Performance of Tao-Mo semilocal density functional in projector-augmented-wave method

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We assess the performance of Tao-Mo semilocal exchange correlation (TM) functional [J. Tao and Y. Mo, Phys. Rev. Lett. 117, 073001 (2016)] using projector-augmented-wave method with the plane wave basis set in Vienna ab initio simulation package (VASP). The meta-GGA level semilocal functional TM is an all purpose exchange-correlation functional which performs accurately for the wide range of molecular and solid state properties. The exchange functional part of TM is designed from the density matrix expansion (DME) technique together with the slowly varying fourth order gradient expansion. The correlation functional of the corresponding exchange is based on Tao-Perdew-Staroverov-Scuseria (TPSS) functional. We assess the performance of TM for solid state lattice constants, bulk moduli, band gaps, cohesive energies and magnetic moments of solids. It has been established that in plane wave basis the TM functional performs accurately in predicting all the solid state properties in semilocal level.

I. INTRODUCTION

The calculations of the electronic structure of molecules and solids are done mostly within the framework of Kohn-Sham (KS) density functional theory. The accuracy of density functional theory (DFT) depends upon the accuracy of the exchange-correlation (XC) functionals which contain all the many electron effects. In principle the exact form of XC functional is unknown. Therefore, one need to approximate it from different physical perspective. The accuracy of the XC functionals are classified through the Jacob’s ladder, where each rung of the ladder adds an extra ingredients. The first three rungs of the Jacob’s ladder are classified as local density approximation (LDA), the generalized gradient approximations (GGAs) and meta-generalized gradient approximations (meta-GGAs). The LDA, GGAs and meta-GGAs utilize density, gradient of density and Kohn-Sham kinetic energy density as its main ingredient, therefore all are semilocal in nature. The XC functionals based on the semilocal quantities are very attractive because of low computational cost and high accuracy. The semilocal functionals are very accurate in describing several thermochemical properties, bond length, equilibrium lattice constants, bulk modulus, cohesive energy and solid state surface properties. Several accurate semilocal density functionals have been developed for localized electron systems, whereas, slowly varying density correction is accurate for solid state systems. The correlation part TM functional has been derived from one electron self-interaction free Tao-Perdew-Staroverov-Scuseria (TPSS) functional. The TM functional is very accurate in describing both the thermochemical and solid state properties in semilocal level. TM functional is extensively tested in all electron code but has not been benchmarked in plane wave basis set. Due to its higher degree of accuracy for solid state properties it is always interesting to test the TM functional using plane wave basis set. Present paper assess the performance of TM functional using projector-augmented-wave (PAW) method with plane wave basis set in Vienna ab initio simulation package (VASP). For the benchmark calculation of TM functional we choose solid state lattice constants, bulk moduli, semiconductor band gaps, cohesive energies and magnetic moments of ferromagnetic materials. We compare the performance of TM functional against other popular semilocal functionals like local spin density approximation (LSDA), Perdew-Burke-Ernzerhof (PBE) functional and its revised form for solid state system (PBEsol), meta-GGA level TPSS, revTPSS and recently proposed strongly constrained and appropriately normed (SCAN) functional. It is shown that the performance of TM functional is very accurate in describing lattice constants, bulk moduli, cohesive energies and magnetic properties except band gap. In describing the band gap, SCAN meta-GGA performs in more satisfactory way. To put our comparison in a broader perspective we also in-

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clude Heyd-Scuseria-Ernzerhof (HSE) hybrid functional for studying magnetic properties.

Present paper is organized as follows. In the following we will discuss the details of the implementation of TM based semilocal functionals in VASP. Next we do the benchmark performance of the TM based functionals with other popular GGA and meta-GGA level semilocal functionals for lattice constants, bulk moduli, band gaps, cohesive energies and magnetic moments of ferromagnetic materials.

II. THEORETICAL BACKGROUND

The PAW method was first proposed by Blöchl and later it is adopted by Kresse and Joubert. The PAW potential reserves both the computational efficiency and accuracy of ultrasoft pseudo-potential (UPP) and all electron (full-)potential. The accuracy of PAW is same as the full potential linearized augmented plane wave (plus local potential) implemented in other codes. In PAW method, any semilocal operator (i.e., kinetic energy operator or density operator) is presented by plane wave (PW) expansion for valance region. The core region is presented by projecting it on the radial grid at the atom center. Therefore, the core region is well presented in this method and its accuracy is same as the all electron (AE) calculation. After doing all these the additional part is subtracted from the additive augmentation of core and valence. The general implementation of all the meta-GGA functional in VASP is based on the method proposed by Sun et al. In this method the KS kinetic energy density also divided in core-valence region. We implemented the TM semilocal functional by locally modifying the meta-GGA routine implemented in VASP code. The self-consistence exchange-correlation potential computed for meta-GGA in VASP is based on generalized KS (gKS) framework. In gKS, the exchange-correlation potential for meta-GGA is defined as,

