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## ABSTRACT

In their recent communication, Tao and Mo [Phys. Rev. Lett. **117**, 073001 (2016)] presented a semi-local density functional derived from the density matrix expansion of the exchange hole localized by a general coordinate transformation. We show that the order-of-limits problem present in the functional, dismissed as harmless in the original publication, causes severe errors in predicted phase transition pressures. We also show that the claim that lattice volume prediction accuracy exceeds that of existing similar functionals was based on comparison to reference data that miss anharmonic zero-point expansion and consequently overestimates accuracy. By highlighting these omissions, we give a more accurate assessment of the Tao–Mo functional and show a possible direction for resolving the order-of-limits problem.

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## I. INTRODUCTION

Many of the advances that have developed the accuracy of Kohn–Sham density functional theory (KS-DFT) have been realized by designing approximations to the exchange–correlation (XC) energy functional from theoretical analysis. This non-empirical approach to functional design is commonly pursued by obeying conditions known for the theoretical exact XC functional, termed exact constraints, and the resulting functionals have enjoyed broad success.<sup>1–6</sup> A complementary approach to functional design, although less well explored in recent years, has been to derive functionals from models of the exact exchange hole.<sup>7,8</sup> A recent advance in this approach was made by Tao and Mo in Ref. 8 in which a new semi-local density functional approximation for the exchange energy was derived from a general coordinate transformation<sup>9</sup> to the density matrix expansion of the exact exchange hole.

The Tao–Mo exchange hole model was used to construct a meta-generalized gradient approximation (meta-GGA) exchange functional from the electron density, electron density gradient, and

the orbital kinetic energy density,  $\tau(\mathbf{r}) = 1/2 \sum_i^{\text{occ}} |\nabla \psi_i(\mathbf{r})|^2$ . The resulting exchange energy density is combined with a modified Tao–Perdew–Staroverov–Scuseria (TPSS) correlation functional<sup>5</sup> with simplified spin polarization and re-parameterized to better fit the exact exchange correlation energy of the one electron Gaussian density. The resulting functional was denoted as “TM.” Combination of the new exchange functional with unmodified TPSS correlation was also suggested and named “TMTPSS” (Tao–Mo–Tao–Perdew–Staroverov–Scuseria).

The resulting non-empirical meta-GGA TM functional properly recovers the uniform electron gas, the slowly varying density limit, and the iso-orbital limits. Its useful accuracy was established in Ref. 8 against equilibrium 0 K lattice constants of 16 solids, alongside atomization energies, Jellium surface energies, dissociation energies of hydrogen bonded complexes, and cohesive energies of solids.

While the TM functional presents an intriguing advance for building functionals from exchange hole models, it contains fundamental issues that limit its accuracy for some classes of problems. Here, we examine the order-of-limits problem and its impact

on phase transition pressure prediction. We also show that the TM functional's accuracy for lattice constants was overestimated in Ref. 8 due to the missing zero-point anharmonic expansion (ZPAE) correction in the reference data used.

## II. ORDER-OF-LIMITS PROBLEM

Like the earlier TPSS exchange functional,<sup>5</sup> TM uses the dimensionless meta-GGA indicator variable,

$$z(\mathbf{r}) = \frac{\tau^{\text{vW}}(\mathbf{r})}{\tau(\mathbf{r})}, \quad (1)$$

where  $\tau^{\text{vW}}(\mathbf{r}) = |\nabla n(\mathbf{r})|^2 / (8n(\mathbf{r}))$  is the single orbital limit for the kinetic energy. In TM,  $z(\mathbf{r})$  is used to identify single orbital and slowly varying densities through the interpolation function,

$$w(\mathbf{r}) = \frac{z(\mathbf{r})^2 + 3z(\mathbf{r})^3}{(1 + z(\mathbf{r})^3)^2}. \quad (2)$$

A different iso-orbital indicator,

$$\alpha(\mathbf{r}) = \frac{\tau(\mathbf{r}) - \tau^{\text{vW}}(\mathbf{r})}{\tau^{\text{UEG}}(\mathbf{r})}, \quad (3)$$

where  $\tau^{\text{UEG}}(\mathbf{r}) = (3/10)(3\pi^2)^{2/3}n(\mathbf{r})^{5/3}$  is the kinetic energy density of the uniform electron gas, occurs in the terms that recover the fourth-order gradient expansion of the exchange energy. These indicators are related as

$$z(\mathbf{r}) = \frac{1}{1 + \frac{3\alpha(\mathbf{r})}{5p(\mathbf{r})}}, \quad (4)$$

$$\alpha(\mathbf{r}) = \frac{5p(\mathbf{r})}{3} \left[ \frac{1}{z(\mathbf{r})} - 1 \right] \quad (5)$$

through square of the reduced density gradient,

$$p(\mathbf{r}) = s(\mathbf{r})^2 = \frac{|\nabla n(\mathbf{r})|^2}{4(3\pi^2)^{2/3}n(\mathbf{r})^{8/3}}, \quad (6)$$

$$= \frac{3}{5} \frac{\tau^{\text{vW}}(\mathbf{r})}{\tau^{\text{UEG}}(\mathbf{r})}. \quad (7)$$

