

# Unexpected cold curve sensitivity to GGA exchange form

S. B. Trickey<sup>1</sup> 

Received: 6 April 2016 / Accepted: 18 July 2016 / Published online: 16 August 2016  
© Springer-Verlag Berlin Heidelberg 2016

**Abstract** Finding the crystalline phase transitions along the zero-temperature equation of state (“cold curve”) of elemental solids has been a triumph of density functional theory even in the simple local-density approximation. The present work shows how quantitatively significant improvement on molecules in a generalized gradient approximation functional can result in unexpected ambiguity in the cold curve. The specific cause is obscure but some possibilities are discussed.

**Keywords** Crystalline phase transition · Cold curve · Equation of state · Approximate DFT functional

## 1 Commendation

One of the hallmarks of Quantum Theory Project from its beginning until the late 1980s was the offering of Winter Institutes. They were intense short courses in many-electron theory and methods and their forefront computational implementation. QTP’s founder, Per-Olov Löwdin, long was interested in educating young scientists from Latin American. By the 1980s, that was increasingly his focus for the Winter Institutes. The focus suited me, as my sons’ maternal grandparents were Mexicans and México long

since had become my second country psychologically and spiritually.

Thus as an instructor in the 1987 Winter Institute I met several Mexican participants, including Alberto Vela. Over the years, as we both worked on density functional theory (DFT) in density fitting codes (deMon [1, 2] for him, GTOFF [3–7] for me), Alberto and I shared many discussions and became personal friends as well. But we did not collaborate, as our career paths differed. That changed in 2006. At the IMRC meeting in Cancún, he insisted that I should look in detail at results [8] he was getting from modifying the PBE exchange–correlation (XC) functional [9]. I am the beneficiary of his insistence. Eventually, after much discussion and many calculations, his original insight led to the VMT XC functional [10] which is the topic of renewed focus here. More broadly, his initiative led to a major collaborative effort which continues to this day, exploring what are the real limits of performance of generalized gradient approximation (GGA) and meta-GGA XC functionals [11–18].

Although Alberto has seen the basic results in this paper in the form of slides in talks, I never had written about the work, because the key aspect of the results still is a puzzle. In that spirit, I offer the puzzle here, with thanks for collaboration, hospitality, and friendship. !Feliz Cumpleaños!

## 2 Formal setting

Offering an attractive balance of accuracy, range of applicability, and computational cost as they do, GGA XC functionals are used widely today, especially for the prediction of structural properties of large molecules, clusters, layered periodic systems, and solids. Though there are more refined rungs of the Perdew–Schmidt ladder of functional complexity [19] those rungs are not at issue here. Rather, the

---

Published as part of the special collection of articles “Festschrift in honour of A. Vela”.

---

✉ S. B. Trickey  
trickey@ufl.edu

<sup>1</sup> Quantum Theory Project, Departments of Physics and Chemistry, University of Florida, Gainesville, FL 32611, USA

challenge is to extract as much physical accuracy over as broad a set of systems as possible from the simple GGA form. The practical motivation is computational speed. The intellectual motivation is the elegant purity of orbital-free DFT.

A GGA for the X energy, the focus of much of the work with Alberto, has the form

$$E_x^{\text{GGA}}[n] = c_x \int d\mathbf{r} n^{4/3}(\mathbf{r}) F_x(s(\mathbf{r})). \quad (1)$$

Here  $n(\mathbf{r})$  is the electron number density, the dimensionless density gradient variable  $s$  is

$$s(\mathbf{r}) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla n(\mathbf{r})|}{n(\mathbf{r})^{4/3}}, \quad (2)$$

and

$$c_x := -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3}. \quad (3)$$

(Hartree atomic units are used unless otherwise stated.) Constraint-based development of  $F_x$  is challenged by a paucity of rigorous information about its behavior. Any reasonable GGA must have  $F_x(s \rightarrow 0) = 1.0$  to maintain accord with the homogeneous electron gas (HEG). Determination of other useful restrictions on the behavior of  $F_x(s)$  is a challenge. Two popular functionals illustrate the point. Supposedly the most heavily cited paper in physics is for the PBE functional [9]. Though PBE was presented as a simplification of the PW-91 GGA [20], from the perspective of constraint-based development, there are notable qualitative differences between them. The PW-91 X enhancement factor  $F_x^{\text{PW91}}$  vanishes in the limit of large reduced density gradient,  $s \rightarrow \infty$ , whereas  $\lim_{s \rightarrow \infty} F_x^{\text{PBE}} = 1.804$ . Thus PW-91 fulfills a known constraint [21], but PBE does not. The constant to which PBE goes is set by imposition of the Lieb–Oxford bound [22, 23],

