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We extend the recently introduced PBEh-3c global hybrid density functional [S. Grimme et al., *J. Chem. Phys.*, 2015, **143**, 054107] by a screened Fock exchange variant based on the Henderson–Janesko–Scuseria exchange hole model. While the excellent performance of the global hybrid is maintained for small covalently bound molecules, its performance for computed condensed phase mass densities is further improved. Most importantly, a speed up of 30 to 50% can be achieved and especially for small orbital energy gap cases, the method is numerically much more robust. The latter point is important for many applications, e.g., for metal–organic frameworks, organic semiconductors, or protein structures. This enables an accurate density functional based electronic structure calculation of a full DNA helix structure on a single core desktop computer which is presented as an example in addition to comprehensive benchmark results.

Due to its excellent accuracy-cost ratio Kohn–Sham density functional theory (KS-DFT, or simply DFT in the following)^{1,2} is the most prominent electronic structure method applied to larger molecules and solids. In practice, DFT is massively used for the routine computation of equilibrium structures, which may be then used in the treatment of various other properties.³ Though recent progress was made in wavefunction based methods for single-point energy calculations,^{4–6} we expect DFT to be the dominant approach for geometry optimizations, vibrational frequency calculations, or molecular dynamics applications in the foreseeable future. With this in mind, a composite method for consistent structures and noncovalent interaction energies

Screened exchange hybrid density functional for accurate and efficient structures and interaction energies†

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by DFT with small atomic orbital basis sets has been developed recently.⁷ Together with the previously proposed three-fold corrected (3c) Hartree–Fock (HF) method (HF-3c),⁸ the new composite scheme (termed PBEh-3c) represents the next member in a hierarchy of “low-cost” electronic structure approaches. They are mainly free of basis set superposition error (BSSE) and account for most interactions in a physically sound and asymptotically correct manner. Excellent equilibrium structures and very good results for noncovalent interaction energies in small and large complexes and molecular crystals could be reported. However, the relatively large amount of global, long-range Fock exchange hampers SCF convergence, which is especially pronounced in condensed systems with metallic characteristics, *i.e.*, with orbital energy gaps of <3.5 eV. Unfortunately, this excludes important classes of solids or other condensed phase systems from a numerically stable description with our proposed scheme. Note that already the naphthalene crystal falls into this category, and we encountered problems with organic semiconductors, most extended protein structures, and pharmaceutically relevant organic polymorph structures.^{9–11}

Here, we solve this problem rather generally by construction of a screened exchange variant based on the Henderson–Janesko–Scuseria (HJS) exchange hole model.^{12,13} The here proposed composite method can basically be seen as an ideal combination of PBEh-3c⁷ and the Heyd–Scuseria–Ernzerhof (HSE06) exchange functional.^{14,15} The method will be dubbed HSE-3c in the following. Its energy can be expressed as

$$\begin{aligned} E^{\text{HSE-3c}} = & E_{\text{xc}}^{\text{HSE-3c}} + E_{\text{disp}}^{\text{D3}} + E_{\text{BSSE}}^{\text{gCP}} \\ E_{\text{xc}}^{\text{HSE-3c}} = & aE_{\text{x}}^{\text{HF,SR}}(\omega) + (1 - a)E_{\text{x}}^{\text{PBEh-3c,SR}}(\omega) \\ & + E_{\text{x}}^{\text{PBEh-3c,LR}}(\omega) + E_{\text{c}}^{\text{PBEh-3c}}. \end{aligned} \quad (1)$$

The exchange–correlation functional is evaluated in an unmodified small Gaussian orbital basis set of double-zeta quality (termed def2-mSVP as introduced in ref. 7). The short-range (SR) Fock mixing parameter is fixed to $a = 0.42$, and the same modified Perdew–Burke–Ernzerhoff (PBE) exchange,¹⁶ and modified PBE correlation as in PBEh-3c is used.⁷ The HJS exchange hole

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† Electronic supplementary information (ESI) available: Full definition of the HSE-3c composite method, individual interaction energies, geometry of the DNA structure, and a numerical example for reproduction purposes. See DOI: 10.1039/c6cp01697a

model is parametrized on this modified functional as described in ref. 17. In this way, we closely reproduce the short-range exchange correlation potential of PBEh-3c. The error function separation (controlled *via* the standard parameter $\omega = 0.11$)¹⁴ switches the HSE-3c potential to a pure generalized gradient approximation (GGA) at long-range.

