

Tests of a ladder of density functionals for bulk solids and surfaces

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The local spin-density approximation (LSDA) and the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) are fully non-empirical realizations of the first two rungs of “Jacob’s ladder” of exchange–correlation density functionals. The recently proposed non-empirical meta-GGA of Tao, Perdew, Staroverov, and Scuseria (TPSS), featuring the kinetic energy density as an additional local ingredient, completes the third rung. A hierarchy of these functionals, complemented by the meta-GGA of Perdew, Kurth, Zupan, and Blaha (PKZB), is tested in self-consistent Gaussian-type orbital calculations of equilibrium lattice constants, bulk moduli, and cohesive energies for 18 solids, and in studies of the jellium surface energy. The ascent of the ladder generally results in better performance, although most of the improvement for bulk solids occurs in the transition from LSDA to PBE. For the jellium surface energy, PBE is less accurate than LSDA, but PKZB and TPSS are more accurate. We support the idea that most of the error of these functionals for bulk solids arises in the description of core–valence interaction, by demonstrating that it can be removed through adjustment of the corresponding term in the equation of state. Overall, TPSS gives the best description of solids and surfaces, as it was found to do for molecules in earlier work.

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I. INTRODUCTION

Kohn-Sham (KS) spin-density functional theory^{1–4} treats the kinetic and classical Coulomb components of the electronic energy exactly. The remaining contribution, the exchange–correlation energy, must be approximated as a functional of the ground-state electron densities $n_{\uparrow}(\mathbf{r})$ and $n_{\downarrow}(\mathbf{r})$. Since the dependence of $E_{xc}[n_{\uparrow}, n_{\downarrow}]$ on $n_{\uparrow}(\mathbf{r})$ and $n_{\downarrow}(\mathbf{r})$ does not have to be explicit, the list of local ingredients of E_{xc} may contain not only $n_{\sigma}(\mathbf{r})$ and their derivatives $\nabla n_{\sigma}(\mathbf{r})$, $\nabla^2 n_{\sigma}(\mathbf{r})$, etc., but also quantities that are indirectly determined by the densities. Such quantities, normally constructed from the KS orbitals, include the kinetic energy density, $\tau_{\sigma}(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla \phi_i^{\sigma}(\mathbf{r})|^2$, and the exact exchange. Ingredients other than the density do more than just enhance flexibility; they are necessary if the approximation is to satisfy known exact constraints on $E_{xc}[n_{\uparrow}, n_{\downarrow}]$.

The type of local ingredients of $E_{xc}[n_{\uparrow}, n_{\downarrow}]$ forms the basis for the “Jacob ladder” classification of density functional approximations.⁵ The ascent of the ladder consists in embedding increasingly complex ingredients and exact properties into $E_{xc}[n_{\uparrow}, n_{\downarrow}]$. At a certain point, functionals designed in this manner are bound to achieve satisfactory accuracy.

The lower three rungs of the ladder are, in ascending order, the local spin-density approximation (LSDA), which employs only n_{σ} , the generalized gradient approximation (GGA), whose ingredients are n_{σ} and ∇n_{σ} , and the meta-GGA (MGGA), which makes use of τ_{σ} (or $\nabla^2 n_{\sigma}$) in addition to the GGA ingredients. The LSDA is exact for a uniform electron gas and agreeably accurate for systems where the electron density does not vary too fast, such as solids. Since the exchange component of the LSDA is known exactly, the design of the ultimate LSDA requires only an accurate parametrization of the correlation energy per electron

$\epsilon_c^{\text{unif}}(n_{\uparrow}, n_{\downarrow})$.⁶ Of several existing forms,^{7–10} the Perdew–Wang parametrization⁹ of this function, which satisfies many exact constraints, has been chosen here.