$$\frac{E_{xc}[n]}{E_x^{\text{LDA}}[n]} \leq \lambda_{\text{LO}} \quad (4)$$

where

$$E_x^{\text{LDA}}[n] = c_x \int d\mathbf{r} n^{4/3}(\mathbf{r}). \quad (5)$$

The LO value for the constant is

$$\lambda_{\text{LO}} = 2.273 \quad (6)$$

Spin-scaling then gives  $\lambda_{\text{LO}}/2^{1/3} = 1.804$  (A slightly more restrictive  $\lambda_{\text{CH}} = 2.215$  was obtained by Chan and Handy [24]. The difference does not matter here.) PW-91 actually satisfies the LO bound on the low side by having a lower maximum value for its enhancement factor than PBE, namely  $F_x^{\text{PW91}} \leq 1.641$ .

The paucity of rigorous information is this. It is well understood that the meaningful range of  $s$  is at most  $0 \leq s \leq 5$  [15, 25, 26] in physical systems. Clearly, the constraints just summarized leave much unspecified for the behavior of  $F_x(s)$  in that range. In fact, the success of PBE might seem to suggest that even the  $s \rightarrow \infty$  limit may be of little consequence. Plots comparing  $F_x^{\text{PW91}}$  and  $F_x^{\text{PBE}}$  are widely available; see Fig. 1 of Ref. [11] for example. Study of such plots amplifies curiosity about optimum design of  $F_x^{\text{GGA}}$  in that region. An example of a redesign is the RPBE functional [27].

Motivated by the notion of locally varying imposition of the LO bound in that  $s$  region, Vela [8] introduced what developed into the VMT functional [10]. It has the form

$$F_x^{\text{VMT}} = 1 + \frac{\mu s^2 \exp(-\alpha s^2)}{1 + \mu s^2} \quad (7)$$

Either  $\mu = \mu_{\text{PBE}} = 0.21951$  from original PBE or  $\mu = \mu_{\text{GEA}} = 10/81$  from the gradient expansion may be used.

Vela et al. [10] give the rationale for the design choices made in VMT on  $0 \leq s \leq 5$ . Retrospectively, the VMT argument can be summarized as follows. The local LO bound is important for universality. That sets  $\alpha$  for a given choice of  $\mu$  ( $F_x^{\text{VMT}}$  has a single maximum). However, large  $s$  corresponds to low densities that are in fact smooth, hence weakly inhomogeneous, so the enhancement factor in that regime should recover the local-density approximation, i.e.,  $F_x^{\text{VMT}} = 1$ . Since experience with PBE seems to show that the exact non-uniform scaling asymptotic constraint [21] is of little consequence, one can ignore that constraint and simply extend the LDA all the way out,  $\lim_{s \rightarrow \infty} F_x^{\text{VMT}} = 1$ .

Thus, VMT X has an enhancement factor which, except at one point, always is tighter than the LO bound and which gives an LDA-like description of systems with both near-zero and large  $s$ . On typical molecular test sets, VMT does better for mean absolute atomization energy errors than PBE by about a factor of two and otherwise is competitive on the slightly better side, except for bond-length errors which are worse by about a factor of two (but small nonetheless). See, for example, Table II of Ref. [15].

### 3 Physical system and computational details

What sets VMT X apart from almost all of the newer functionals from our collaboration [11–13, 15, 17] is the strong reliance on the HEG limit,  $F_x = 1$ . Given the importance of free-electron metals, that reliance almost immediately spurs the question of VMT versus LDA performance in such systems. Note that our VT{8,4} functional [18], which has a plateau around  $F_x^{\text{VT}\{8,4\}} = 1$  for intermediate values of  $s$ ,

is close to VMT in this sense. Designed as a modification of VMT X, one would expect that test calculations with VT{8,4} would be less decisive than those with VMT, so only VMT is considered here.

Crystalline Li is the obvious physical system choice. That choice actually raises more subtle challenges than the simple free-electron system issue. While the zero-temperature equilibrium for Li generally is characterized as nearly-free-electron, it has been known since the middle 1980s that the compressed system is rather more complicated [28–31]. That insight was very substantially deepened in 1999 when Neaton and Ashcroft predicted low-symmetry phases [32] under pressure. By now, the Li phase diagram is known to be quite complicated [33]. Review of the substantial literature is well beyond the scope of this work. The essential point is that this richness of phases along the cold curve (zero-temperature equation of state) suggests that comparative calculations for various functionals that treat intermediate-magnitude regions of  $s$  distinctly might be instructive. In particular, how does a functional such as VMT, with its LDA-like behavior at both small and large  $s$ , handle the deviation from HEG-behavior found in the compressed phases of Li?

