Reply to Comment on "Using Kohn−Sham Orbitals in Symmetry-Adapted Perturbation Theory To Investigate Intermolecular Interactions"

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It appears that the main point being made in Jansen and Hesselmann's (JH's) Comment is that that our approach is "... not potentially exact to second order in the interaction energy...", and we certainly agree with this. Of course, nowhere in the paper was this claim made or implied. We had assumed this fact was self-evident since we gave the explicit (and very simple) form of our Hamiltonian operator on p 651, i.e., $H = K + V$, with $K = K_A + K_B$. In the second to the last paragraph JH state, "The shortcomings of the DFT-SAPT hybrid approach presented by WC do not imply, however, that a potentially exact hybrid approach cannot be devised. Yet, this requires a more careful derivation." We chose the Hamiltonian in the paper because it provides a much-simplified computational alternative to the "potentially exact" form. We most certainly did *not* settle on this simplified Hamiltonian due to a less "careful" derivation. They now go on to give the reader a form for the operator that would be potentially exact "if carried out to infinite order in $H_0 - K$". It should be emphasized that there was a very good reason for not choosing such a form, and JH give this reason in their Comment; "... the resulting expressions are not simpler than those occurring in conventional many-body SAPT." What JH are saying is that such a potentially "exact" Hamiltonian would require the same degree of computational effort as the existing, conventional SAPT Hamiltonian. While utilizing such an "exact" hybrid Hamiltonian might be an interesting theoretical endeavor, it would totally defeat our primary purpose for this work, which was to come up with a simplified approach that could calculate reliable intermolecular interaction energies between larger molecules (e.g., DNA base pairs) in a computationally tractable way. Our simplified Hamiltonian provides this computational efficiency, but with the usual tradeoff in accuracy. The paper then goes on to study how much accuracy was sacrificed in each interaction energy term in order to gain this computational efficiency. Hence, JH's comments concerning this "potentially exact" form for the Hamiltonian fall outside the scope and goals of our paper.

JH do offer a good explanation for why one might expect $E^{(1)}_{\text{elst}}$ to be more accurate in our approach than the $E^{(1)}_{\text{exch}}$ term, and we agree with their statements. For a reader who is less familiar with symmetry adapted perturbation theory (SAPT) than are JH, these might be useful elaborations.

Their next comment states that our hybrid Hamiltonian is "...inconsistent and by no means equivalent to the original Hamiltonian." We hope that this is glowingly obvious from our presentation in the paper. In fact, the entire paper hangs upon the fact that the "hybrid" Hamiltonian used therein is fundamentally different from the "original Hamiltonian" used in the conventional SAPT. They then make a comment about the fact that we are combining a Kohn−Sham operator "K" that defines a system of "noninteracting particles", with an intermolecular interaction operator "V" that "describes the interactions of electrons". This is true, but they do not explain why this needs to be repeated. The origins of "K" and "V" have already been stated in the paper where we say that we are combining a Kohn−Sham operator with the conventional intermolecular interaction energy operator "V" from SAPT. It is worth mentioning that the "potentially exact to second order" Hamiltonian given by JH also contains these two operators.

In the same paragraph they point out to the reader that we are using a "sum over states (SOS)" formula in describing the second-order terms. They then state that "This corresponds to using an 'uncoupled'[4] or 'nonrelaxed'[5] approximation of the static density−density response function ...". First, it is clearly stated in our paper that we are doing a sum over states method for our second-order corrections, so we did not repeat it. Second, the SAPT codes we used can calculate this orbital or charge relaxation through coupled Hartree−Fock, and indeed this was done (and so stated and referenced in the paper) for our benchmark results given in the tables. However, to perform a coupled Kohn−Sham calculation to relax the DFT densities would require additional coding within the DFT-SAPT package. While this is something worth exploring, and is planned as a part of further developments for this method, it has not yet been done. One should keep in mind that if DFT-SAPT were to account for the bulk of intramolecular correlation effects (one of the motivations for using DFT), then the difference between interaction energy terms (such as the induction terms) for "uncoupled" versus "coupled" monomer densities will be smaller in this approach than in the conventional double perturbation theory SAPT for a given order of intermolecular interaction energy. In the case of infinite-order MPBT corrections to the intramolecular correlation energy, the two approaches are identical, i.e.,

$$\sum_{i=0}^{\infty} E^{2i}_{\text{ind}} = \sum_{i=0}^{\infty} E^{2i}_{\text{ind,resp}}$$

Obviously, assessing the usefulness of such possible refinements can only be done by examining actual data. Therefore, we look forward to JH's upcoming publication that is in preparation.

JH inform us that, within this future publication, they will report yet another approach to calculating intermolecular interaction energies, i.e., one based on density matrices. If a reader is interested in such an approach, we would like to direct their attention to a paper coauthored by one of us (H.L.W.) entitled "Many-body Theory of Exchange Effects in Intermolecular Interactions. Density Matrix Approach and Applications to He−F$^-$, He−HF, H$_2$−HF, and Ar−H$_2$ Dimers" [Moszynski, R; Jeziorski, B.; Rybak, S.; Szalewicz, K.; Williams, H. L. *J. Chem. Phys.* **1994**, *100*, 5080−5093]. This reference was not included in our DFT-SAPT paper since it seemed to have no direct bearing on the issues being tested in that work.

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