Doubly Hybrid Functionals Close to Chemical Accuracy for Both Finite and Extended Systems: Implementation and Test of XYG3 and XYGJ-OS

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ABSTRACT: While being widely used to understand the chemical reactions in heterogeneous catalysis or other multidisciplinary systems, a great challenge that semilocal and hybrid density functional approximations (DFAs) are facing is to deliver a uniformly accurate description for both finite and extended systems. Herein, we perform reliable and well-converged periodic calculations of two doubly hybrid approximations (DHAs), XYG3 and XYGJ-OS, and demonstrate that the good accuracy of DHAs achieved for molecules is transferable to the semiconductors and insulators. Such an accuracy is not only for energetic properties but also for the first- and second-order response properties, which is general for different kinds of chemical environments, including simple cubic bulks, perovskite-type transition metal oxides like TiO$_2$, and heterogeneous systems like CO adsorption on the NaCl(100) surface. The present finding has strengthened the predictive power of DFT, which not only will inspire the future development of the top-rung DFAs but also will boost their applications in multidisciplinary studies with high accuracy and efficiency.

KEYWORDS: DFT, doubly hybrid approximation, periodic boundary conditions, condensed-matter systems

Kohn–Sham density functional theory (DFT) has been the method of choice for quantitative understanding and design of complex systems in either quantum chemistry or computational materials science. However, it remains a great challenge in the quest for a general purpose density functional approximation (DFA) that is capable of delivering a uniform accuracy in describing both finite and extended systems, offering the predictive power of DFT in multidisciplinary studies such as catalysis where small molecules react on the surface of a catalyst.

In the past decade, doubly hybrid approximations (DHAs) have been emerging quickly in quantum chemistry. DHAs introduce unoccupied Kohn–Sham orbitals in the form of the second-order perturbation theory (PT2) and thus stand on the top (fifth) rung of Jacob’s Ladder for DFA. Taking the XYG3 method investigated in this Letter as an example, the corresponding exchange-correlation energy is written as

$$E_{xc}^{XYG3} = a_1 E_{xc}^{HF} + (1 - a_1) E_{xc}^{LDA} + a_2 \Delta E_{xc}^{B88} + a_3 E_{xc}^{PT2} + (1 - a_3) E_{xc}^{LYP} \tag{1}$$

where $E_{xc}^{LDA}$ and $\Delta E_{xc}^{B88}$ are the exchange contribution in local density approximation and the Becke88 gradient-correction, respectively, while $E_{xc}^{LYP}$ is the contribution from the Lee–Yang–Parr correlation. “Doubly hybrid” means that both the Hartree–Fock (HF)-like exact exchange $E_{xc}^{HF}$ and the PT2 correlation $E_{xc}^{PT2}$ are linearly mixed with the commonly used DFA terms, using several empirical parameters optimized here against the heats of formation of some small molecules in the G3/99 set. The other DHA studied in this work, XYGJ-OS, shares a similar formula. The key difference is to replace $E_{xc}^{PT2}$ by its opposite-spin (os) variant $E_{xc}^{osPT2}$ for a speedup. XYG3 proposed by the Xu group defines a family of DHAs (xDH), which insists to use the self-consistent field (SCF) orbitals from a conventional lower-rung DFA for a good density while adopting another higher-rung functional for a good final energy. Hence, both XYG3 and XYGJ-OS belong to the xDH@B3LYP model, that is, the DHA energies are evaluated in a non-SCF (self-consistent field) manner, using orbitals and densities from the SCF calculations with the B3LYP functional.

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Extensive investigations have shown that the PT2-based DHAs improve over the conventional DFAs in the lower rungs with unprecedented accuracy in describing various kinds of chemical interactions and properties for finite molecules. It is not obvious whether the PT2-based DHAs can be equally successful for condensed-matter systems. Unfortunately, due to the inherent computational complexity of the calculations under the periodic boundary conditions, there are only a few results to date that mainly focused on the molecular crystals, often using small basis sets and/or local (or fragment-based) approximations. The performance of the DHAs for condensed-matter systems is yet to answer.

