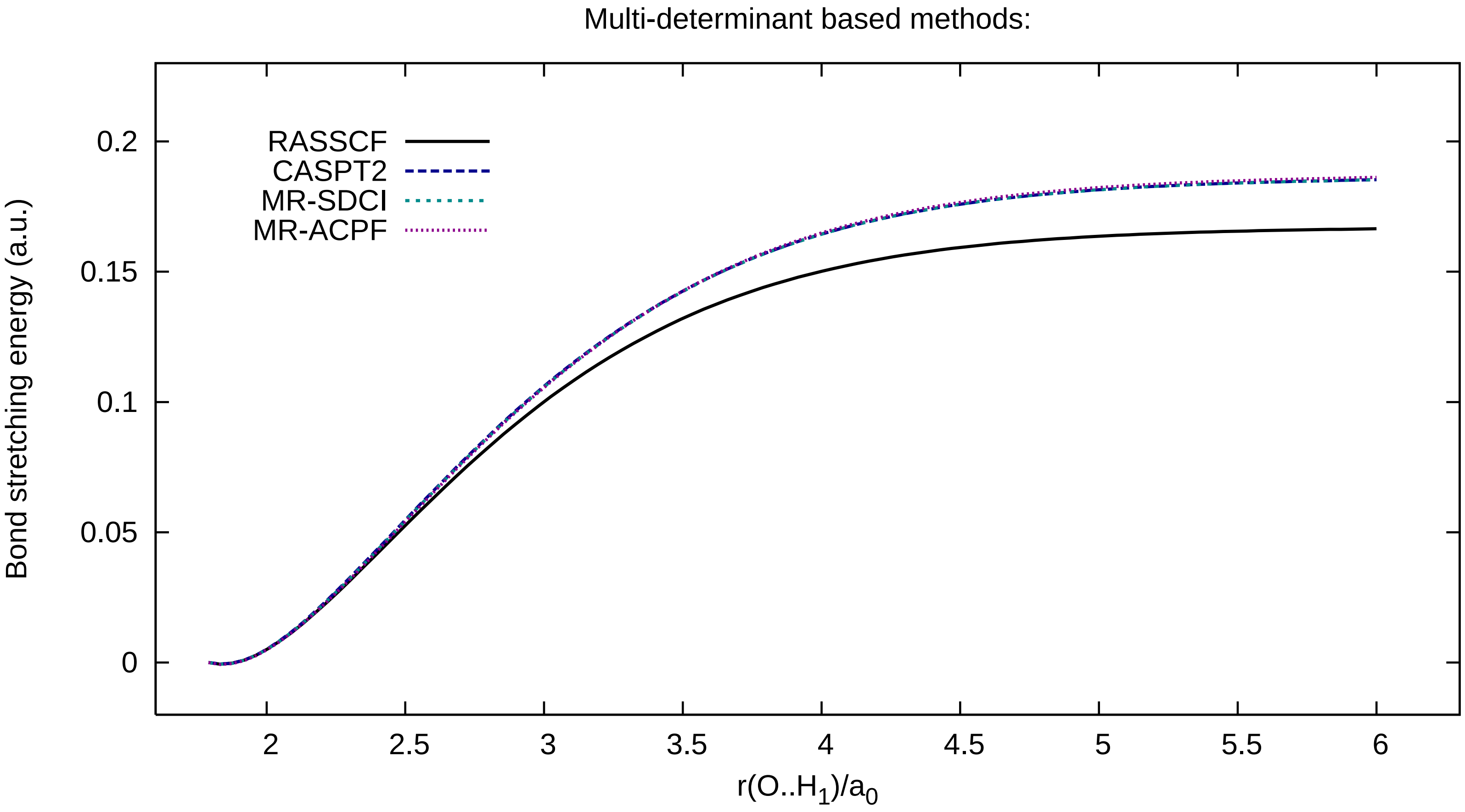
Single-determinant (-based) methods.



Multi-determinant methods.



Multi-determinant methods.



Different references.

We know the answer of course: We do need the kind of correlation computed by MP2 and similar programs, but they must be able to deal with the multi-determinant character of the wave function of e.g. radicals and excited states on an equal footing to the closed-shell cases. Even a simple bond-breaking is not properly treated by single-determinant methods.

