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Emmanuel Fromager, Nikitas Gidopoulos, Paola Gori-Giorgi, Trygve Helgaker, Pierre-Francois Loos, Thomas Malcomson, Katarzyna Pernal, Andreas Savin, Donald Truhlar, Meilani Wibowo, et al.

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## Strong correlation in density functional theory: general discussion

Emmanuel Fromager, Nikitas Gidopoulos, Paola Gori-Giorgi,<sup>1</sup> Trygve Helgaker, Pierre-François Loos, Thomas Malcomson,<sup>2</sup> Katarzyna Pernal,<sup>3</sup> Andreas Savin,<sup>3</sup> Donald G. Truhlar,<sup>3</sup> Meilani Wibowo<sup>3</sup> and Weitao Yang

**Pierre-François Loos** opened the discussion of the paper by Katarzyna Pernal: At the very end of your paper, you say “One should note, however, that there are several outliers for which the CASIIDFT errors exceed 0.5 eV. Some of them could be explained by the possible inaccuracy of the chosen theoretical benchmark if compared with experimental values.” I don't think you can compare your theoretical vertical values to the experimental values which are usually 0-0 energies (*i.e.*, it takes into account the geometrical relaxation of the excited state as well as the ZPE corrections from both ground state and excited state).

Therefore, you're going to miss vibronic effects as well as geometrical relaxation. These effects usually decrease the excitation energies, *i.e.*, the 0-0 energies are usually lower than the corresponding vertical energy for a given excitation. See the discussion at the end of ref. 1.

If your vertical excitations fit the experimental values better than the TBEs, it means that your values are usually too low. This is typically what happens with CASPT2 values.

As a rule of thumb, CC3 is usually really good and CCSD usually overestimates the vertical excitation energies.<sup>2</sup>

In ref. 2, we provide both TBEs for the aug-cc-pVTZ basis as well as a set of basis set corrected TBEs. In the case of CASIIDFT, because you're using DFT correlations, your correlation energy must converge faster than typical wave function theory methods.<sup>3</sup> Therefore, it might be safer to compare your CASIIDFT numbers to TBE/CBS values.

1 P.-F. Loos and D. Jacquemin, *J. Phys. Chem. Lett.*, 2020, **11**(3), 974–980.

2 P.-F. Loos, F. Lipparini, M. Boggio-Pasqua, A. Scemama and D. Jacquemin, *J. Chem. Theory Comput.*, 2020, **16**(3), 1711–1741.

3 E. Giner, A. Scemama, P.-F. Loos and J. Toulouse, *J. Chem. Phys.*, **152**, 174104.

**Katarzyna Pernal** responded: Indeed, better agreement of CASIIDFT excitation energies with experimental values than with TBE's (theoretical best estimates) of Schreiber *et al.*<sup>1</sup> might indicate underestimation of the CASIIDFT predictions.

The largest deviations of CASIIDFT from the TBE of Schreiber *et al.*<sup>1</sup> are observed for pyrimidine and pyridazine molecules. A comparison with TBE's of Loos *et al.*<sup>2</sup> leads to the same conclusion, *i.e.*, that the excitation energies of CASIIDFT are underestimated.

1 M. Schreiber, M. R. Silva-Junior, S. P. A. Sauer and W. Thiel, *J. Chem. Phys.*, 2008, **128**, 134110.

2 P.-F. Loos, F. Lipparini, M. Boggio-Pasqua, A. Scemama and D. Jacquemin, *J. Chem. Theory Comput.*, 2020, **16**(3), 1711–1741.

**Trygve Helgaker** asked: In your CASIIDFT method, you obtain the dynamical correlation energy by adding a DFT-type correlation functional to the CASSCF energy. Would it be possible or even meaningful to add your dynamical correlation correction in a self-consistent manner or would this lead to a variational collapse?

**Katarzyna Pernal** replied: CASIIDFT is not variational by construction, *i.e.*, it is an approximation which is not, by its nature, bound from below by the exact ground (or excited) state energy. Considering that the CASIIDFT energy obtained for the small CAS wavefunction is close to the CBS limit for ground states, it is certain that self-consistent calculation would result in the total energy below the exact value, at least for ground states. Since the correlation function  $P[x]$  used in the IIDFT correlation function is bound ( $P[x]$  is greater or equal to 0 and smaller than 2.5 for  $x$  from the range  $[0, 1.3]$ ), and so is the correlation energy density functional, the energy collapse is not possible. The CASIIDFT energy expression is not a density functional (not even implicitly) so SCF would not be meaningful. But if it improves the accuracy of the excitation energies, or is used to compute linear response property, so it may be worth exploring.