Here, we announce an efficient periodic implementation of XYG3 and XYGJ-OS in the FHI-aims package using the numeric atom-centered orbital (NAO) basis set. The most time-consuming and resource-demanding part is obviously the calculation of the canonical PT2 correlation energy:

$$E_{PT2} = -\frac{1}{N^2} \sum_{k,k'q} \sum_{\alpha\beta} \left[ 2 \left( \epsilon_{q\alpha q\beta} + \epsilon_{q\alpha q\beta} - \epsilon_{kq\alpha} - \epsilon_{k'q\beta} \right) \right]$$

(2)

As a generalization of the closed-shell sum-overstate canonical PT2 formula under the periodic boundary conditions, eq 2 contains three extra loops over all the k-grid points with $k_i$ and $k_j$ connected to the occupied (occ) orbitals $i$ and $j$, respectively, while $q_i$ and $q_j = q_i + k_i - k_j$ to the unoccupied virtual (vir) orbitals $a$ and $b$, respectively. Equation 2 reveals that the computational expense of any PT2-based DHAs, including XYG3 and XYGJ-OS, scales formally as $N_s^2 N^2$, where $N_s$ is the total k-grid number and $N$ denotes the system size of the unit cell. Hereby, an efficient periodic PT2 implementation is crucial to the intensive XYG3 and XYGJ-OS calculations with large basis sets and a dense k-grid setting in this work. Meanwhile, the corresponding massive parallelization is known to be essentially communication bound, particularly in storing and manipulating the electronic repulsion integral (ERI) of $(i|q\alpha q|j|b\beta q)$. To overcome this long-standing problem and to gain the desired parallel efficiency, our DHA implementation takes the advantage of a local variant of the resolution-of-identity (RI-LVL) approximation to decompose ERIs in the reciprocal space using an auxiliary basis set that is not predefined but produced on-the-fly in each specific calculation. Such a RI-LVL scheme has been demonstrated before to be accurate and efficient under the periodic boundary conditions for hybrid DFAs and beyond.

In this Letter, we present the results from the first attempt to obtain numerically well-converged cohesive energies per atom $E_{coh}$, lattice constants $a_0$ and bulk modulus $B_0$ for a set of condensed-matter systems with finite energy gaps, that is, semiconductors and insulators. The DFAs examined include not only XYG3 and XYGJ-OS but also four other popular semilocal DFAs and their hybrid counterparts, that is, BLYP, B3LYP, PBE, PBE0, M06-L, M06, SCAN, and SCAN0. The latter DFAs are lower-rung functionals, representing the historical and/or current working horses in quantum chemistry and computational materials science, respectively. We also present results for 142 bond dissociation energies of small molecules (Bond142), the relative stability of rutile and anatase TiO$_2$, as well as CO adsorption on the NaCl(100) surface. We find that the unprecedentted accuracy of XYG3 and XYGJ-OS achieved for molecules is transferable to the semiconductors and insulators, making them appealing for applications in the complex systems where molecules meet extended solids as, for example, in catalytic chemistry. Moreover, the numerically stable performance of XYG3 and XYGJ-OS clearly demonstrates that the periodic implementation is technically feasible for any mainstream PT2-based DHAs. These DHAs include other xDHs like ωB97M(2), xrevDSD-PBEP86-D4, and XYG7, which represent the top-level accuracy of KS-DFT currently available for the main-group chemistry, as well as B2PLYP and its variants, that optimize orbitals based on neglecting the PT2 component of the functionals, and the recently proposed BL1P functional with the density and orbitals from the Hartree–Fock approximation.

Here, we briefly outline the key aspects essential to perform reliable calculations of XYG3 and XYGJ-OS on solids. As in the calculations for molecules, the periodic XYG3 and XYGJ-OS results reported in this Letter are all evaluated based on the B3LYP density and orbitals as well. We have studied 14 main-group cubic crystals with strong covalent bonding and/or ionic bonding characters, including C and Si with diamond structure, LiH, LiF, LiCl, NaF, NaCl, MgO, and MgS with rock-salt structure, and BeS, BN, BP, SiC, and AlP with zincblende structure. In aid of the down-sampling technique, the periodic DHA results are extrapolated to the complete basis set (CBS) and the complete k-mesh (CKM) limits, using modified valence-correlation consistent NAO basis sets (NAO-VCC-nZ, with $n = 2$ and 3) and based on the results from the Γ-center k-grids of $6 \times 6 \times 6$ and $8 \times 8 \times 8$. The optimized total energy, lattice constant, and bulk modulus are then obtained by fitting the calculated energy-volume data in terms of the Birch–Murnaghan (B-M) equation of state (EOS). The computational details, as well as the raw data of all calculations are provided in the Supporting Information (SI).