Some methods have been successfully extended to handle many-determinant wave functions.

In the Molcas suite of programs, these are the CASPT2 and MRCI programs. The latter can also compute MR-ACPF.

Also, there is some limited capability of the CPF program to handle *single-configuration* open-shell cases, and the CCSDT program can use an open-shell reference state with two open shells. The HF and DFT codes can do UHF and U-DFT. This covers important and common special cases, but none of them can be used reliably for excited states, or when the wave function changes character due to near-degenerate configurations.

Programs and methods.

Program	Methods	Type	Size extensive	Reference
MBPT2	MP2	Perturbative	Yes	HF
CASPT2	CASPT2	Perturbative	Approx	General CASSCF
CCSDT	CCSD, CCSD(T), . . .	Neither/Both	Yes	HF, ROSHF
MRCI	(MR)-SDCI	Variational	No	General
MRCI	(MR)-ACPF	Variational	Approx	General
CPF	CPF	Variational	Approx	ROSHF
CPF	MCPF	Variational	Approx	ROSHF

All methods work properly only if the reference wave function is already a reasonable approximation to the final wave function.

The perturbative methods can fail completely if this is not true. The variational methods will work, but the the quality of the results will deteriorate. The variational methods have a lowest bound on the energy, but only for MRCI do the eigenstates bracket true eigenvalues of the exact Schrödinger equation.

For more than ten-fifteen electrons, a size extensive method should be used. However, for MR-SDCI, a large reference can partly overcome the deficiency, and anyway, there are good correction estimates (Davidson, ACPF).

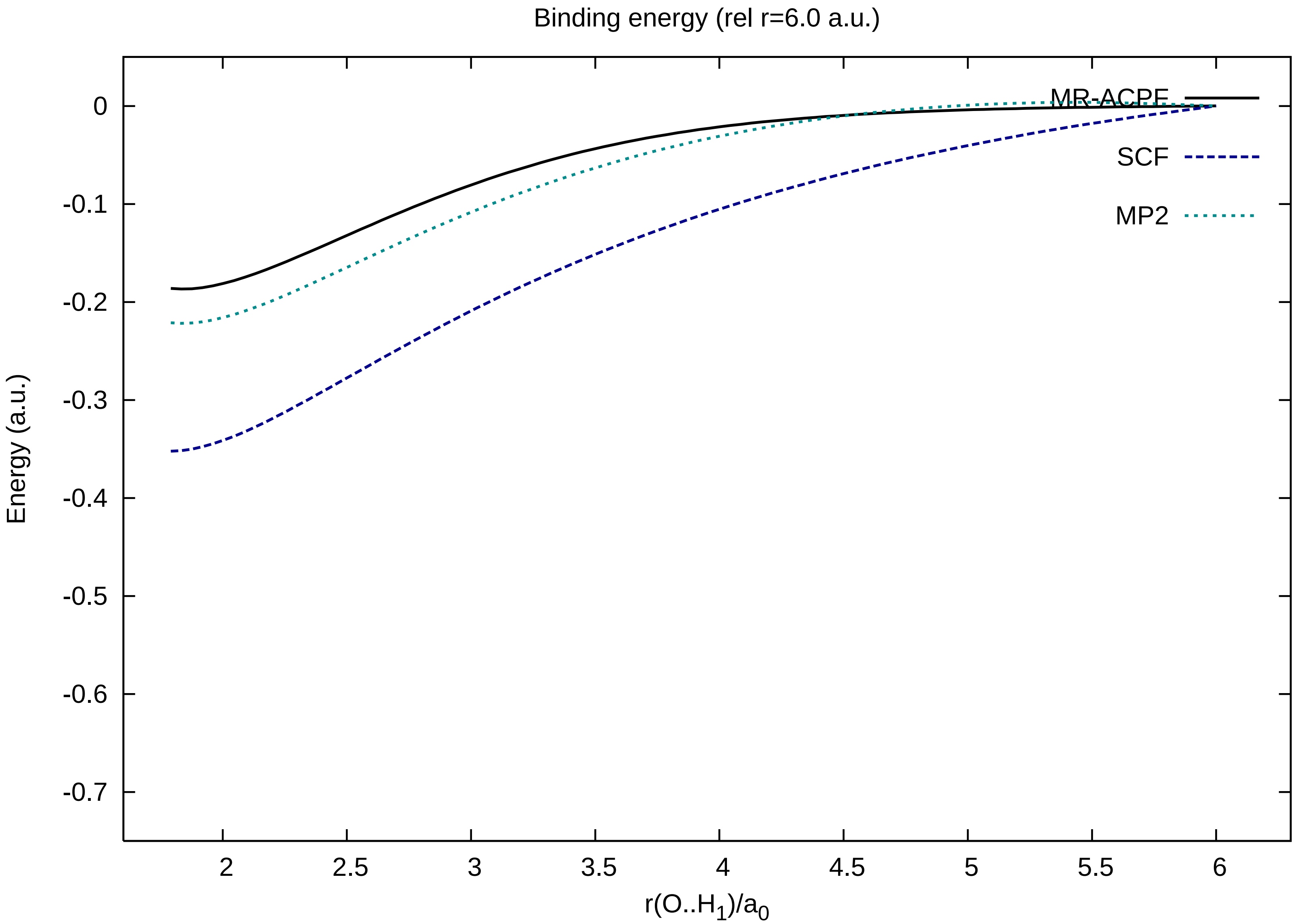
The MBPT2 program

```
 &SCF &END
Title
 H2O ANO(321/21).
Lumorb
ITERATIONS
 40
Occupied
  4  1
End of input

  &MBPT2 &END
Title
  H2O ANO(321/21).
Frozen
  1  0
End of Input
```

