

Strong Electron Correlation and Multireference Methods

Jacob Wardzala

Abstract

A wide range of popular and efficient quantum mechanical methods rely on single Slater determinants. While effective for many chemical systems, they often fall short for systems of interest, especially in modern research applications. Single Slater determinants fail to properly characterize systems including heavy metal complexes (like transition metals, lanthanides and actinides) and far from equilibrium interactions like bond breakings. Such systems are common in a wide range of interesting applications, from superconductors to metal-insulator transitions. Instead, these strongly correlated materials are more readily modeled by multireference methods. Such methods go beyond the single determinant representation by including both the ground state electron configuration and a range of excited state configurations. Application uses the Maple Quantum Chemistry Toolbox.

Introduction

Correlation energy is defined as the difference between the exact energy and the Hartree Fock (HF) energy [1]:

$$E_{corr} = E_{exact} - E_{HF}$$

Multireference methods, like other post Hartree-Fock methods, serve to determine this correlation energy to correct for the shortcoming in HF. Hartree-Fock makes use of the mean-field approximation and a single determinant representation, leading to this missing energy [1].

The mean-field approximation simplifies many-body interactions to interactions within an averaged field, reducing complexity to an effective single body problem. This simplification, while clearly useful in making more approachable calculations, breaks down as the assumption of independent electrons fails. Dynamical mean field theory methods address such dynamical/weak correlation between electrons. This correlation is often described as the instantaneous repulsion of electrons and generally produces a quantitative error.

Given the existence of dynamical correlation, it follows that static (or strong) correlation makes up the other part of correlation energy. Static correlation becomes important in systems which are only well defined by more than one determinant. These determinants can be nearly degenerate, such as in molecules with ground states that are quasi-degenerate with low-lying excited states. In these situations, a linear combination of close lying states is necessary to accurately define the electronic structure. Methods like CASSCF and CASCI address this qualitative error.

Other methods, like perturbation theory and coupled cluster methods, also serve to address the electron correlation problem. They do so by introducing higher level excitations to their calculations. However, they still rely on a single reference determinant representation dominating the wavefunction. By contrast, multiconfigurational methods do not assume a single determinant wavefunction. Density functional theory also attempts to collect electron correlation through the exchange correlation functional.

Theory

Multireference Methods

Multiconfigurational Self Consistent Field (MCSCF) is a method which uses a linear combination of configuration state functions to describe the exact wavefunction. Such a representation is given by:

