Self-consistent Kohn-Sham calculations with adiabatic connection models

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Abstract

Adiabatic connection models (ACMs) are powerful tools to build accurate exchange-correlation functionals. In this work we introduce a fully self-consistent-field (SCF) implementation of some popular ACM based functionals. To this purpose we also introduce new GGA approximations, beyond the usual point-charge-plus-continuum model, for the strong correlation functional and its first derivative, showing their robustness and reliability. Then we assess the SCF-ACM functionals for molecular systems and for strong-correlation problems. We find that they perform well for both the total energy
and the electronic density, being in line or superior to SCF double-hybrid methods, and that the impact of SCF orbitals is directly connected to the accuracy of the ACM functional form. For the H\textsubscript{2} dissociation the SCF-ACM functionals yield significant improvements, also thanks to the use of the new GGA strong-correlation formulas.

Kohn-Sham (KS)\textsuperscript{1} density functional theory (DFT) is the most used electronic structure computational approach for molecular and solid-state systems.\textsuperscript{2-4} Its accuracy depends on the choice of the approximation for the exchange-correlation (XC) functional which, at the highest-rung of the Jacob’s ladder,\textsuperscript{5} involves all the occupied and virtual KS orbitals as well as the eigenvalues. Then, the XC approximation is no more an explicit functional of the density and, to stay within the pure KS formalism, the optimized effective potential (OEP) method\textsuperscript{6,7} must be employed. Early OEP approaches included exact-exchange (EXX) and approximated the correlation using the second-order Görling-Levy perturbation theory (GL2).\textsuperscript{8} However this led to a large overestimation of correlation effects and to convergence problems.\textsuperscript{9-15}

Actually two different main approaches have been explored to solve this issue: going beyond the second-order approximation\textsuperscript{16-23} or using a semicanonical trasformation\textsuperscript{9,10,15}. Another possible path is the adiabatic connection (AC) formalism\textsuperscript{24-26} which is a general, powerful tool for the development of XC functionals. Since several decades it has been used to justify the introduction of hybrid\textsuperscript{27-29} and double hybrid (DH) functionals\textsuperscript{30-32} and successively it has been directly employed to construct high-level XC functionals based on AC models (ACM) interpolating between known limits of the AC integrand.\textsuperscript{33-40} Recently it has also been employed in the context of the Hartree-Fock (HF) theory\textsuperscript{41} to develop corrections to the Møller-Plesset perturbation series.\textsuperscript{42}

The XC functionals based on ACMs have the general form

\[
E_{xc}^{ACM} = f^{ACM}(W) = \int_0^1 W_\lambda^{ACM}(W) d\lambda.
\]  

(1)
where $W = (W_0, W'_0, W_\infty, W'_\infty)$, with $W_0 = E_x$ is the exact exchange energy, $W'_0 = 2E_c^{GL2}$ is twice the GL2 correlation energy, and $W_\infty$ and $W'_\infty$ are the indirect part of the minimum expectation value of the electron-electron repulsion and the potential energy of coupled zero-point oscillations, respectively. The model $W^{ACM}_\lambda$ is designed to mimic the exact but unknown $W_\lambda$, in particular by considering the known asymptotic expansions. 

\begin{align}
W_{\lambda \rightarrow 0} & \sim W_0 + \lambda W'_0 + \cdots \\
W_{\lambda \rightarrow \infty} & \sim W_\infty + \frac{1}{\sqrt{\lambda}} W'_\infty + \cdots.
\end{align}

In the last years several ACMs have been tested for various chemical applications showing promising results, especially in the description of non-covalent interactions. Most of these recent studies have focused, however, on post-HF calculations while only little attention has been devoted to DFT-based ones. The main reason for this is that in the HF case the ACM is applied on top of the HF ground state, which is a simple and well defined reference; on the contrary, in the DFT framework the ACM-based XC functional should be applied inside the KS equations in a self-consistent-field (SCF) fashion. This requirement is not trivial because ACM-based functionals are not simple explicit functionals of the density but are instead complicated expressions depending on KS orbitals and orbital energies as well (through $E_x$ and $E_c^{GL2}$). Thus, in practice, also in the context of DFT, ACMs are applied in a post-SCF scheme using precomputed DFT densities and orbitals. In this way the results depend significantly on the choice of the reference density and orbitals, making the whole method not very reliable. On the other hand, an exploratory study of the XC potential derived from ACM models has shown that this possesses promising features, indicating that SCF calculations with ACM-based functionals might be an interesting path to explore.

