

01 January 2017

Prof. Anne McCoy
Deputy Editor
Journal of Physical Chemistry

Dear Prof. McCoy:

We are grateful for the detailed and helpful comments by the reviewers of our manuscript, "Frozen Virtual Natural Orbitals for Coupled Cluster Linear-Response Theory." We have made the following changes, in the same order as the reviewers' comments:

Reviewer #1

1. I suggest to include a paragraph in the introduction outlining the structure of the paper (what is included in the theory and results sections), which provides a clear picture of the goal and scope of this study. For example, Section 2A presents the theoretical background for FVNO.

The final sentence of the Introduction explains the purpose of this work. Given that this is a relatively short paper, we have chosen not to unnecessarily extend the introduction with an outline.

2. It worthwhile commenting in the introduction about the connection between spectral properties of model Hamiltonian and properties (which is apparent from SOS expressions), and why imbalance introduced by FNOs In the description of the ground and excited states can affect properties.

Given that we have chosen not to focus on sum-over-states (SOS) expressions but the non-canonical formulation, in our opinion this would be distracting from the central point of the work.

3. Very important point left under the rag: Orbital relaxation. On page 14, the authors say that orbital relaxation has been neglected for computational convenience. It is indeed the standard practice in response calculations, but the reason for omitting orbital relaxation is not just convenience. Orbital response has been shown to mess up pole structure of response functions (by inheriting HF pole structure) and that is why it is omitted. This should be clarified in the introduction or in the theory section. This said, in the context of this paper, orbital response might be important, because it will be accounting for FNO truncation. I strongly recommend to include finite difference calculations of static polarizabilities with FNO and with canonical frozen virtuals to see what would be the effect of orbital relaxation in this context. I suspect that the FNO polarizabilities computed as full derivative (including orbital response) will behave better.

The reviewer is correct that orbital relaxation is important, though we did not claim to have ignored it in our polarizability calculations strictly for computational convenience. (This remark was solely in reference to the formulation of the derivative of the one-electron density in Eq. 14.) More importantly, the reviewer is also correct that inclusion of the orbital relaxation does mostly account for the poor behavior of the NO virtual space. Although we cannot take this into account in a "conventional" response calculation due to the need to avoid spurious poles in the polarizability dispersion, this is still an illuminating observation. We have thus added a figure and a paragraph discussing this issue at the end of p.10.

Invent the Future

4. Computational details state that calculations for dimethylallene and methyloxirane have been reported, but there is no data or figures for these systems in the paper. Please provide relevant information in the SI. Further, in the same section, the sentence “While the aDZ basis set was used for most test calculations, the larger aug-cc-pVTZ (aTZ) and aug-cc-pVQZ (aQZ) basis sets were also employed for selected analyses.” is very vague. Please give specific details about each calculation performed. Also, (very important) the value of the frequency “omega” used in the calculations of dynamic polarizabilities is not specified anywhere in the text.

We have added data on the additional test cases to the SI, as requested, as well as for the larger basis sets for hydrogen peroxide. The value of omega is specified multiple times in Figure captions.

5. In the results on page 8, it says “Similar results are obtained for larger basis sets, for which even more aggressive truncation of the virtual space is effective.” Why these results are not provided?

As noted in our response to point #4, we have added data on larger basis sets to the SI.

6. Missing references on page 8-9 for the comment: “It is well known that diffuse basis sets are essential for the accurate descriptions of a variety of response properties, such as dipole polarizabilities.”

We have added a reference to the 1994 paper by Woon and Dunning.

7. On page 10, it says “For additional insight into the above observations, we examine errors arising in dynamic polarizabilities as a function of truncation of specific wavefunction parameters in either the CMO or NO basis.” and then “Note that, in this analysis, only the specified amplitudes associated with the selected CMOs are forced to zero; the CMOs remain active for all other wave function components.” What are the truncation criteria for these amplitudes?