MBPT means Many-Body Perturbation Theory. The most common form is *Møller-Plessett* perturbation theory, and the MBPT2 program uses this form to compute a 2nd order correlation energy, MP2. This is a simple and fast calculation, and does not need much input.
In this case, we just give the number of frozen – uncorrelated – orbitals. It is not a good idea to correlate the core orbitals.

The MBPT2 program.

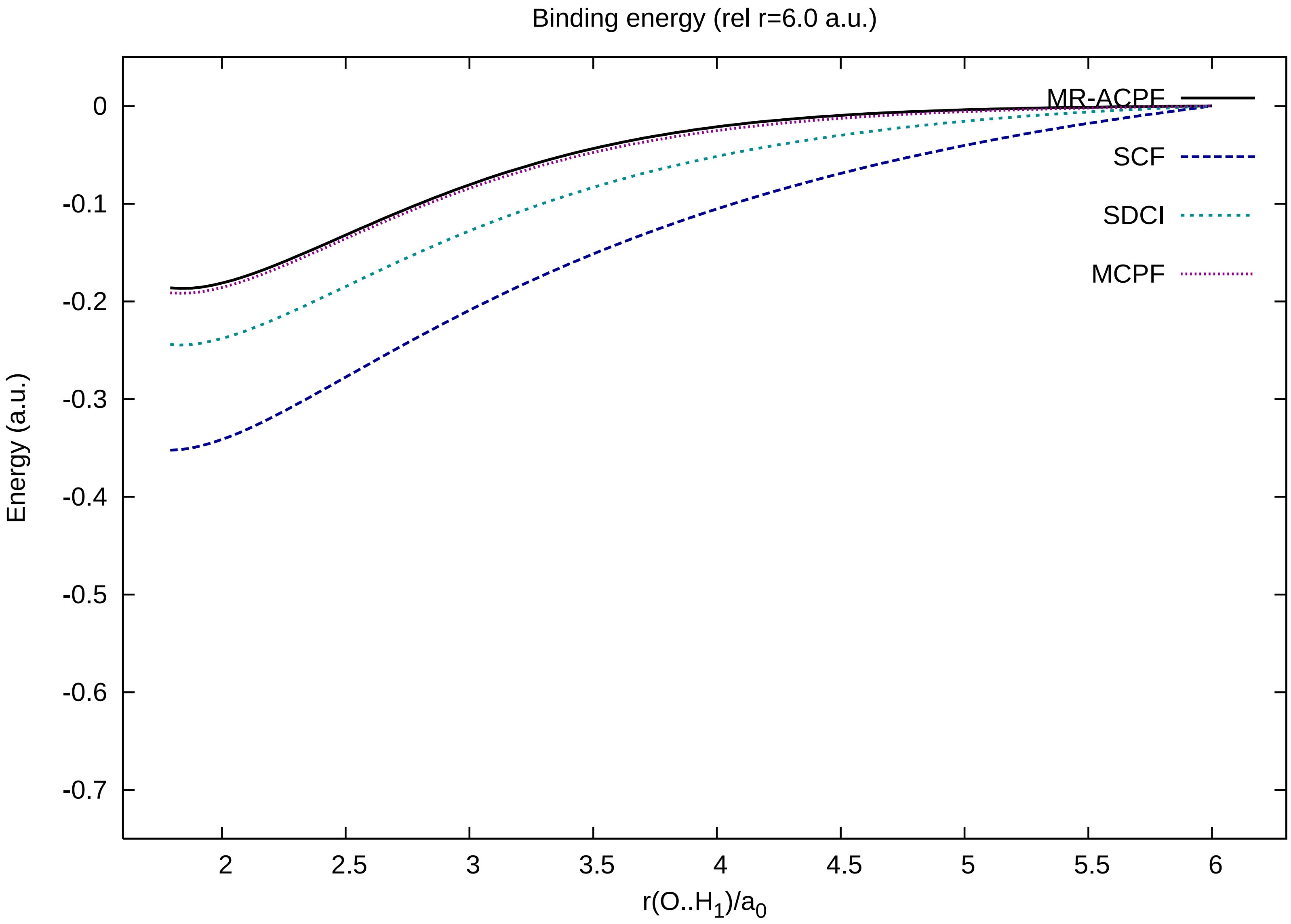


The MRCI/CPF programs, single ref.

```
 &GUGA &END
Title
 H2O ANO(321/21).
Electrons
    8
Spin
    1
Symmetry
    2
Inactive
    3    1
Active
    0    0
CiAll
    1
End of Input
```

```
 &MOTRA &END
Title
 H2O ANO(321/21).
LumOrb
Frozen
 1 0
End of input
 &MRCI &END
Title
 H2O ANO(321/21).
SDCI
End of input
 &CPF &END
Title
 H2O ANO(321/21).
Mcpf
End of input
```

The SDCI and MCPF results.

