jz-2022-00730x.R1

Name: Peer Review Information for "Hierarchy Configuration Interaction: Combining Seniority Number and Excitation Degree"

First Round of Reviewer Comments

Reviewer: 1

Comments to the Author

This manuscript is very well presented and pleasant to read. The figures and the extensive supporting information are very much appreciated.

Strongly correlated electronic systems are difficult to treat in a Slater determinant basis. At equilibrium, "excitation-based" CI converges quickly, while at dissociation, (oo-) seniority based CI is better. The authors present a way to combine these ideas in a single hierarchy to try to get the advantages of both, and they do: hCI is better at dissociation than excitation CI, and better at equilibrium than seniority CI. Viewed as CI methods, I agree entirely that hCI is superior as it is much cheaper than seniority CI and scales similar to excitation CI.

I strongly recommend publication with one minor caveat:

- The authors cite refs 14-30 which show that seniority zero CI is essentially the same as a mean-field of seniority zero pairs, which has O(N^4) cost. I feel this point is rather important as oo-seniority zero CI is itself intractable, and the authors could modify the statement citing refs 14-30.

The presentation is professional. I have a lot of respect for this group, and I will cite this paper at the next opportunity.

Author's Response to Peer Review Comments:

Dr Pierre-François Loos
Université Paul Sabatier
Laboratoire de Chimie et Physique Quantiques
Toulouse, France

Telephone: +33 5 61 55 73 39
Email: loos@irsamc.ups-tlse.fr

April 6, 2022

To the Editors of the The Journal of Physical Chemistry Letters,

Dear Editors,

Please find attached a revised version of the manuscript entitled *"Hierarchy Configuration Interaction: Combining Seniority Number and Excitation Degree"*. We thank the reviewer for the positive appreciation of our work and the suggestion, which we agree to be pertinent. Our detailed response can be found below. For convenience, changes are highlighted in red in the revised version of the manuscript.

We look forward to hearing from you.

Sincerely, the authors.

Authors' answer to Reviewer #1

This manuscript is very well presented and pleasant to read. The figures and the extensive supporting information are very much appreciated.

Strongly correlated electronic systems are difficult to treat in a Slater determinant basis. At equilibrium, "excitation-based" CI converges quickly, while at dissociation, (oo-) seniority based CI is better. The authors present a way to combine these ideas in a single hierarchy to try to get the advantages of both, and they do: hCI is better at dissociation than excitation CI, and better at equilibrium than seniority CI. Viewed as CI methods, I agree entirely that hCI is superior as it is much cheaper than seniority CI and scales similar to excitation CI.

I strongly recommend publication with one minor caveat: - The authors cite refs 14-30 which show that seniority zero CI is essentially the same as a mean-field of seniority zero pairs, which has $\mathcal{O}(N^4)$ cost. I feel this point is rather important as oo-seniority zero CI is itself intractable, and the authors could modify the statement citing refs 14-30.

The presentation is professional. I have a lot of respect for this group, and I will cite this paper at the next opportunity.

We thank the reviewer for the supportive comments.

Concerning the point raised, we have included a sentence on page 1, which reads "In particular, coupled cluster restricted to paired double excitations, which is the same as the antisymmetric product of 1-reference orbital geminals, provides very similar energies as DOCI, and at a very favourable polynomial cost".