We start by establishing the accuracy of various DFAs for the cohesive properties of solids. Table 1 shows the mean absolute errors (MAEs) in the calculated $a_0$ and $B_0$ of the aforementioned 14 solids with covalent bonding and/or ionic bonding characters; while the errors in the calculated $E_{coh}$ for the same set (CE14) are individually plotted in Figure 1a with the corresponding MAEs in Figure 1b. The present work confirms the well-known failure of empirical BLYP and its hybrid counterpart B3LYP for solids, while they are the historically most popular DFAs in quantum chemistry. For example, B3LYP produces similarly unsatisfactory MAE as BLYP for cohesive energies of the CE14 set (8.45 and 10.67 kcal/mol, respectively), which are dramatically worse than that of PBE (3.82 kcal/mol), a nonempirical semilocal DFA with overwhelming popularity currently in computational materials science.

The deficiency of B3LYP for solids has been attributed to its empirical way of construction, optimizing for a specific description of some finite molecules and the LYP correlation for being incapable of attaining the exact electron gas limit. These arguments are applicable to metals but may not be so obvious to semiconductors and insulators. On the other hand, the hybrid M06 functional is currently one of the most widely used DFAs in quantum chemistry, which contains several tens empirical parameters optimized against a set of finite molecules. As shown in Figure 1b, M06 clearly
outperforms PBE and its nonempirical hybrid counterpart PBE0 for the description of the cohesive energies in CE14. However, Table 1 shows that the errors of M06 are, on average, of the same order as for B3LYP in the calculations of \( a_0 \) and \( B_0 \). Among the tested (hybrid) semilocal DFAs, the SCAN functional, recently proposed by Sun, Ruszinszky, and Perdew, produces the best performance for all three properties (\( a_0 \), \( B_0 \), and \( E_0 \)) of solids. Such consistent improvement of SCAN over PBE for solids can be partly understood by the fact that SCAN not only obeys more (17 in total) known exact constraints for the exchange and/or correlation functionals but also unlocks several parameters by fitting the electronic properties of some rare-gas atoms, dimers, and the jellium surfaces.

Although hybrid DFAs, such as PBE0, have now gained increasing use in computational materials science,\(^5\)\(^3\) they are not comparable in popularity to their semilocal counterparts, such as PBE. It is not only because of the higher computational cost but also, as illustrated in Figure 1b, due to the fact that the inclusion of the exact exchange does not bring in consistent and noticeable improvements for solids.\(^3\)

Return to the failure of BLYP and B3LYP for solids. Figure 1a uncovers the significant underestimation of BLYP for the cohesive energies in CE14, with the absolute errors all larger than 3.0 kcal/mol. The inclusion of the exact exchange reduces the wrong tendency, but the results of B3LYP are by no mean satisfactory. As a natural extension of BLYP and B3LYP to the doubly hybrid level of theory, both XYG3 and XYGJ-OS inherit the LYP correlation in their formula and include three to four empirical parameters fitting against the experimental heats of formation of small molecules. Moreover, the total energies of XYG3 and XYGJ-OS are established based on the SCF orbitals of B3LYP. In a nutshell, XYG3 and XYGJ-OS share all the characters that the failure of BLYP and B3LYP has been ascribed to. Encouragingly, XYG3 and XYGJ-OS deliver an excellent performance for all cohesive properties of the 14 tested semiconductors or insulators, leading to the MAEs of only 1.44 and 1.21 kcal/mol for cohesive energies, 1.4 and 1.0 pm for lattice constants, and 3.6 and 3.1 GPa for bulk moduli, respectively. Figure 1a reveals that the doubly hybrid strategy is capable of effectively compensating the intrinsic limitation in the semilocal BLYP approximations for solids with nonzero band gaps, which notably shifts up and shrinks the error distribution for the CE14 set. In consequence, both XYG3 and XYGJ-OS deliver the best error distribution with 9 out of 14 (more than 60%) test cases reaching the chemical accuracy.

Note that another important view of the B3LYP failure for metals emphasized its use of the HF exchange at long-range,\(^5\)\(^4\) arguing that a screened long-range exchange should be used, which corresponds to introducing an electron correlation effect that is not present in the HF theory. As a reasonable assumption to partially associate the poor performance of B3LYP for semiconductors and insulators with its failure for metals aforementioned, the notable improvement made by XYG3 and XYGJ-OS for the CE14 test set suggests that the subtle many-electron correlated motion (or screening) at long-range in solids can be properly described to some extent by the combination of the HF-like exact exchange and the PT2 correlation, in particular, the osPT2 correlation, in the context of doubly hybrid strategy. For comparison, MP2 and RPA results are listed in Tables S2—S4 in the SI for various properties of solids. MP2 and RPA may be considered as the nonempirical top-rung DFAs from the perspective of Görling–Levy perturbation theory\(^5\)\(^6\)\(^7\) and the adiabatic-connection fluctuation–dissipation theory,\(^5\)\(^6\)\(^7\) respectively. However, none of them present a better performance than PBE, in particular for the cohesive energy. Such errors have been traced back to the lack of high-order many-body correlation in MP2,\(^5\)\(^8\) and the heavy self-interaction errors in RPA.\(^5\)\(^9\)