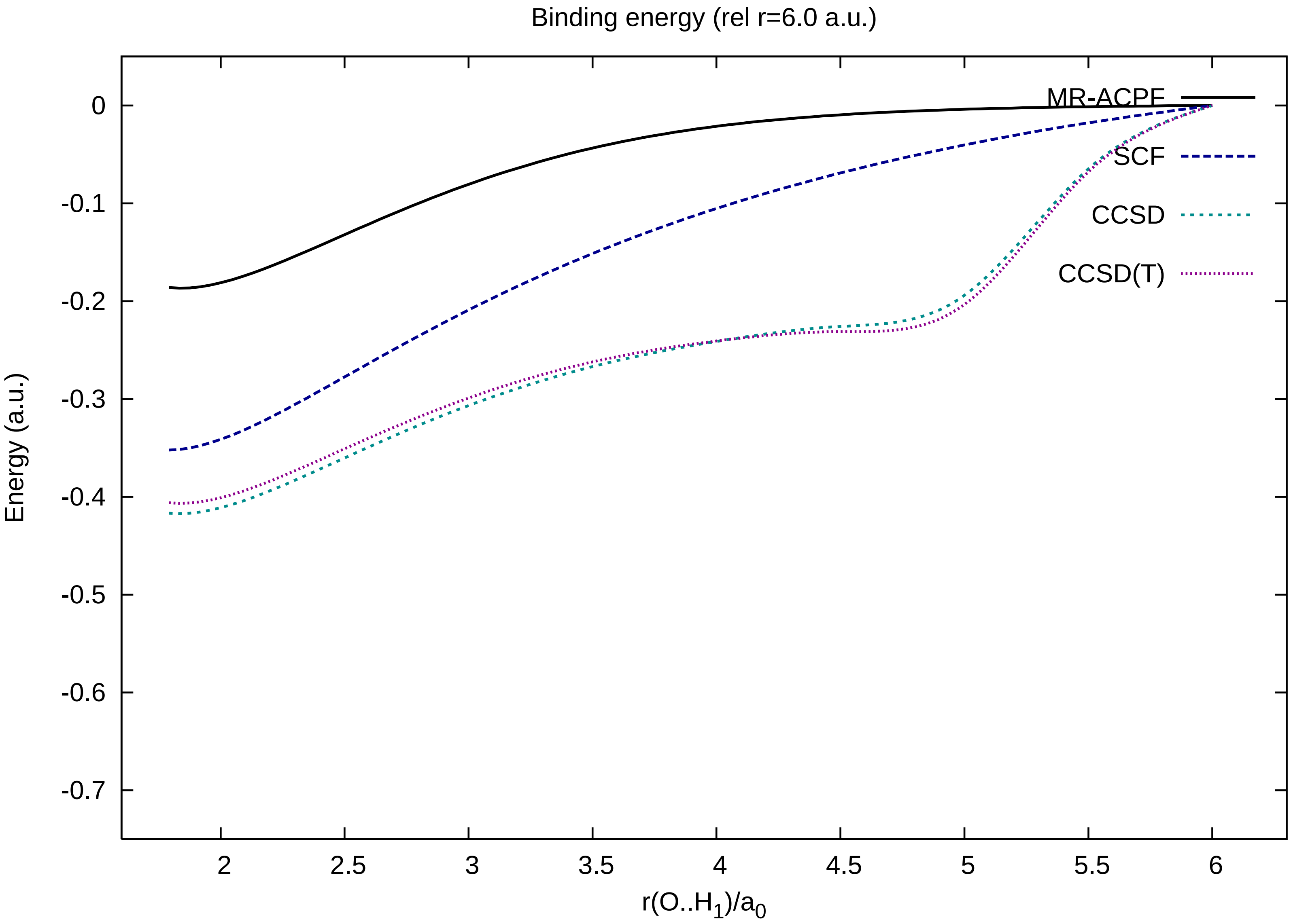


The CCSDT program

```
 &CCSDT &END
Title
 H2O ANO(321/21).
CCT
Iterations
20
Triples
3
End of input
```

With input requesting the triples correction to be computed, also the CCSD energy, as well as a number of different contributions to the triples energy, is computed.

The CCSD and CCSD(T) results.



Multi-configuration methods: RASSCF.

```
 &RASSCF &END
Title
 H2O ANO(321/21).
Lumorb
InActive
 2  0
Ras2
 5  1
NActEl
 6  0  0
CIRoots
 3  3  1
End of input
```

The RASSCF program is mostly used for CASSCF calculations. The wave function is a linear combination of many configuration functions (CSF's, spin-coupled combinations of determinant functions).
The coefficients of the linear combination are optimized, as in CI, but the number of orbitals that are correlated (*active orbitals*) is smaller than in a CI. Also the orbitals are optimized.

The name 'Complete Active Space Self-Consistent Field' means that *all* determinants that can be formed by distributing the active electrons among active orbitals are used in the CI (CAS) and that the orbitals are optimized (SCF).

This calculation is small: 6 active electrons in 6 active orbitals, giving 30 CSF's of symmetry 1 and spin 1 ($^1A'$).

Multi-configuration methods: CASPT2, MRCI, ACPF.

