# ⟨G|QC|J⟩

# 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

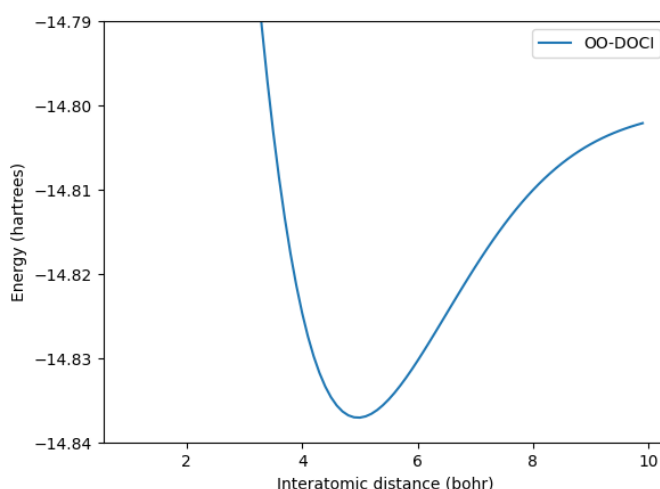All hydrogen polymer chains dissociation curves were easily computed and yielded smooth results.

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**Fig. 1** OO-DOCI dissociation curve of $Li_2$ in the STO-6G orbital basis

#### 2.1.2  Homonuclear diatomics

Smooth dissociations curves have been obtained for $Li_2$ and $F_2$ (see figures 1 and 2), with preliminary results for $N_2$ and $O_2$ (see figure 4) suggesting these curves should be obtained without significant hurdles as well.
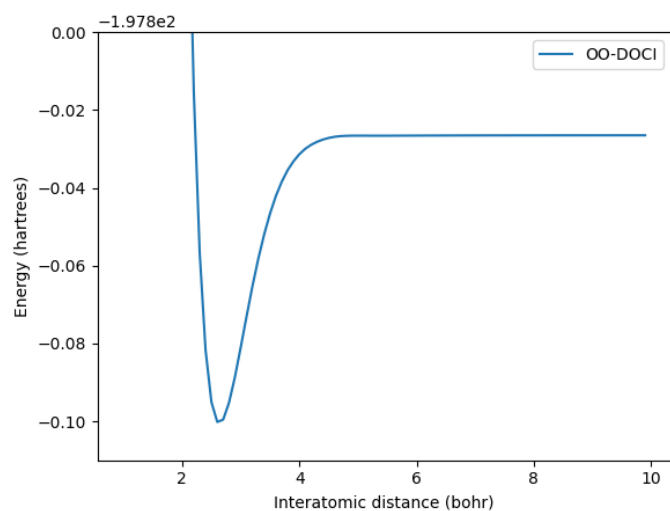
For the larger systems ($N_2$, $O_2$ and $F_2$), some points sometimes yielded results that layed outside the curve. However, it has generally been possible to recompute those points to get adequate results, thus these invalid results were attributed to bad convergence of the optimisation algorithm (CMA-ES, which has a stochastic nature).