\[ v_{xc} \Psi_i = \left[ \frac{\partial (\rho_{xc})}{\partial \rho} - \nabla \left( \frac{\partial (\rho_{xc})}{\partial \nabla \rho} \right) \right] \Psi_i - \frac{1}{2} \nabla \left( \frac{\partial (\rho_{xc})}{\partial \tau} \right) \nabla \Psi_i - \frac{1}{2} \frac{\partial (\rho_{xc})}{\partial \tau} \rho^2 \Psi_i \right]. \tag{1} \]

Therefore, in addition to the partial derivative of XC functional with respect to density and gradient of density, one need to perform the partial derivative with respect to KS kinetic energy density. Thus, for meta-GGA one need to calculate the partial derivative of XC functional with respect to density, gradient of density and KS kinetic energy density. In terms of enhancement factor the general formulation of the exchange functional in meta-GGA level is described as,

\[ E_x = - \int d\mathbf{r} \rho(\mathbf{r}) v_{xc}^{\text{unif}} f_x^{\text{meta-GGA}} [\rho, \nabla \rho, \tau]. \tag{2} \]

In the present case of TM functional the enhancement factor becomes,

\[ F_x^{\text{meta-GGA}} [\rho, \nabla \rho, \tau] = F_x^{TM}, \tag{3} \]

which have the following semilocal form,

\[ F_x^{TM} = w F_x^{DME} + (1 - w) F_x^{sc}, \tag{4} \]

where \( F_x^{DME} = 1/f^2 + 7R/(9f^4) \) is the density matrix expansion based enhancement factor \(^{24}\) (with \( R = 1 + 595(2\lambda - 1)^2p/54 - (\tau - 3\lambda^2 - \lambda + 1/2)/\tau^{\text{unif}} - (\nabla \rho)^2/(72p) \)) and \( F_x^{sc} = 1 + 10\left( (10/3) + (50/27) p + 146/2025 \right) \) is the slowly varying forth order gradient expansion to the TM semilocal functional. In TM functional \( w \) is used as the weight factor between DME expansion and slowly varying density correction, which is the functional of meta-GGA ingredient \( z = \tau_W/\tau \) (where \( \tau_W \) is the von Weizsäcker kinetic energy density). For the details of the mathematical expression and parameter related to the TM functional readers are suggested to go through the refs. \(^{24,35}\).

It is noteworthy to mention that the discontinuity effect and convergence issue of the terms related to the \( z \) in TM functional is removed as it was suggested by Sun et al. \(^{34}\). In meta-GGA subroutine of the VASP code we calculate analytically the terms related to the partial derivatives i.e., \( \partial (\rho_{xc})/\partial \rho \), \( \partial (\rho_{xc})/\partial \nabla \rho \) and \( \partial (\rho_{xc})/\partial \tau \). This completes the implementation of exchange part of TM functional. The correlation of TM functional is based on the Tao-Perdew-Staroverov-Scuseria (TPSS) correlation. TM modifies the correlation part to be used for slowly varying density correction. This leads to the two functional – TM-TPSS (which uses TM exchange plus TPSS correlation) and TM (which uses TM exchange plus modified TPSS correlation). Here we assess the performance of both TM-TPSS and TM for all our solid state calculations. The spin density scaling relation is used in the VASP implementation of TM functional. To test the accuracy of all the functionals under study we calculate mean (relative) error (ME/MRE), mean absolute (relative) error (MAE/MARE) and the standard deviation of the (relative) error (STDE/STDRE) which are defined as,

\[ ME = \frac{1}{N} \sum_{i=1}^{N} (Y_i - y_i), \text{ MAE} = \frac{1}{N} \sum_{i=1}^{N} |Y_i - y_i|, \text{ STDE} = \left[ \sum_{i=1}^{N} (Y_i - y_i)^2 / \sum_{i=1}^{N} |Y_i - y_i| \right]^{1/2}, \text{ MRE} = \sum_{i=1}^{N} (Y_i - y_i)/y_i, \text{ MARE} = \sum_{i=1}^{N} |Y_i - y_i|/|y_i| \]

and

\[ \text{STDRE} = \left[ \sum_{i=1}^{N} (Y_i/y_i)^2 / \sum_{i=1}^{N} (Y_i/y_i) \right] \]