**Meilani Wibowo** commented: In the results and discussion section, there is an issue with the state ordering which is not consistent with the best estimate. For instance, in pyrimidine the order of the  $1^1A_2$  and  $1^1B_2$  states is incorrect due to the underestimation of the  $1^1B_2$  energy. What is the cause of this behaviour? Could it be due to the state-specific or state-average approximation? Or, could it be due to the choice of active space?

**Katarzyna Pernal** responded: In the case of the states in question, the ordering is not correct if a state-specific CAS calculation is used instead of state-averaged. The active space could make a difference. We used the active spaces from Schreiber *et al.*<sup>1</sup> work. They work well for the perturbation method, PT2, but they do not have to be optimal for our method. Ideally the active space is minimal and only accounts for the nondynamic correlation. The choice of the active spaces for CASIIDFT is a problem to be explored further in our future work.

1 M. Schreiber, M. R. Silva-Junior, S. P. A. Sauer and W. Thiel, *J. Chem. Phys.*, 2008, **128**, 134110.

**Meilani Wibowo** asked: Have you also tried to compute the triplet excited state?

**Katarzyna Pernal** replied: The current formulation of the IIDFT correlation functional is based on the physical meaning of the  $x(\mathbf{r})$  ratio which holds for opposite spin electrons (a depletion or enhancement of electron density with respect to “conventional” density “measured” by  $x(\mathbf{r})$  works, by construction, only for opposite spins). The presented CASIIDFT approach is dedicated to singlet states and it is not expected to be reliable for other spin states. Extension of IIDFT to states other than the singlet is feasible and it is work in progress.

**Weitao Yang** remarked: If you can define the dynamic correlation energy in your approach mathematically, that would be very helpful. Related to this, if you don't have a precise mathematical definition, would different active-space CAS calculations alter the results dramatically? Because at the full CI limit with all the determinants, the dynamic correlation energy contribution is wrong. At what active-space CAS is the dynamic correlation term appropriate?

**Katarzyna Pernal** replied: There is one definition for the dynamic correlation: it is the difference of the exact energy of the state of interest and the MCSCF (in our case it is CASSCF) energy. For a given molecule, the value of such defined correlation energy depends, obviously, on the used multireference wavefunction and it will vanish in the limit when the MC wavefunction approaches FCI. In the CASIIDFT method, the IIDFT correlation functional has been constructed to be sensitive to the amount of electron correlation (mainly the static one) in the wavefunction part, and to some degree it adjusts accordingly to avoid correlation double-counting. By construction, the correlation IIDFT functional performs best if it is coupled with the wavefunction part where only static correlation is accounted for, implying that small active spaces should be used. Since the correlation ratio  $x(\mathbf{r})$ , the main variable of the correlation function  $P[x]$  employed in IIDFT, does not vanish if  $x(\mathbf{r})$  is constructed from the FCI wavefunction (it vanishes only if the nondynamic correlation suppresses fully the dynamic one, *i.e.*, when the conditional density achieves zero) the IIDFT correlation energy will not vanish.

**Emmanuel Fromager** opened the discussion of the paper by Donald G. Truhlar: If I understood correctly, in the construction of your effective Hamiltonian, DFT only contributes to the diagonal elements. In a way, your approach could be referred to as a DFT-based dressing technique. Is that correct?

**Donald G. Truhlar** responded: Yes, the on-top density functional only contributes to the diagonal elements in the intermediate representation of the model space. We have not used the language of “DFT-based dressing”.

**Emmanuel Fromager** addressed Donald G. Truhlar and Katarzyna Pernal :Your methods use the same ingredients, namely a CASSCF wave function, its density and on-top pair density. I was wondering what makes the two methods different, in particular for ground states.