Other iso-orbital indicator functions are also known.<sup>10,11</sup>

Combined dependence on  $\alpha$  and  $z$  introduces an order-of-limits problem into TM that was first identified for TPSS in Ref. 12. This problem was identified in the initial publication of TM<sup>8</sup> but disregarded as harmless. To the contrary, the order-of-limits problem has been shown to be the leading cause of error in TPSS predictions of phase transition pressures<sup>13</sup> and we will show here that the same is true for TM.

The order-of-limits discontinuity can be seen when the enhancement factor,  $F_x$  [Eq. (11) of Ref. 8], is expressed in terms of  $p$  and  $\alpha$  using Eqs. (4)–(7). Taking the limit of  $p \rightarrow 0$  followed by the limit  $\alpha \rightarrow 0$  gives

$$\lim_{\alpha \rightarrow 0} \left[ \lim_{p \rightarrow 0} [F_x(p, \alpha)] \right] = 1.0137, \quad (8)$$

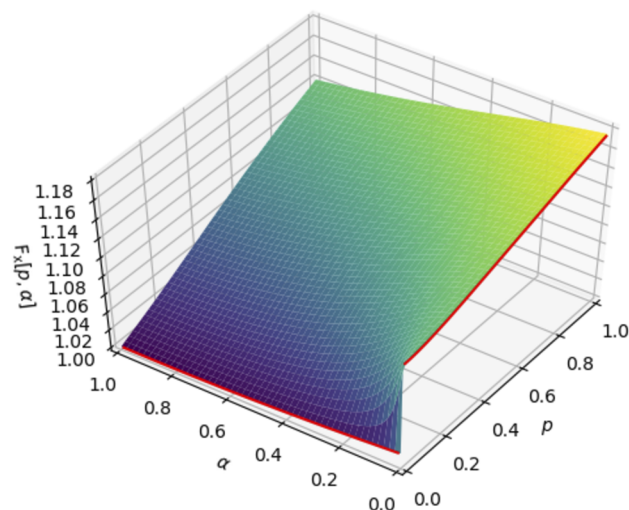
whereas reversing the order and taking the limit of  $\alpha \rightarrow 0$  followed by  $p \rightarrow 0$  gives

$$\lim_{p \rightarrow 0} \left[ \lim_{\alpha \rightarrow 0} [F_x(p, \alpha)] \right] = 1.1132. \quad (9)$$

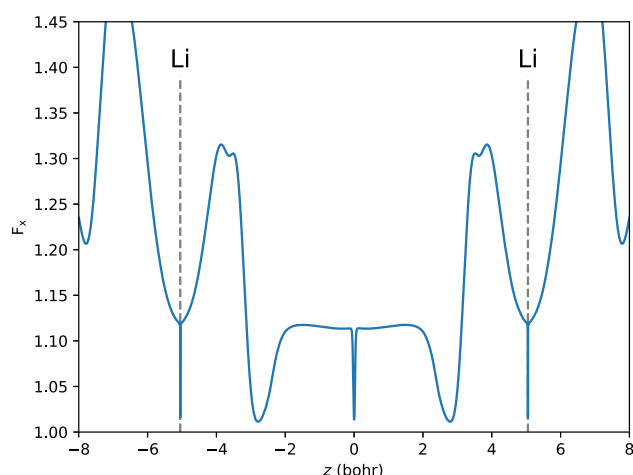
This discontinuity is shown graphically in Fig. 1, which plots the TM exchange enhancement as a function of  $p$  and  $\alpha$ . Following the  $F_x[p = 0, \alpha]$  and  $F_x[p, \alpha = 0]$  edges, highlighted red, reveals the discontinuity at  $F_x[p = 0, \alpha = 0]$ .