III. RESULTS AND DISCUSSIONS

A. Lattice constants

We first perform the benchmark calculations for equilibrium lattice constant of TM-TPSS and TM against
| Solids | LSDA | PBE | PBEsol | TPSS | revTPSS | SCAN | TM-TPSS | TM | Expt. |
|--------|------|-----|--------|------|---------|------|---------|----|-------|
| C (A2) | 3.536 | 3.573 | 3.557 | 3.572 | 3.563 | 3.555 | 3.560 | 3.554 | 3.567 |
| Si (A2) | 5.400 | 5.467 | 5.433 | 5.450 | 5.426 | 5.425 | 5.423 | 5.411 | 5.430 |
| Ge (A2) | 5.648 | 5.785 | 5.704 | 5.754 | 5.710 | 5.687 | 5.691 | 5.672 | 5.652 |
| SiC (B3) | 4.332 | 4.379 | 4.359 | 4.365 | 4.357 | 4.352 | 4.351 | 4.354 | 4.358 |
| BN (B3) | 3.583 | 3.625 | 3.607 | 3.624 | 3.618 | 3.605 | 3.615 | 3.609 | 3.607 |
| BP (B3) | 4.490 | 4.546 | 4.521 | 4.545 | 4.531 | 4.521 | 4.522 | 4.510 | 4.538 |
| BAs (B3) | 4.742 | 4.817 | 4.778 | 4.810 | 4.787 | 4.779 | 4.775 | 4.763 | 4.777 |
| BSb (B3) | 5.198 | 5.280 | 5.234 | 5.270 | 5.242 | 5.257 | 5.257 | 5.212 | n/a  |
| AlP (B3) | 5.433 | 5.504 | 5.470 | 5.489 | 5.480 | 5.478 | 5.463 | 5.450 | 5.460 |
| AlAs (B3) | 5.637 | 5.732 | 5.681 | 5.707 | 5.685 | 5.670 | 5.656 | 5.656 | 5.658 |
| AlSb (B3) | 6.120 | 6.232 | 6.168 | 6.208 | 6.185 | 6.150 | 6.143 | 6.143 | 6.136 |
| β−GaN (B3) | 4.503 | 4.588 | 4.547 | 4.581 | 4.569 | 4.542 | 4.559 | 4.549 | 4.531 |
| GaP (B3) | 5.425 | 5.533 | 5.474 | 5.523 | 5.499 | 5.457 | 5.482 | 5.464 | 5.448 |
| GaAs (B3) | 5.627 | 5.763 | 5.684 | 5.737 | 5.699 | 5.664 | 5.681 | 5.664 | 5.648 |
| GaSb (B3) | 6.067 | 6.226 | 6.130 | 6.190 | 6.144 | 6.117 | 6.126 | 6.102 | 6.096 |
| InP (B3) | 5.878 | 6.001 | 5.932 | 5.989 | 5.965 | 5.938 | 5.945 | 5.923 | 5.866 |
| InAs (B3) | 6.472 | 6.651 | 6.543 | 6.611 | 6.565 | 6.545 | 6.546 | 6.521 | 6.479 |
| ZnS (B3) | 5.403 | 5.440 | 5.355 | 5.401 | 5.358 | 5.370 | 5.388 | 5.364 | 5.409 |
| ZnSe (B3) | 5.570 | 5.734 | 5.634 | 5.681 | 5.625 | 5.652 | 5.658 | 5.633 | 5.668 |
| ZnTe (B3) | 5.905 | 6.178 | 6.064 | 6.115 | 6.048 | 6.077 | 6.082 | 6.056 | 6.089 |

| ME(A) | -0.055 | 0.076 | 0.002 | 0.061 | 0.039 | 0.020 | 0.019 | 0.000 | -   |
| MAE(A) | 0.072 | **0.078** | 0.041 | 0.065 | 0.053 | 0.041 | 0.045 | **0.038** | -   |
| STDRE(Å) | 0.082 | 0.076 | 0.079 | 0.079 | 0.081 | 0.074 | 0.077 | 0.075 | -   |
| MRE(%) | -1.045 | 1.361 | 0.027 | 1.059 | 0.657 | 0.310 | 0.274 | -0.065 | -   |
| MARE(%) | 1.375 | 1.406 | 0.738 | 1.157 | 0.961 | 0.753 | 0.854 | 0.753 | -   |
| STDRE(%) | 1.573 | 1.407 | 1.469 | 1.483 | 1.537 | 1.423 | 1.524 | 1.478 | -   |
TABLE II. Bulk moduli, $B_0$ (GPa) of 20 solids are shown for different functionals. The LSDA, PBE, PBEsol, TPSS, revTPSS results for Ag, Al, C, GaAs, Ge, Li, LiCl, LiF, NaF, Pd, Rh are collected from ref.\(^{41}\). For rest of the solids and functionals we perform self consistence calculations followed by the fitting of $E$ vs $V$ curve using Murnaghan equation of states\(^{57}\) sing VASPKIT\(^{54}\) post-processing code. The structures consider here are the same as it is given in Table-I. All the experimental values are collected from ref.\(^{37,49}\).

