COMMENTS

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

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Recently, Williams and Chabalowski (WC) published a paper on a hybrid approach for calculating intermolecular interaction energies using density functional theory (DFT) to describe correlated molecular properties of the monomers and symmetry-adapted perturbation theory (SAPT) to describe the interactions between the monomers.[1] They give a list of five attributes that should be fulfilled by such a hybrid approach, among them the criterium that the electrostatic, exchange, inductive and dispersive interaction energies should be calculated with equal accuracy. Referring to their new method, WC state that "this DFT-SAPT hybrid approach should exhibit the aforementioned five attributes" and continue "the issue then becomes the accuracy one can expect ... with a given exchange-correlation functional".

In the present Comment we point out that the hybrid scheme presented by WC is not potentially exact to second order in the interaction energy; i.e., with this scheme most of the first- and second-order interaction energy contributions cannot be exactly calculated even if the exact exchange-correlation potential would be known and employed to determine the occupied and virtual molecular orbitals and orbital energies of the Kohn−Sham scheme. The approach presented by WC thus cannot strictly fulfill the aforementioned criterium. The reason for this is fundamental: it is the inadequacy of the Hamiltonian upon which the derivation of their hybrid scheme is based. In standard ab initio SAPT the Hamiltonian H of the dimer is partitioned as $H = H_0 + V$ with $H_0 = H_A + H_B$ being the sum of the Hamiltonians of the isolated, noninteracting monomers A and B and V as the sum of the Coulomb interactions between the electrons and nuclei of A and B. WC propose a new SAPT Hamiltonian $H = K + V$, where $K = K_A + K_B$ is the sum of Kohn−Sham operators for the monomers and V is the same interaction operator as above. This Hamiltonian, however, is inconsistent and by no means equivalent to the original Hamiltonian: the zeroth-order part of it, K, refers to the famous "noninteracting particles" with fermion characteristics of the Kohn−Sham theory[2] while part of the perturbation potential V describes interactions between *electrons*. The ground and excited-state eigenfunctions of K_A and K_B are simple Slater-determinants and the ground state determinants will yield the same one-particle densities as the true electronic ground states − if the exact exchange-correlation potential has been used. Yet, one should not confuse the eigenfunctions of K_A and K_B with *electronic* wave functions.

As a consequence, the only term that is potentially exact in WCs hybrid approach is the first-order electrostatic energy $E^{(1)}_{\mathrm{elst}}$. The first-order exchange correction $E^{(1)}_{\mathrm{exch}}$ does not share this property: it depends on density *matrices* (on the one- and two-particle density matrices if the single-particle-exchange approximation is employed), and already the Kohn−Sham one-particle density matrix is neither the exact electronic density matrix nor is it guaranteed to be a good approximation to it[3]—even if the exact exchange-correlation potential would have been employed. With this in mind WCs (unexplained) finding that the first-order electrostatic contributions tend to be in better agreement with benchmark values than the first-order exchange contributions is no longer surprising. Furthermore, the derivation given by WC results in a "sum over states" (SOS) formula to calculate the second-order induction contribution $E^{(2)}_{\mathrm{ind}}$. This corresponds to using an "uncoupled"[4] or "nonrelaxed"[5] approximation of the static density−density response function (polarization propagator) in which the changes in the Coulomb and exchange-correlation potentials due to the perturbation-induced change of the electron density have been neglected. Thus the induction energy in this scheme is not potentially exact. Essentially the same remarks apply to the second-order dispersion contribution $E^{(2)}_{\mathrm{disp}}$, which, using the Casimir-Polder trick,[6] can be rewritten in terms of uncoupled dynamic density−density response functions and, in consequence, to the second-order exchange corrections. Additionally, the exchange corrections again suffer from the fact that (response) density *matrices* enter their calculation.

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. One route to such an approach is to use K as the zeroth-order Hamiltonian, as proposed by WC. The subsequent perturbation theory, however, has to be a *double*-perturbation theory with V as one perturbation and $H_0 - K$ as the other. The scheme presented by WC is just the zeroth-order (in $H_0 - K$) approximation to such a potentially exact (if carried out to infinite order in $H_0 - K$) hybrid approach. A disadvantage of the double-perturbation scheme is that the resulting expressions are not simpler than those occurring in conventional many-body SAPT. Furthermore, since $E^{(1)}_{\mathrm{elst}}$ is potentially exact already in zeroth order of $H_0 - K$ the sum of all higher order contributions should be zero and cutting it at some order different from zero will *not* improve $E^{(1)}_{\mathrm{elst}}$. Yet, the double-perturbation scheme might be of practical value for the other contributions. Note that in practice the exact exchange-correlation potential is not available so that even $E^{(1)}_{\mathrm{elst}}$ might be systematically improvable with the double-perturbation approach.

Another way to conceive a hybrid approach is to formulate the intermolecular perturbation theory in terms of densities, density−density response functions, density matrices, and

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response density matrices. Potentially exact static and dynamic density−density response functions required to calculate $E_{\mathrm{ind}}^{(2)}$ and $E_{\mathrm{disp}}^{(2)}$ can be obtained from (coupled-perturbed) time-dependent DFT.[7] As stated above, the density matrices and response density matrices from the Kohn−Sham scheme and, in consequence, the exchange corrections will not be potentially exact. They are, however, at least in principle improvable in a double-perturbation scheme, as indicated above. Furthermore, already the unimproved density matrices might come sufficiently close to the exact ones for the purpose at hand, as it has recently been proposed by us.[8] Investigations along these lines have been carried out in our group, first results have been presented on several occasions[9] and a detailed publication is underway.

References and Notes

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