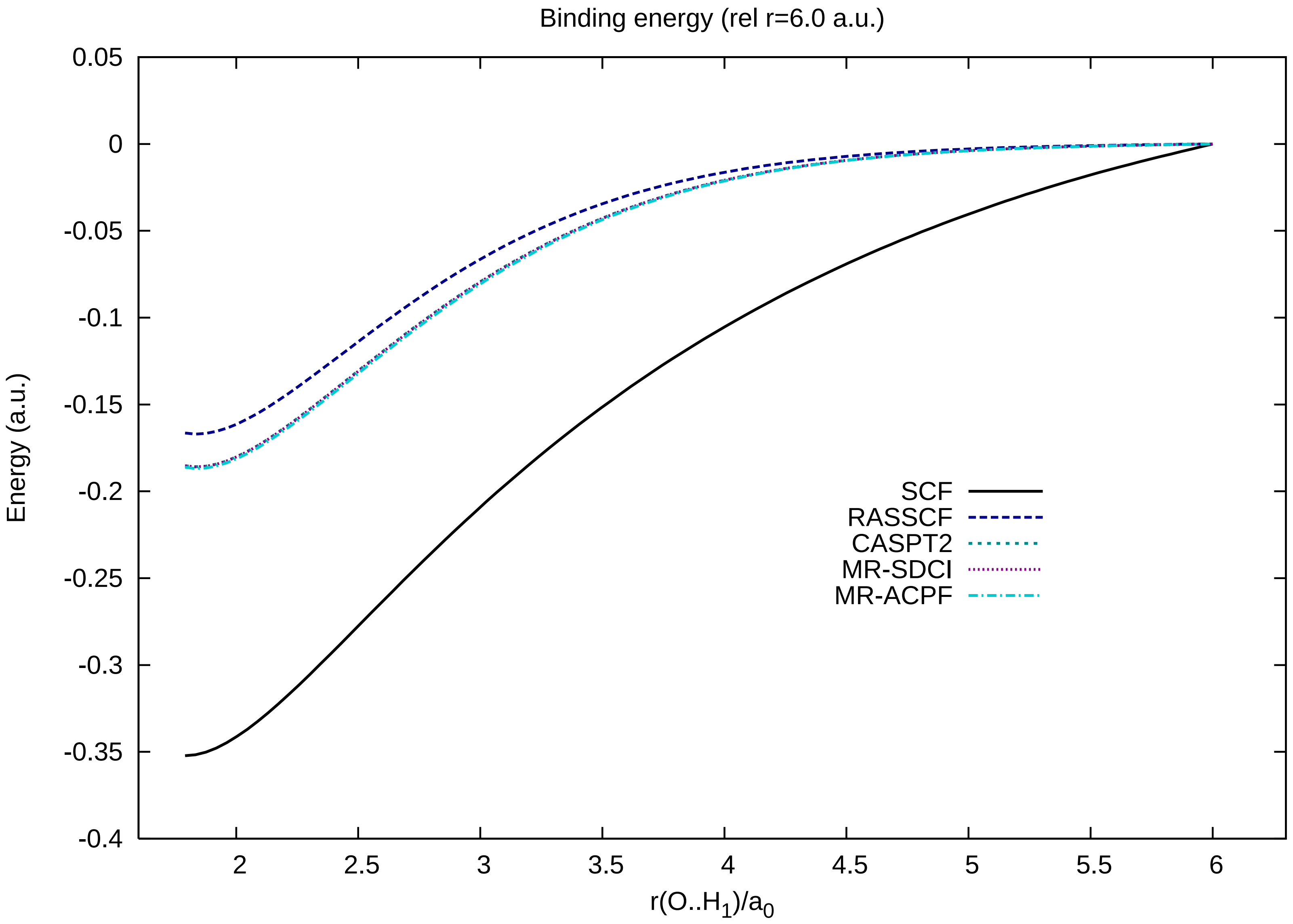
```
 &CASPT2  &END
Frozen
  1   0
Multistates
  3
  1  2  3
End of Input
*------------
 &MRCI &END
Title
 H2O ANO(321/21).
SDCI
NrRoots
  3
End of input
*------------
```

```
 &MRCI &END
Title
 H2O ANO(321/21).
ACPF
NrRoots
  3
End of input
```

The CASPT2 and MRCI programs are also useful for excited state calculations. The simplest inputs are identical to those for a lowest state. The CASPT2 program requires that RASSCF, with the CIROOTS keyword, has generated the root functions. The MRCI program will generate its own reference states within the reference space defined in GUGA.

The GUGA and MOTRA inputs, needed for MRCI, are identical to the ones for only one root. All these methods can also be used with root functions and/or orbitals individually computed for each state, but a common *Average State* reference is much simpler.

The RASSCF results.



Multi-configuration methods, excited states.