| Solids | LSDA | PBE | PBEsol | TPSS | revTPSS | SCAN | TM-TPSS | TM | Expt. |
|--------|------|-----|--------|------|---------|------|---------|----|-------|
| Ag     | 138.5| 90.9| 118.9  | 110.0| 120.5   | 111.5| 111.3   | 115.1| 109.0 |
| Al     | 83.7 | 77.3| 81.9   | 85.6 | 85.7    | 85.7 | 85.7    | 85.7 | 79.4  |
| AlAs   | 74.5 | 67.4| 71.6   | 70.3 | 72.2    | 72.2 | 75.5    | 75.7 | 76.4  |
| AlP    | 89.0 | 82.0| 85.9   | 84.9 | 86.1    | 90.7 | 89.4    | 90.7 | 86.0  |
| BP     | 168.0| 156.2|162.5  |155.7 |158.3   |166.5 |164.4   |165.8 |173.0 |
| C      | 465.8| 433.2|450.2  |430.3 |439.5   |461.4 |447.9   |455.2 |443.0 |
| Cu     | 185.4| 139.4|165.4  |158.6 |172.4   |161.7 |170.1   |173.2 |142.0 |
| GaAs   | 75.1 | 60.5| 69.9   |64.8 |66.8    |73.3 |71.7    |74.1 |75.6  |
| GaN    | 209.8| 183.5|197.1  |188.9|191.2   |210.2 |197.3   |200.5|190.0 |
| GaP    | 90.7 | 78.0| 85.3   |79.6 |82.5    |90.7 |87.5    |90.1 |88.0  |
| Ge     | 70.5 | 59.4| 65.8   |60.2 |65.0    |71.4 |58.4    |58.4 |75.8  |
| K      | 4.6  | 3.7 | 3.8    | 3.4 | 3.4    | 3.7 | 4.0    | 4.0 | 3.7  |
| Li     | 15.1 | 13.8| 13.7   |13.3 |13.4    |13.2 |14.6    |14.6 |13.0  |
| LiCl   | 41.5 | 31.7| 35.4   |33.4 |34.0    |35.8 |36.2    |36.7 |35.4  |
| LiF    | 86.7 | 66.9| 72.2   |66.2 |68.9    |81.2 |79.6    |80.2 |69.8  |
| NaF    | 61.5 | 45.2| 48.8   |42.9 |44.0    |55.9 |59.5    |59.9 |51.4  |
| Pd     | 226.3| 169.4|205.2  |195.4|209.7   |194.8|191.3   |199.5|195.0 |
| Rh     | 315.6| 256.4|295.0  |281.9|296.1   |290.9|283.4   |291.2|269.0 |
| Si     | 95.4 | 87.9| 92.7   |91.3 |93.0    |98.7 |96.3    |98.4 |99.2  |
| SiC    | 221.5| 205.1|213.7  |217.7|221.3   |225.7|217.8   |221.1|225.0 |

| ME (GPa) | 10.695 | -9.870 | 1.335 | -3.545 | 0.935 | 0.485 | 2.745 | 4.650 |
| MAE (GPa) | 13.255 | 9.950 | 7.615 | 7.285 | 8.235 | 7.785 | 7.195 | 8.290 |
| STDE (GPa) | 16.432 | 7.385 | 10.384 | 8.783 | 11.897 | 11.644 | 9.795 | 10.653 |
| MRE(%) | 9.752 | -8.521 | -0.331 | -4.617 | -1.384 | -1.797 | 2.748 | 4.435 |
| MARE(%) | 12.260 | 9.136 | 6.380 | 7.389 | 7.518 | 7.105 | 7.684 | 8.282 |
| STDRE(%) | 12.115 | 7.225 | 7.746 | 8.287 | 9.425 | 9.048 | 9.945 | 9.986 |
TABLE III. Band gaps using different functionals at their equilibrium lattice constant are shown here. The mean absolute error is mentioned in the last row. All the experimental references are collected from ref. The structures consider here are the same as it is given in Table-1.