The curves for $Be_2$, $B_2$ and $C_2$ however, consistently produced curves that aren't completely smooth throughout dissociation (see figures 5 6 and 7). Specifically, $C_2$ presents an avoided crossing whereas $Be$ presents two, and $B_2$ actually produces a double-well. Before moving forward, it must be determined whether these avoided crossings are to be expected for OO-DOCI results in this basis or whether they indicate a failure of the orbital optimisation to converge on the correct orbital rotation.
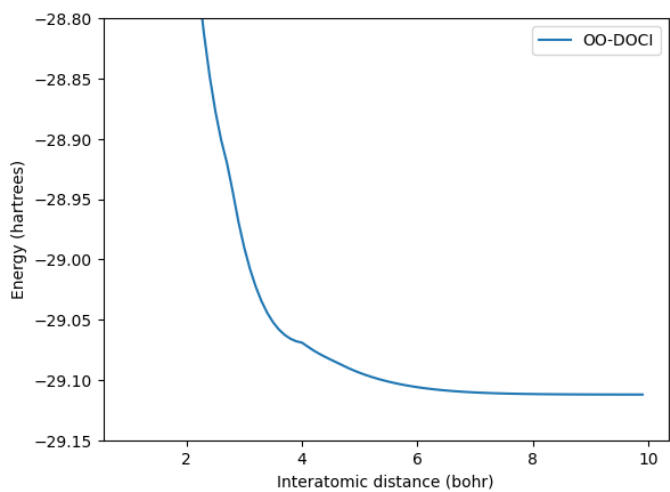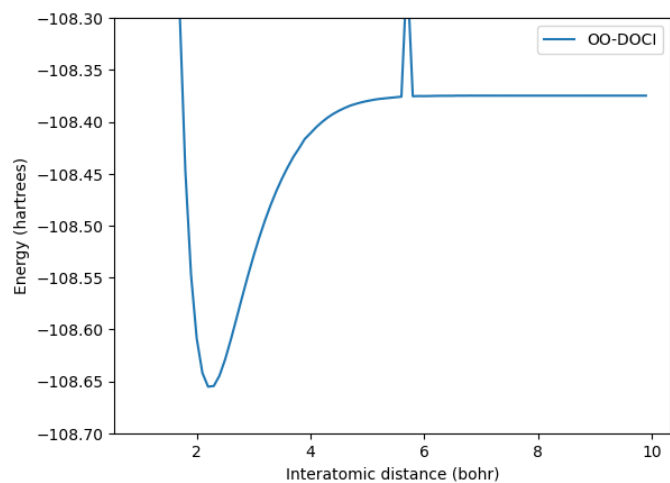
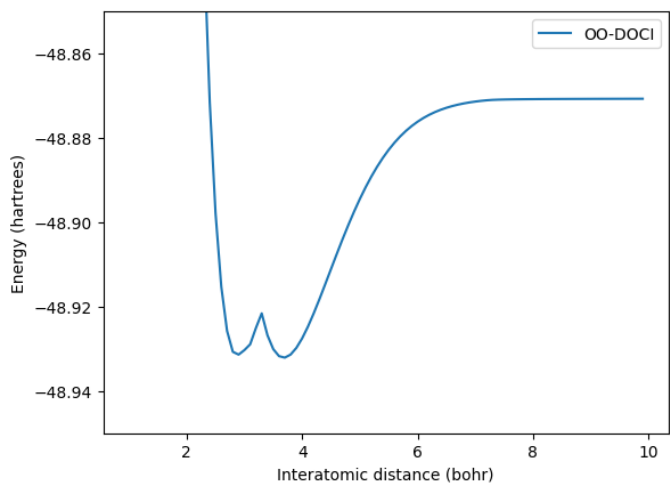Various approaches have been attempted (with $B_2$ and $C_2$

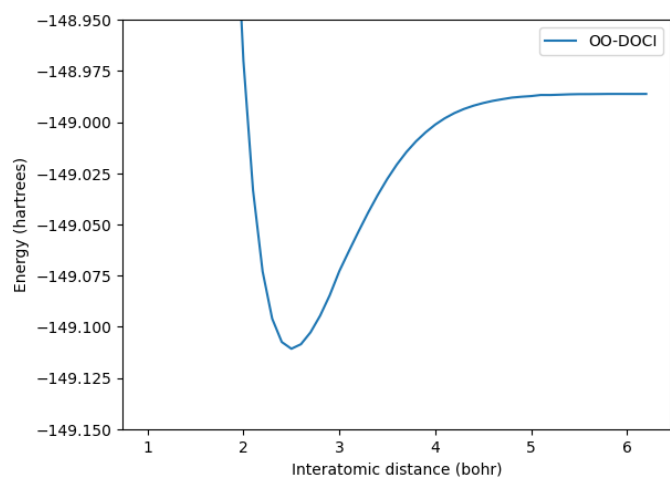**Fig. 2** OO-DOCI dissociation curve of $F_2$ in the STO-6G orbital basis