As a semilocal GGA is not able to describe long-range London dispersion interactions (also known as attractive van der Waals force), we include the semi-classical D3 dispersion energy correction.¹⁸ The ‘dispersion problem’ has been mostly solved in the last decade and many modern and accurate schemes within the DFT framework exist.^{18–23} Two recent review article describe their different construction principles.^{24,25} Here, the D3 energy expression is used in its most recent rational damping version²⁶ and in addition to the leading order fluctuating-dipole–fluctuating-dipole (C_6 based) energy, we include the three-body C_9 (dipole–dipole–dipole) contributions.^{18,27}

The small atom-centered single-particle basis set used leads to significant BSSE that is effectively removed by the geometric counterpoise correction gCP.^{28,29} Due to the density independent energy contributions, HSE-3c is not a generalized Kohn-Sham density functional, unlike HSE itself, and is therefore referred to as density functional based composite method. Explicit definitions of all HSE-3c model parameters are given in the ESI.† Because of its close relation to PBEh-3c, especially in the short-range regime, the overall performance of the new scheme for covalent geometries, thermochemistry, and kinetics will closely follow its parent model which has been tested for general thermochemistry rather extensively.⁷ Due to the relatively small orbital basis set, the results for thermochemistry and kinetics will be only of medium quality, *e.g.*, a weighted mean absolute deviation on the large GMTKN30 database of about 5 kcal mol⁻¹ is expected (compare with ref. 7 for details). The range-separation is expected to mostly affect interactions in the noncovalent regime, which is therefore tested in detail below.

A number of benchmark sets are analyzed and a summary is given in Table 1. Additional test sets, an extended statistical evaluation, and comparisons to other density functionals is given in the ESI.† For comparison we show PBEh-3c and standard, uncorrected HSE06 results evaluated in the same def2-mSVP orbital basis set. Note that we expect the performance of HSE06

to be substantially improved when it is calculated in a converged basis set (*e.g.* of projector-augmented plane wave type^{30,31}) and corrected for missing London dispersion interaction (*e.g. via* the D3 scheme¹⁸) as demonstrated recently.²⁷ Such a treatment is, however, not applicable to the intended large-scale geometry optimizations and we therefore use the comparison to highlight the impact of gCP and D3 contributions. We separate covalent bond lengths into light main group bonds (LMGB, first and second row of periodic table), heavy main group bonds (HMGB, third row and higher), and 3d-transition metal complexes (TMC).³² The good performance of PBEh-3c is maintained indicating that HSE-3c indeed reproduces the PBEh-3c short-range inter-atomic potential.

Rotational constants indirectly measure the size and shape of molecules and are analyzed with the ROT34 set.^{33,34} High accuracy of triple-zeta AO basis set, second-order perturbation theory (MP2/TZ) level can be reached by both PBEh-3c and HSE-3c at a tiny fraction of the computational effort. The systematically too large molecules (ROT34) computed by HSE06 in the def2-mSVP basis highlights the necessity of the rather large amount of short-range Fock exchange in order to compensate basis set incompleteness errors. For systems with stronger static electron correlation effects (TMC32), this leads to slightly better results. The S66x8 benchmark set^{36,37} has been used to adjust the empirical parameters in the D3 and gCP schemes and a good performance for these sets is mandatory for an accurate condensed phase method. HSE-3c fulfills this requirement with small MADs of 0.5 kcal mol⁻¹ and 1.5% for the interaction energy and center-of-mass distances, respectively. For further analysis of the noncovalent interactions, we tested the benchmark sets S22,³⁸ L7,³⁹ the GMTKN30 subsets IDISP, ADIM, (C,A,P,CY)CONF (averaged),⁴⁰ and the conformer set YMPJ.⁴¹ The computed MADs of 0.4, 1.9, 2.4, 0.2, 0.8 and 1.1 kcal mol⁻¹ for HSE-3c are rather small and in the typical range found for *e.g.* dispersion corrected density functionals like TPSS in a converged basis set expansion. Modern parametrized hybrid density functionals like wB97X-V evaluated in larger basis sets yield MADs on S22 and S66 by a factor of two smaller.⁴² If this translates into good performance on larger complexes has yet to be tested. The here proposed method gains a speed-up of about one to two orders of magnitude compared to those functionals for large gap molecular complexes and even more for small gap and periodic systems.

As a more realistic cross-check, we fully optimize the X23 benchmark set of organic crystals^{43,44} and show for two examples lattice energy curves. We compare with experimentally measured sublimation enthalpies and X-ray geometries that have been back-corrected for zero-point vibrational and thermal effects.^{43,44} With increasing π character in the series benzene, naphthalene, and anthracene, HSE-3c shows a speed-up compared to PBEh-3c of 30, 38, and 45%. This is due to the faster convergence of both the numerical Brillouin zone sampling as well as the more efficient exchange integral screening.