In this work we tackle this issue by introducing an SCF implementation of the ACM potential and applying it to some test problems in order to verify its ability to describe different properties and systems. To this purpose, we need to deal with the potential arising
from the functional derivative of the energy of Eq. (1), that is,

\[ v_{xc,\sigma}^{ACM}(r) = \frac{\delta E_{xc}^{ACM}}{\delta \rho_\sigma(r)} = \]  

\[ = D_{E_x}^{ACM} \frac{\delta E_x}{\delta \rho_\sigma(r)} + D_{E_{cGL2}}^{ACM} \frac{\delta E_{cGL2}}{\delta \rho_\sigma(r)} + \]

\[ + D_{W_\infty}^{ACM} \frac{\delta W_\infty}{\delta \rho_\sigma(r)} + D_{W'_\infty}^{ACM} \frac{\delta W'_\infty}{\delta \rho_\sigma(r)}, \]  

where \( D_j = \partial f^{ACM}/\partial j \) with \( j = E_x, E_{cGL2}, W_\infty, W'_\infty \). As discussed in Ref. 48, the potential in Eq. (4) requires a combination of OEP (for \( E_x \) and \( E_{cGL2} \)) and GGA approaches (for \( W_\infty \) and \( W'_\infty \)). Thus it resembles the OEP-SCF implementation of the double-hybrid (DH) functionals reported in Ref. 49,50 (Further details can be found in Refs. 14,51,52). However, there is a significant difference between ACM and DH approaches: in the former the coefficients \( D_{E_x}^{ACM} \) and \( D_{E_{cGL2}}^{ACM} \) are not fixed empirical parameters as in DH, but are well defined (non-linear) functions of \( E_x, E_{cGL2}, W_\infty, W'_\infty \). Another important issue is related to \( W_\infty \) and \( W'_\infty \), which describe the \( \lambda \to \infty \) limit of the AC integrand. It can be proven that both \( W_\infty \) and \( W'_\infty \) display a highly non-local density dependence. This is accurately described by the strictly-correlated electrons (SCE) model, which is however computationally very demanding and non trivial to evaluate. Therefore, the \( \lambda \to \infty \) limit is usually approximated by simple semilocal gradient expansions (GEA) derived within the point-charge-plus-continuum (PC) model,

\[ W^{PC}_\infty[\rho] = \int d^3r \ A \rho^{4/3}(1 + \mu_w s^2), \]  

\[ W'^{PC}_\infty[\rho] = \int d^3r \ C \rho^{3/2}(1 + \mu_{w'} s^2), \]  

where \( s = |\nabla \rho|/[2(3\pi^2)^{1/3} \rho^{4/3}] \) is the reduced gradient of the density, \( A = -9(4\pi/3)^{1/3}/10 \), \( C = \frac{1}{2}(3\pi)^{1/2} \), \( \mu_w = -3^{1/3}(2\pi)^{2/3}/35 \approx -0.1403 \), and \( \mu_{w'} = -0.7222 \) (slightly different estimates are possible for \( \mu_{w'} \), see e.g. Refs. 33,36). The GEAs of Eqs. (5) and (6) yield, at least for small atoms, energies that are quite close to the accurate SCE values. However, when
s is large, e.g. in the tail of an exponentially decaying density, they fail, giving functional
derivatives that diverge. This is a severe drawback that does not allow to directly use these
approximations in a SCF implementation.

To remedy to this limitation we consider here a simple GGA approximation, named
harmonium PC (hPC) model, based on the Perdew-Burke-Ernzerhof (PBE) exchange en-
hancement factor, that recovers the GEAs of Eqs. (5) and (6) in the slowly-varying regime,
is well behaved everywhere, and reproduces as close as possible the SCE values for both $W_\infty$ and $W'_\infty$. Thus, we have

$$W^{hPC}_\infty = \int d^3\mathbf{r} \, A \rho^{4/3} \left[ \frac{1 + s^2 \mu_w \frac{\kappa_w+1}{\kappa_w}}{1 + s^2 \mu_w / \kappa_w} \right],$$  