**Fig. 5** OO-DOCI dissociation curve of $Be_2$ in the STO-6G orbital basis presenting two avoided crossings
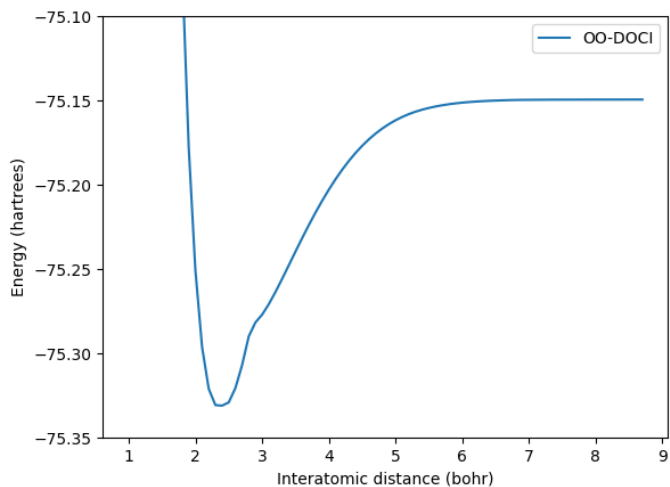


**Fig. 3** OO-DOCI dissociation curve of $N_2$ in the STO-6G orbital basis with a badly converged point
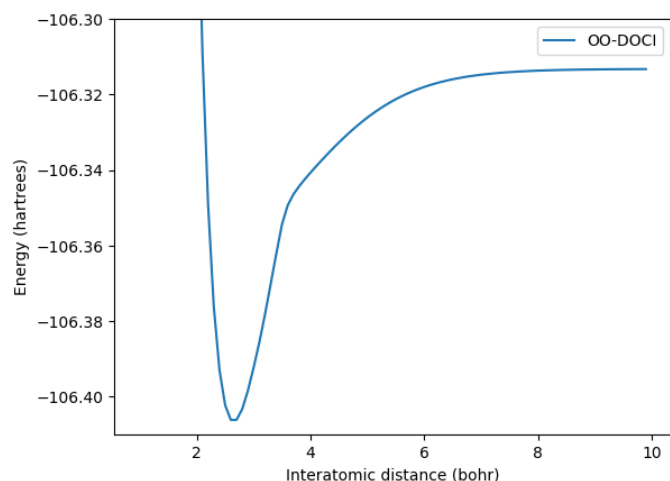


**Fig. 6** OO-DOCI dissociation curve of $B_2$ in the STO-6G orbital basis presenting an avoided crossing in the form of a double potential well
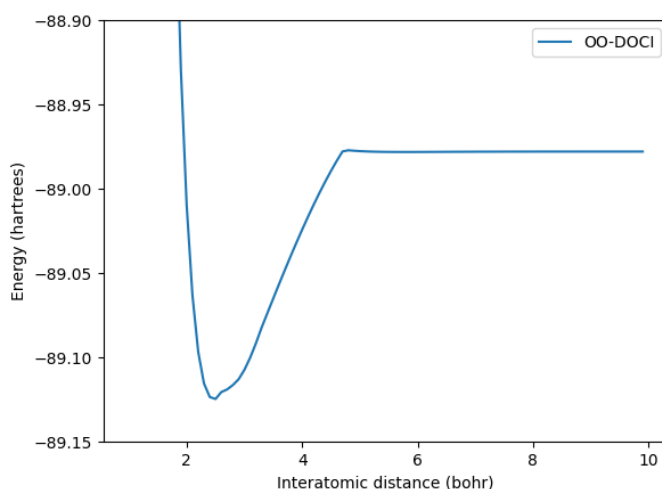


**Fig. 4** Incomplete OO-DOCI dissociation curve of $O_2$ in the STO-6G orbital basis



**Fig. 7** OO-DOCI dissociation curve of $C_2$ in the STO-6G orbital basis presenting an avoided crossing

**Fig. 8** OO-DOCI dissociation curve of $LiF$ in the STO-6G orbital basis presenting an avoided crossing

specifically) to improve the optimisation's results :

- 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.

All these approaches converged on the same results as the initial brute-force attempt.

### 2.1.3  12-electron diatomics

Similarly to some of the homonuclear diatomics mentioned, all 12-electron dissociation curves present avoided crossings (see figures 8, 9, 10, 11 and 12).