The truncation criterion is just as stated in the quoted sentence: any amplitudes associated with the selected CMOs are forced to zero. There is no other cutoff implied.

8. On page 10, it says “(Not surprisingly, freezing both \hat{T}_1 and \hat{T}_2 amplitudes together have essentially the same effect as freezing \hat{T}_2 amplitudes alone.)”. Is there a formal reason for this? It is not obvious to me.

This statement follows from the previous sentence in the paragraph where we note that freezing T_1 amplitudes alone has no impact on the property.

9. On page 10, it says “A key observation is that, within the domain of the first 23 virtual CMOs, the positive errors introduced by truncation of \hat{T}_2 is cancelled almost exactly by the negative errors arising from the truncation of \hat{X}_2 .” I would like to remind the authors that X_2 is simply the first-order response of T_2 (or first derivative of T_2 in the analytic-derivative approach). If a T_2 -component is frozen, would the inclusion of the corresponding X_2 -component be formally correct? Further, the same analysis on page 11 for NOs reveal that freezing out T_2 -amplitudes introduces no significant errors, but freezing out X_2 does. Is there a formal explanation for this? I would not hold back the publication of this article to these points, but if there is an obvious explanation for this, please provide it.

We agree that, in a full model, inclusion of perturbed amplitudes corresponding to deleted unperturbed amplitudes would be inappropriate. However, given that our purpose for this truncation here is merely to investigate sources of error, we consider the truncation to be reasonable. On the second point, we provide an explanation of this in the next sentence, viz., “This behavior is expected, because the T_2 amplitudes are, by

construction, sparse in the virtual NO basis such that orbitals with low occupation numbers are associated with T_2 amplitudes of smaller magnitude.”

10. Last line on page 10: Fig. 3 or Fig. 7?

The reference to Fig. 3 is correct.

11. On page 11, it says “However, unlike the virtual CMO case, neglecting \hat{X}_1 amplitudes corresponding to specific virtual NOs introduces large negative errors in the polarizability even from the first NO removed, and the total error obtained by truncating both \hat{X}_1 and \hat{X}_2 amplitudes is almost the same as the error due to truncation of the \hat{X}_1 amplitudes alone. Indeed, in both the CMO and NO bases, the greatest contribution ($> 90\%$) to the total polarizability errors arises from the perturbed singles amplitudes.” The paragraph starts by saying that X_1 amplitudes are not important in CMO case and ends by saying that X_1 contributes $>90\%$ of the total polarizability errors. However, Fig. 6 for CMO tells a different story. X_1 only dominates after a few virtual CMOs are frozen.

We agree that the phrasing is misleading, and thus we have removed the reference to the CMO basis in the offending sentence.

12. A minor point: “Perturbed density” on page 14 = “unperturbed density” + “perturbation to density”. What the authors call “perturbed density” is actually the “perturbation to the density”

We disagree with this point, as it is common in perturbation theories to refer to “perturbed wave functions” even though they are perturbations to the wave function. Similarly, in analytic gradient theory, the derivative of the density (which we are using in Eq. 14) is commonly referred to as the “perturbed density”.

13. How is the “perturbed density” independent of the frequency for the calculation of dynamic polarizability? Equation 14 has $D_{ij}^{ac} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_c$. Is there no dependence on ω ? I think this is incorrect.

There is no frequency dependence because we have built only the derivative of the density with respect to a static field. (In the lead paragraph to this section, we refer to this as the gradient of the density.)

14. Equation 15 also has no frequency dependence (while equation 13 shows frequency dependence). I would guess the criterion for dynamic polarizability would be dependent on frequency.

As we are attempting to construct a phenomenological truncation criterion, rather than a complete model, the neglect of the frequency dependence is reasonable. We have added a sentence to the paragraph following Eq. (15) to indicate this choice.