I explored these questions with a series of all-electron calculations. To confine the problem in a reasonable scope, I examined the relative energetics of the hcp, fcc, and bcc phases. The experimental low-temperature equilibrium phase of Li generally is thought to be a complicated hexagonal one, usually taken to be 9R [34, 35]. Matters are more subtle however, as there is substantial evidence of polytype behavior as well [36–39]. For present purposes, the subtlety of the rearrangement energetics of hcp  $\rightarrow$  fcc is itself an important test.

All-electron calculations are preferable in this setting: They enable as nearly exclusive a focus as possible on effects of the XC functional. Which all-electron basis? One must be careful in doing compression studies with cellularly decomposed basis sets such as linearized augmented-plane-wave (LAPW); see Ref. [40] for brief discussion. So I used the Gaussian basis GTOFF code [3–7].

Gaussian basis sets for crystalline systems under compression also require some care in construction. After considerable testing, I found that for the Kohn–Sham orbitals the uncontracted 10s6p3d set constructed long ago [41] was not only difficult to improve upon but had the additional virtue of providing continuity with earlier calculations. See Table II of Ref. [41] for the orbital exponents. For the variational Coulomb charge density fitting basis and XC fitting basis, I used an 11s set which was derived from a 9s set developed by Boettger [42]. The exponents are 958.00, 239.00, 112.00, 46.29, 19.32, 7.78, 3.24, 1.41, 0.610, 0.270, and 0.080. Brillouin Zone scan densities were  $24 \times 24 \times 24$  for the cubic systems (413 total points in the

irreducible wedge of the BZ) and  $24 \times 24 \times 12$  for hcp (427 points in the irreducible wedge).

GTOFF does not support analytical geometry optimization, so calculations were done at eight cell volumes per atom,  $1.078 \Omega_0$ ,  $1.025 \Omega_0$ ,  $1.00 \Omega_0$ ,  $0.976 \Omega_0$ ,  $0.931 \Omega_0$ ,  $0.854 \Omega_0$ ,  $0.732 \Omega_0$ , and  $0.640 \Omega_0$ , with  $\Omega_0 = 142.4 \text{ au}^3/\text{atom}$  the reference equilibrium experimental volume [43] used by Boettger and Albers [31]. For one functional, VMT with  $\mu_{\text{GE}}$ , three additional volumes were used for hcp and fcc,  $0.8235 \Omega_0$ ,  $0.793 \Omega_0$ , and  $0.7625 \Omega_0$ . The hcp calculations were done at ideal  $c/a = \sqrt{8/3}$ . Calculated total energies per atom were fitted to the stabilized jellium equation of state (SJEOS) [42] to extract energy minima, the corresponding lattice parameters, and bulk moduli for each phase separately. Standard deviations of those energy fits were  $< 1 \times 10^{-4}$ , in many cases an order of magnitude or two smaller. It is known that the pressure-induced population shifts between bands (shells) are a very smooth function of compression; see for example Fig. 2 in Ref. [29].

As already noted, DFT calculations of the Li crystalline phases date from the 1980s. Unlike now, at that time various versions of the local-spin-density approximation were in use. For the sake of historical continuity and demonstration of reproducibility, two of those, Hedín–Lundqvist (HL) [44] and Rajagopal–Singhal–Kimball (RSK) [45, 46] were included, as well as simple local exchange, Eq. (5). In the early literature of DFT calculations on Li, that was called KSG, a convention I follow here for ease of comparison. Modern functionals are the Perdew–Zunger (PZ) LDA [47], PBE GGA [9], and its PBEsol variant [48]. VMT with  $\mu_{\text{PBE}}$  (denoted VMT<sub>PBE</sub>) is the counterpart to PBE, while VMT with  $\mu_{\text{GE}}$ , denoted VMT<sub>GE</sub>, is the PBEsol counterpart. Both used PBE correlation.

