Electron correlation analysis of H_2

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1 The case of cc-pVDZ

The first case study was carried out for the H_2 molecule, using for all the calculations cc-pVDZ and cc-pVTZ as a basis set. All the calculations were performed using ORCA, except for CASSCF and CASPT2 calculations which were performed using OpenMolcas.

1.1 The ground state S_0

The dissociation energy curve for H_2 was constructed by comparing all the methods that were used for the ground state study. In this case, as can be seen in figure 1, the dissociation energy values obtained are in agreement with those reported experimentally and theoretically. Where for the equilibrium distance, which is 0.741 Å for the ground state, an exact dissociation energy of -109.5 Kcal/mol (at 0 K) is reported [1].

Energy minima were reached using FCI and CCSD, which is to be expected since they consider a full correlation energy, and because H_2 is a two electron system, CCSD can be analogous to a full CI. The opposite is true for RHF, which has the highest energy values, in particular in long range where Coulomb repulsion is overestimated. In FCI the minimum energy was reached at a distance of 0.8 Å in which an energy of -103.033349 Kcal/mol was obtained, considering that the molecule was not in its optimized geometry. Since the correlation energy is defined as the energy difference between the FCI energy and the HF energy, the energy difference observed in the hydrogen dissociation curve can be understood as the correlation energy of H_2. Because CASSCF describes the static correlation energy very well, the difference between HF and CASSCF can be stated as the static correlation energy, while the energy difference between FCI and CASSCF can be interpreted in this case as the dynamic correlation.

Figure 1
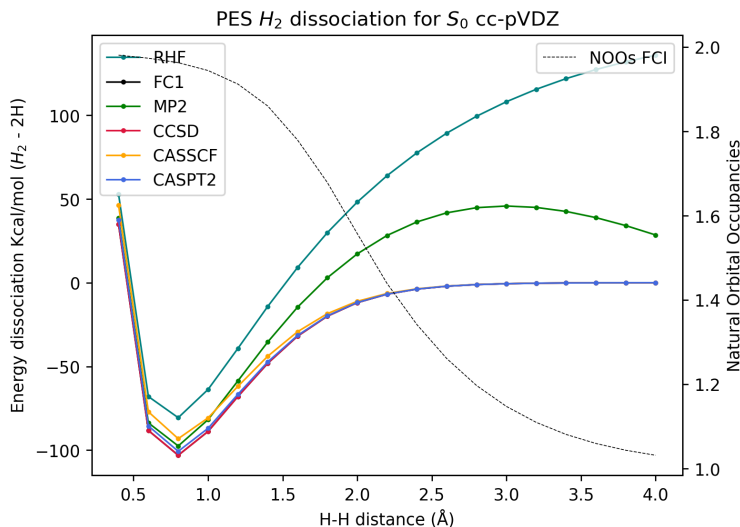
The natural orbitals occupancies (NOOs) are represented for the case of a close shell systems, as shown

in Figure 2, and therefore the NOOs are close to 2 and 0 for short distances. As the molecule approaches the dissociation limit, the occupancy number approaches one, since the orbitals acquire a similar energy and the appropriate linear combination of them will reproduce the 1s states of the hydrogen atoms. This agrees with other investigations where the H atoms being at a distance close to 4 Å, the NOOs approach one [5].

It is important to mention that in this case the representation of the natural orbitals (NOs) is given only for the first two orbitals, which in this case are the σ_g and σ_u, since in the case of a system with two electrons they are the most relevant. Moreover, it has been shown that only a small number of NOs have a significant number of occupancy numbers, even for highly correlated wavefunctions.