GGA functionals retain most of the correct features of the LSDA and greatly advance the accuracy,¹¹ especially for molecular binding energies, which are severely overestimated by LSDA. Semi-empirical GGAs are fitted to reproduce particular sets of experimental data, while non-empirical approximations avoid optimized parameters in favor of satisfying exact constraints. The non-empirical GGA of Perdew, Burke, and Ernzerhof¹² (PBE) is the most complete embodiment of the second rung of Jacob’s ladder. Although the PBE GGA is not always as accurate for molecules¹³ as some semi-empirical GGAs (e.g., BLYP^{14,15}), it incorporates more exact properties and thus is more universal in applicability.¹¹ The PBE has two different derivations leading to the same GGA: one based upon exact properties of the exchange–correlation energy,¹² and one based upon exact properties of the exchange–correlation hole.¹⁶ The latter derivation also produces the Perdew–Wang 1991 (PW91) GGA,¹⁷ which is typically very close to PBE.

Meta-GGAs strive to improve upon the GGA by employing the kinetic energy density $\tau_{\sigma}(\mathbf{r})$ as an indicator¹⁸ of one-electron regions of $n_{\sigma}(\mathbf{r})$ and forcing the correlation energy density to vanish there. The presence of $\tau_{\sigma}(\mathbf{r})$ also enables one to reproduce gradient expansions of exchange and correlation energies for slowly varying densities through higher orders in ∇ than is possible in the GGA. Given expectations of a high return from these new constraints, it came as a surprise that the meta-GGA of Perdew, Kurth, Zupan, and Blaha¹⁹ (PKZB) proved less accurate than PBE for all molecular properties except atomization energies.^{11,20,21} The problems of PKZB have been identified and corrected in the meta-GGA approximation of Tao, Perdew, Staroverov, and

Scuseria²² (TPSS), which essentially completes the meta-GGA rung of Jacob's ladder. Other meta-GGAs have also been proposed recently,^{23–28} but, except for VSXC²⁵ and KCIS,^{27,29} they have not been tested extensively and some have yet to be implemented self-consistently.

The LSDA and the non-empirical PBE and TPSS are “universal” functionals based upon universal constraints and limits. Recent molecular tests³⁰ revealed an impressive increase in accuracy in the order LSDA < PBE < TPSS for atomization energies and a more moderate improvement for vibrational frequencies and hydrogen-bond properties; for other properties, the order is generally LSDA < PBE ≈ TPSS. Moreover, TPSS was found to match and occasionally exceed in accuracy the best semi-empirical and hybrid GGA functionals.

The LSDA as well as many GGAs and meta-GGAs were tested for twelve bulk solids and for jellium surfaces by Kurth, Perdew, and Blaha.¹¹ They found that semi-empirical functionals fitted to chemical data typically did not perform even as well as LSDA. The best results were obtained with functionals that were exact in the uniform-density limit and had no (LSDA, PBE) or one (PKZB) empirical parameter. In this work, we continue tests of the LSDA–PBE–TPSS ladder and focus on periodic systems and jellium surfaces. The PKZB functional, as a predecessor to TPSS, is also included for comparison.

II. DESCRIPTION OF THE FUNCTIONALS

The exchange components of the four functionals of the ladder are evaluated by the spin-scaling relation³¹

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} E_x[2n_\uparrow] + \frac{1}{2} E_x[2n_\downarrow], \quad (1)$$

where $E_x[n]$ is the corresponding functional for a spin-unpolarized system. In the case of LSDA,

$$E_x^{\text{LSDA}}[n] = \int n \epsilon_x^{\text{unif}}(n) d^3r, \quad (2)$$

where $\epsilon_x^{\text{unif}}(n) = -(3/4\pi)(3\pi^2n)^{1/3}$ is the exact LSDA exchange energy per particle. For the PBE GGA,¹²

$$E_x^{\text{PBE}}[n] = \int n \epsilon_x^{\text{unif}}(n) F_x^{\text{PBE}}(n, \nabla n) d^3r, \quad (3)$$

where $F_x^{\text{PBE}}(n, \nabla n)$ is an enhancement factor given by

$$F_x^{\text{PBE}}(n, \nabla n) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2 / \kappa}, \quad (4)$$

in which $s = |\nabla n| / (2n(3\pi^2n)^{1/3})$ is a dimensionless density gradient, while μ and κ are non-empirical constants.