15. The authors could comment whether the same virtual space is used for both the energy/dipole moment calculations as the one used for calculating the polarizabilities in both the CMO/NO cases. An analysis/validation of the analytic “static” polarizabilities for a given truncated space against numerical differentiation of either the energy or the dipole moment calculated in the same truncated space would be a nice inclusion in this paper. Also, the figures showing errors in energy and polarizabilities against number of frozen virtuals (figs. 1-5) can be merged (with two y-axes) for a given ordering of virtuals frozen out.

Yes, the same virtual space is used in the energy and perturbation calculation, as they must be in order for finite-difference and analytic results to match. We have added a sentence to the computational methods section, as well as an appropriate reference. We have chosen not to merge Figs. 1-5 as they present very different points.

16. The authors may also comment on size-consistency of these response properties with this method.

The size-consistency/size-extensivity of the response properties is unaffected by truncation of the virtual space, and we have added a sentence to the end of the Computational Methods section indicating this.

Other minor corrections:

1. "higher order" and "coupled cluster theory" should be "higher-order" and "coupled-cluster theory" in the abstract and the rest of the text.

Corrected.

2. On page 4, last line of introduction is "present work is on the extension of the NO approach to linear-response properties, especially the cases of frequency-dependent dipole polarizabilities and optical rotations of chiral compounds." However, the paper simply focuses on dipole polarizabilities and not the optical rotations (agreed that both properties are given as linear response functions). The authors may rephrase this sentence. Also, the spelling of frequency is wrong in the above sentence.

Indeed, the reviewer is correct. The original scope of the work included chiroptical properties, but we chose during production to separate this aspect of the work for a future publication. This has been corrected.

3. I Theory section: Why do we need normal ordering in OPDM definition? I would suggest to remove it for more clear presentation, since it is not needed for anything.

We disagree that the normal-ordering notation has a negative impact on the presentation. Indeed, given that we focus only on properties associated with the correlated wave function, normal ordering is important here.

4. Please define PNOs. It is not clear what does it mean "... the virtual-virtual MO block is constructed...." (lines 53-56 on page 2).

This is defined in the same sentence in which we use the acronym "PNO", and elaborated upon in the Theoretical Background section.

Reviewer #2

1. The acronym CI is never defined

Corrected

2. misspelled "frequency" on page 4, line 10

Corrected

3. misspelled "virtual-" on page 5

Corrected

4. In the sentence "we take an average of the three cartesian components of the density is taken" (page 14) the words "is taken" should be removed

Corrected

5. Page 15, a square parenthesis is missing: "[cf. Eqs. (4) and (14)."

Corrected

6. Page 15: "our preliminary analyses" ... "suggest" (and not suggests)

Corrected

7. Page 16: "ALTHOUGH the use of external space corrections... REDUCES.." (missing word and singular conjugation)

Corrected

Editorial Changes

1. The manuscript title must be presented in title case format (i.e., capitalize the first letter of each principal word).

Corrected

2. Check all reference formatting to make sure it conforms with recommended JPC/ACS style (please refer to the attached Reference guide). References should have article titles listed in the journal references. Please use either sentence case or title case. Titles written in "mixed" case are not acceptable. When reformatting your references, please make sure that there is only one citation number per reference (e.g., no 1a, 1b, etc).

Done

3. References with more than 10 authors should list the first 10 authors, followed by "et al"; otherwise, all author names should be listed.

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4. Include a TOC graphic illustrating the significance of the paper. The TOC graphic should be something that is representative of your entire work. Color schemes or illustrations typically make good choices. TOC graphic must be original and free from any copyright issues. The TOC graphic must be submitted in the actual size to be used for the web table of contents. That is, it should fit in an area no larger than 3.25 in. × 1.75 in. (approx. 8.5 cm × 4.75 cm) and should have adequate resolution and clarity. Confirm that all text is legible at this size. Present the TOC graphic on the last page of the manuscript by itself. Please label the TOC as "TOC Graphic". A caption describing the TOC is not needed.

The TOC has been included at the end of the document

We hope that our paper will now be acceptable for publication in the *Journal of Physical Chemistry*.

Sincerely,



Prof. T. Daniel Crawford