Figure 2: Natural Orbital Occupancies. Solid line for σ_g and dashed line for σ_u
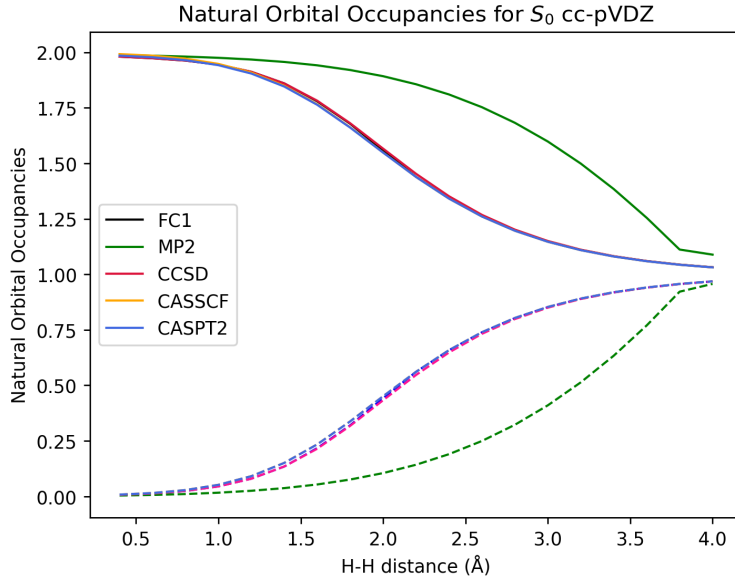
1.1.1 Indices of electron correlacion

The indices for dynamic, non-dynamic and static correlation where calculated using Matito's formulas [6], considering a close shell system and using the for size-intensive version:

$$I_{ND} = \frac{1}{2N} \sum_i n_i(2 - n_i)$$

$$I_D = \frac{1}{4N} \sum_i [n_i(2 - n_i)]^{1/2} - I_{ND}$$

$$I_T = I_{ND} + I_D$$

Figure 3 shows the electronic correlation indices, where the left side shows the correlation indices for CCSD, CASSCF and CASPT2.The values obtained for this case are similar to those previously reported by Matito and collaborators using the same formulas [3]. Where a maximum total correlation of approximately 0.5 is obtained at a distance of 2 Å to constant. While for short distances there is no non-dynamic correlation, even at the equilibrium distance the I_{ND} correlation is almost zero. However, as the distance between the H atoms gets longer, the non-dynamic correlation starts to become important and the dynamic correlation starts to decay to zero, which is an indicator of the dissociation limit. This is due to the fact that as the H atoms are moving away from each other, the electrons get farther away from each other and the interaction decreases, so the dynamic correlation loses relevance as the two electrons are

isolated. In the case of CASSCF, it is to be expected that it is the one with the lowest I_D indices (CCSD has almost double), since it theoretically do not have dynamic electron correlation included.

It was decided to represent separately the correlation indices for the case of MP2 since they are a special case. As can be seen in the image on the right there comes a point where MP2 no longer describes correctly the I_T and I_D which occurs at a distance of approximately 1.5 Å, this was because the NOOs values for the last orbitals had negative values so that the calculation of the correlation indices becomes impossible. These values could be omitted, however for this case it was decided not to omit them in order to get a general idea of how the method can break down for long distances. This may be due to the fact that MP2 is a simple reference method, based on HF, and as it is known, the latter fails for long distances. Although theoretically MP2 is unable to describe non dynamic correlation, for the case of a two electron system it adds some static correlation when the atoms are at a long distance.

