

Improving coupled cluster theory for strongly correlated molecules with Kohn-Sham density encoding

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Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Zamani and coworkers present analysis of electronic structure methods that mix density functional theory with coupled cluster wave function theory. This area has been somewhat recognized over the years, including the idea that swapping the reference state from Hartree Fock to DFT can improve coupled cluster results, for instance DFT/CCSD(T). Adding to this area, this work hits the challenge of strong correlation, and shows how improvements in predictions of properties can be achieved without too much sensitivity to choice of density functional. The core argument is that the reference density is the key factor, rather than the DFT orbitals. Overall this work is merited but needs some improvements before publication.

The authors should recognize the significant need for clarity in their presentation of the theoretical aspects of this work. For example, this work semi-canonicalizes the KS orbitals. It should be shown why specifically that needs to be done, as I would think CC theory is invariant to precisely this type of rotation. Or perhaps it matters, due to details in the implementation of the CC equations in a particular code, which makes use of the orbital eigenvalues. Altogether, I think it is necessary to go into the precise working equations of CCSD and point out where the change from HF to DFT reference affects the relevant quantities. This can be done in brief in the main paper and in more detail in the SI.

When referring to the Fock matrix, F , for instance on page 3 line 74, be specific about which Fock matrix it is. There is a KS Fock and a HF Fock, either of which can be expressed in either KS or HF orbitals (or (semi-)canonicalized in some way). Along the same lines, show specifically the expression where the KS density leads to terms in the CC equations (that would be different than HF density).

The paper might be easier to read without some of the acronyms (there are many. For instance the SC, NBS, and STG acronyms. The first overlaps with SCF and the latter two aren't particularly standard. In addition, while it is okay to not spell out the DFT functional names, other acronyms need to be defined before being used.

On page 4, "Since orbital energies after SC become similar (but not necessarily identical) p 98 to their canonical HF values under the action of the same Fock operator, their eigenvectors must 99 be similar to the canonical HF MOs." I do not see why this would necessarily be the case, unless the overlap between KS and HF determinants were close to 1. So, it may help here to provide quantification of the overlap.

In the key intermediate region of the Cr2 dissociation curve, the PW91 and PBE references flatten out, indicating an inability to capture the full (likely multireference) electronic structure transition that is occurring in this region. Because one would not know these KS references were "best" a priori, I would not place as much value on the conclusion that the accuracy of CCSD(T) for Cr2 is a just matter of finding a good reference density. Though, I do think the KS reference is still better than that of HF.

A reference associated with BTE is needed in the text (rather than just the figure caption).

On page 9, "These changes allow useful Thouless rotations that drive KS-CC toward the exact solution." I find it likely that the singles terms like this are responsible for the differences in CC results, though I also find it hard to see what a "useful" rotation really means. It is possible to choose a DFT functional that gives a Fock matrix that is worse than HF.

Along the lines mentioned just above, there needs to be some discussion of cancellation of errors. It is likely that error cancellation is operative here in some degree, as it appears GGAs provide better density references than some higher-rung functionals. The GGA densities are likely to give lower accuracy densities.

Is the metric based on DeltaP sensitive to basis selection? One would not need to evaluate CC to know this. The authors should see Herbert's paper in JCTC 2024: doi.org/10.1021/acs.jctc.4c01085 and note whether the invariance criterion is met.

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)

The manuscript "Kohn-Sham density encoding rescues coupled cluster theory for strongly correlated molecules" presents a compelling and timely investigation into the origin of improved performance in coupled cluster (CC) calculations when using Kohn-Sham (KS) references. By carefully dissecting the role of semi-canonicalization and the resulting effective Fock operator, the authors demonstrate that the key factor is not the KS orbitals themselves but rather the encoded one-particle density matrix.

Overall, this is a well-executed and conceptually insightful study. The topic is highly relevant to the electronic structure community, particularly given the ongoing challenges associated with treating strong correlation in transition-metal systems. The analysis is thorough, and the results, especially the recovery of the Cr₂ potential energy surface and the systematic improvements in bond dissociation energies, are impressive and convincing. The introduction of the NNED metric as a low-cost diagnostic for multireference character is also a valuable and potentially impactful contribution.

I recommend minor revision, primarily for clarification and improved presentation of several methodological and conceptual points.

1. A central conclusion of the manuscript is that the improvement of KS-CC arises from density differences rather than orbital characteristics. This is an important and insightful perspective. However, it may be helpful for the authors to briefly discuss the extent to which residual orbital effects may still play a secondary role. A short clarification acknowledging this interplay would further strengthen the conceptual framework and avoid potential overinterpretation.

2. The proposed NNED metric is a particularly interesting aspect of the work, offering a low-cost way to assess multireference character and guide reference selection. To further enhance its utility, it would be helpful if the authors could clarify: (1) how sensitive NNED is to basis set choice and system size, (2) whether the proposed thresholds are expected to be broadly transferable or system-dependent.