### Table 1. Performance of Different Methods in the Calculated Lattice Constants (\( a_0 \) in Picometer, pm) and Bulk Moduli (\( B_0 \) in GPa) of 14 Solids with Covalent Bonding or Ionic Bonding Characters\(^\text{a}\)

| Method | MAE \( a_0 \) | MAE \( B_0 \) | Max(+) | Max(−) |
|--------|---------------|---------------|--------|--------|
| BLYP   | 10.1          | 19.8          | 19.7   | −55.1  |
| B3LYP  | 5.7           | 7.8           | 13.1   | −24.5  |
| PBE    | 5.8           | 11.9          | 13.0   | −38.2  |
| PBE0   | 2.3           | 4.1           | 8.1    | −0.8   |
| M06-L  | 2.5           | 5.7           | 9.6    | −2.2   |
| M06    | 6.0           | 7.1           | 17.4   | −1.0   |
| SCAN   | 1.2           | 3.8           | 3.7    | −1.2   |
| SCAN0  | 1.3           | 7.4           | 1.8    | −3.8   |
| XYG3   | 1.4           | 3.8           | 2.2    | −5.2   |
| XYGJ-OS| 1.0           | 3.3           | 1.3    | −4.6   |

\(\text{a}\) The two methods with the best performance are labeled in bold. (See Supporting Information for more details.) Positive error indicates overestimation and vice versa. Max(+) and Max(−) are the maximal positive and negative errors, respectively.

**Figure 1.** (a) Errors (Calc. – Ref.) in the calculated cohesive energies per atom (\( E_0 \) in kcal/mol) of 14 solids (CE14) with strong covalent bonds (‘○’ in blue) or ionic bonds (‘×’ in orange). Positive error indicates overestimation and vice versa. Errors falling in the area with green background reach the chemical accuracy of [−1.0, 1.0 kcal/mol]. Yellow background marks the errors within [−3.0, −1.0 kcal/mol] and [1.0, 3.0 kcal/mol]. The numbers on the red background count the errors larger (or smaller) than 3.0 kcal/mol (−3.0 kcal/mol), (b) MAEs in the calculated \( E_0 \) (in kcal/mol) for the CE14 set. (c) MAEs in 142 calculated bond dissociation energies of small molecules (Bond142).
Figure 1c shows the performance of various DFAs on 142 bonding dissociation energies (BDEs) of small molecules (Bond142).\textsuperscript{45} BDE is a central concept in chemistry. Accurate description of BDE is of vital importance for the understanding of the relevant chemical reactions. By using the NAO-VCC-4Z basis set, XYG3 leads to MAE = 2.1 kcal/mol. This accuracy has surpassed those of all (hybrid) semilocal DFAs using the same basis set, while the best performance is given by XYGJ-OS, yielding an MAE of only 0.86 kcal/mol. The excellent performances on both cohesive properties for solids and BDEs for small molecules clearly manifest the versatility of XYG3 and, in particular, XYGJ-OS to resolve the aforementioned failure of their ancestors BLYP and B3LYP. Hence, for the top-rung functionals, it is possible to give an equally good and balanced description for both finite and extended systems. Note that SCAN leads to MAE = 6.83 kcal/mol for BDEs, much worse than that for PBE (MAE = 4.63 kcal/mol). Thereby, as the mirror of the B3LYP failure, the good performance for solids does not necessarily ensure a comparable accuracy for molecules for the lower rung functionals.

Next, we turn to the relative stability of TiO\textsubscript{2} as a challenging case in materials science. The rutile phase is arguably the most stable phase at \( T = 0 \) K when the zero-point energy contribution is excluded.\textsuperscript{46,47} However, it remains challenging to determine the relative stability in theory. Most of the popular DFAs in computational materials science, such as PBE and SCAN, predict the anatase phase to be more stable than rutile. DFT+U corrects the ordering, which, however, often significantly deteriorates the description of the structure parameters. As shown by Figure 2, our results confirm the wrong phase stability calculated by PBE and SCAN. Using the tight NAO basis set in FHI-aims, the calculated relative energies per formula unit between rutile and anatase (\( \Delta E_{\text{rel}} \)) of PBE and SCAN are 9.26 and 2.81 kJ/mol, respectively, which differ from the values using the plane-wave basis sets by only 0.02\textsuperscript{46} and 0.35 kJ/mol,\textsuperscript{47} respectively. Again, we are happy to see from Figure 2 and Table S5 that, with the same