| Solids | LSDA | PBE | PBEsol | TPSS | revTPSS | SCAN | TM-TPSS | TM | Expt. |
|--------|------|-----|--------|------|---------|------|---------|----|-------|
| C      | 4.17 | 4.13| 4.03   | 4.17 | 4.04    | 4.15 | 4.09    | 5.48 |
| Si     | 0.46 | 0.64| 0.48   | 0.67 | 0.57    | 0.85 | 0.85    | 1.17 |
| Ge     | 1.38 | 1.47| 1.34   | 1.42 | 1.30    | 1.82 | 1.47    | 2.42 |
| SiC    | 4.48 | 4.52| 4.36   | 4.52 | 4.38    | 5.04 | 4.59    | 6.22 |
| BP     | 1.17 | 1.28| 1.14   | 1.29 | 1.15    | 1.55 | 1.28    | 2.4  |
| BAs    | 1.14 | 1.22| 1.10   | 1.21 | 1.10    | 1.44 | 1.19    | 1.46 |
| BSB    | 0.70 | 0.75| 0.65   | 0.65 | 0.54    | 0.88 | 0.61    | 0.57 |
| ALP    | 1.47 | 1.68| 1.50   | 1.73 | 1.64    | 1.95 | 1.75    | 2.51 |
| ALAs   | 1.36 | 1.54| 1.38   | 1.59 | 1.51    | 1.79 | 1.59    | 2.23 |
| ALSb   | 1.11 | 1.24| 1.13   | 1.32 | 1.23    | 1.39 | 1.25    | 1.68 |
| β−GaN | 1.82 | 1.41| 1.54   | 1.31 | 1.28    | 2.05 | 1.47    | 1.48 |
| GaP    | 1.45 | 1.51| 1.52   | 1.72 | 1.60    | 1.89 | 1.46    | 2.35 |
| GaAs   | 0.50 | 0.15| 0.39   | 0.38 | 0.57    | 0.80 | 0.80    | 1.52 |
| GaSb   | 0.11 | 0.00| 0.00   | 0.00 | 0.17    | 0.12 | 0.39    | 0.46 |
| InP    | 0.52 | 0.37| 0.48   | 0.54 | 0.59    | 0.87 | 0.71    | 1.42 |
| InAs   | 0.00 | 0.00| 0.00   | 0.00 | 0.00    | 0.00 | 0.00    | 0.41 |
| InSb   | 0.00 | 0.00| 0.00   | 0.00 | 0.00    | 0.00 | 0.05    | 0.23 |
| ZnS    | 1.89 | 2.02| 2.09   | 2.29 | 2.33    | 2.71 | 2.32    | 3.66 |
| ZnSe   | 1.28 | 1.15| 1.24   | 1.45 | 1.51    | 1.80 | 1.60    | 2.70 |
| ZnTe   | 1.31 | 1.07| 1.24   | 1.42 | 1.58    | 1.62 | 1.63    | 2.38 |
| CdS    | 0.97 | 0.90| 1.04   | 1.23 | 1.18    | 1.47 | 1.23    | 2.55 |
| CdSe   | 0.43 | 0.49| 0.48   | 0.71 | 0.70    | 0.94 | 0.81    | 1.90 |
| CdTe   | 0.66 | 0.59| 0.93   | 0.82 | 0.82    | 0.97 | 1.01    | 1.92 |
| MgO    | 5.13 | 4.53| 4.68   | 4.77 | 4.72    | 5.77 | 4.96    | 7.22 |
| MgS    | 3.14 | 3.34| 3.35   | 3.63 | 3.64    | 4.19 | 3.80    | 5.4  |
| MgSe   | 1.80 | 1.84| 1.85   | 2.14 | 2.16    | 2.51 | 2.23    | 2.47 |
| MgTe   | 2.41 | 2.32| 2.35   | 2.66 | 2.72    | 3.03 | 2.89    | 3.6  |
| CaS    | 2.00 | 2.40| 2.18   | 2.47 | 2.46    | 2.84 | 2.54    | 2.43 |
| CaSe   | 1.73 | 2.10| 1.90   | 2.18 | 2.18    | 2.55 | 2.26    | 2.15 |
| CaTe   | 1.33 | 1.57| 1.37   | 1.64 | 1.63    | 2.14 | 1.71    | 1.80 |
| SrS    | 2.14 | 2.52| 2.30   | 2.59 | 2.54    | 2.92 | 2.57    | 2.47 |
| SrSe   | 1.91 | 2.25| 2.05   | 2.32 | 2.29    | 2.67 | 2.33    | 2.23 |
| SrTe   | 1.43 | 2.09| 2.12   | 2.31 | 2.38    | 2.74 | 2.51    | 2.44 |
| BaS    | 1.14 | 2.17| 1.98   | 2.26 | 2.19    | 2.52 | 2.16    | 2.08 |
| BaSe   | 1.67 | 1.97| 1.79   | 2.05 | 2.01    | 2.33 | 2.01    | 3.58 |
| BaTe   | 1.30 | 1.61| 1.41   | 1.67 | 1.63    | 1.94 | 1.66    | 3.08 |