$$W'^{hPC}_\infty = \int d^3\mathbf{r} \, C \rho^{3/2} \left[ \frac{1 + s^2 \mu'_w \frac{\kappa'_w+1}{\kappa'_w}}{1 + s^2 \mu'_w / \kappa'_w} \right],$$

where $\kappa_W = -7.11$ and $\kappa'_{W'} = -99.11$ have been fixed such that $W^{hPC}_\infty$ and $W'^{hPC}_\infty$ recover exactly the corresponding SCE values for the harmonium atom at $\omega = 0.5$. We note that the mPC approach of Ref. also employs GGA expressions for $W_\infty$ and $W'_\infty$ but they are quite far from recovering the PC values, in particular for $W'_\infty$ that does not even recover the PC model in the small $s$ limit. In fact, the mPC model has been derived for the quasi-two-dimensional density regime and its application in three-dimensional systems, e.g. for the total correlation of atoms, is highly based on an error cancellation between the quite inaccurate values of $W_\infty$ and $W'_\infty$.

To understand the performances of the different approaches we report in Fig. 1 the differences between values of $W_\infty$ and $W'_\infty$ computed with various methods and the respective $W^{PC}_\infty$ and $W'^{PC}_\infty$ values, for the Hooke atom at different confinement strengths $\omega$. We see that, unlike mPC, the hPC model is much closer to the PC one and it also reproduces very well both the $W_\infty$ and $W'_\infty$ accurate SCE values, being comparable to and even superior than the original PC model (see Table S1 in the Supporting Information). This performance is not trivial since hPC was parametrized only on a single instance of the Hooke’s atom.
Figure 1: Differences between the values of $W_\infty$ and $W'_\infty$ computed with hPC and mPC formulas and the corresponding $W'^{PC}_\infty$ and $W'^{mPC}_\infty$ data ($W^{Method}_\infty - W^{PC}_\infty$; $W'^{Method}_\infty - W'^{PC}_\infty$) for the harmonium atom at various values of the confinement strength $\omega$. For reference also some available accurate SCE values are reported.61

(\omega = 0.5) but turns out to be very accurate for the whole range of confinement strengths. In particular, in the small $\omega$ range (strong interaction limit of the Hooke’s atom) hPC yields the best estimation of the XC energy $E_{xc} = W_\infty + 2W'_\infty$ (see Fig. S1 in the Supporting Information), being slightly better than PC, while the mPC method fails completely. Similar trends are confirmed also for real small atoms both for energies and potentials, see Table S2 and Figure S2 in the Supporting Information, respectively, indicating the robustness of the hPC method.

Having all the necessary tools we have performed a series of SCF ACM calculations to investigate the performance of these methods in the KS framework. In particular, we have considered the Interaction-Strenght-Interpolarinon (ISI)33 and Seidl-Perdew-Levy (SPL)37 ACMs as well as the bare OEP-GL29 approach. The ISI model for $W_\lambda$ has in general a larger deviation from linearity than SPL (which does not depend on $W'_\infty$ too), whereas GL2 corresponds to the linear approximation $W_\lambda = 2E_{GL2}\lambda$. Thus the comparison of ISI with SPL and GL2 gives information on the importance of the shape of the ACM interpolation form.

For a better assessment the results to those of the PBE-QIDH62 (69.33\% EXX contribution) and PBE-mIDH63 (86.75\% EXX contribution) DH. The latter calculations have been performed using the methodology developed in ?? taking into account the MP2 correlation
term in SCF calculations. We remark, that both DH functionals have been selected since they include a similar EXX contribution as in our AC functionals (80% to 100%, see ??). Full computational details are given in the Supporting Information. Reference results are obtained from CCSD(T) in the same basis set.