A brief comment on these points would make the diagnostic more accessible to practitioners.

3. While the manuscript is generally well written, several acronyms and notations appear without clear definition upon first use. For clarity, the authors may wish to explicitly define the following terms when they first appear: MO, SCF, CBS, MR, etc. Although these are well-known acronyms in the field of quantum chemistry, addressing these points would improve readability, particularly for a broader audience.

With these clarifications, the manuscript will be even clearer and more accessible to the community. Overall, this is a strong and insightful contribution that advances our understanding of how density functional references influence correlated wavefunction methods.

(Remarks on code availability)

This is a well-known commercial code. No need to review.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I appreciate the updates made by the authors to the manuscript, which is now sufficiently improved and ready to move forward for publication.

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)

The authors clarified all my previous concerns. As such I agree to the publication of this manuscript.

(Remarks on code availability)

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Author responses are highlighted in blue. Reviewer comments are italicized.

Reviewer #1:

The authors thank Reviewer #1 for their detailed comments. The reviewer's insights on CC theory and suggestions for enhancing readership understanding have strengthened the impact and clarity of the manuscript.

The authors should recognize the significant need for clarity in their presentation of the theoretical aspects of this work. For example, this work semi-canonicalizes the KS orbitals. It should be shown why specifically that needs to be done, as I would think CC theory is invariant to precisely this type of rotation. Or perhaps it matters, due to details in the implementation of the CC equations in a particular code, which makes use of the orbital eigenvalues.

We thank the reviewer for these important remarks. Semi-canonicalization is a specific operational choice made by almost all practical implementations, as it greatly simplifies the use of non-HF orbitals in the CC equations. We now emphasize on line 73 that this is the typical choice across implementations. We also add emphasis on lines 109-112 that *any* orbitals could be used (even localized KS orbitals) so long as the span of these MOs is preserved.

Altogether, I think it is necessary to go into the precise working equations of CCSD and point out where the change from HF to DFT reference affects the relevant quantities. This can be done in brief in the main paper and in more detail in the SI.

We thank the reviewer for making this important point about the clarity of our communication. We now show the non-Brillouin terms for perturbative methods and the relevant portion of the CCSD amplitude equations in equations 1 and 2 of the revised text.

When referring to the Fock matrix, F , for instance on page 3 line 74, be specific about which Fock matrix it is. There is a KS Fock and a HF Fock, either of which can be expressed in either KS or HF orbitals (or (semi-)canonicalized in some way). Along the same lines, show specifically the expression where the KS density leads to terms in the CC equations (that would be different than HF density).

We agree that clarity in our notation could be improved. We now specifically define the KS Fock matrix and distinguish it from the Hartree-Fock *operator* in lines 74-77. As stated above, we also include terms from the CC equations that include occupied/virtual Fock matrix elements, which we specifically claim encode the changes imposed by the KS density.

The paper might be easier to read without some of the acronyms (there are many. For instance the SC, NBS, and STG acronyms. The first overlaps with SCF and the latter two aren't particularly standard. In addition, while it is okay to not spell out the DFT functional names, other acronyms need to be defined before being used.

We appreciate these suggestions. We have removed the use of non-standard/unfamiliar acronyms and expanded them out in the main text. We have retained the NBS acronym as it is used in cited literature, but we are sure to clearly define this.

On page 4, "Since orbital energies after SC become similar (but not necessarily identical) 98 to their canonical HF values under the action of the same Fock operator, their eigenvectors must 99 be similar to the canonical HF MOs." I do not see why this would necessarily be the case, unless the overlap between KS and HF determinants were close to 1. So, it may help here to provide quantification of the overlap.

We thank the reviewer for this comment. Rather than saying something that may be incorrect, we have changed the wording in the main text to avoid making a definitive assertion.

In the key intermediate region of the Cr₂ dissociation curve, the PW91 and PBE references flatten out, indicating an inability to capture the full (likely multireference) electronic structure transition that is occurring in this region. Because one would not know these KS references were "best" a priori, I would not place as much value on the conclusion that the accuracy of CCSD(T) for Cr₂ is a just matter of finding a good reference density. Though, I do think the KS reference is still better than that of HF.

This is a noteworthy observation. Indeed, even the best KS-CC methods do not achieve the softer shelf structure like the (truly multireference) best theoretical estimate. We now emphasize that our conclusions apply to single-reference KS-CC in the Discussion section to avoid any suggestion that we are directly capturing multireference effects. Otherwise, our

discussion is quite general, stating only our hypothesis as to why KS-CC appears to outperform HF-CC in this case.

A reference associated with BTE is needed in the text (rather than just the figure caption). We have cited the now well-known 2022 paper on Cr₂ in the main text.