## 4 Results and discussion

Begin with the predicted equilibria. To facilitate comparison and confirm reproducibility, first consider the historical functionals, KSG, HL, and RSK, then the modern ones, PZ, PBE, VMT<sub>PBE</sub>, PBEsol, and VMT<sub>GE</sub>. For the historical functionals, Table 1 gives the lowest-energy lattice parameters  $a_e$  in au, the associated cell volume per atom  $\Omega_e$  in  $\text{au}^3/\text{atom}$ , equilibrium total energies  $E$  per atom (from the present calculations only), and the inter-phase energy differences per atom (both in Hartree au), and the hcp bulk modulus  $B_0$  in Mbar. The energy differences are ordered as in the subscripts, thus  $\Delta E_{\text{hcp-fcc}} = E_{\text{hcp}} - E_{\text{fcc}}$ . The earlier calculations are labeled with the initials of the authors: “BA” for the linearized muffin-tin-orbital (LMTO) calculations from Boettger and Albers, [31], “BT” for the gaussian orbital calculations by Boettger and Trickey with the

**Table 1** Calculated equilibrium properties for hcp, fcc, and bcc Li from older functionals. See text for notation and references. Lowest-energy lattice parameters (au), with corresponding cell volume peratom ( $\text{au}^3/\text{atom}$ ) in parentheses, followed by equilibrium total energies  $E$  per atom (present work only, Hartree/atom), inter-phase energy differences  $\Delta E$  (Hartree/atom), and hcp bulk modulus (Mbar)

	KSG	KSG (BT)	KSG (BA)	HL	HL (NTBS)	RSK	RSK (BT)
$a_e$ hcp	5.866 (142.7)	–	5.91 (146.0)	5.646 (127.3)	5.659 (128.1)	5.617 (125.3)	–
$a_e$ fcc	8.282 (142.0)	8.28 (141.9)	8.36 (146.1)	7.974 (126.8)	–	7.943 (125.3)	7.94 (125.1)
$a_e$ bcc	6.597 (143.6)	6.59 (143.1)	6.63 (145.7)	6.350 (128.0)	–	6.334 (127.1)	6.32 (126.2)
$E_{\text{hcp}}$	–7.2375144	–	–	–7.4160294	–	–7.4613234	–
$E_{\text{fcc}}$	–7.2374170	–	–	–7.4159794	–	–7.4613144	–
$E_{\text{bcc}}$	–7.2371312	–	–	–7.4156194	–	–7.4609362	–
$\Delta E_{\text{hcp-fcc}}$	–0.000097	–	–0.000035	–0.000050	–0.00004	–0.000009	–
$\Delta E_{\text{hcp-bcc}}$	–0.000383	–	–0.00014	–0.000410	–0.00016	–0.000387	–
$\Delta E_{\text{fcc-bcc}}$	–0.000286	–0.00025	–0.00011	–0.000360	–0.00012	–0.000378	–0.00045
$B_0$ , hcp	0.127	–	0.159	0.159	–	0.152	–

**Table 2** As in Table 1 for modern functionals. See text for notation.  $B_0$  for bcc added. Lattice parameters, cell volumes, and  $B_0$  values for the bcc phase from Csonka et al. [49] also added in brackets below the corresponding values from the present calculations

	PZ	PBE	VMT <sub>PBE</sub>	PBEsol	VMT <sub>GE</sub>
$a_e$ hcp	5.644 (127.1)	5.777 (136.3)	5.810 (138.7)	5.774 (136.2)	5.776 (136.2)
$a_e$ fcc	7.974 (126.8)	8.164 (136.0)	8.212 (138.4)	8.163 (136.0)	8.163 (136.0)
$a_e$ bcc	6.350 (128.0)	6.492 (136.8)	6.516 (138.3)	6.490 (136.7)	6.516 (138.4)
	[6.355 (128.3)]	[6.480 (136.0)]	–	[6.478 (135.9)]	–
$E_{\text{hcp}}$	–7.4086898	–7.5207440	–7.5307576	–7.4588113	–7.4632081
$E_{\text{fcc}}$	–7.4086397	–7.5207271	–7.5307415	–7.4587855	–7.4631803
$E_{\text{bcc}}$	–7.4082775	–7.5203174	–7.5303326	–7.4583712	–7.4627352
$\Delta E_{\text{hcp-fcc}}$	–0.000050	–0.000017	–0.000016	–0.000026	–0.000028
$\Delta E_{\text{hcp-bcc}}$	–0.000412	–0.000427	–0.000425	–0.000440	–0.000472
$\Delta E_{\text{fcc-bcc}}$	–0.000362	–0.000410	–0.000409	–0.000414	–0.000406
$B_0$ , bcc	0.156	0.144	0.145	0.140	0.137
	[0.152]	[0.138]	–	[0.138]	–
$B_0$ , hcp	0.158	0.144	0.140	0.141	0.128

BNDPKG code [28], and “NTBS” for the WIEN code full-potential LAPW (FLAPW) calculations by Nobel et al. [40].