**Donald G. Truhlar** answered: The key difference between our method (MC-PDFT) and that presented by Pernal (CASIIDFT) is as follows. In CASIIDFT, one adds a pair-density functional contribution to the total CASSCF energy. Because

the CASSCF energy includes full exchange and some correlation energy, only a correlation functional is used, and it is scaled to try to be consistent with the amount of correlation already present at the CASSCF level. In MC-PDFT, one throws away the total CASSCF energy calculated by wave function theory. One adds the kinetic energy and the classical electrostatic energy from the CASSCF calculation to a pair-density functional contribution that includes both exchange and correlation.

**Thomas Malcomson** commented: The method you're putting forward certainly seems to have some promising applications for upcoming research. If I am understanding your presentation correctly, with regards to the transition dipole moments needed to calculate two-photon absorption properties, your application of DFT methodologies while having an effect on the energy of the system, leaves the CAS wavefunction intact and, as such, would have no effect on these values?

**Donald G. Truhlar** replied: We do not change the SA-CASSCF orbitals, but we do recombine the SA-CASSCF states.

**Thomas Malcomson** queried further: And therefore, in obtaining these values, there would be no need to proceed beyond the initial CAS to obtain these values?

**Donald G. Truhlar** answered: The multi-state step in VMS-PDFT or XMS-PDFT uses the same orbitals as SA-CASSCF, but it takes new linear combinations of the model-space SA-CASSCF eigenvectors to obtain the final states. The transition moments should be computed with these new eigenvectors that are obtained by diagonalizing the small model-space effective Hamiltonian.

**Weitao Yang** asked: The use of kinetic energy from CAS is a very interesting component in your theory. My first question is how this kinetic energy is compared with the single-determinant Kohn-Sham kinetic energy? How the difference is addressed in the kinetic energy contribution to the correlation energy in the DFT functionals?

**Donald G. Truhlar** answered: In Kohn-Sham theory, the exchange–correlation energy must include the difference between the kinetic energy calculated from the Slater determinant reference function and the exact kinetic energy. In MC-PDFT, the on-top energy should include the difference between the kinetic energy calculated from the multi-configurational reference function and the exact kinetic energy. We made a detailed study of the kinetic energy contributions in test cases, and we found in the cases studied that for small and moderate sizes of the active space, the increase in kinetic energy upon increasing the active space is more than compensated by the change in the on-top energy, so this increase does not seem to be a major source of error.<sup>1</sup> In fact, for practical active spaces, the MC-PDFT total energy is less dependent on the active space than is either of these other quantities. Nevertheless, to be safe we recommended that MC-PDFT should be employed with an active space large enough to account for near-degeneracy correlation, but not so large as to include significantly more dynamic correlation.

1 P. Sharma, D. G. Truhlar and L. Gagliardi, *J. Chem. Theory Comput.*, 2018, **14**, 660–669.

**Weitao Yang** continued: My second question is on the approach you have used to construct what you call intermediate states described in your paper. You maximize the sum of the diagonal elements and thus minimize the DFT correlation contributions to the diagonal. It looks like you want to use it, but with the least amount. And then in the off diagonals you completely ignore the DFT contribution. Would not the least amount be not using it at all for the diagonals as well? What's the thinking behind this differential treatment for the diagonals and off diagonals in the Hamiltonian?

**Donald G. Truhlar** replied: MC-DFT does not have a separate DFT correlation contribution; it adds the on-top energy (which includes exchange and correlation) to the kinetic energy and Coulomb energy of a correlated calculation. If one did not include the on-top energy in the diagonal matrix elements, one would simply have the SA-CASSCF energies, and these are not quantitatively reliable. This deficiency is corrected by replacing the diagonal Hamiltonian matrix elements by MC-PDFT energies. The reason for treating the diagonal and off-diagonal elements differently is to keep the theory practical and simple. The MC-PDFT treatment of the diagonal elements and the configuration interaction treatment of the off-diagonal elements are both straightforward, and so we combine them into a practical hybrid computational method.

**Weitao Yang** asked: How much is the variation? A lot, or a tiny bit?

**Donald G. Truhlar** responded: The variation in going from SA-CASSCF to MC-PDFT is very large. SA-CASSCF often has errors in excitation energies that are more than twice as large as those of MC-PDFT. Table 1 compares the mean unsigned error in molecular excitation energies for some cases<sup>1–8</sup> where we have compared the theory to CASSCF or SA-CASSCF.