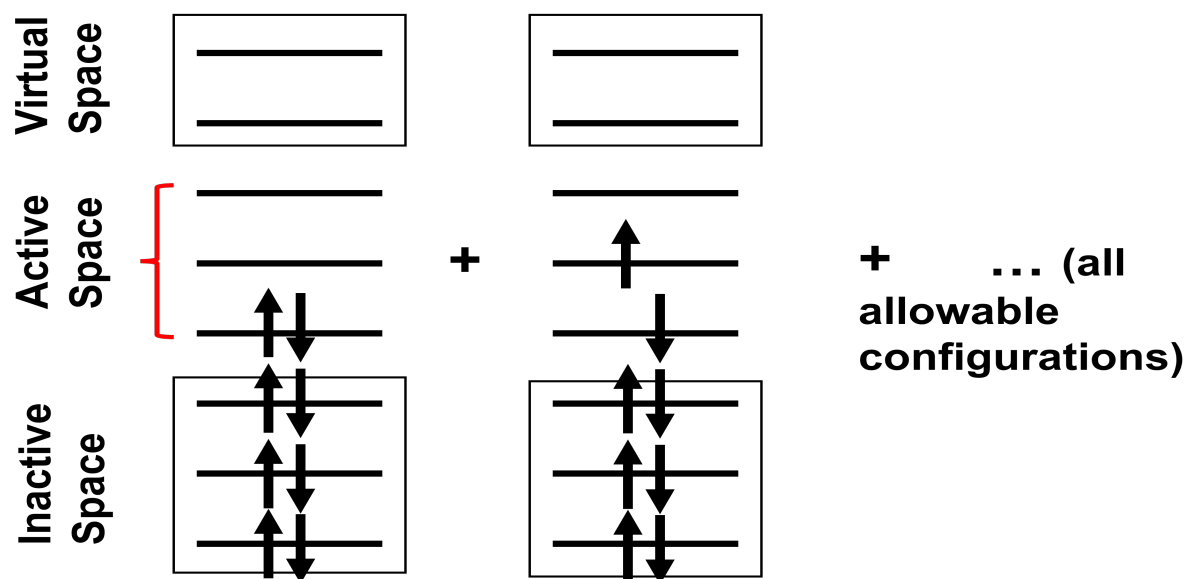
$$\Psi_{MCSCF} = \sum_n^N c_n \Psi_n$$

MCSCF includes a wide range of methods with varying advantages and disadvantages. To perform a MCSCF calculation, both the molecular orbitals, Ψ_n , and the expansion coefficients, c_n , are optimized according to the variational principle. This is done to obtain the lowest possible energy for the given approximate wavefunction, which remains an upper bound on the energy, just like in a standard HF calculation. From a general perspective, a MCSCF calculation is equivalent to a HF-SCF calculation, with a wavefunction approximated as a linear combination of determinants instead of the single determinant used in HF.

Under the umbrella of MCSCF, Complete Active Space Self Consistent Field (CASSCF) is particularly popular and well implemented. In CASSCF, there exists an active space (set of orbitals) for which all possible configurations are included. Other methods exist that are forms of MCSCF, such as Restricted Active Space Self Consistent Field (RASSCF), where a subset of the active space configurations are restricted. For the scope of this worksheet, the focus will be placed on CASSCF.

CASSCF

In CASSCF, the orbitals are divided into three subspaces [3]. These are the inactive space, the aforementioned active space, and the virtual space. The inactive space, also referred to as the core, encompasses full or doubly occupied orbitals. The active space is treated with full configuration interaction. In this space, orbitals have occupations between zero and two. As with FCI calculations, active electrons can occupy any active orbital as long as they abide by the conservation of spin [3]. This is the most complex part of the calculation, scaling as a factorial of the number of active electrons. Finally the virtual space is composed of unoccupied orbitals. The core and virtual orbitals are treated identically to such orbitals in HF. The active space for a given calculation is generally given by (n,m), where n is the number of active electrons and m the number of active orbitals. The splitting of an orbital space with an active space of (2, 3) is visualized in the following figure:



This method helps to decrease the number of determinants describing the system at play by focusing the multiconfigurational character on a subset of the total orbitals. Thus the active space should be chosen to include the orbitals which bring the most multireference character, or the strongest correlation, to the problem as a whole. While this is more efficient than treating the entire system as the active space, it requires added chemical intuition that other methods may not [4]. In choosing the active space, apriori knowledge about the molecule of interest can be used to understand the best choice of electrons and orbitals. Beyond such knowledge, lower theory calculations can be performed in an effort to improve the choice of active spaces. For example, MP2 orbital occupations can be used to find a reasonable active space. When considering relatively small molecules, all valence electrons/orbitals can be included in the active space. However, in larger systems, this is not feasible, increasing the challenge of choosing the active space. For example, treating a conjugated pi system might be done by choosing the pi orbitals and their corresponding electrons to be the active orbitals. The simplest active space is generally one that includes only the HOMO and LUMO.

CASCI

The complete active space group of methods also includes Complete Active Space Configuration Interaction (CASCI). CASCI operates like CASSCF, with one exception. While CASSCF variationally optimizes both the expansion coefficients and orbitals, CASCI forgoes orbital optimization [5]. Thus, CASCI requires more work to find ideal orbitals, but can potentially offer more flexibility in orbital representation.