On page 9, "These changes allow useful Thouless rotations that drive KS-CC toward the exact solution." I find it likely that the singles terms like this are responsible for the differences in CC results, though I also find it hard to see what a "useful" rotation really means. It is possible to choose a DFT functional that gives a Fock matrix that is worse than HF.

We agree that the term "useful" is ambiguous. We now avoid the use of this word, and on lines 284-286 we now focus on what we really meant by this. Essentially, in most cases, the KS reference gives better results than HF-CC at lower excitation order. This is accomplished through the KS density, as encoded in the occupied/virtual KS-Fock matrix elements of equation 2.

Along the lines mentioned just above, there needs to be some discussion of cancellation of errors. It is likely that error cancellation is operative here in some degree, as it appears GGAs provide better density references than some higher-rung functionals. The GGA densities are likely to give lower accuracy densities.

We agree that it is important to address this point more clearly. We already discuss a balancing/cancellation of errors in paragraph 2 of the Discussion section. However, to the reviewer's excellent point regarding the apparent failure of Jacob's Ladder as a sensible guide, we have cited the work of Martin Kaupp on the so-called "zero-sum game" of DFT. Essentially, this deterioration of the well-known rung structure of Jacob's Ladder is commonly encountered in truly multireference systems like the ones that we investigate, so GGAs often *do* outperform higher-rung functionals due to a strange manifestation of self-interaction errors that conspire to improve GGA predictions in such cases. We thank the reviewer for suggesting clarification here, as it further motivates the need for a metric like NNED that can offer some insights into the underlying density changes that KS densities bring to the table.

Is the metric based on DeltaP sensitive to basis selection? One would not need to evaluate CC to know this. The authors should see Herbert's paper in JCTC 2024: doi.org/10.1021/acs.jctc.4c01085 and note whether the invariance criterion is met.

Thank you for this question. The normalized number of electrons displaced (NNED) should converge towards a basis set limit in a manner similar to the SCF energies (ie quite quickly).

We now include this remark in the methods section of the main text. A basis set convergence example is now included in Figure 53 of the SI. We do indeed find that the difference in the NNED for triplet BN is a mere 0.0012 between cc-pV6Z and cc-pVDZ basis sets.

We also note that the difference density exhibits unitary invariance by means of

$$U^\dagger(P''^\# - P^\$%)U = U^\dagger(P''^\#)U - U^\dagger(P^\$%)U$$

Reviewer #2:

We thank the reviewer for their thoughtful comments on the clear communication of our manuscript.

1. A central conclusion of the manuscript is that the improvement of KS-CC arises from density differences rather than orbital characteristics. This is an important and insightful perspective. However, it may be helpful for the authors to briefly discuss the extent to which residual orbital effects may still play a secondary role. A short clarification acknowledging this interplay would further strengthen the conceptual framework and avoid potential overinterpretation.

We thank the reviewer for this comment. We remark on the complicated interplay between the orbital energies, electron repulsion integrals, and the non-Brillouin terms in paragraph 4 of the Discussion section. We have added some clarifying language in lines 279-280 that highlights the fact that no particular orbital representation is sacred, but that the changes we observe come from the space those orbitals span (captured in the density).

2. The proposed NNED metric is a particularly interesting aspect of the work, offering a low-cost way to assess multireference character and guide reference selection. To further enhance its utility, it would be helpful if the authors could clarify: (1) how sensitive NNED is to basis set choice and system size, (2) whether the proposed thresholds are expected to be broadly transferable or system-dependent.

A brief comment on these points would make the diagnostic more accessible to practitioners.

We thank the author for their attention to detail and interest in the performance of the NNED metric. In general, the NNED should converge towards a basis set limit in a manner similar to the SCF energies. We include this remark in the methods section of the main text. We have added Figure 53 to our supplemental information, which details the (small) basis set dependence of the NNED metric, which differs by only 0.0012 from cc-pVDZ to cc-pV6Z.

We indicate already that the NNED is functional dependent, so our proposed decision tree in the supplementary information considers the class of density functional being applied. On size-dependent effects, the NNED is normalized to the number of electrons specifically to point out differences between the HF and DFT densities without a dependence on the number of electrons, so we expect the NNED to be consistent across system sizes by construction. For example, take results for B3LYP/def2-QZVPPD: ZnS has a NNED of 0.017, Carbon atom has a NNED of 0.018, and BN has a NNED of 0.037.

3. While the manuscript is generally well written, several acronyms and notations appear without clear definition upon first use. For clarity, the authors may wish to explicitly define the following terms when they first appear: MO, SCF, CBS, MR, etc.

Although these are well-known acronyms in the field of quantum chemistry, addressing these points would improve readability, particularly for a broader audience.

We thank the reviewer for considering the clarity of our communication. We now carefully define every acronym before it is used in the main text.