Figure 3: Indices of electron correlation. I_D (solid line) I_{ND} (dotted line) and I_T (dashed line)
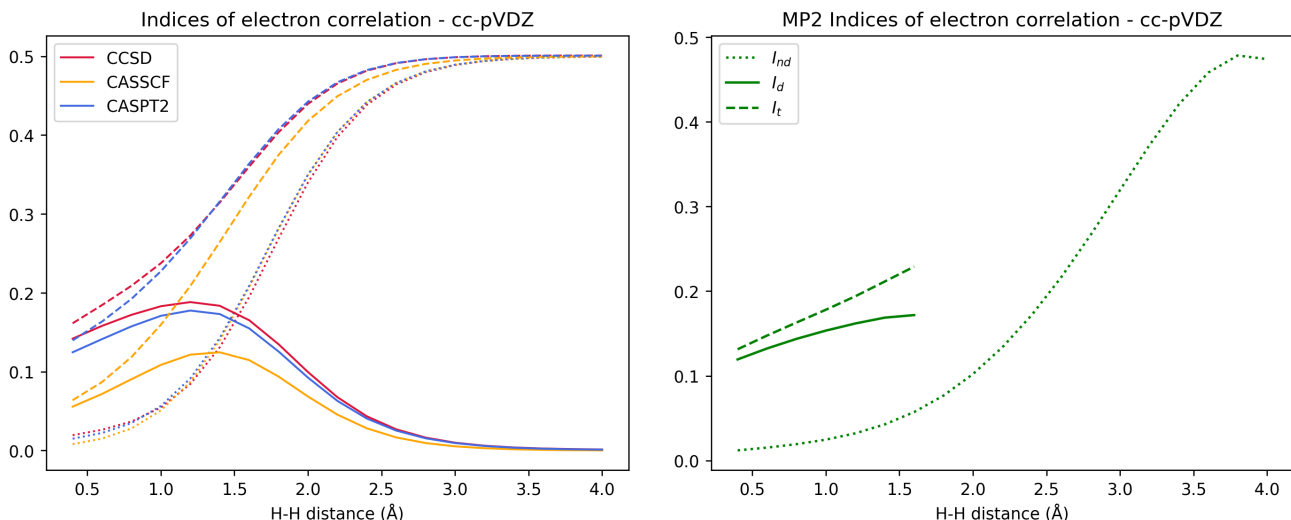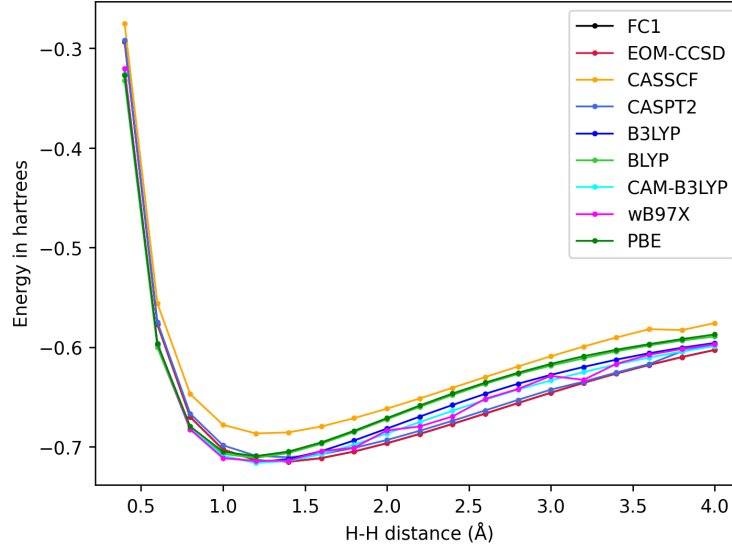

1.2 The first excited state S_1

The potential energy curve of all the methods used is represented in figure 4. In this case 5 functionals where used to the study of the first excited state:

- Gradient-corrected approximation (GGA): PBE and BLYP

- Hybrid-GGA: B3LYP

- Range-separated hybrids: wB97X and CAM-B3LYP

The minimun energy obtained is in agreement with the one previously reported, in which for an equilibrium distance of 1.0319 Å a minimum energy of -0.717961 hartrees for the first excited state is obtained [4]. As expected, the energetic minimum is established by FCI, and in this case EOM-CCSD has almost the same values as FCI, taking into account that it is a two-electron system. This is followed by CASPT2 as in the ground state case. However, there is a clear difference between the functionals, where the range-separated hybrids are the ones with a better performance. This is due to the fact that RSH functionals use different functionals forms for the short-range and long-range parts of the exchange-correlation interaction and this allows a more accurate treatment of electron correlation. While GGA functionals focus on incorporate the gradient of the electron density in addition to the local density and only capture local and short-range

correlation effects. Thus, as the distance between H atoms increases, the energetic difference between PBE and wB97X (for example) becomes clearer.