Applications

To show the role of electron correlation, an example comparing multiconfigurational methods with HF is implemented here with the the Quantum Chemistry Toolbox in Maple. Two situations are presented. In the first example we examine the stretching of diatomic hydrogen. In the second we explore the titanium atom and its ionization energy.

> with(QuantumChemistry) :

Looking at the hydrogen molecule, we explore a range of H-H bond distances in an effort to understand the role of electron correlation as the system moves away from equilibrium.

H₂ in the Dissociation Limit

> *moleculesH2* := [seq([["H", 0, 0, 0], ["H", 0, 0, r]], r in seq(r, r=0.5..4.1, 0.2))]:

For the range of bond distances, calculations are carried out with HF, CASSCF, CASCI and FCI. The energies for each method at each interatomic distance are reported below.

> *EnergiesHF* := [seq(*Energy*(*molecule*, *method* = *HartreeFock*, *basis* = "cc-pVDZ"), *molecule* in *moleculesH2*)];

EnergiesHF := [-1.04880056, -1.12692469, -1.11639130, -1.08117078, -1.04093874, (4.1.1)
 -1.00219275, -0.96699945, -0.93591768, -0.90886890, -0.88548552, -0.86533012,
 -0.84798761, -0.83308637, -0.82030129, -0.80935143, -0.79999297, -0.79201046,
 -0.78521027, -0.77941758]

> *EnergiesDFT* := [seq(*Energy*(*molecule*, *method* = *DensityFunctional*, *xc* = "B3LYP", *basis* = "cc-pVDZ"), *molecule* in *moleculesH2*)];

EnergiesDFT := [-1.08263980, -1.16398667, -1.15740457, -1.12656014, -1.09113886, (4.1.2)
 -1.05769645, -1.02824500, -1.00319642, -0.98233356, -0.96517814, -0.95118594,
 -0.93983737, -0.93066752, -0.92327639, -0.91733084, -0.91255846, -0.90873657,
 -0.90568153, -0.90324116]

> *EnergiesCASSCF* := [seq(*Energy*(*molecule*, *method* = *ActiveSpaceSCF*, *active* = [2, 2], *basis* = "cc-pVDZ"), *molecule* in *moleculesH2*)];

EnergiesCASSCF := [-1.06114927, -1.14397743, -1.13968432, -1.11244939, (4.1.3)
 -1.08232713, -1.05612538, -1.03586447, -1.02153426, -1.01213211, -1.00632483,
 -1.00289724, -1.00094037, -0.99985074, -0.99925526, -0.99893383, -0.99876135,
 -0.99866880, -0.99861886, -0.99859158]

> *EnergiesCASCI* := [seq(*Energy*(*molecule*, *method* = *ActiveSpaceCI*, *active* = [2, 2], *basis* = "cc-pVDZ"), *molecule* in *moleculesH2*)];

EnergiesCASCI := [-1.04963746, -1.12918139, -1.12192054, -1.09279875, (4.1.4)
 -1.06191285, -1.03568865, -1.01575526, -1.00179335, -0.99263605, -0.98694778,
 -0.98357373, -0.98165419, -0.98061008, -0.98007473, -0.97982457, -0.97972719,
 -0.97970623, -0.97971914, -0.97974346]