MAE (eV) 1.158 1.154 1.173 1.033 1.055 0.736 0.949 0.996 –

the LSDA, PBE, PBEsol, TPSS, revTPSS and SCAN functional. For the benchmark test set we consider 47 crystalline structures which include (i) semiconductor diamond structures C, Si and Ge, (ii) zinc blende structures Sic, BN, BP, BAs, BSB, AlP, AlAs, AlSb, β−GaN, GaP, GaAs, GaSb, InP, InAs, InSb, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, MgS, MgTe, (iii) ionic structures MgO, MgSe, CaS, CaSe, CaTe, SrS, SrSe, SrTe, BaS, BaSe, BaTe, LiCl, LiF, NaCl, LiF, NaCl, NaF, and (iv) metal structures Li, K, Al, Cu, Pd, Ag. All the calculations are performed using 11x11x11 Monkhorst-Pack k meshes with tetrahedron method. The self-consistence calculation of meta-GGAs (TPSS, revTPSS, SCAN, TM-TPSS and TM) are performed starting from the converged wavefunction obtained in PBE calculations.

In Table-I, we list the benchmark calculations of TM-TPSS and TM with other semilocal functionals. There we also calculate the mean (relative) error (ME/MRE), mean absolute (relative) error (MAE/MARE) and the standard deviation of the (relative) error (STDE/STDRE). We obtain the maximum MAE using PBE and local density approximate (LSDA) functional. The MAE of PBE and LSDA are obtained to be 0.078 Å and 0.072 Å respectively. LSDA has the tendency to underestimate the lattice constant while PBE overestimates the lattice constant. The reduction in MAE is observed using meta-GGA TPSS and revTPSS functionals. The TPSS functional performs slightly better than PBE while the revised version of TPSS (revTPSS) reduces the MAE significantly. Recently proposed SCAN meta-GGA by Sun et. al. gives the same MAE as obtain from the PBEsol GGA functional. Interestingly, the lowest MAE is obtained from TM functional (with MAE 0.038 Å ). The unmodified
TABLE IV. Cohesive energies of 9 solids in eV/atom using different functionals at static-lattice constant are shown. The experimental reference values are taken from ref. The structures consider here are the same as it is given in Table-I.

| Solids | LSDA | PBE | PBEsol | TPSS | revTPSS | SCAN | TM-TPSS | TM | Expt. |
|--------|------|-----|--------|------|---------|------|--------|----|-------|
| Li     | 1.786| 1.583| 1.653  | 1.738| 1.625   | 1.545| 1.664  | 1.662| 1.658 |
| C      | 8.867| 7.714| 8.215  | 7.420| 7.504   | 7.899| 7.624  | 7.845| 7.545 |
| SiC    | 7.305| 6.356| 6.779  | 6.298| 6.380   | 6.689| 6.478  | 6.478| 6.478 |
| Si     | 5.194| 4.464| 4.810  | 4.444| 4.531   | 4.811| 4.628  | 4.788| 4.685 |
| LiF    | 3.739| 3.332| 3.467  | 6.442| 3.430   | 3.632| 3.551  | 3.551| 3.586 |
| NaF    | 3.438| 3.085| 3.197  | 6.389| 3.199   | 3.438| 3.349  | 3.326| 3.337 |
| MgO    | 5.982| 5.152| 5.441  | 5.271| 5.295   | 5.654| 5.439  | 5.496| 5.203 |

ME(eV/atom) -0.163 0.068 -0.080 -0.139 0.147 -0.007 0.053 |
MAE(eV/atom) 0.201 0.153 0.152 0.139 0.171 0.041 0.053 |
STDE(eV/atom) 0.153 0.258 0.162 0.077 0.137 0.067 0.109 |
MRE(%) 4.696 2.670 3.496 3.349 3.326 3.337 |
MARE(%) 8.593 4.696 2.670 3.496 3.349 3.326 3.337 |
STDRE(%) 4.229 2.976 3.935 3.960 1.594 1.331 1.478 |