In Table 1 we compare the mean absolute errors (MAEs) and the mean absolute relative errors (MAREs) for the correlation and total energies computed with the various methods for a test set of 16 closed-shell atoms and small molecules, namely He, Be, Ne, Mg, Ar, HF, CO, H2O, H2, He2,Cl2,N2,Ne2,HCl,NH3 ,C2H6. Full results are in Tables S3 and S4 in the Supporting Information. We see that ISI@SCF and SPL@SCF perform quite well, being twice better than OEP-GL2 and slightly better than the DHs. This result confirms that the ACMs at the base of these functionals are quite effective to mimic the AC curve. Nevertheless, we have to acknowledge that the performance has further margins of improvement. For example the MAREs of MP2 and OEP2-sc (see Table S3 in the Supporting Information) for the same test are 7.1% and 6.0%, respectively. We can trace back most of this difference to the fact that the use of KS eigenvalues, as in ISI, SPL and OEP-GL2, requires a quite large
AC curvature to yield accurate results, whereas this is not the case for MP2 and OEP2-sc that employ HF-quality eigenvalues. Then, KS based methods need much more accurate ACMs to compete with HF based ones. This is also confirmed observing that in Tab. 1, ISI is generally better than SPL, as the former is a more advanced ACM than the latter.

A second, related observation is that the ISI and SPL results suffer from a small relaxation error that worsens slightly the performance (with respect using EXX orbitals). For a given property E (e.g. the energy) we defined the quantity

$$\Delta[E] = |E^{@SCF} - E^{ref}| - |E^{@EXX} - E^{ref}|$$

which considers the absolute error difference (with respect the reference, i.e. CCSD(T)) going from EXX orbitals to SCF orbitals (a negative value means that SCF orbitals give better accuracy than EXX orbitals). This is reported in the last columns of Tab. 1. Despite the $\Delta[E]$ values are all positive (i.e. calculations using EXX orbitals are more accurate) they decrease going from GL2 to SPL and then from SPL to ISI, showing again that increasing the complexity/accuracy of the ACM can yield better SCF potentials and relaxed total energies.

Interestingly an opposite behavior of the relaxation is found in harmonium atom, as shown in Fig. where (for both ISI and SPL) the SCF results are better with respect to the EXX ones, especially at small values of the confinement strength where relaxation becomes more important. This also traces back to the use of hPC which yields accurate strong-correlation potentials; we note in fact the accuracy of both ACMs with the hPC model is very high (compare e.g. with Figure 3 of Ref. 47).

As a next step, therefore, we consider, the correlation potentials, for two typical systems, the Ne atom and the CO molecule. In the top panels of Fig. we see that the ACM based potential provides a quite good description of the correlation potential for the two systems, improving significantly over GL2. Nevertheless, with respect to reference data, there are still some limitations, e.g. a moderate overestimation of the correlation potential in valence
regions. This characteristic corresponds to an overestimation of shell oscillations in the SCF density, as indicated in the bottom panels of Fig. 3, where we report the correlation density $\rho_c$, i.e. the difference between the density obtained with a correlated method and its exchange-only version.

In the central panels of Fig. 3, we report the values $\Delta [v_c (r)]$, which show, point-by-point if the SCF procedure improves or not the correlation potential with respect to EXX orbitals. As also found for energies, the SCF correlation potentials are less accurate, but the error reduces with more accurate ACM functionals. This feature is also evident for the correlation density, see bottom panels. In this context, we should however point out that the ACM-SCF density does not correspond to the exact linear response density.$^{64–66}$

As a final case we consider in Fig. 4 the potential energy surface for the dissociation of the H$_2$ molecule, in a restricted formalism,$^{68}$ which is one of the main DFT challenges,$^{68,69}$ and previously investigated in ACM framework.$^{40,70,71}$ While both MP2 and GL2@EXX diverge at large distances, ISI@SCF nicely reproduces the exact FCI curve, much better than ISI@EXX , see also Ref. $^{44}$. Thus the SCF procedure turns out to be quite important showing that, despite some limitations discussed above, it is crucial to include important correlation effects into the orbitals. For SPL (see Fig. S3 of the Supporting Information)
similar trends are found.

The limit for very large distances, which can be numerically tricky, can be instead computed exactly using the hydrogen atom with fractional spins, $H(1/2,1/2)$, i.e. with half spin up and half spin down. For this system we have $E_{GL2} \to -\infty$ so that the total ISI energy reduces to

$$E^{ISI}_{xc} \to W_\infty + 2W'_\infty (1 - \frac{1}{q} \ln(1 + q))$$

with $q = (E_x - W_\infty)/W'_\infty$. The potential is thus a simple linear combination of the EXX potential and the GGA potential from $W_\infty$ and $W'_\infty$. For the SPL approach, we have simply that $E^{SPL}_{xc} \to W_\infty$ and thus the potential is just $\delta W_\infty/\delta \rho(r)$.