### 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 (see figures 13, 14, 15 and 16).

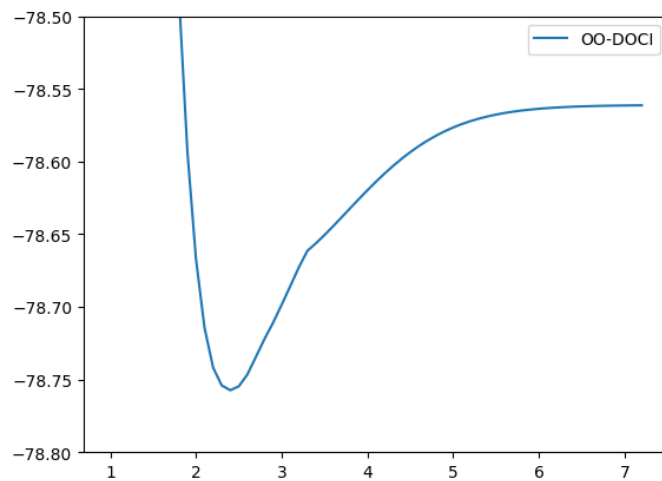### 2.2  cc-pVDZ

### 2.2.1  Hydrogen polymer chains

Computations underway. Preliminary results seem to produce a smooth dissociation curves.
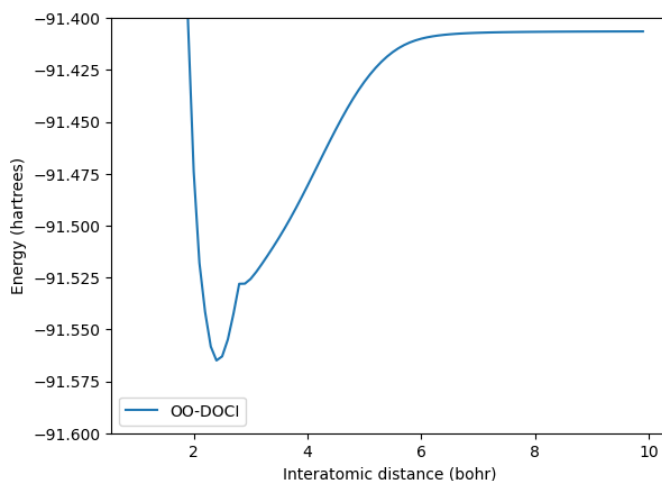
### 2.2.2  Homonuclear diatomics

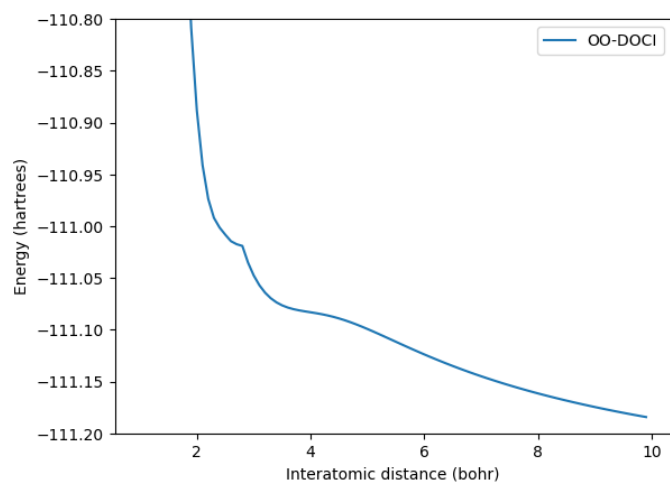Computations underway.

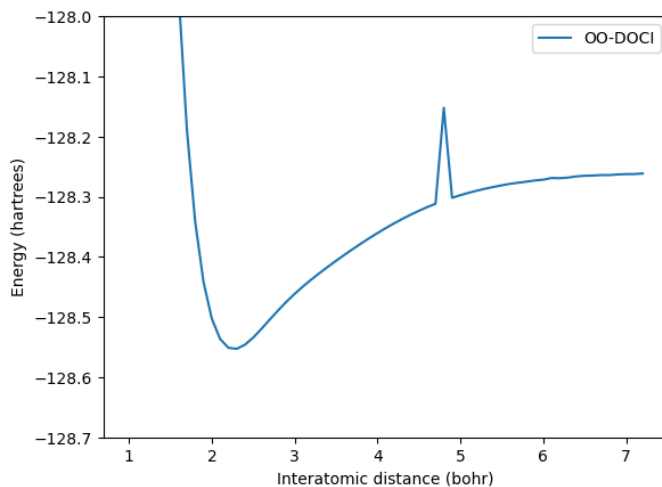### 2.2.3  12-electron diatomics

Computations underway.