- 1 G. Li Manni, R. K. Carlson, S. Luo, D. Ma, J. Olsen, D. G. Truhlar and L. Gagliardi, Multiconfiguration pair-density functional theory, *J. Chem. Theory Comput.*, 2014, **10**, 3669–3680.
- 2 S. Ghosh, A. L. Sonnenberger, C. E. Hoyer, D. G. Truhlar and L. Gagliardi, Multiconfiguration pair-density functional theory outperforms Kohn-Sham density functional theory and multireference perturbation theory for ground-state and excited-state charge transfer, *J. Chem. Theory Comput.*, 2015, **11**, 3643–3649.

Table 1 Mean unsigned error (in eV) for molecular excitation energies

System(s)	Final state <sup>a</sup>	(SA-)CASSCF	MC-PDFT	Ref.
singlet → singlet				
7 molecules	S <sub>1</sub>	1.4	0.5	1
NH <sub>3</sub> ...HNO <sub>2</sub>	CT at 9 distances	1.1	0.4	2
HCHO	Ryd	1.0	0.4	3
23 cases	18 Val, 2 Ryd, 3 CT	0.7	0.2	4
C <sub>6</sub> H <sub>6</sub>	4 Val	0.7	0.4	5
2 cyclohexadienes	3 Val, 7 Ryd	1.3	0.2	6
doublet → doublet				
CN	D <sub>1</sub> , D <sub>2</sub> , D <sub>3</sub>	0.3	0.03	7
10 radicals	5 states each	0.4	0.2	8

<sup>a</sup> S: Singlet; D: Doublet; Val: Valence; Ryd: Rydberg; CT: charge transfer

- 3 C. E. Hoyer, L. Gagliardi and D. G. Truhlar, Multiconfiguration pair-density functional theory spectral calculations are stable to adding diffuse basis functions, *J. Phys. Chem. Lett.*, 2015, **6**, 4184–4188. The result given is for the best basis with each method.
- 4 C. E. Hoyer, S. Ghosh, D. G. Truhlar and L. Gagliardi, Multiconfiguration pair-density functional theory is as accurate as CASPT2 for electronic excitation, *J. Phys. Chem. Lett.*, 2016, **7**, 586–591. The MUE averaged over Val, Ryd, and CT, each weighted 1/3.
- 5 P. Sharma, V. Bernales, D. G. Truhlar and L. Gagliardi, Valence  $\pi\pi^*$  excitations in benzene studied by multiconfiguration pair-density functional theory, *J. Phys. Chem. Lett.*, 2019, **10**, 75–81.
- 6 J. Ning and D. G. Truhlar, The valence and Rydberg states of dienes, *Phys. Chem. Chem. Phys.*, 2020, **22**, 6176–6183.
- 7 J. J. Bao, L. Gagliardi and D. G. Truhlar, Multiconfiguration pair-density functional theory for doublet excitation energies and excited state geometries: the excited states of CN, *Phys. Chem. Chem. Phys.*, 2017, **19**, 30089–30096.
- 8 J. J. Bao, S. S. Dong, L. Gagliardi and D. G. Truhlar, Automatic selection of an active space for calculating electronic excitation spectra by MS-CASPT2 or MC-PDFT, *J. Chem. Theory Comput.*, 2018, **14**, 2017–2025.

**Nikitas Gidopoulos** continued the discussion of the paper by Katarzyna Pernal: A way to avoid double-counting of correlation would be to keep only the one-body reduced density matrix from the CASSCF calculation and use it in an approximate reduced density matrix functional theory expression to obtain the total energy. Do you expect the accuracy of the resulting total energy expression to be good compared with your results?

**Katarzyna Pernal** answered: In a CAS one-electron reduced density matrix only a handful of the natural orbitals are occupied, the rest are unoccupied. Employing such a density matrix in an approximate reduced density matrix functional would recover mostly nondynamic correlation (for a dynamic correlation SCF calculations would be necessary). Adding correlation energy from the density matrix functional to CAS would lead to nondynamic correlation energy double-counting and lack of dynamic correlation, therefore this is not the way to go.