Table 1 confirms that the present and early KSG results from two independent Gaussian basis codes agree well on lattice parameters and fcc–bcc energy difference. The BA cellular basis lattice parameters are longer. There is also consistency between the present calculation and the NTBS WIEN FLAPW calculation of  $a_{e,\text{hcp}}$  for the HL functional. Both results are consistent with the physical argument, borne out by experience, that the internal structure of such basis sets results in prediction of stiffer crystals than from gaussian basis sets. In contrast to those modest differences, however, the various calculated interphase energy shifts differ substantially. In most instances, the interphase energy differences from gaussian basis calculations are larger in magnitude than for the cellular basis (LMTO, FLAPW) calculations. To the extent comparison is

possible, the phase ordering nevertheless is the same. That these agreements and disparities long have been known is evident from the age of several of the results in that Table. In any event, there are no significant inconsistencies of the present calculations with well-established findings. Reproducibility is verified.

Now consider the equilibrium phase description given by the modern functionals. Table 2 presents results for PZ, PBE, VMT<sub>PBE</sub>, PBEsol, and VMT<sub>GE</sub>. (Isolated atom total energies from all five modern functionals are given for the Appendix.) To provide comparison, results for bcc symmetry from plane-wave, projector augmented wave calculations by Csonka et al. using the VASP code [49] for PZ, PBE, and PBEsol functionals are given as well. The bcc lattice parameters from PZ, PBE, and PBEsol calculated in the present work agree within 0.012 au or better with the VASP PAW results. The bcc bulk moduli from VASP are lower for all three functionals than from the GTOFF

**Table 3** Comparison of calculated pressure-induced phase transition from hcp to fcc. Transition pressures in Mbar (1 Mbar = 100 GPa). Compressions at the transition,  $\Omega_{\text{hcp-fcc}}/\Omega_{\text{hcp,e}}$ , relative to hcp equilibrium volume for the particular XC functional also are tabulated

	KSG	HL	RSK	PZ	PBE	VMT <sub>PBE</sub>	PBEsol	VMT <sub>GE</sub>
P	0.065	0.039	0.068	0.045	0.028	0.031	0.052	0.032
$\Omega_{\text{hcp-fcc}}/\Omega_{\text{hcp,e}}$	0.73	0.83	0.76	0.81	0.86	0.84	0.78	0.76

calculations but by 4 % or less. Presumably, the difference traces to the PAW technique. I expect that inter-code differences for the hcp bulk moduli would be similarly small.

It is reassuring that all five modern functionals (as well as old-fashioned KSG) give the same relative ordering of hcp, fcc, and bcc energies at equilibrium, with roughly the same energy intervals. Second, it is remarkable that the simplest Slater LDA (KSG) gives a bcc equilibrium lattice parameter, 6.597 au, quite close to the fixed-node diffusion Monte Carlo value, 6.58 au [50]. The presumably more accurate, more soundly based PZ LSDA substantially worsens that, the usual LDA over-binding story, so that what the GGA then must do is to compensate.

All of the calculated cell constants are short. In that context, despite its favoring LDA limits, VMT does as expected of a GGA X functional and lengthens lattice parameters compared to LDA. VMT does so slightly more than its PBE counterparts:  $a_{\text{bcc,VMT}_{\text{PBE}}} = a_{\text{bcc,VMT}_{\text{GE}}} = 6.516$  versus 6.492 au (PBE) and 6.490 au (PBEsol). In the hcp case, the VMT<sub>PBE</sub> lengthening relative to PBE is 0.03 au, but VMT<sub>GE</sub> lengthening relative to PBEsol is negligible. The same behavior occurs for fcc;  $a_c$  is 0.05 au longer for VMT<sub>PBE</sub> than for PBE, but unchanged for VMT<sub>GE</sub> versus PBEsol.

In the midst of the general consistency of lattice constant results in equilibrium quantities, there is a striking anomaly. Namely, the  $B_{0,\text{hcp}}$  from VMT<sub>GE</sub> is much lower than any other GGA value, 0.128 Mbar, essentially the same as the KSG result (0.127 Mbar). I return to this anomaly below. Before that, consider the behavior with pressure.