Reference 8 asserts that the discontinuity at  $p = \alpha = 0$  is not a practical concern, stating that such behavior only occurs close to the nuclei. This assertion is incorrect and important counter examples are found at the center of stretched covalent single bonds.<sup>12–14</sup> An example of this is shown in Fig. 2, which plots  $F_x$  along the bond axis of stretched  $\text{Li}_2$ . The effect of the order-of-limits discontinuity is clearly seen at the bond center (as well as at the nuclei) as downwards spikes caused by the exchange enhancement jumping between the two limits. We were not able to converge the self-consistent field cycle for stretched  $\text{Li}_2$  when using the LibXC<sup>15</sup> implementation of TM, while other meta-GGA functionals converged without trouble. We rationalize this as the discontinuities at stretched bond centers causing numerical instabilities. As a result, Fig. 2 is evaluated for self-consistent PBE<sup>3</sup> orbitals.

Far from being harmless, the order-of-limits problem was identified in Refs. 13 and 14 as the leading source of errors for TPSS in crystal structure energy differences and in the cohesive energies of insulating solids. We refer the reader to these publications for a full analysis of effect of the order-of-limits problems on transition pressures. The degradation of accuracy that the order-of-limits problem causes in the TM functional is clearly shown by comparing the



**FIG. 1.** The exchange enhancement factor for the TM functional of Ref. 8 as a function of  $p$  and  $\alpha$ . The order-of-limits discontinuity is visible at  $(0, 0)$ . Edges  $p = 0$  and  $\alpha = 0$  are highlighted in red.



**FIG. 2.** The exchange enhancement factor of the TM functional<sup>8</sup> along the  $\text{Li}_2$  internuclear axis evaluated for self-consistent PBE<sup>3</sup> orbitals in the aug-cc-pVQZ basis.<sup>16</sup> Order-of-limits discontinuities are visible at the nuclei (indicated with dashed vertical lines) and at the bond center  $z = 0$ .

accuracy for a small but representative set of phase transitions calculated by TM, that suffers the order-of-limits problem, with those calculated by the SCAN functional,<sup>6</sup> which does not.

Table I summarizes the accuracy of transition pressure predictions for a test set comprised of semiconductor–metal, metal–metal, and semiconductor–insulator transitions for which thermal effects are small enough to allow direct comparison between experimental and predicted results. All calculations were made following the procedure of Ref. 17, using the Vienna *ab initio* simulation package (VASP)<sup>18,19</sup> with PBE projector augmented waves that include the kinetic energy density component for B, N, Si, O, and C and fully occupied *d*-shell electrons with kinetic energy density components for Ga, As, Pb, and Ge. Gamma-centered Monkhorst–Pack *k*-mesh was used throughout. The *k*-mesh point densities and cutoff energy for the plane wave basis are detailed in Table S1 of the supplemental material of Ref. 17.

**TABLE I.** Transition pressures (GPa) for structural phase transitions. Mean error (ME) and mean absolute error (MAE) are given relative to the experiment.<sup>20</sup> Computational details given in the main text.

	SCAN	TM	Expt. <sup>20</sup>
Si	14.5	3.9	12.0
Ge	11.3	6.7	10.6
GaAs	17.1	8.2	15.0
$\text{SiO}_2$	4.6	1.0	7.5 <sup>a</sup>
Pb	16.4	10.0	14.0
BN	2.8	−1.2	5.0
ME	0.4	−5.9	
MAE	2.1	5.9	

<sup>a</sup>Reference 21.

The order-of-limits problem causes the TM functional to strongly underestimate the phase transition energy for every system in the set, with qualitatively incorrect phase ordering seen for BN. A similar performance for TPSS was reported in Ref. 14, which has the same order-of-limits problem. In contrast, the SCAN functional that does not suffer the order-of-limits problem predicts accurate phase transition pressures for every system. This poor accuracy of the TM functional stands in contrast to its good performance for lattice constants, which are not so affected. Lattice constant accuracy is discussed in Sec. III. We must therefore conclude that, contrary to Ref. 8, the order-of-limits problem in TM cannot be dismissed as harmless in all applications.

In principle, the order-of-limits problem could be removed from the TM functional to make a revised-TM functional analogous to the regularized-TPSS proposed in Ref. 13. The order-of-limits problem stems from the interpolation function, Eq. (2), that joins the slowly varying exchange enhancement factor to the density matrix expansion exchange enhancement factor.<sup>8</sup> If this interpolation function were replaced by a function of  $\alpha$  under the constraint that

$$w(\alpha = 1) = 0, \quad (10)$$

then the order-of-limits problem would be resolved. The fourth order gradient correction term,  $F_x^{\text{SC}}$  in Ref. 8, should be suitably modified to maintain the correct gradient expansion for the new interpolation function.