The potential energy surface (PES) of the benzene crystal is shown as prototypical example with high level coupled cluster reference data⁴⁵ in Fig. 1(a). We additionally show the PES of oxalic acid as a strongly hydrogen bonded system, which are

Table 1 Mean absolute or relative deviations for various geometry (first four rows, S66-CMA, X23-DENS) and non-covalent interaction energy (INT) benchmark sets^a

	HSE-3c	PBEh-3c	HSE06
LMGB35 [pm]	0.9	0.9	1.1
HMGB11 [pm]	0.9	0.8	0.9
TMC32 [pm]	3.5	3.3	2.8
ROT34 [%]	0.4	0.4	0.6
S66-CMA [%]	1.5	1.5	5.2
S66-INT [kcal mol ⁻¹]	0.5	0.5	2.2
X23-DENS [%]	2.6	2.7	8.4
X23-INT [kcal mol ⁻¹]	1.3	1.3	4.9

^a Details of all sets are given in ref. 7.

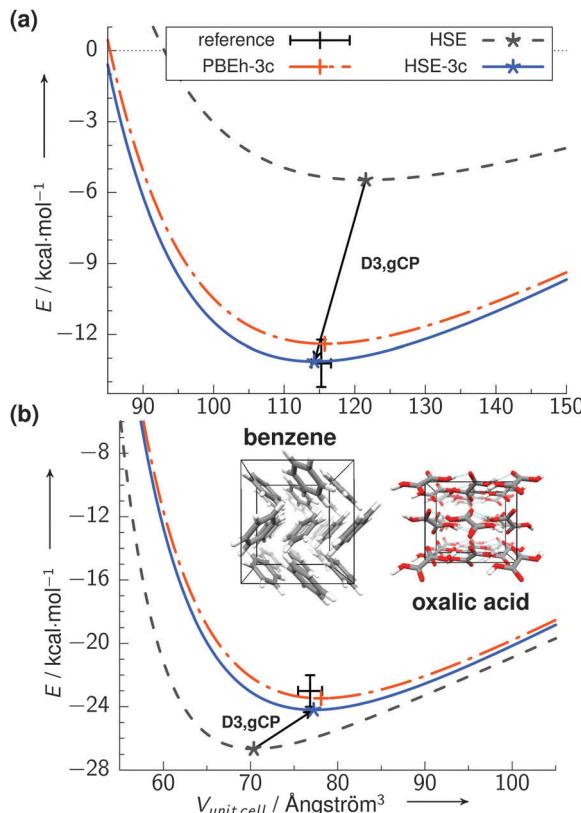


Fig. 1 Lattice energy of the (a) benzene and (b) oxalic acid α crystal based on constrained volume optimized TPSS-D3³⁵ structures and single-point energy evaluations of the presented methods. Each cross shows the position of the energy minimum and the arrow indicates the effect of the added energy corrections.

typically more difficult to describe than unpolar π systems. As expected, the uncorrected HSE functional cannot properly describe the noncovalently bound systems. Interestingly, the benzene crystal is bound too weakly while oxalic acid is bound too strongly. These different compensation effects between BSSE on the one hand and missing London dispersion on the other has been analyzed previously.⁴⁶ When accounting for both effects *via* the gCP and D3 scheme, respectively, an excellent agreement of the HSE-3c equilibrium position within the uncertainties of the reference data can be achieved. For benzene the D3 dispersion interaction is most dominant contributing 9 kcal mol⁻¹ to the lattice energy. The gCP correction is significantly smaller but still important and reduces the binding by 1 kcal mol⁻¹. For the oxalic acid polymorph the relative contributions to the lattice energy are interchanged with 8 and 9 kcal mol⁻¹ for the D3 and gCP correction, respectively. A very similar analysis holds for the equilibrium unit cell volume, where the HSE-3c errors for benzene and oxalic acid are very small with 0.9% and 0.5%, respectively.