With one exception, also discussed in detail below, the first pressure-induced phase transition is hcp to fcc for all of the XC functionals. Transition pressures in Mbar (1 Mbar = 100 GPa) and compressions (relative to calculated equilibrium hcp volume) are given in Table 3. For comparison, Boettger and Albers [31] reported  $P_{\text{hcp-fcc}} = 0.08$  Mbar at volume compression  $\Omega_{\text{hcp-fcc}}/\Omega_{\text{hcp,e}} = 0.73$  for the HL functional, whereas Nobel et al. [40] reported  $\Omega_{\text{hcp-fcc}}/\Omega_{\text{hcp,e}}$  between 0.72 and 0.89 for the HL functional, but did not report  $P_{\text{hcp-fcc}}$ .

For VMT<sub>PBE</sub>, the hcp  $\rightarrow$  fcc transition pressure goes up a little compared to PBE, so there is a hint of favoring LDA, but not a strong one. It is technically a bit difficult to find the hcp  $\rightarrow$  fcc transition in PBEsol, but it is there. In contrast, the VMT<sub>GE</sub> transition is indistinct, to the point

that I am not entirely comfortable with stating that it was located. Only by adding the three additional volumes mentioned above was I able to get the transition volume value shown in Table 4 for VMT<sub>GE</sub>. Superficially the resulting SJEOS fit puts the transition at about  $\Omega/\Omega_0 = 0.76$ . However, examination of the data along the fitted EOS does not really support that conclusion. From 120.6 au<sup>3</sup>/atom down to 110 au<sup>3</sup>/atom, the fitted  $E_{\text{hcp}}$  lies about 10 micro-Hartree below the fitted  $E_{\text{fcc}}$  curve. Then for 109.6 au<sup>3</sup>/atom down to 103.6 au<sup>3</sup>/atom, the two energies are identical, then fcc lies below by about 10 micro-Hartree/atom down through 101.6 au<sup>3</sup>/atom, then the energies of the two phases are equal again, etc. In essence, for VMT<sub>GE</sub> the two curves (hcp, fcc) run almost parallel.

The standard reasoning regarding the value of the gradient expansion coefficient,  $\mu$ , in PBE is that  $\mu_{\text{GE}}$  is needed to get solids right from PBE (i.e., shift to PBEsol), whereas  $\mu = 0.27583$  improves the performance on molecules as compared with the original  $\mu_{\text{PBE}}$  [17]. In that context, the Li results from VMT<sub>GE</sub> are a bit puzzling and not easy to explain. As reported above, VMT<sub>GE</sub> notably lowers the bulk modulus of the equilibrium hcp phase compared to modern LDA and to the other GGAs, even compared to PBEsol. On this quantity, VMT<sub>GE</sub> replicates simplest KSG X, an outcome consistent with the interpretation that VMT<sub>GE</sub> favors LDA but inconsistent with the PZ LDA result.

Taken at face value, the fitted hcp  $\rightarrow$  fcc transition pressure for VMT<sub>GE</sub> is consistent with the bulk modulus softening. But beneath that consistency is the striking result that VMT<sub>GE</sub> yields near-coexistence of the hcp and fcc phases without a clear transition between them. In the great variety of DFT calculations of martensitic phase transitions in elemental solids that sort of behavior has not, to my knowledge, been encountered before.

As mentioned already, there is evidence that the ground state of Li may not be of a pure crystalline symmetry but a polytype [36–39]. Most recently, Pichl et al. [39] proposed that the experimental ground state of Li is fcc with 9R (hexagonal) as a metastable phase induced experimentally by the environment. Superficially, it seems that VMT<sub>GE</sub> is mimicking this behavior. If so, the mimicry would have to arise via the combination of the VMT reduced density gradient dependence ( $\mu_{\text{GE}} = 10/81$ ) and the VMT  $s$ -dependence that maps to the HEG in two regimes of  $s$ , but not in between. The fact that finding the hcp  $\rightarrow$  fcc transition

in PBEsol requires some computational care is consistent with that interpretation. Supposing that interpretation to be true, what would remain unresolved is why the details of VMT<sub>GE</sub> differ just enough from PBEsol, VMT<sub>PBE</sub>, and even from simple LDA (KSG), to give this peculiar physics.

Although a large-scale computational survey of many GGA functionals applied to Li could be undertaken to explore this issue, it seems more plausible that first we need more insight into the physics that should be incorporated into a GGA X functional on  $1 \leq s \leq 5$ . In that sense, the puzzle may present an opportunity, though how to exploit it is not obvious. One possibility would be to extract the effective enhancement factor  $F_x^{GGA}$  from the Monte Carlo data [50]. In addition to the numerical work required, an underlying challenge in doing that would be to separate the exchange and correlation contributions appropriately.