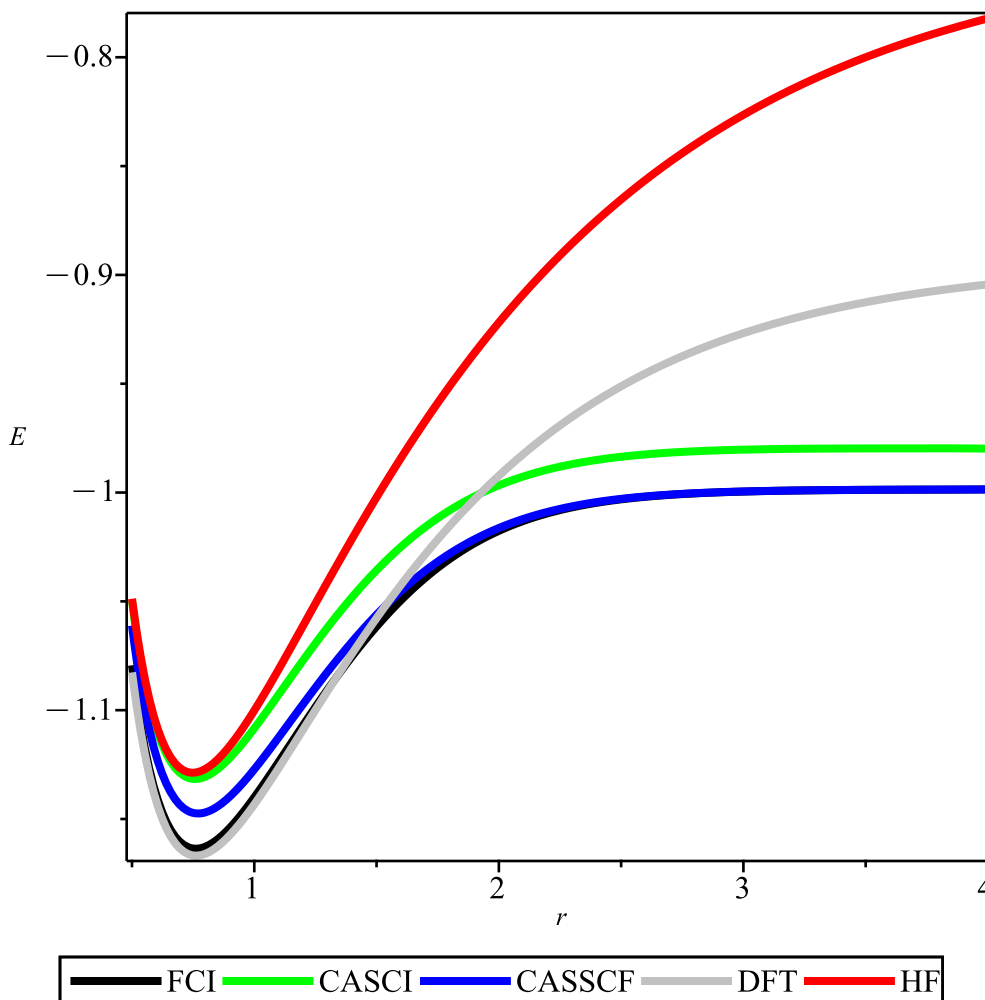
> *EnergiesFCI* := [seq(*Energy*(*molecule*, *method* = *FullCI*, *basis* = "cc-pVDZ"), *molecule* in *moleculesH2*)];

Now, the energy can be plotted as a function of internuclear distance with the following set of commands. First, the data from each method is fit to a polynomial, then each fitted curve is plotted.

EnergiesFCI := [-1.07937005, -1.16090468, -1.15408171, -1.12373524, -1.09049387, (4.1.5)
 -1.06153495, -1.03911335, -1.02332228, -1.01305946, -1.00679094, -1.00312925,
 -1.00105660, -0.99991007, -0.99928643, -0.99895083, -0.99877106, -0.99867463,

