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Multiconfigurational self-consistent field (MCSCF)

- MCSCF is a CI on steroids:
both the **coefficients in front of the determinants** and the **MOs used for constructing the determinants** are optimised
- MCSCF optimisation is **iterative** like the SCF procedure in HF or KS
- MCSCF are much harder to converge and prone to converge on solutions that are not minima (2nd-order SCF procedure)
- MCSCF wave function is usually smaller than CI because **harder to optimise**
- MCSCF (**orbital relaxation**) do not recover a large fraction of the correlation energy: **static correlation**
- CI recovers a large fraction of the correlation energy: **dynamic correlation**

The two faces of correlation energy

Static correlation energy

Energy lowering introduced by adding enough **flexibility in the wave function to be able to qualitatively describe the system**. This is essentially the effect of allowing orbitals to become (partly) singly-occupied instead of forcing double occupation, i.e. describing near-degeneracy effects (two or more configurations having almost the same energy)

Dynamic correlation energy

The remaining energy lowering by correlating the **motion of the electrons** and the **electronic cusp**. The problem is that there is no rigorous way of separating **dynamic** and **static** correlation

Take-home message 1

MCSCF methods are mainly used for generating a qualitatively correct wave function, i.e. recovering the “static” part of the correlation

Complete active space self-consistent field (CASSCF)

- In CASSCF, the selection of configurations is done by partitioning the MOs into **active** and **inactive** spaces
- The **active MOs** will typically be some of the **highest occupied** and some of the **lowest unoccupied MOs** from HF calculation
- The **inactive MOs** have **either 2 or 0 electrons**, i.e. always either doubly occupied or empty
- **[n, m]-CASSCF**: n electrons are distributed in all possible ways in m orbitals
- CASSCF gets the “**static**” part of the correlation energy
⇒ **CASPT2** is used to get the “**dynamical**” part

[n, n]-CASSCF

Number of configurations generated in an [n, n]-CASSCF wave function

n	Number of CSFs
2	3
4	20
6	175
8	1764
10	19404
12	226,512
14	2,760,615

Restricted active space self-consistent field (RASSCF)

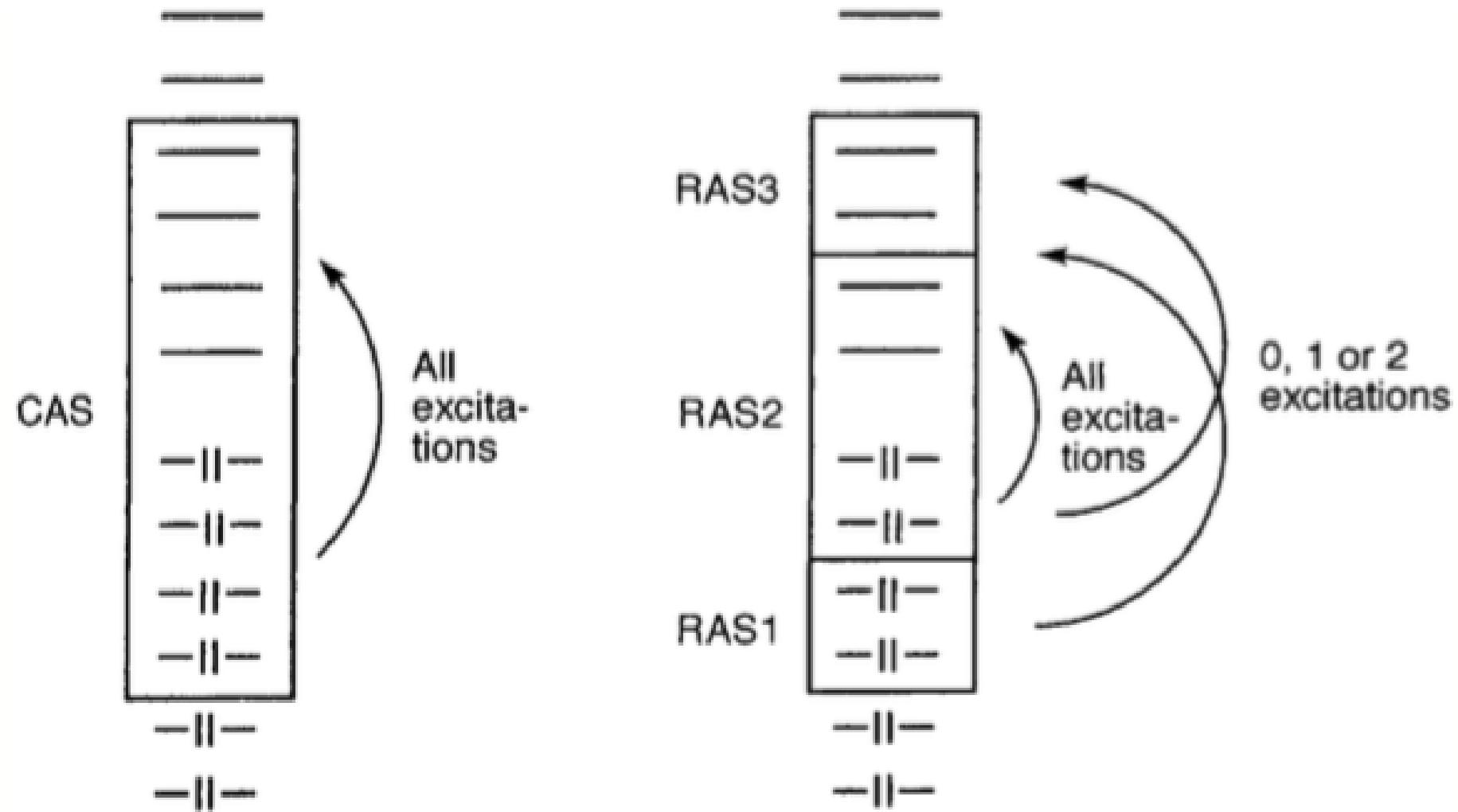
- The active MOs are divided into three spaces: **RAS1**, **RAS2** and **RAS3**
 - ① **RAS1** consists of MOs that are doubly occupied in HF reference determinant
 - ② **RAS2** is generated by a FCI (analogously to CASSCF)
 - ③ **RAS3** consists of MOs that are empty in HF reference determinant
- FCI within **RAS2**
- CISD from **RAS1** to **RAS3** and from **RAS2** to **RAS3**
- This procedure can be customised if required

Take-home message 2

MCSCF methods ain't BLACK BOX!!

How do we choose the active space?! valence orbitals, natural orbitals

CASSCF vs RASSCF



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