TABLE V. Comparison between the calculated magnetic moments ($M_s$/atom) and the experimental total magnetic moments of Fe, Co and Ni using different functionals. Values are in $\mu_B$. The Fe (bcc) and Ni (fcc) values of LSDA, PBE, PBEsol, TPSS and revTPSS are taken from ref. 41.

| Solids | Magnetic Ordering | LSDA | PBE | PBEsol | TPSS | revTPSS | SCAN | TM-TPSS | TM | HSE06 | Expt. |
|--------|------------------|------|-----|--------|------|---------|------|--------|----|-------|-------|
| Fe (bcc) | FM | $a_0$ | 2.747 | 2.829 | 2.803 | 2.794 | 2.844 | 2.811 | 2.803 | 2.903 | 2.853 (2.861)$^a$ |
|          | $M_s$ | 1.97 | 2.18 | 2.11 | 2.19 | 2.20 | 2.64 | 2.64 | 2.25 | 2.22 | 2.896 |
| Co (fcc) | FM | $a_0$ | 3.420 | 3.514 | 3.460 | 3.479 | 3.468 | 3.479 | 3.481 | 3.469 | 3.547–3.558$^b$ |
|          | $M_s$ | 1.49 | 1.61 | 1.57 | 1.61 | 1.62 | 1.77 | 1.77 | 1.64 | 1.60 | 1.852 |
| Ni (fcc) | FM | $a_0$ | 3.428 | 3.520 | 3.463 | 3.481 | 3.465 | 3.456 | 3.468 | 3.469 | 3.504 (3.516)$^c$ |
|          | $M_s$ | 0.56 | 0.62 | 0.60 | 0.63 | 0.65 | 0.66 | 0.66 | 0.61 | 0.60 | 0.839 |

$^a$ ref. 41  
$^b$ ref. 62  
$^c$ ref. 63  
TPSS correction coupled with TM exchange produce the equivalent MAE as obtain from PBEsol and SCAN. It is noteworthy to mention that the experimental lattice constants we consider here are not corrected for zero point anharmonic expansion (ZPAE) and all the experimental lattice constant are taken from ref. 37, 51. The results we obtain here using the TM-TPSS and TM can be compared to the all electron calculation performed using Gaussian09, 58 which is given in ref. 37. In ref. 37, the lowest mean absolute error is also reported using TM.

B. Bulk moduli

The bulk modulus is defined as the change in the volume of the crystalline structures upon acting the pressure. In terms of total energy of the cell $E$, the bulk modulus is expressed as $K = V \frac{\partial^2 E}{\partial V^2}$. In density functional theory the bulk modulus is calculated at the equilibrium lattice constant $a_0$ by scanning over the range of lattice constant (or volume). Several equation of states (EOS) are available to fit the energy versus volume curve to obtain the bulk modulus. In our present case we used the post-processing code VASPKIT to fit and obtain the bulk modulus of all the crystalline solids we compared here. The $E$ vs $V$ output from VASP is used as an input of VASPKIT. The VASPKIT is very well established post-processing code which is used to obtain several post-processing calculations. In VASPKIT, Murnaghan equation of states is used for the fitting. The test set we use here and the performance of all the corresponding functionals are listed in Table-II. For few selected solids we collect the values of LSDA, PBE, PBEsol, TPSS, revTPSS from ref. 41. For all other functionals and solids the calculation is performed using the same k points meshes as mentioned in subsection-A. From the results reported in Table-II it is indicative that the performance of TM-TPSS is best compared to all other functionals. The MAE of TM-TPSS even better than SCAN functionals with MAE 7.195 GPa compared to MAE 7.785 GPa obtain from SCAN. The performance of SCAN, PBEsol and TPSS almost equivalent. It is also indicative that TM-TPSS performs better than TM functional though the performance of TM is better than TM-TPSS in predicting lattice constant. The maximum MAE is obtained from LSDA functional. The
performance of PBE is better than LSDA. The results we obtain using the TM functional are also very close to that obtained using G09 all electron calculation reported by Mo et al.\textsuperscript{37}.