$-0.99862254, -0.99859403]$

- > $HF_fit := \text{interp}([seq(r, r=0.5 ..4.1, 0.2)], \text{EnergiesHF}, r) :$
- > $DFT_fit := \text{interp}([seq(r, r=0.5 ..4.1, 0.2)], \text{EnergiesDFT}, r) :$
- > $CASSCF_fit := \text{interp}([seq(r, r=0.5 ..4.1, 0.2)], \text{EnergiesCASSCF}, r) :$
- > $CASCI_fit := \text{interp}([seq(r, r=0.5 ..4.1, 0.2)], \text{EnergiesCASCI}, r) :$
- > $FCI_fit := \text{interp}([seq(r, r=0.5 ..4.1, 0.2)], \text{EnergiesFCI}, r) :$
- > $p_HF := \text{plot}(HF_fit, r=0.5 ..4, \text{axes} = \text{boxed}, \text{labels} = ['r', 'E'], \text{color} = \text{red}, \text{thickness} = 3) :$
 $p_DFT := \text{plot}(DFT_fit, r=0.5 ..4, \text{axes} = \text{boxed}, \text{labels} = ['r', 'E'], \text{color} = \text{grey}, \text{thickness} = 3) :$
 $p_CASSCF := \text{plot}(CASSCF_fit, r=0.5 ..4, \text{axes} = \text{boxed}, \text{labels} = ['r', 'E'], \text{color} = \text{blue}, \text{thickness} = 3) :$
 $p_CASCI := \text{plot}(CASCI_fit, r=0.5 ..4, \text{axes} = \text{boxed}, \text{labels} = ['r', 'E'], \text{color} = \text{green}, \text{thickness} = 3) :$
 $p_FCI := \text{plot}(FCI_fit, r=0.5 ..4, \text{axes} = \text{boxed}, \text{labels} = ['r', 'E'], \text{color} = \text{black}, \text{thickness} = 3) :$
- > $\text{plots}:-\text{display}(\{p_HF, p_DFT, p_CASSCF, p_CASCI, p_FCI\});$



From this plot, we can see the importance of electron correlation far from equilibrium, even in a species as simple as diatomic hydrogen. Near the equilibrium bond distance, there are differences between the methods, but each predicts a similar distance and fairly similar energy. Moreover, the curves are qualitatively similar. However, as that bond is stretched towards the infinite limit, it becomes clear that HF is lacking the electron correlation component to energy which is recovered by the three high level

methods. DFT with the B3LYP functional also fails to describe the cleavage of the H-H bond properly. This can be explained by the fact that as the hydrogen-hydrogen bond is pulled apart, the molecule becomes better represented by a linear combination of two determinants. Thus the single determinant method employed by HF fails, predicting a $H^+ + H^-$ product instead of $2H$. The persistent difference between CASSCF and CASCI can be explained by the lack of orbital relaxation in CASCI.

> *MOOccupations(moleculesH2[19], method = HartreeFock, basis = "cc-pVDZ")*

$$\begin{bmatrix} 2.00000000 \\ 0. \\ 0. \\ 0. \\ 0. \\ 0. \\ \vdots \end{bmatrix}$$

10 element Vector[column]

(4.1.6)

> *MOOccupations(moleculesH2[19], method = ActiveSpaceSCF, active = [2, 2], basis = "cc-pVDZ")*

$$\begin{bmatrix} 1.02661519 \\ 0.97338481 \\ 0. \\ 0. \\ 0. \\ 0. \\ \vdots \end{bmatrix}$$

10 element Vector[column]

(4.1.7)

The orbital occupations back up this understanding of the bond dissociation plot. With HF, a single orbital is occupied by both electrons, even at the furthest distance examined. By contrast, using CASSCF, the first two orbitals each have roughly one electron, corresponding to the expected bond breaking.

1st Row Transition Metal Atom

The second example involves the transition metal titanium. Transition metal containing complexes are of interest in a variety of applications, and they generally necessitate multiconfigurational methods due to their strongly correlated electrons and many low lying excited states.