Figure 4: Potential energy curve for S_1

For the occupancies of the natural orbitals for the first excited state, these are expected to have values close to one for σ_g and σ_u^*. In Figure 5 these values are represented, where on the right are the occupancies for σ_g and on the right are the occupancies for σ_u^*. It is observed that at long distances, at about 3.6 Å, CASSCF and CASPT2 behave in an odd way, where the electrons end up occupying mostly the same σ_g orbital, while the other methods have almost the same behavior throughout the dissociation of the H_2.
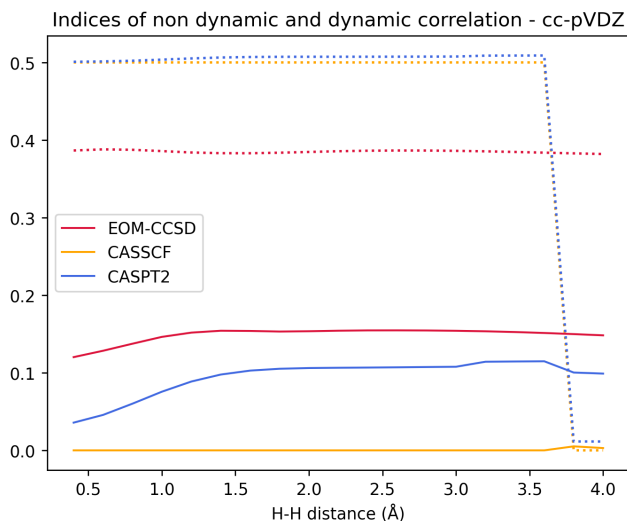
Figure 5
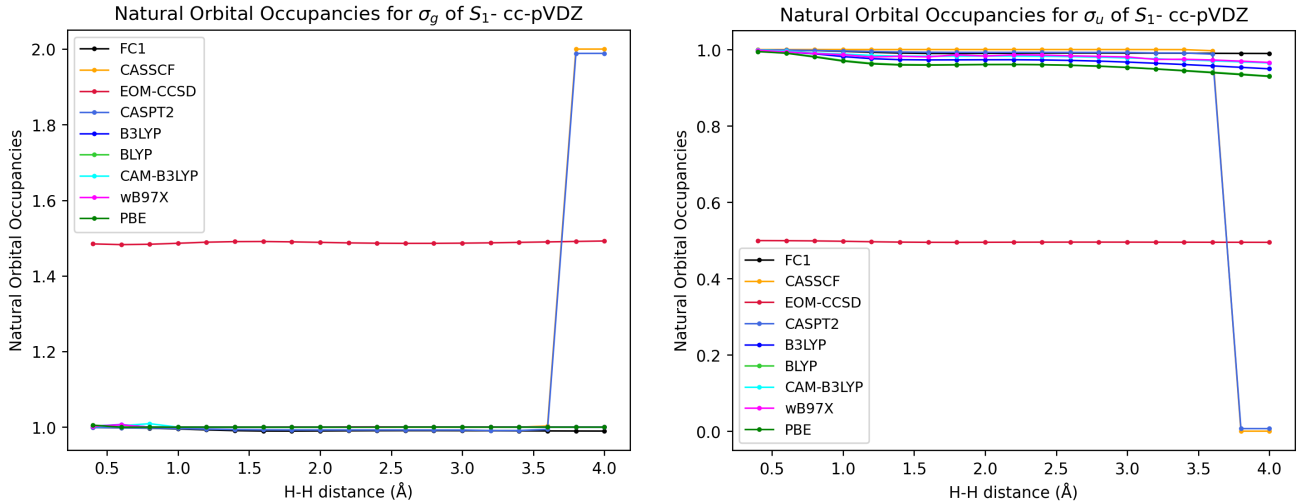
As shown in Figure 6, for CASSCF, CASPT2 and EOM-CCSD the dynamic correlation indices are lower compared to those obtained for S_0, and these have minimal variation. However, would be expected that dynamic correlation exhibits an increase due to the ionic character of the state, contrary to what was observed for S_0. It is quite representative how CASSCF does not add dynamic correlation along the H dissociation, which when compared with Figure 3 for S_0, at short distances a few dynamic correlation was

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observed. It is expected that EOM-CCSD is the one that best represents dynamic correlation, however for this case, as the NOOs values remain constant, so do the correlation indices, whose variation along the separation of the atoms is almost null.