C. Band gaps

The band gap calculation using semilocal functional is fraught with difficulties due to the absence of inherent non-locality and many electron self-interaction (MESI).\textsuperscript{47} The hybrid functional proposed using semilocal exchange hole are very popular in predicting the band gap for semiconductor materials accurately.\textsuperscript{47} It has been observed that the meta-GGA functional implemented in generalized KS formalism give more realistic band gap than GGA functionals.\textsuperscript{59} Therefore, the improvement in band gap is observed using meta-GGA type semilocal functionals compared to LSDA and GGA functionals. Here, we assess the performance of TM-TPSS and TM for 37 semiconductors at their equilibrium lattice constant (reported in Table-I) of each functionals.

From Table-III, it is evident that all the density functionals underestimate the band gap of all semiconductor which is obvious due to the absence of non-locality and MESI. Interestingly, using SCAN meta-GGA we obtain more realistic band gap within all semilocal functionals. TPSS, revTPSS, TM-TPSS and TM perform equivalently in predicting band gaps. It is indicative from the obtained results of the SCAN, TM-TPSS and TM that the SCAN functional outperformed the TM based functionals almost in every cases. Interestingly, for Ge, InAs and InSb which are the difficult cases within semilocal formalism, SCAN, TM-TPSS and TM perform extremely well and predict non-zero band gap except only one for InAs. For Ge and InSb TM functional have non-zero band gap, whereas, for Ge both SCAN and TM based functionals predict non-zero values. Also, in all these cases the TM functional performs better than SCAN functional. This is actually a most attractive feature of TM based functional than other semilocal functionals.

D. Cohesive energies

Cohesive energy is equivalent to the molecular atomization in the case of crystalline solids. It is defined as the energy difference of the solid from its neutral from as an atom. Finally the cohesive energy (in eV) per atom is obtained by dividing the energy difference of the atoms in the unit cell. Here, we consider a set of 9 crystalline solids to perform the benchmark calculations of all the functionals. Among all the functionals under consideration TM-TPSS is accurate with MAE of 0.041 eV/atom. In this case TM-TPSS is more accurate than TM functional. From Table-IV, we observed that the performance of TM-TPSS and TM are accurate compared to all other GGA and meta-GGA based functionals with MAE 0.041 eV/atom and 0.053 eV/atom respectively. It is also noteworthy that TM has tendency to overestimate the cohesive energy for all the crystalline solids considered here, whereas, TM-TPSS overestimates the cohesive energies for few cases and underestimate for few cases. Overall, TM-TPSS performs accurately in predicting cohesive energy of all the solids.

E. Magnetic properties

Studying strongly correlated systems within semilocal density functional is quite difficult because of the different levels of interaction of $d$ and $f$ blocks. In Table-V we calculate the magnetic moments and lattice constant of ferromagnetic Fe, Ni and Co. Here the results of all the semilocal functionals are also compared with the range separated hybrid functional HSE06. All magnetic moments are calculated by optimizing the structure with the corresponding semilocal functionals.

The results presented in Table-V show that for all the semilocal functional predicts the lattice constant quite appropriately. In the case of magnetic moment, all the functionals are accurate except LSDA and SCAN functional. For LSDA the underestimation of magnetic moment is observed. While SCAN overestimates the magnetic moment. In this case, both TM-TPSS and TM predict the magnetic moment accurately. In the case of Co, PBE is better than all other semilocal functional in predicting the lattice constant. LSDA underestimate magnetic moment of Co, while SCAN is close to the experimental values. All other semilocal functional perform equivalently in predicting magnetic moment. In case of Ni, both the lattice constant and magnetic moment are obtained accurately within all the semilocal functionals. Now we come to the discussion of range separated hybrid HSE06 in predicting all properties. HSE06 predicts accurately various properties but computationally very expensive. In this case, HSE06 accurately predict lattice constant for all the solids but overestimate the magnetic moments due to the inclusion of too much HF exchange. This drawback has been discussed by Paier et al.\textsuperscript{49}.

IV. CONCLUSIONS

We assess the performance of TM functional in projector-augmented-wave method with plane wave basis set for solid state band gaps, bulk moduli, cohesive energies and magnetic properties. It has been shown that the performance of TM-TPSS and TM are quite accurate within the popular semilocal functionals in predicting all the properties except semiconductor band gaps. In that case SCAN meta-GGA performs better than TM. The TM-TPSS functional is accurate for bulk moduli and cohesive energies, whereas, TM is accurate in predicting lattice constants. For the band gap the performance of TM-TPSS is second best after SCAN. In particular,
TM-TPSS and TM predict non-zero band gap for several semiconductor for which LSDA, PBE, PBEsol, TPSS and revTPSS predict metallic. Lastly we conclude that the TM functional can be used with confidence using plane wave basis in predicting all the solid state properties accurately over the GGA and meta-GGA functionals.
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