As there is no simple mapping between  $z$  and  $\alpha$  and functional performance is likely to be sensitive to the exact nature of  $w(\alpha)$ , deriving and testing a revised TM functional is expected to be non-trivial and is beyond the scope of the current communication. Inspiration for possible  $w(\alpha)$  could be taken from other non-empirical interpolation based meta-GGA functionals.<sup>6,22–24</sup>

### III. ANHARMONIC CORRECTION TO LATTICE CONSTANTS

Accurate prediction of lattice constants is an important indicator of functional performance both as a measure directly relevant to experiment and as a property that underpins many others. Direct comparison of calculated lattice constants to experimental data is complicated by zero-point phonon effects in the experimental data that cause an ZPAE of measured lattice constants. The impact of ZPAE was calculated in Ref. 25 and found to expand lattice constants by around 0.015 Å ( $\approx 0.35\%$ ) for a set of 24 solids.

The experimental reference data used in Ref. 8 were obtained by extrapolating finite temperature experimental lattice constants to 0 K. Extrapolating in this way implicitly includes anharmonic ZPAE effects, so such data are not directly comparable with single point electronic structure calculations in which the nuclei are treated with harmonic potentials. Hence, neglecting to control for anharmonic ZPAE introduced a small but systematic error into the assessment of TM performance for lattice constants.

The original assessment in Ref. 8 was made from 13 bulk crystalline solids. This set includes main-group metals (Li and Al), semiconductors (diamond, Si,  $\beta$ -SiC, and GaAs), ionic crystals (NaCl, NaF, LiCl, LiF, and MgO), and transition metals (Cu and Ag). Comparable SCAN data are available from Ref. 17 and are included here.

**TABLE II.** Mean error (ME) and mean absolute error (MAE) for lattice constants (Å) of 13 bulk crystalline solids calculated with zero-point expansion (ZPAE) correction and without (as used in Ref. 8).

	ZPAE-Uncorrected		ZPAE-Corrected	
	ME	MAE	ME	MAE
SCAN	−0.013	0.018	0.004	0.011
TM	−0.001	0.012	0.015	0.019
TMPSS	0.008	0.015	0.024	0.028

We repeat the analysis of Ref. 8 using reference data properly corrected for anharmonic ZPAE, the results of which are presented in Table II. Computational details follow those detailed in Sec. II.

The uncorrected reference data used in Ref. 8 indeed suggest the conclusion that TM, and to a lesser extent TMPSS, predicts lattice constants with slightly higher accuracy than SCAN. The reference data with proper anharmonic ZPAE corrections show error of this conclusion, however, with SCAN instead having slightly higher accuracy than both TM and TMPSS. The change in error statistics following ZPAE correction is small but important given the impressive accuracy of both TM and SCAN.

#### IV. CONCLUSION

While Ref. 8 presents an appealing non-empirical functional, assessment of its performance was flawed in two important aspects. First, the order-of-limits problem is more severe for TM than initially claimed and we have shown that it causes significant error for transition pressure predictions. One route to revising the functional to remove this problem is to redesign the interpolation function as a function of  $\alpha$ , although this may require significant care to ensure that the otherwise good performance is not lost. Second, while both TM and TMPSS make accurate predictions of lattice constants, the lack of anharmonic ZPAE correction in the reference data caused Ref. 8 to incorrectly conclude that TM is more accurate than other meta-GGA functionals, such as SCAN, for this property. When the assessment is repeated with properly ZPAE-corrected reference data, the apparent accuracy is worsened with TM and TMPSS showing worse accuracy than SCAN, although we stress that all three functionals are impressively accurate. Given the compelling theoretical foundations of TM, we feel that the functional would be well served by a revision that solves the order-of-limits problem.

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#### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