| Energies (kJ/mol) | Rutile | Anatase | Rutile/Anatase | Anatase/Rutile | SCAN/Rutile | XYGJ-OS/Rutile | XYG3/Rutile |
|------------------|--------|---------|----------------|---------------|-------------|----------------|------------|
| 28               | 30.0   | -10.0   | 20             | 10            | 5           | 15             | 5          |
| 30               | 28.0   | -12.0   | 15             | 7.5           | 10          | 17.5           | 10         |
| 32               | 30.0   | -14.0   | 20             | 10            | 5           | 15             | 5          |
| 34               | 32.0   | -16.0   | 25             | 12.5          | 10          | 22.5           | 12.5       |
| 36               | 34.0   | -18.0   | 30             | 15            | 10          | 25             | 15         |
| 38               | 36.0   | -20.0   | 35             | 17.5          | 15          | 32.5           | 17.5       |

In summary, the present study sets out to provide the first comprehensive assessment of doubly hybrid approximations for condensed-matter systems with nonzero band gaps. Demonstrated by the excellent performance of XYG3 and XYGJ-OS, the unprecedented accuracy of the PT2-based DHAs for molecules is transferable to the description of semiconductors and insulators. Note that the current implementation of XYG3 and XYGJ-OS is based on the canonical PT2 formula (eq 2). In consequence, the computations can be much more intensive than those with the lower rung functionals. For example, in the anatase-type TiO\textsubscript{2} calculations with 200 orbitals per unit cell and 4 \( \times \) 4 \( \times \) 4 k-grids, we employed 160 cores of Intel Gold 6126 CPUs. It took 100–110 s for each B3LYP SCF iteration, while the post-SCF PT2 evaluation spent about 3.5 h. In this consideration, XYGJ-OS is recommended, not only because of its overall best performance on diversely bonding systems due to its different treatment of the same- and the opposite-spin contributions\textsuperscript{83–85} but also because of its potential applicability to large systems due to the use of only osPT2 in the formula. Low-scaling implementation of XYGJ-OS has been realized for molecules.\textsuperscript{81} The generalization to the extended systems is under way, although it is nontrivial and needs extra coding efforts.\textsuperscript{66,67}
For metallic systems, the PT2 energies diverge, because the orbitals become degenerate, which appear in the denominator of the sum-over-state formula of the PT2 model (see eq 2). Regarding this fundamental limitation of the PT2-based DHAs, the development of a more sophisticated correlation model that goes beyond the PT2 model in the context of a doubly hybrid strategy is crucial but has been demonstrated to be unsuccessful by directly borrowing the advanced correlation models from wave function theory. In a recent review, we have proposed a development strategy for the next-generation DHAs. As a renormalization of the standard PT2, the osRPT2 correlation model recently developed in our group is a promising candidate for DHAs. The osRPT2 model, with a similar computational cost as that of PT2, can properly capture the nondynamic correlation effect in the molecular dissociation limit with closing energy gaps and thus holds a strong promise to the extended systems with metallic character. In the future work, we will develop and implement the osRPT2-based DHAs for extended solids, which we expect to deliver a universally higher accuracy and a broader applicability for both molecules and extended solids.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00011.

Computational details; k-grid settings used for different methods; lattice constants, bulk moduli, and cohesive energies of cubic crystals; equilibrium volumes, bulk moduli, and energy differences of Rutile and Anatase TiO2; bond dissociation energies; optimized heights of carbon atoms to the NaCl(100) surface; CO vibrational frequencies; absorption energies; optimized coordinates (PDF)

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Figure 3. (A) Adsorption energies (kJ/mol) against the height of the carbon atom to the NaCl(100) surface (dZ, in Å) for varying DFAs. Experimental adsorption energy and dZ (18 kJ/mol, 2.592 Å) were located to the panel center (marked with “+”). Calculations were performed for 1 × 1 surface unit cells. Undesired lateral CO–CO interactions have been removed in the calculated adsorption energies. The PBE results are the PBE results using plane-wave basis sets, which, together with PBE-D3 and PBE-MBD results, were collected from ref 48. (B) 13C18O frequency shifts of adsorbed CO monolayer with C-down configuration (blue) and O-down configuration (red). Experimental and XYGJ-OS frequency shifts are rendered on a light purple background. Experimental reference frequency comes from the crystal CO on multilayers, where lateral CO–CO interactions exhibit noticeable influence on the CO frequency. To include such kind of influence, computational reference frequencies were obtained from the CO molecule on periodic boundary conditions with the same lattice constants of adsorbed CO monolayer. (See the SI for more computational details).
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