It may be, however, that the Li cold curve is simply too subtle to describe with a GGA. At first thought, such a finding would be not only somewhat unexpected but also a seemingly serious threat to the orbital-free DFT (OFDFT) agenda. An alternative perspective is that the physics of co-existing metastable phases (polytype) suggests that there is an important real-space non-locality. That in turn suggests pursuing the OFDFT agenda via a combination of a one-point functional (GGA) and a supplemental two-point functional, namely  $E_x = E_x^{GGA} + E_x^{(2)}$  with

$$E_x^{(2)}[n] = c_x \int d\mathbf{r}_1 d\mathbf{r}_2 n^{2/3}(\mathbf{r}_1) \kappa_x(n(\mathbf{r}_1); n(\mathbf{r}_2)) n^{2/3}(\mathbf{r}_2). \quad (8)$$

There is a history of approximations of the form of  $E_x^{(2)}$  by itself that is, as Ref. [51] suggests, not too encouraging. However, the two-point form represents an alternative to the conventional OFDFT route to approximate non-locality, which rapidly becomes quite cumbersome as higher-order spatial derivatives (beyond Laplacians) are included. And while the computational cost of a two-point functional obviously is higher than for one-point OFDFT approximations, the OFDFT scaling with system size would be preserved.

**Acknowledgments** Thanks go to J.C. Boettger for several helpful conversations about basis set design and GTOFF technical issues, as well as for providing a copy of his SJEOS code. Support came from the U.S. National Science Foundation under DMR-1515307.

## Appendix

For reference and to enable extraction of cohesive energies from the crystalline data presented here, the associated spin-polarized atomic energies are in Table 4. Those were

**Table 4** Isolated Li atom (spin-polarized) energies (Hartree)

Functional	$E_{\text{atom}}$
KSG	−7.19326525
HL	−7.35441804
RSK	−7.39343494
PZ	−7.34254058
PBE	−7.46203592
VMT <sub>PBE</sub>	−7.47317477
PBEsol	−7.39742123
VMT <sub>GE</sub>	−7.40266556

computed with an uncontracted 12s basis constructed by adding two diffuse orbitals, exponents 0.063, 0.028, to the 10 s KS manifold used in the solid calculations.

## References

- Geudtner G, Calaminici P, Carmona-Espíndola J, del Campo J, Domínguez-Soria VD, Flores-Moreno R, Gamboa GU, Goursot A, Köster AM, Reveles JU, Mineva T, Vásquez-Pérez JM, Vela A, Zuñiga-Gutierrez B, Salahub DR (2012) *Comput Mol Sci* 2:548. doi:10.1002/wcms.98
- Köster AM, Calaminici P, Casida ME, Flores-Moreno R, Geudtner G, Goursot A, Heine T, Ipatova A, Janetzko F, Martín del Campo J, Patchkovskii S, Reveles JU, Salahub DR, Vela A (2006) deMon2K; The deMon developers. Cinvestav, Mexico
- Trickey SB, Alford JA, Boettger JC (2004) In: Leszczynski J (ed) *Computational materials science*, vol 15 of *Theoretical and computational chemistry*. Elsevier, Amsterdam, p 171
- Boettger JC (2000) *Phys Rev B* 62:7809
- Birkenheuer U, Boettger JC, Rösch N (1994) *J Chem Phys* 100:6826
- Boettger JC (1993) *Int J Quantum Chem S27*:147
- Mintmire JW, Sabin JR, Trickey SB (1982) *Phys Rev B* 26:1743
- Vela A (2006) The Lieb–Oxford bound and the large gradient correction in the exchange energy. XVth Internat. Materials Research Congress, Acad. Mexicana de Ciencia de Materiales, Cancún México, 22 August 2006
- Perdew JP, Burke K, Ernzerhof M (1996) *Phys Rev Lett* 77:3865; erratum *Phys Rev Lett* 78:1396 (1997)
- Vela A, Medel V, Trickey SB (2009) *J Chem Phys* 130:244103
- Pacheco-Kato JC, del Campo JM, Gázquez JL, Trickey SB, Vela A (2016) *Chem Phys Lett* 651:268
- Carmona-Espíndola J, Gázquez JL, Vela A, Trickey SB (2016) *Theoret Chem Acc* 135:120
- Carmona-Espíndola J, Gázquez JL, Vela A, Trickey SB (2015) *J Chem Phys* 142:054105
- Trickey SB, Vela A (2013) *J Mex Chem Soc* 57:105
- del Campo JM, Gázquez JL, Alvarez-Mendez RJ, Trickey SB, Vela A (2013) In: Deb BM, Ghosh SK, Chattaraj PK (eds) *Concepts and methods in modern theoretical chemistry*, vol 1. CRC Press, Boca Raton, p 295
- del Campo JM, Vela A, Gázquez JL, Trickey SB (2012) *Chem Phys Lett* 543:179
- del Campo JM, Gázquez JL, Trickey SB, Vela A (2012) *J Chem Phys* 136:104108