Figure 6 b shows the correlation indices for the different functionals studied. In this case it is interesting to see how in general the GGA functionals are the ones with the highest dynamic and non-dynamic correlation indices, even though they theoretically do not add correctly the long-range correlation. However, in general, TDDFT has lower I_D values than those observed for EOM-CCSD and CASPT2 so they tend not to be good descriptors for dynamic correlation compared to CASPT2.

Figure 6: Indices of electron correlation. I_D (solid line) I_{ND} (dotted line).

(a) EOM-CCSD, CASSCF and CASPT2 comparation

(b) Functionals TD-DFT comparation
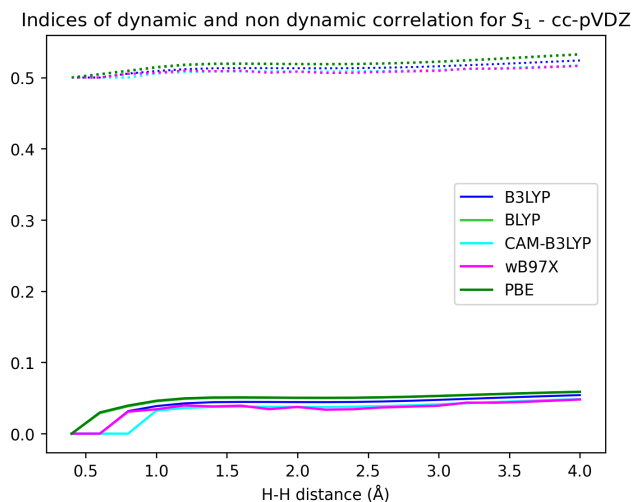
In figure 7 the indices for total correlation are represented. Because CASPT2 adds dynamic correlation to CASSCF it is expected that as a reference it will be among those with the highest correlation indices. In this case EOM-CCSD should have a similar or better performance than CASPT2, but due to the number of NOOs obtained at the moment, its values tend to be low. I_T values tend to be greater than 0.5, where for S_0 this was the maximum value reached, this is due to the fact that in general for the excited system, there is a higher dynamic correlation contribution.

Figure 7

Indices of total correlation for S_1 of H_2 - cc-pVDZ
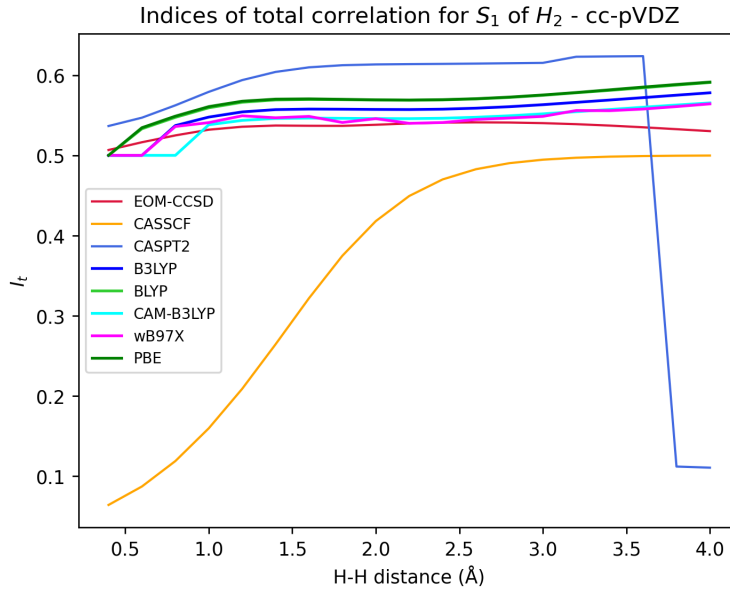
2 Comparation with cc-pVTZ

2.1 Ground state S_0

As the bases set size increases, more virtual orbitals are available, as in the case of cc-pVDZ for H_2, which has one occupied orbital and 9 virtual orbitals. When the basis set is increased to cc-pVTZ there are then 27 virtual orbitals. Each of these virtual orbitals as they move away contribute less to the total energy of the system, however these configurations must be considered for the dynamical correlation case. Figure 8 shows the comparation between cc-pVDZ and cc-pVTZ for the ground state of H_2.

