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Orbital optimisation for Richardson-Gaudin wavefunctions†

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Do *not* write an abstract. That will be done when the outline has matured into a completed paper.

1 Introduction

Orbital-optimised doubly-occupied configuration interaction (OO-DOCI) computations yield the most precise result one can expect to obtain through a geminal approach with a given orbital basis set. In other words, for a given set of orbitals, this approach gives the exact solution to the seniority-zero coulomb Hamiltonian. Incidently, its optimised orbitals are also the optimal orbitals for any geminal-based approach.

This makes this method an very useful reference tool as we develop a variationnal Richardson-Gaudin (varRG) approach based on wavefunction ansatz made from products of Richardson-Gaudin geminals [1] [2] , both as a source for the optimal orbitals (until we develop an independent orbital-optimisation routine) and as a comparison standard for the precision we can hope to achieve.

It is therefore relevant to compute OO-DOCI dissociation curves for various small systems as a reference point. We are notably interested in the following systems, for the STO-6G and cc-pVDZ orbital basis :

- Hydrogen polymer chains : H_4, H_6 and H_8

- Homonuclear diatomics : He_2, Li_2, Be_2, B_2, C_2, N_2, O_2, F_2 and Ne_2 (cc-pVDZ only)

- 12-electron diatomics : LiF, BeO, BN, CN^+ and CO^{2+} (and C_2)

- 14-electron diatomics : CN^-, CO, NO^+ and O_2^{2+} (and N_2)

2 Results and discussion

2.1 STO-6G

2.1.1 Hydrogen polymer chains

All hydrogen polymer chains dissociation curves were easily computed and yielded smooth results.

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2.1.2 Homonuclear diatomics

Smooth dissociations curves have been obtained for Li_2 and F_2, with preliminary results for N_2 and O_2 suggesting these curves should be obtained without significant hurdles as well.

For the larger systems (N_2, O_2 and F_2), some points sometimes yielded results that layed outside the curve; however, it was possible to recompute those points to get adequate results, thus these invalid results were attributed to bad convergence of the optimisation algorithm (CMA-ES, which has a stochastic nature).

The curves for Be_2 and C_2, however, consistently produced unexpected shoulders between the minimum and dissociation (see figures 1 and 2), whereas B_2 shows an unphysical double well (see figure 3). Note that an avoided crossing is expected in the C_2 dissociation curve, but the shoulder obtained does not match the expected result quantitatively (the shoulder doesn't occur at the right interatomic distance) nor qualitatively (the shoulder does not match the shape expected for an avoided crossing).
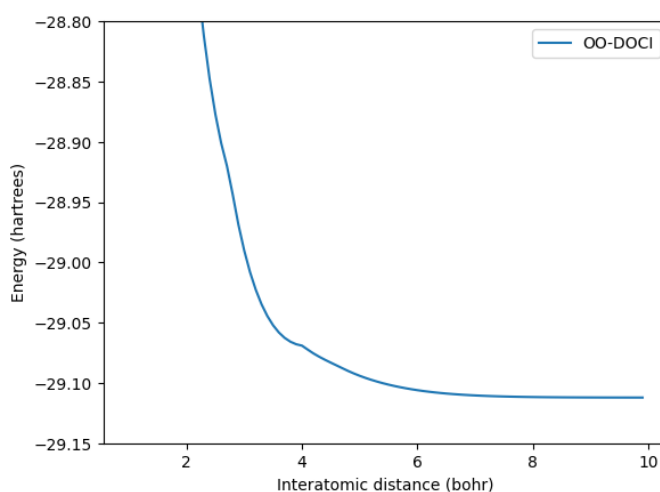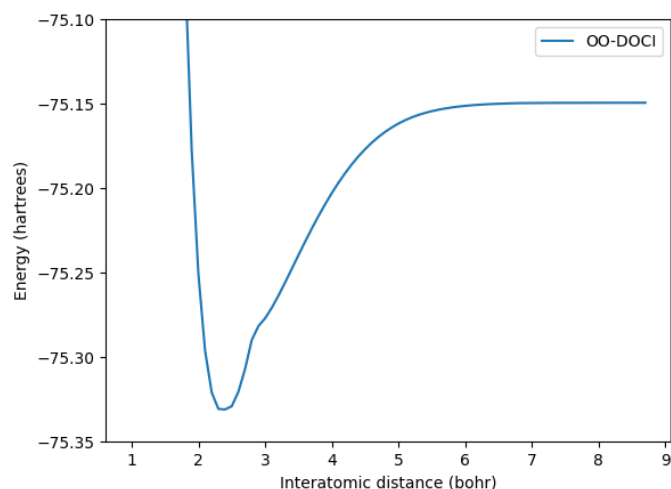