The error for different methods and orbital are reported in Tab. 2. At the exact density ($\rho(r) = \exp(-2r)/\pi$) SPL-PC gives extremely accurate total energy. The SPL-mPC
Figure 4: The total energy of the H$_2$ molecule as it is stretched calculated with the various methods. The inset presents the same data around the equilibrium distance.

Table 2: Total energy error for H(1/2,1/2) in kcal/mol for different methods and orbitals, using a very large uncontracted basis-set. Last column reports the integrated density difference error (IDD), i.e. $\int dr 4\pi r^2 |\rho(r) - \rho^{\text{exact}}(r)|$

|            | @EXACT | @SCF | IDD  |
|------------|--------|------|------|
| PBE        | 54.7   | 51.5 | 0.103|
| EXX        | 196.1  | 178.6| 0.260|
| SPL-PC     | -0.4   | no   | no   |
| SPL-mPC    | -109.8 | -114.9| 0.125|
| SPL-hPC    | -21.0  | -21.4| 0.024|
| ISI-PC     | 27.4   | no   | no   |
| ISI-mPC    | 90.2   | 83.7 | 0.151|
| ISI-hPC    | 23.6   | 19.4 | 0.107|

Note that the good accuracy of the ISI-hPC is not related to a large error cancellation between an incorrect SCF density and an incorrect energy. In fact, the integrated density...
difference (IDD) error shows that the density is quite accurate and almost exact for the SPL-hPC approach. The accuracy of the ISI-hPC@SCF approach for the H\textsubscript{2} dissociation limit is thus quite significant, considering that it uses full exact exchange and a combination of GL2 and a GGA functional without empirical parameters, in contrast to other approaches that use more complex constructions or extensive fitting on molecular data.\textsuperscript{69,73}

In conclusion, in this paper we have shown that it is possible to use ACM-based XC functionals in a fully SCF procedure. This solves a long-standing issue in DFT as all previous calculations with ACM functionals had been done in a post-SCF fashion using GGA or exact-exchange orbitals. For strong-correlated systems, such as the harmonium atom and the hydrogen molecule at dissociation limit, the ACM SCF calculations yield very accurate results taking advantage of the incorporated strong-correlation limit and also thanks to the novel hPC functional for \( W_\infty \) and \( W'_\infty \) that proved to be very accurate for these cases. For molecular systems, we find that the overall accuracy using SCF orbitals depends on the quality of the correlation functional form, in line with the Refs. 21 and 22. In any case the ISI-hPC yields already quite correct SCF potentials and total energies, comparable and/or even better than double hybrids. Thus, despite some limitations, the overall accuracy of our ACM SCF implementation is overall satisfactory especially considering that: i) we do not employ any parameter obtained from molecular systems, ii) the approach is within a pure KS formalism with a local potential. Thus our work open the path towards the development of more accurate ACM functional forms (see e.g. Ref. 42) as well as further development of \( W_\infty \) and \( W'_\infty \), with improved accuracy for molecular systems, as well as to application and testing to other systems.

**Supporting Information**

The Supporting Information is available free of charge at (URL)

Computational details, full total and correlation energy data, additional Hooke’s atom
results, strong correlation results for real atoms, and H₂ dissociation with SPL functional.

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References

(1) Kohn, W.; Sham, L. J. Phys. Rev. 1965, 140, A1133.

(2) Burke, K. J. Chem. Phys. 2012, 136, 150901.

(3) Becke, A. D. J. Chem. Phys. 2014, 140, 18A301.

(4) Jones, R. O. Rev. Mod. Phys. 2015, 87, 897–923.

(5) Perdew, J. P.; Schmidt, K. AIP Conf. Proc. 2001, 577, 1–20.

(6) Engel, E. In A Primer in Density Functional Theory; Fiolhais, C., Nogueira, F., Marques, M. A., Eds.; (Springer, Berlin, 2003.

(7) Kümmel, S.; Kronik, L. Rev. Mod. Phys. 2008, 80, 3–60.

(8) Görling, A.; Levy, M. Phys. Rev. A 1994, 50, 196–204.

(9) Grabowski, I.; Hirata, S.; Ivanov, S.; Bartlett, R. J. J. Chem. Phys. 2002, 116, 4415–4425.