In the three cases, both for CASSCF and CASPT (left a) and for CCSD (right b), it is observed that the change of bases does not affect the non-dynamic correlation indices. However, the base change does affect the dynamic correlation indices, where it becomes evident that as the basis set size increases, the dynamic correlation indices increase, since in this case, as the number of available virtual orbitals increases, a greater number of configurations must be considered.

Figure 8: Indices of electron correlation. I_D (solid line) I_{ND} (dotted line) and I_T (dashed line).

(a) CASSCF and CASPT2 cc-pVDZ vrs cc-pVTZ
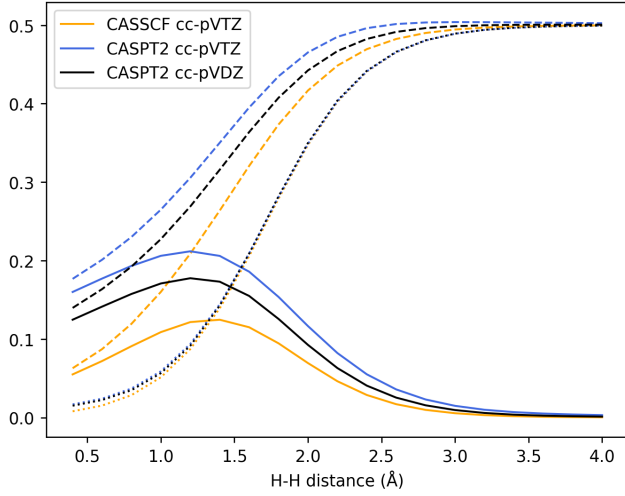
(b) CCSD cc-pVDZ vrs cc-pVTZ
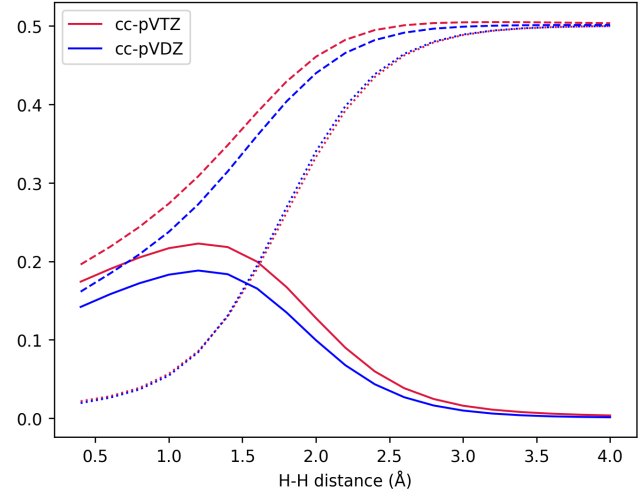
2.2 First excited state S_1

The same behavior is observed for the case of the first excited state of H_2, where as the base set size increases, the dynamic correlation indices increase, while for the non-dynamic correlation the base change has no relevance. In this case CASSCF and CASPT2 have the same behavior compared to cc-pVDZ S_1, where increasing the distance between the atoms reaches a point where the occupancy of the natural orbitals changes completely.