18. Vela A, Pacheco-Kato JC, Gázquez JL, del Campo JM, Trickey SB (2012) *J Chem Phys* 136:144115
19. Perdew JP, Schmidt K (2001) *AIP Proc Conf* 577:1
20. Perdew JP (1991) In: Ziesche P, Eschrig H (eds) *Electronic structure of solids '91*. Akademie Verlag, Berlin, p 11
21. Levy M, Perdew JP (1993) *Phys Rev B* 48:11638; erratum *Phys Rev* 55:13321 (1997)
22. Lieb EH, Oxford S (1981) *Int J Quantum Chem* 19:427
23. Lieb EH (1979) *Phys Lett* 70A:444
24. Chan GK-L, Handy NC (1999) *Phys Rev A* 59:3075
25. Zupan A, Perdew JP, Burke K (1997) *Int J Quantum Chem* 61:835
26. Zupan A, Burke K, Ernzerhof M, Perdew JP (1997) *J Chem Phys* 106:10184
27. Hammer B, Hansen LB, Norskov JK (1999) *Phys Rev B* 59:7413
28. Boettger JC, Trickey SB (1985) *Phys Rev B* 32:3391
29. Zittel WG, Meyer-ter-Vehn J, Boettger JC, Trickey SB (1985) *J Phys F Met. Phys* 15:L247
30. Meyer-ter-Vehn J, Zittel WG (1988) *Phys Rev B* 37:8674
31. Boettger JC, Albers RC (1989) *Phys Rev B* 39:3010
32. Neaton JB, Ashcroft NW (1999) *Nature* 400:141
33. Marqués M, McMahon MI, Gregoryanz E, Hanfland M, Guillaume CL, Pickard CJ, Ackland GJ, Nelmes RJ (2011) *Phys Rev Lett* 106:095502 (and refs. therein)
34. Overhauser AW (1984) *Phys Rev Lett* 53:64
35. Smith HG (1987) *Phys Rev Lett* 58:1228
36. Schwarz W, Blaschko O (1990) *Phys Rev Lett* 65:3144
37. Krystian M, Pichl W (2000) *Phys Rev B* 62:13956
38. Vigreux C, Loiseau P, Binet L, Gourier D (2000) *Phys Rev B* 61:8759
39. Pichl W, Krystian M, Prem M, Krexner G (2003) *J. Phys. IV France* 112:1095
40. Nobel JA, Trickey SB, Blaha P, Schwarz K (1992) *Phys Rev B* 45:5012
41. Boettger JC, Trickey SB (1984) *Phys Rev B* 29:6425
42. Alchagirov AB, Perdew JP, Boettger JC, Albers RC, Fiolhais C (2001) *Phys Rev B* 63:224115
43. Anderson MS, Swenson CA (1985) *Phys Rev B* 31:668
44. Hedin L, Lundqvist BI (1971) *J Phys C* 4:2064
45. Rajagopal AK, Singhal SP, Kimball J (1979) apparently unpublished
46. Rajagopal AK (1979) *Adv Chem Phys* 41:59
47. Perdew JP, Zunger A (1981) *Phys Rev B* 23:5048
48. Perdew JP, Ruzsinszky A, Csonka GI, Vydrov OA, Scuseria GE, Constantin LA, Zhou XL, Burke K (2008) *Phys Rev Lett* 100:136406
49. Csonka GI, Perdew JP, Ruzsinszky A, Philipsen PHT, Lebégue S, Paier J, Vydrov OA, Ángyán JG (2009) *Phys Rev B* 79:155107
50. Rasch K, Mitas L (2015) *Phys Rev B* 92:045122
51. Engel E, Dreizler RM (2011) In: *Density functional theory: an advanced course*. Springer, Heidelberg, p 201 (Section 4.6 and refs. therein)