> *mol := ["Ti", 0, 0, 0]*

mol := ["Ti", 0, 0, 0]

(4.2.1)

Calculations using HF and CASSCF are carried out for this system. The electron correlation energy is also reported.

```
> dataHF := HartreeFock(mol, basis = "cc-pVTZ") :
> dataCASSCF := ActiveSpaceSCF(mol, active=[4, 6], basis = "cc-pVTZ"):
> dataCASSCF[e_corr]
                                -0.32172931
                                                                (4.2.2)
```

```
> MOOccupationsPlot(mol, method = HartreeFock, basis = "cc-pVDZ")
0.....
```

```
2.....
```

```
> MOOccupationsPlot(mol, method = ActiveSpaceSCF, active = [4, 6], basis = "cc-pVDZ")
```


$$\text{Moccs_CASSCF} = \begin{bmatrix} 1.83178620 \\ 0.99548125 \\ 0.99547930 \\ 0.07658426 \\ 0.05033835 \\ 0.05033064 \\ \vdots \end{bmatrix} \quad (4.2.4)$$

11 element Vector[column]

Exploring the orbital occupations, we see a more dramatic version of what was seen with the dissociation of hydrogen. With HF, the valence electrons can be found in two orbitals, corresponding to the 4s and first 3d orbital. In contrast, CASSCF shows the valence electrons primarily occupying the 4s and first 2 3d orbitals. This better aligns with the conventional expectations of orbital filling. Beyond this, higher energy orbitals see small average occupations as a result of titanium's low lying excited states.

> *dataHFE* := *HartreeFock*(*mol*, *basis* = "cc-pVTZ", *charge* = 1) :

> *dataCASSCF_E* := *ActiveSpaceSCF*(*mol*, *active* = [5, 6], *basis* = "cc-pVTZ", *charge* = 1) :

$$\begin{aligned}
 > \text{IE_HF} &= (\text{dataHFE}[e_tot] - \text{dataHF}[e_tot]) \cdot 27.211 \text{ eV} \\
 &\quad \text{IE_HF} = 0.54837920 \text{ eV} \quad (4.2.5)
 \end{aligned}$$

$$\begin{aligned}
 > \text{IE_CASSCF} &= (\text{dataCASSCF_E}[e_tot] - \text{dataCASSCF}[e_tot]) \cdot 27.211 \text{ eV} \\
 &\quad \text{IE_CASSCF} = 6.12526600 \text{ eV} \quad (4.2.6)
 \end{aligned}$$

Finally, the first ionization energies are reported for each method. Here, it is clear that the correlation energy components of the absolute energies do not cancel out when calculating a more relevant quantity. The CASSCF ionization energy is roughly an order of magnitude larger than the HF energy, and much more closely aligned with experimental results.

Discussions/Conclusion

Single reference methods have notable shortcomings for systems with strong electron correlation and low lying excited states that are nearly degenerate with the ground state. While some single determinant methods (CC, MP) successfully recover the correlation energy for many systems, they can still struggle for those that are challenging to define with a single Slater determinant. Multireference methods, including the popular CASSCF and CASCI define a set of active orbitals for which all allowable configurations are included. This allows this portion of the system with the most multireference character to be properly treated, while the core and virtual orbitals can be treated with the comparatively cheap HF method. These and other multireference methods are crucial for examining systems with strong electron correlation, like transition metal complexes and some far from equilibrium scenarios.

References

1. Szabo, A.; Ostlund, N.S.; *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure*; Dover, New York, 1996
2. Helgaker, T.; Jorgensen, P.; Olsen, J., *Molecular electronic structure theory*; John Wiley & Sons, England, 2004.
3. Townsend, J; Kirkland, J; Vogiatzis, K; *Mathematical Physics in Theoretical Chemistry*; Elsevier, 2019.
4. Veryazov, V.; Malmqvist, P. Å.; Roos, B. O., 2011. How to Select Active Space for Multiconfigurational Quantum Chemistry? *Int. J. Quantum Chem.* 111, 3329-3338.
5. Levine, B.G., Durden, A.S., Esch, M.P., Liang, F., Shu, Y., 2021. CAS without SCF—Why to use CASCI and where to get the orbitals. *The Journal of Chemical Physics* 154, 090902.
6. Cramer, Christopher J. *Essentials of Computational Chemistry: Theories and Models*. J. Wiley & Sons, England, 2004.