**Paola Gori-Giorgi** asked: My question concerns the fact that the CAS wave function has regions in which  $x(\mathbf{r})$  is larger than 1: is it always due to the CAS wave function not being exact? In other words, for the exact wave function (in particular for excited states) is it known that  $x(\mathbf{r}) > 1$  can never happen? You use this condition to signal that you need more dynamical correlation (*i.e.*, that you need to correct for this  $x(\mathbf{r}) > 1$ , which you assume to be always wrong) so it would be interesting to know that, indeed, this needs to be always corrected.

**Katarzyna Pernal** answered: For the CAS wavefunction  $x(\mathbf{r})$  may be greater than 1 if the (excited) state is ionic, *i.e.*, the ionic configuration dominates in the wavefunction. When the active space of CAS is extended, configurations other than ionic start playing a role and in the limit of the FCI function they are likely to take over and mask the ionic character, leading to  $x(\mathbf{r})$ , see Fig. 1.

**Trygve Helgaker** continued the discussion of the paper by Donald G. Truhlar: For the VMS-PDFT method, you maximize the sum over states of the MC-PDFT energies by a Fourier approximation rather than a complete variational calculation (FMS). How much difference is there, and how large is the difference in energy compared to a full maximization?

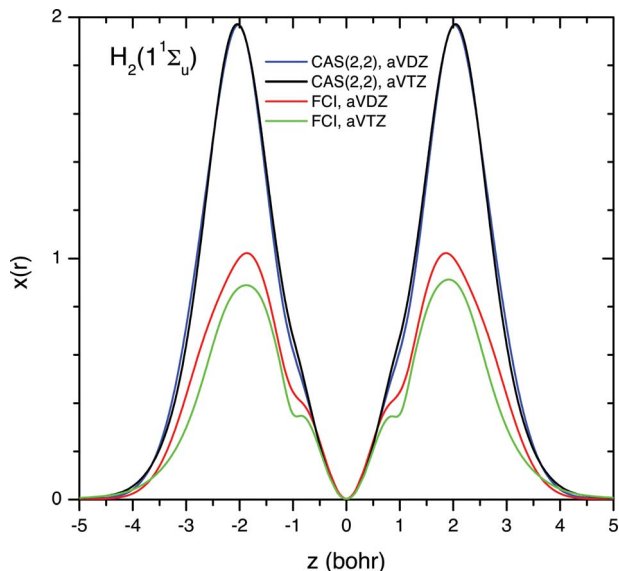


Fig. 1 Plots of the  $x(r)$  function along the bond axis of the  $H_2$  molecule at  $R_{H_2} = 2$  a.u. CAS(2,2) and FCI wavefunctions obtained in aug-cc-pVDZ and aug-cc-pVTZ basis sets.

**Donald G. Truhlar** responded: The transformation is parameterized by a rotation angle as indicated in eqn 15 of our article. Table 2 compares the Fourier approximation to full variational optimization for LiF. We see that the rotation angle obtained by Fourier analysis is within  $0.3^\circ$  of the fully optimized one. We also see that the difference in energy is usually less than  $10^{-3}$  eV.

**Andreas Savin** continued the discussion of the paper by Katarzyna Pernal: You described situations where correlation can bring together electrons, instead of separating them. You showed that this happens through CASSCF functions. It was asked whether this can happen for the exact wave function. I think that it can for excited states. Consider the stretched  $H_2$  molecule. The single determinant wave

Table 2 Comparison of VMS-PDFT to FMS-PDFT for LiF as a function of internuclear distance ( $R$ ): Rotation angles ( $\theta$ ), their difference ( $\Delta\theta$ ), and differences in energy ( $\Delta E$ ) for the ground state (GS) and excited state (ES)

$R$ (Å)	$ \theta_{VMS} $ ( $^\circ$ )	$ \theta_{FMS} $ ( $^\circ$ )	$\Delta \theta $ ( $^\circ$ )	$\Delta E_{GS}$ (FMS – VMS) (meV)	$\Delta E_{ES}$ (FMS – VMS) (meV)
0.8	26.4	26.3	−0.1	−0.7	0.7
1.6	5.1	5.4	0.3	−0.1	0.5
2.4	15.7	16	0.3	1.0	−1.0
3.2	28.7	28.8	0.1	1.0	−1.0
4.0	38.5	38.5	0.0	−0.4	0.4
4.8	13.0	13.0	0.0	0.0	0.0
5.6	4.1	4.3	0.2	−4.0	4.0
6.4	1.4	1.5	0.1	−0.9	1.0
7.2	0.4	0.6	0.2	−0.2	0.4
8.0	0.2	0.1	−0.1	0.0	0.1
10	0.0	0.1	0.1	0.1	0.1



function is a mixture of the covalent and ionic structures. The ground state is described by the covalent structure: the electrons are pushed away. To obtain the ionic excited state, the electrons are brought together, on the same center.