(10) Bartlett, R. J.; Grabowski, I.; Hirata, S.; Ivanov, S. J. Chem. Phys. 2005, 122, 034104.

(11) Jiang, H.; Engel, E. J. Chem. Phys. 2005, 123, 224102.
(12) Schweigert, I. V.; Lotrich, V. F.; Bartlett, R. J. J. Chem. Phys. 2006, 125, 104108.

(13) Mori-Sánchez, P.; Wu, Q.; Yang, W. J. Chem. Phys. 2005, 123, 062204.

(14) Grabowski, I.; Teale, A. M.; Śmiga, S.; Bartlett, R. J. J. Chem. Phys. 2011, 135, 114111.

(15) Grabowski, I.; Lotrich, V.; Bartlett, R. J. J. Chem. Phys. 2007, 127, 154111.

(16) Verma, P.; Bartlett, R. J. J. Chem. Phys. 2012, 136, 044105.

(17) Furche, F. J. Chem. Phys. 2008, 129, 114105.

(18) Grüneis, A.; Marsman, M.; Harl, J.; Schimka, L.; Kresse, G. J. Chem. Phys. 2009, 131, 154115.

(19) Heßelmann, A.; Görling, A. Mol. Phys. 2010, 108, 359–372.

(20) Heßelmann, A.; Görling, A. Phys. Rev. Lett. 2011, 106, 093001.

(21) Bleiziffer, P.; Heßelmann, A.; Görling, A. J. Chem. Phys. 2013, 139, 084113.

(22) Bleiziffer, P.; Krug, M.; Görling, A. J. Chem. Phys. 2015, 142, 244108.

(23) Zhang, I. Y.; Rinke, P.; Perdew, J. P.; Scheffler, M. Phys. Rev. Lett. 2016, 117, 133002.

(24) Langreth, D.; Perdew, J. Sol. State Commun. 1975, 17, 1425 – 1429.

(25) Gunnarsson, O.; Lundqvist, B. I. Phys. Rev. B 1976, 13, 4274–4298.

(26) Savin, A.; Colonna, F.; Pollet, R. Int. J. Quantum Chem. 2003, 93, 166–190.

(27) Becke, A. D. J. Chem. Phys. 1993, 98, 5648–5652.

(28) Perdew, J. P.; Ernzerhof, M.; Burke, K. J. Chem. Phys. 1996, 105, 9982–9985.

(29) Fabiano, E.; Constantin, L. A.; Cortona, P.; Della Sala, F. J. Chem. Theory Comput. 2015, 11, 122–131.
(30) Sharkas, K.; Toulouse, J.; Savin, A. J. Chem. Phys. 2011, 134, 064113.

(31) Brémond, E.; Adamo, C. J. Chem. Phys. 2011, 135, 024106.

(32) Brémond, E.; Ciofini, I.; Sancho-García, J. C.; Adamo, C. Accounts of Chemical Research 2016, 49, 1503–1513.

(33) Seidl, M.; Perdew, J. P.; Kurth, S. Phys. Rev. Lett. 2000, 84, 5070–5073.

(34) Seidl, M.; Perdew, J. P.; Kurth, S. Phys. Rev. A 2005, 72, 029904.

(35) Seidl, M.; Perdew, J. P.; Kurth, S. Phys. Rev. A 2000, 62, 012502.

(36) Gori-Giorgi, P.; Vignale, G.; Seidl, M. J. Chem. Theory Comput. 2009, 5, 743–753.

(37) Seidl, M.; Perdew, J. P.; Levy, M. Phys. Rev. A 1999, 59, 51.

(38) Liu, Z.-F.; Burke, K. Phys. Rev. A 2009, 79, 064503.

(39) Ernzerhof, M. Chem. Phys. Lett. 1996, 263, 499 – 506.

(40) Teale, A. M.; Coriani, S.; Helgaker, T. J. Chem. Phys. 2010, 132, 164115.

(41) Seidl, M.; Giarrusso, S.; Vuckovic, S.; Fabiano, E.; Gori-Giorgi, P. J. Chem. Phys. 2018, 149, 241101.

(42) Daas, T. J.; Fabiano, E.; Della Sala, F.; Gori-Giorgi, P.; Vuckovic, S. J. Chem. Phys. Lett. 2021, 12, 4867–4875.