Figure 9

CASPT2 and CASSCF for S_1
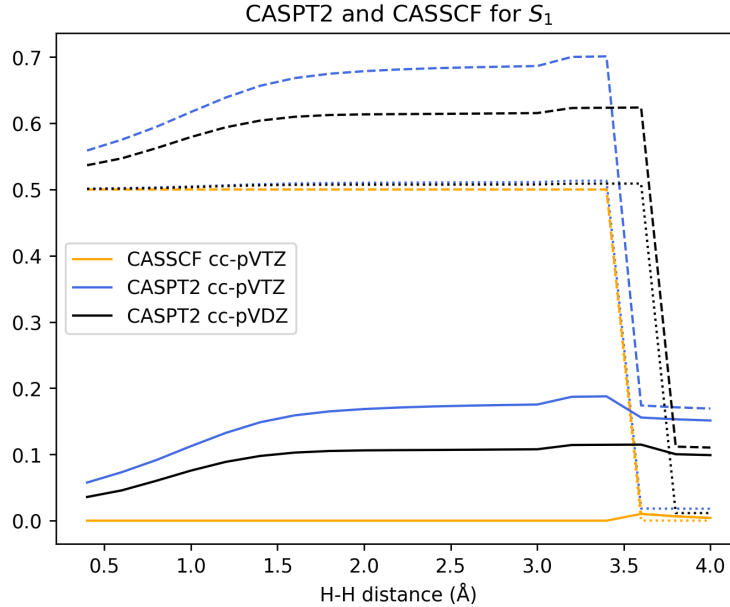
3 Using $Tr[^2\Delta]$

The formula referred to in the article and from which it was originally taken [2] was used for clarity on which part to take the sum of the NOOs. These theorem formulate that the trace of the first order

reduced density matrix 1-RDM can be written as the sum of the 1-RDMS's eigenvalues, therefore the trace of the cumulant 2-RDM can also be expressed in terms of the 1-RDM's eigenvalues n_i. Then the formula using spin σ is (see formula 23 of the reference):

$$Tr[\Delta] = \sum_i n_i^2 - N$$

Dividiendo dentro de dos porque los Natural Orbital Occupancies se representan para close shell system (los valores van de 0 a 2), por lo que tambien N se debe de dividir dentro de dos para mantenerse en su forma original en el lado derecho de la ecuacion:

$$Tr[^2\Delta] = \sum_i (n_i/2)^2 - (N/2)$$

Debido a que se trata de un sistema con dos electrones la ecuacion final queda:

$$Tr[^2\Delta] = \sum_i (n_i)^2 - 1$$

Figure 10
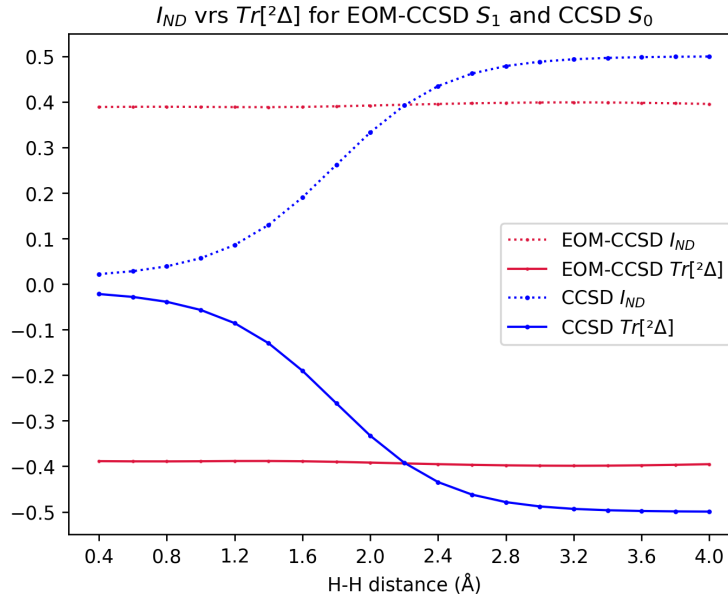
As can be observed for the case of CCSD, using the formula $Tr[\Delta]$, a value between -0.4 and -0.5 is reached at a distance of 2.4 Å, until reach a minium of -0.5 at a distance of 3.2 Å, thus having the same behavior but opposite in sign to Matito's formula for non-dynamic correlation. The same happens with EOM-CCSD, however, as it does not show variation in NOOs along the dissociation, the values remain constant.

References

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