#### REFERENCES

- W. Kohn and L. J. Sham, “Self-consistent equations including exchange and correlation effects,” *Phys. Rev.* **140**, A1133 (1965).
- S. H. Vosko, L. Wilk, and M. Nusair, “Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis,” *Can. J. Phys.* **58**, 1200 (1980).
- J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” *Phys. Rev. Lett.* **77**, 3865 (1996).
- A. Cancio, G. P. Chen, B. T. Krull, and K. Burke, “Fitting a round peg into a round hole: Asymptotically correcting the generalized gradient approximation for correlation,” *J. Chem. Phys.* **149**, 084116 (2018).
- J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, “Climbing the density functional ladder: Non-empirical meta-generalized gradient approximation designed for molecules and solids,” *Phys. Rev. Lett.* **91**, 146401 (2003).
- J. Sun, A. Ruzsinszky, and J. P. Perdew, “Strongly constrained and appropriately normed semilocal density functional,” *Phys. Rev. Lett.* **115**, 036402 (2015).
- A. D. Becke and M. R. Roussel, “Exchange holes in inhomogeneous systems: A coordinate-space model,” *Phys. Rev. A* **39**, 3761 (1989).
- J. Tao and Y. Mo, “Accurate semilocal density functional for condensed-matter physics and quantum chemistry,” *Phys. Rev. Lett.* **117**, 073001 (2016).
- J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, V. N. Staroverov, and J. Tao, “Exchange and correlation in open systems of fluctuating electron number,” *Phys. Rev. A* **76**, 040501 (2007); [arXiv:0702283](https://arxiv.org/abs/0702283) [cond-mat].
- Y. Zhao and D. G. Truhlar, “A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and non-covalent interactions,” *J. Chem. Phys.* **125**, 194101 (2006).
- J. W. Furness and J. Sun, “Enhancing the efficiency of density functionals with an improved iso-orbital indicator,” *Phys. Rev. B* **99**, 041119 (2019).
- J. P. Perdew, J. Tao, V. N. Staroverov, and G. E. Scuseria, “Meta-generalized gradient approximation: Explanation of a realistic nonempirical density functional,” *J. Chem. Phys.* **120**, 6898 (2004).
- A. Ruzsinszky, J. Sun, B. Xiao, and G. I. Csonka, “A meta-GGA made free of the order of limits anomaly,” *J. Chem. Theory Comput.* **8**, 2078 (2012).
- B. Xiao, J. Sun, A. Ruzsinszky, J. Feng, R. Haunschild, G. E. Scuseria, and J. P. Perdew, “Testing density functionals for structural phase transitions of solids under pressure: Si, SiO<sub>2</sub>, and Zr,” *Phys. Rev. B* **88**, 184103 (2013).
- S. Lehtola, C. Steigemann, M. J. T. Oliveira, and M. A. L. Marques, “Recent developments in LIBXC—A comprehensive library of functionals for density functional theory,” *SoftwareX* **7**, 1 (2018).
- R. A. Kendall, T. H. Dunning, and R. J. Harrison, “Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions,” *J. Chem. Phys.* **96**, 6796 (1992).
- N. Sengupta, J. E. Bates, and A. Ruzsinszky, “From semilocal density functionals to random phase approximation renormalized perturbation theory: A methodological assessment of structural phase transitions,” *Phys. Rev. B* **97**, 235136 (2018).
- G. Kresse and J. Hafner, “Ab initio molecular dynamics for open-shell transition metals,” *Phys. Rev. B* **48**, 13115 (1993).
- G. Kresse and J. Furthmüller, “Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set,” *Phys. Rev. B* **54**, 11169 (1996).
- A. Mujica, A. Rubio, A. Muñoz, and R. J. Needs, “High-pressure phases of group-IV, III-V, and II-VI compounds,” *Rev. Mod. Phys.* **75**, 863 (2003).
- D. R. Hamann, “Generalized gradient theory for silica phase transitions,” *Phys. Rev. Lett.* **76**, 660 (1996).
- J. Sun, R. Haunschild, B. Xiao, I. W. Bulik, G. E. Scuseria, and J. P. Perdew, “Semilocal and hybrid meta-generalized gradient approximations based on the

understanding of the kinetic-energy-density dependence Semilocal and hybrid meta-generalized gradient approximations based on the understanding of the kinetic-energy-density depend,” *J. Chem. Phys.* **138**, 044113 (2013).

<sup>23</sup>J. Sun, B. Xiao, Y. Fang, R. Haunschild, P. Hao, A. Ruzsinszky, G. I. Csonka, G. E. Scuseria, and J. P. Perdew, “Density functionals that recognize covalent, metallic, and weak bonds,” *Phys. Rev. Lett.* **111**, 106401 (2013).

<sup>24</sup>J. Sun, J. P. Perdew, and A. Ruzsinszky, “Semilocal density functional obeying a strongly tightened bound for exchange,” *Proc. Natl. Acad. Sci. U. S. A.* **112**, 685 (2015).

<sup>25</sup>P. Hao, Y. Fang, J. Sun, G. I. Csonka, P. H. T. Philipsen, and J. P. Perdew, “Lattice constants from semilocal density functionals with zero-point phonon correction,” *Phys. Rev. B* **85**, 014111 (2012).