(43) Seidl, M.; Gori-Giorgi, P.; Savin, A. Phys. Rev. A 2007, 75, 042511.

(44) Fabiano, E.; Gori-Giorgi, P.; Seidl, M.; Della Sala, F. J. Chem. Theory Comput. 2016, 12, 4885–4896.

(45) Giarrusso, S.; Gori-Giorgi, P.; Della Sala, F.; Fabiano, E. J. Chem. Phys. 2018, 148, 134106.
(46) Vuckovic, S.; Gori-Giorgi, P.; Della Sala, F.; Fabiano, E. J. Phys. Chem. Lett. 2018, 9, 3137.

(47) Šmiga, S.; Constantin, L. A. J. Chem. Theory Comput 2020,

(48) Fabiano, E.; Šmiga, S.; Giarrusso, S.; Daas, T. J.; Della Sala, F.; Grabowski, I.; Gori-Giorgi, P. J. Chem. Theory Comput. 2019, 15, 1006–1015.

(49) Šmiga, S.; Franck, O.; Mussard, B.; Buksztel, A.; Grabowski, I.; Luppi, E.; Toulouse, J. J. Chem. Phys. 2016, 145, 144102.

(50) Šmiga, S.; Grabowski, I.; Witkowski, M.; Mussard, B.; Toulouse, J. J. Chem. Theory Comput. 2020, 16, 211–223.

(51) Šmiga, S.; Della Sala, F.; Buksztel, A.; Grabowski, I.; Fabiano, E. J. Comput. Chem. 2016, 37, 2081–2090.

(52) Grabowski, I.; Fabiano, E.; Teale, A. M.; Šmiga, S.; Buksztel, A.; Sala, F. D. J. Chem. Phys. 2014, 141, 024113.

(53) Buttazzo, G.; De Pascale, L.; Gori-Giorgi, P. Phys. Rev. A 2012, 85, 062502.

(54) Cotar, C.; Friesecke, G.; Klüppelberg, C. Comm. Pure Appl. Math. 2013, 66, 548–599.

(55) Cotar, C.; Friesecke, G.; Klüppelberg, C. Arch. Ration. Mech. An. 2018, 228, 891–922.

(56) Lewin, M. C. R. Math. 2018, 356, 449–455.

(57) Colombo, M.; Di Marino, S.; Stra, F. arXiv 2021, 2106.06282.

(58) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865–3868.

(59) Kooi, D. P.; Gori-Giorgi, P. Theor. Chem. Acc. 2018, 137, 166.

(60) Constantin, L. A. Phys. Rev. B 2019, 99, 085117.
(61) Kooi, D. P.; Gori-Giorgi, P. *Theor. Chem. Acc.* 2018, 137, 1–12.

(62) Brémond, E.; Sancho-García, J. C.; Pérez-Jiménez, A. J.; Adamo, C. *J. Chem. Phys.* 2014, 141, 031101.

(63) Jana, S.; Šmiga, S.; Constantin, L. A.; Samal, P. *J. Chem. Theory Comput.* 2020, 16, 7413–7430.

(64) Voora, V. K.; Balasubramani, S. G.; Furche, F. *Phys. Rev. A* 2019, 99, 012518.

(65) Jin, Y.; Su, N. Q.; Chen, Z.; Yang, W. *Faraday Discuss.* 2020, 224, 9–26.

(66) Yu, J. M.; Nguyen, B. D.; Tsai, J.; Hernandez, D. J.; Furche, F. *J. Chem. Phys.* 2021, 155, 040902.

(67) Wu, Q.; Yang, W. *J. Chem. Phys.* 2003, 118, 2498–2509.

(68) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. *Chem. Rev.* 2012, 112, 289–320.

(69) Kirkpatrick, J. et al. *Science* 2021, 374, 1385–1389.

(70) Peach, M. J. G.; Teale, A. M.; Tozer, D. J. *J. Chem. Phys.* 2007, 126, 244104.

(71) Teale, A. M.; Coriani, S.; Helgaker, T. *J. Chem. Phys.* 2009, 130, 104111.

(72) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. *J. Chem. Phys.* 2008, 129, 121104.

(73) Zhang, I. Y.; Xu, X. *WIREs Comput. Mol. Sci.* 2021, 11, e1490.