

# Orbital optimisation for Richardson-Gaudin wavefunctions<sup>†</sup>

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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. Incidentally, 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<sup>12</sup>, 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.

#### 2.1.2 Homonuclear diatomics

$Li_2$ ,  $N_2$ ,  $O_2$  and  $F_2$  dissociations curves were relatively easily computed to obtain smooth results. For the larger systems ( $N_2$ ,  $O_2$  and  $F_2$ ), some points 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).

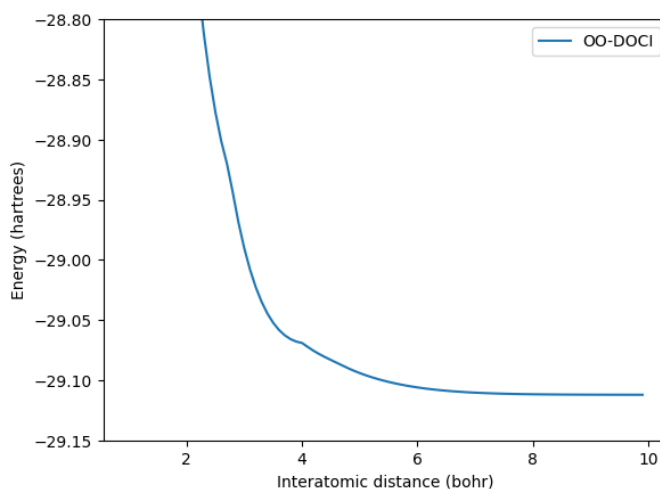


Fig. 1 OO-DOCI dissociation curve of  $Be_2$  in the STO-6G orbital basis

Various alternatives for the initial guess for the orbitals have been used (with  $B_2$  and  $C_2$  specifically) to obtain better results :

- 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).

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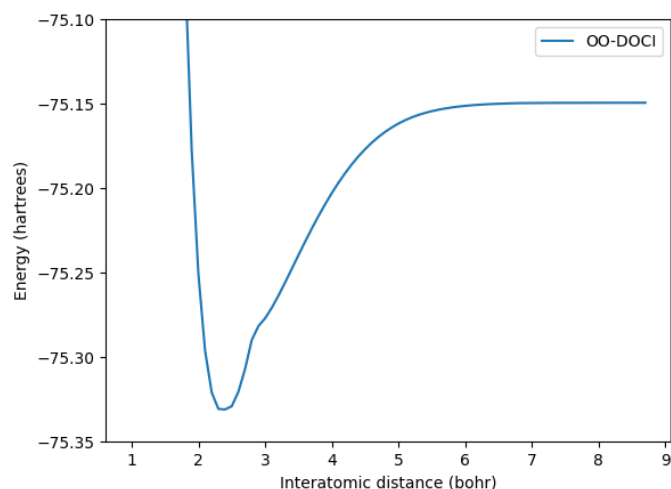


Fig. 2 OO-DOCI dissociation curve of  $C_2$  in the STO-6G orbital basis

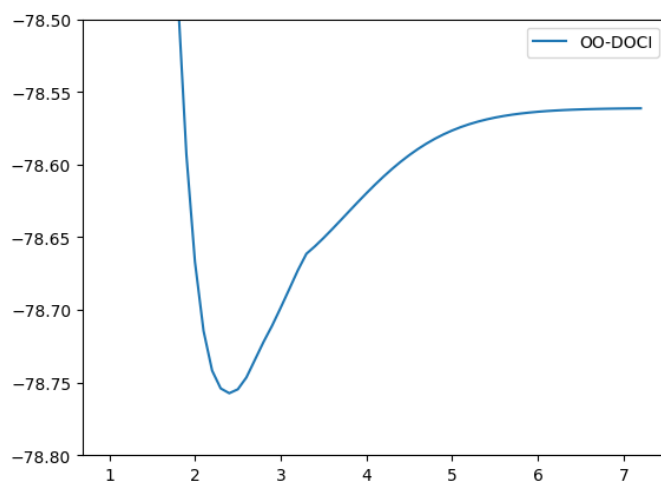


Fig. 4 OO-DOCI dissociation curve of  $BN$  in the STO-6G orbital basis

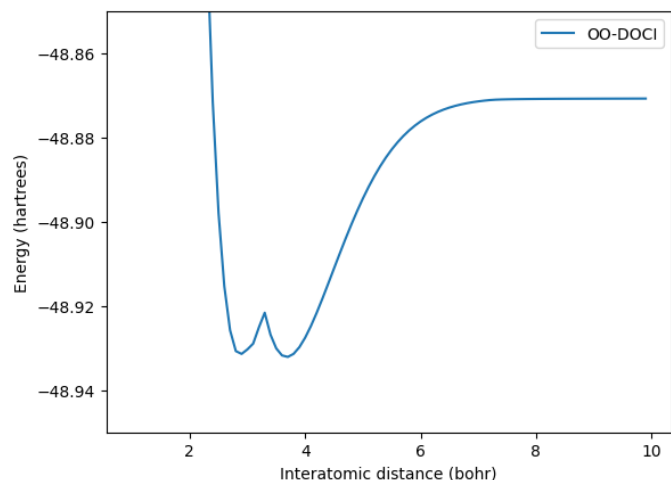


Fig. 3 OO-DOCI dissociation curve of  $B_2$  in the STO-6G orbital basis

- 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 unexpected shoulders. The same approaches that had been attempted for  $B_2$  and  $C_2$  have been used with  $B_N$  as well, to no avail.

### 2.1.4 14-electron diatomics

Like for 12-electron systems, most 14-electron dissociation curves present unexpected shoulders. The one exception is  $CN^-$ , which yielded a smooth curve.

## 2.2 cc-pVDZ

### 2.2.1 Hydrogen polymer chains

Computations underway.

### 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 if 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

- 1 P. A. Johnson, C.-E. Fecteau, F. Berthiaume, S. Cloutier, L. Carrier, M. Gratton, P. Bultinck, S. De Baerdemacker, D. Van Neck, P. Limacher, and P. W. Ayers, *Journal of Chemical Physics* **153**, 104110 (2020).
- 2 C.-E. Fecteau, S. Cloutier, J.-D. Moisset, J. Boulay, and P. A. Johnson, *Journal of Chemical Physics* **156**, 194103 (2022).