Fig. 1 OO-DOCI dissociation curve of Be_2 in the STO-6G orbital basis

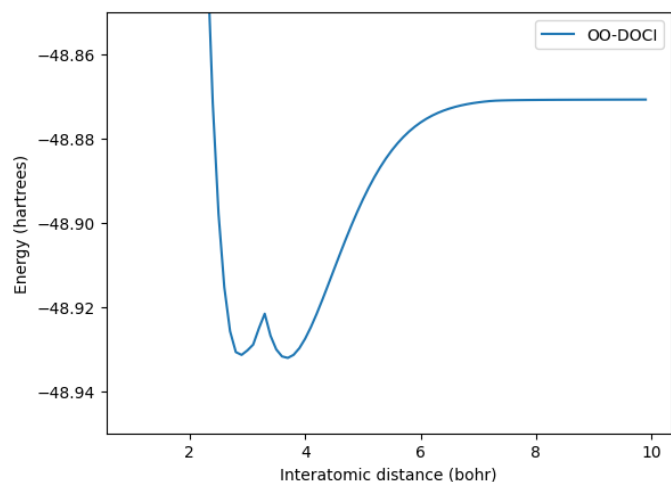Various approaches have been attempted (with B_2 and C_2 specifically) to obtain better results :

Fig. 2 OO-DOCI dissociation curve of C_2 in the STO-6G orbital basis

Fig. 3 OO-DOCI dissociation curve of B_2 in the STO-6G orbital basis

- Points were computed with a significantly higher maximum number of iterations for the CMA-ES algorithm.

- Points were computed reusing the orbital rotation of the previous point in the curve, approaching from both the right and the left.

- Computations were done using DFT orbitals as an initial guess (using B3lyp, LDA, PBE and PW91 functionals).

- Computations were done using CISD natural orbitals as an initial guess.

Unfortunately, none of these approaches helped in obtaining better dissociation curves, instead they all converged on the same results as the initial brute-force approach.

2.1.3 12-electron diatomics

Similarly to some of the homonuclear diatomics mentioned, all 12-electron dissociation curves present shoulders. The same approaches that had been attempted for B_2 and C_2 have been used with BN as well, to no avail.
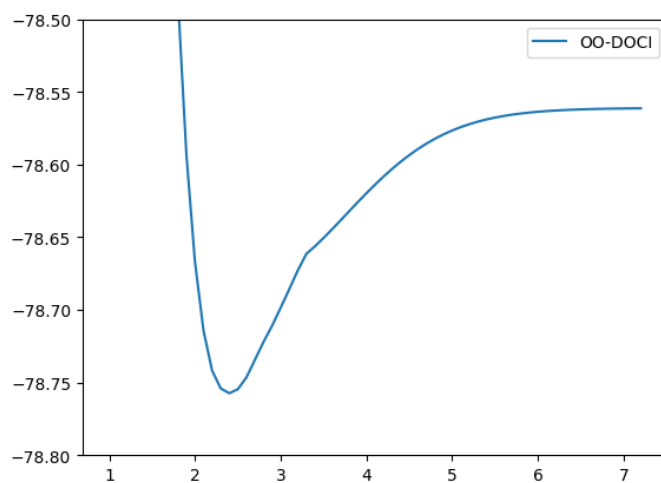

Fig. 4 OO-DOCI dissociation curve of BN in the STO-6G orbital basis

2.1.4 14-electron diatomics

Preliminary results indicate a smooth curve dissociation curve for 14-electron systems, although some curves present outlying points that require recomputation.

2.2 cc-pVDZ

2.2.1 Hydrogen polymer chains

Computations underway. Preliminary results seem to produce a smooth dissociation curve.

2.2.2 Homonuclear diatomics

Computations underway.

2.2.3 12-electron diatomics

Computations underway.

2.2.4 14-electron diatomics

Computations underway.

One issue that arises when computing these dissociation curves (as well as those for N_2, O_2, F_2 and Ne_2) is that the maximal computation time allowed on some compute canada clusters is 7 days, but the computation of even a single point for systems with 14 electrons or more in the cc-pVDZ orbital basis takes more time than that. The cluster cedar allows for longer computations, but the possibility of segmenting CMA-ES optimisation for a single point should be investigated and implemented if possible.

3 Conclusions

4 Acknowledgements

5 Appendix

Notes and references

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