As density functional approximations are thought to model the ground state, one can ask if electrons can be brought together (at least for some spatial regions) in the ground state, too. For years, I asked people, and the best answer I got up to now was from Helene Bolvin (Universite Paul Sabatier, Toulouse, France). She mentioned the existence of systems with *negative U*.

**Katarzyna Pernal** responded: Even for the a  $H_2$  molecule in the first excited ( $\sum_u$ ) state, the ratio  $x(\mathbf{r})$  is greater than one, in the physically meaningful regions (regions of nonvanishing electron density), only if a small CAS wavefunction is used. If  $x(\mathbf{r})$  is constructed from the FCI wavefunction the value of  $x$  drops below 1, see Fig. 1. The same behavior is observed for larger molecules in excited states of ionic character. In the small-CAS-wavefunction description, when the ionic configuration is dominating, the enhancement of the correlation [ $x(\mathbf{r}) > 1$ ] is observed. When larger active space is used the ratio  $x(\mathbf{r})$  may not exceed 1 any

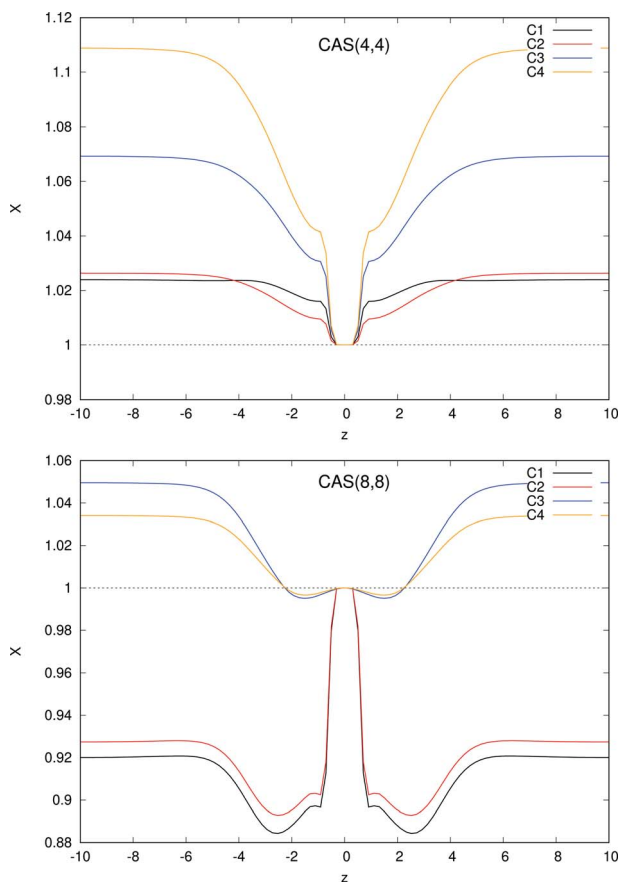


Fig. 2 The  $x(\mathbf{r})$  function along the  $2p_z$  orbital direction on the carbon atoms for the excited ( $2^1B_u$ ) state of octatetraene for the CAS(4,4) and CAS(8,8) reference (cc-pVTZ basis set).

longer. This is due to the fact that the presence of other than ionic configurations in a wavefunction takes over and masks the ionicity. The example of such a situation is presented in Fig. 2, showing the  $x(\mathbf{r})$  ratio of the octatetraene molecule in the  $2^1B_u$  state. The CAS(4,4) function leads to  $x(\mathbf{r}) > 1$  in the carbon atoms regions. This behavior partially vanishes when the active space is extended to 8 electrons in 8 orbitals. When it comes to the question if enhancement of electron correlation ( $x > 1$ ) is feasible in ground states, we cannot provide a definite answer. From our observations it seems unlikely.