The two shown systems are rather representative for the whole X23 set and hence the statistical analysis follows the same trends as given above. The MAD for the lattice energy is 1.3 kcal mol⁻¹ and the MARD for the mass density (which is directly related to the unit cell volume) is 2.6%. This compares

well with the PBEh-3c results and is comparable to more expensive calculations within a converged plane wave basis set.²⁷

As mentioned previously, biologically important structures can exhibit artificially small band gaps in GGA treatments^{47,48} often preventing SCF convergence. Furthermore, the slowly decaying Fock-exchange potential in the dense and highly polar systems makes the application of PBEh-3c problematic. Recently, the dispersion corrected B3LYP functional was applied to compute the structure of a crambin crystal.⁴⁹ While the study nicely shows the power of modern electronic structure codes to get insight into the quantum nature of biologically relevant systems, its routine application is still hindered by large computational requirements and BSSE artifacts. As a prototypical system, we study here a one-dimensional (periodic) DNA helix based on the nucleobases adenine and thymine poly(dA)-poly(dT). A graphical representation is shown in Fig. 2. The power of the here presented HSE-3c method is three-fold:

(1) We can exploit the rotational-translational symmetry group (CRYSTAL14^{50–52}), *i.e.*, only two nucleobases describe the full one-dimensional periodic helix.

(2) The small def2-mSVP orbital basis set in combination with our geometrical counterpoise correction increases the speed substantially, while avoiding most of the BSSE.

(3) The included short-range Fock exchange ensures a mostly self-interaction error (SIE) free treatment accompanied with additional speed up by efficient exchange integral screening compared to PBEh-3c.

Together, this enables the full geometry relaxation of the DNA helix structure at the density functional HSE-3c level on a standard desktop computer. Some computed results are summarized in Table 2. The binding energy per base pair of 16.2 kcal mol⁻¹ compares well to the value of 17.5 kcal mol⁻¹ of an isolated adenine-thymine dimer. Similar to the above given

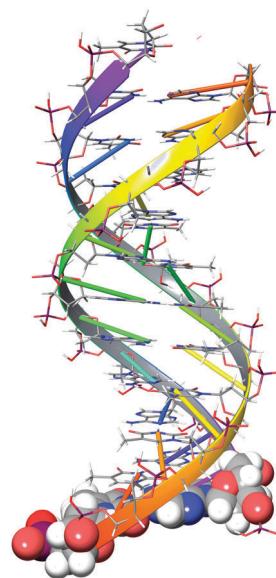


Fig. 2 Graphical representation of the primitive unit cell of the poly(dA)-poly(dT) helix structure. The irreducible atoms are highlighted as space-filling balls.

Table 2 Computed (HSE-3c) properties of the adenine–thymine double helix structure (DNA) compared to the corresponding single stranded helices

	DNA	Adenine	Thymine
Cell parameter ^a [Å]	34.2	35.6	31.1
Direct orbital energy gap [eV]	4.8	5.5	5.5
Inter-strand binding energy ^b [kcal mol ⁻¹]	16.2	—	—

^a Corresponding to the distance of one full helix turn. ^b Normalized to the interaction of one base pair.

analysis, inclusion of both, the dispersion interaction and counterpoise contribution to the geometry and binding energy is crucial. Neglecting one or both leads to large errors in the binding energy of 15% to 40%, respectively. A similar optimization of a guanine and cytosine based DNA helix shows a reasonable trend of less close packing (*i.e.*, enlarged cell parameter of 36.5 Å).⁵³ Note that these properties can not be directly compared to experimental measurements. A meaningful comparison would require the inclusion of solvation effects and probably inclusion of temperature effects (*e.g.* by molecular dynamics). In principle, one can describe the surrounding water implicitly by a dielectric screening (*e.g.*, *via* a COSMO model⁵⁴) or explicitly by including water molecules within the electronic structure calculation. However, this is beyond the scope of the current study and remains for future investigations.

We have presented the HSE-3c composite quantum chemical density functional method which is based on our previously published PBEh-3c model. The replacement of the global hybrid exchange functional by the analogous screened (short-range) HSE exchange variant was accomplished while keeping the BSSE and dispersion corrections. Both the accuracy and capability of HSE-3c to describe extended organic systems was demonstrated. According to the benchmark results, HSE-3c is expected to yield consistent and practically exact equilibrium structures for a wide range of nonmetallic molecular and condensed phase systems. Compared to PBEh-3c, the new method can be consistently applied to condensed large as well as small gap systems and computational speedups of a factor of two are observed at essential no loss of accuracy.

PBEh-3c can still be routinely used and is preferred for large gap and medium sized molecular systems due to its implementation in the fast program packages TURBOMOLE and ORCA. We suggest HSE-3c as general and robust electronic structure method in both theoretical chemistry and solid state physics of large systems especially in periodic boundary conditions and for small orbital gap cases. The strengths of both methods are the description of structures and noncovalent interactions but still providing reasonable chemical energetics of typical DFT accuracy.

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