**Fig. 9** OO-DOCI dissociation curve of $BeO$ in the STO-6G orbital basis presenting two avoided crossings



**Fig. 10** Incomplete OO-DOCI dissociation curve of $BN$ in the STO-6G orbital basis presenting an avoided crossing
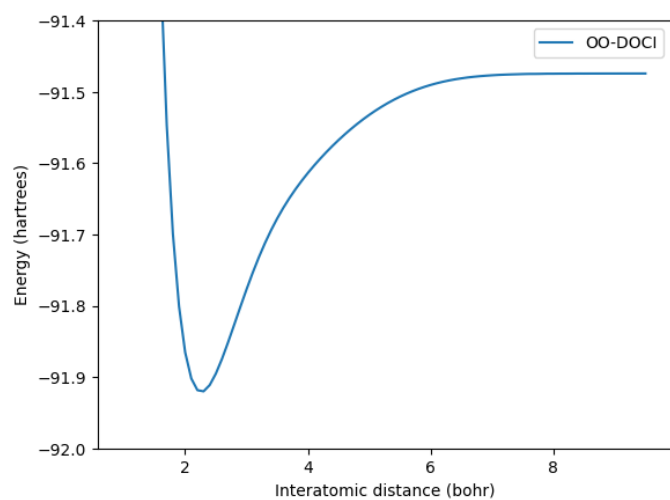


**Fig. 11** OO-DOCI dissociation curve of $CN^+$ in the STO-6G orbital basis presenting an avoided crossing
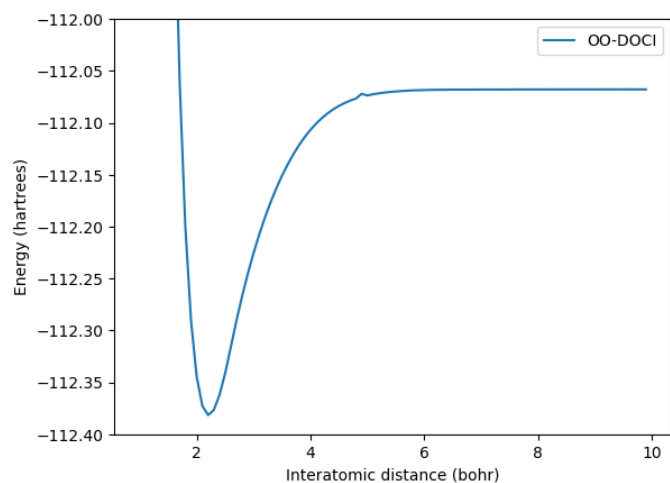
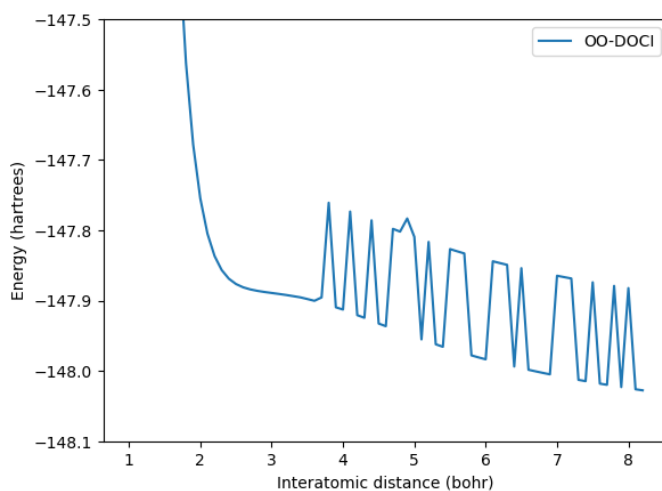**Fig. 12** OO-DOCI dissociation curve of $CO^{2+}$ in the STO-6G orbital basis presenting an avoided crossing



**Fig. 13** Incomplete OO-DOCI dissociation curve of $CN^-$ in the STO-6G orbital basis



**Fig. 14** OO-DOCI dissociation curve of $CO$ in the STO-6G orbital basis with a badly converged point



**Fig. 15** Incomplete OO-DOCI dissociation curve of $NO^+$ in the STO-6G orbital basis with some badly converged points



**Fig. 16** Incomplete OO-DOCI dissociation curve of $O_2^{2+}$ in the STO-6G orbital basis with some badly converged points

### 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

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).