The exchange components of the PKZB¹⁹ and TPSS²² meta-GGAs can be both represented by

$$E_x^{\text{MGGGA}}[n] = \int n \epsilon_x^{\text{unif}}(n) F_x^{\text{MGGGA}}(n, \nabla n, \tau) d^3r. \quad (5)$$

The enhancement factor is

$$F_x^{\text{MGGGA}}(n, \nabla n, \tau) = 1 + \kappa - \frac{\kappa}{1 + x/\kappa}, \quad (6)$$

where x is a complicated function of variables n , ∇n , and τ , which has different forms in PKZB and TPSS. When using Eq. (1), ∇n and τ in Eqs. (3) and (5) must be scaled by a factor of 2 just like the density.

Correlation components of the LSDA, PBE, PKZB, and TPSS functionals are not resolved into spin-up and spin-down components. The LSDA correlation is simply

$$E_c^{\text{LSDA}}[n_\uparrow, n_\downarrow] = \int n \epsilon_c^{\text{unif}}(n_\uparrow, n_\downarrow) d^3r, \quad (7)$$

where $n = n_\uparrow + n_\downarrow$. As indicated earlier, we used the Perdew–Wang parametrization for $\epsilon_c^{\text{unif}}(n_\uparrow, n_\downarrow)$. The PBE correlation has the form¹²

$$E_c^{\text{PBE}}[n_\uparrow, n_\downarrow] = \int n \epsilon_c^{\text{PBE}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) d^3r, \quad (8)$$

where

$$\epsilon_c^{\text{PBE}} = \epsilon_c^{\text{unif}}(n_\uparrow, n_\downarrow) + H(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow). \quad (9)$$

Here H is a gradient correction to the LSDA correlation. The function H is such that $H = 0$ if $n_\sigma(\mathbf{r}) = \text{const}$.

Both PKZB and TPSS are based upon self-correlation corrections to PBE. The PKZB correlation is given by¹⁹

$$E_c^{\text{PKZB}}[n_\uparrow, n_\downarrow] = \int \left\{ n \epsilon_c^{\text{PBE}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) \times \left[1 + C \left(\frac{\sum_\sigma \tau_\sigma^W}{\sum_\sigma \tau_\sigma} \right)^2 \right] - (1 + C) \times \sum_\sigma \left(\frac{\tau_\sigma^W}{\tau_\sigma} \right)^2 n_\sigma \epsilon_c^{\text{PBE}}(n_\sigma, 0, \nabla n_\sigma, 0) \right\} d^3r, \quad (10)$$

where $\tau_\sigma^W = |\nabla n_\sigma|^2 / 8n_\sigma$ is the Weizsäcker kinetic energy density and C is a (non-empirical) constant.

Finally, the TPSS correlation is given by²²

$$E_c^{\text{TPSS}}[n_\uparrow, n_\downarrow] = \int n \epsilon_c^{\text{revPKZB}} \left[1 + d \epsilon_c^{\text{revPKZB}} \left(\frac{\tau^W}{\tau} \right)^3 \right] d^3r, \quad (11)$$

where $\tau^W = |\nabla n|^2 / 8n$, d is a constant, and $\epsilon_c^{\text{revPKZB}}$ is the revised PKZB correlation energy per particle,

$$\begin{aligned} \epsilon_c^{\text{revPKZB}} = & \epsilon_c^{\text{PBE}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) \left[1 + C(\zeta, \xi) \left(\frac{\tau^W}{\tau} \right)^2 \right] \\ & - [1 + C(\zeta, \xi)] \left(\frac{\tau^W}{\tau} \right)^2 \sum_\sigma \frac{n_\sigma}{n} \\ & \times \max[\epsilon_c^{\text{PBE}}(n_\sigma, 0, \nabla n_\sigma, 0), \epsilon_c^{\text{PBE}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)]. \end{aligned} \quad (12)$$

Note that, in TPSS, C is a function of the spin polarization $\zeta = (n_\uparrow - n_\downarrow)/n$ and a variable $\xi = |\nabla \zeta|/2(3\pi^2 n)^{1/3}$. $C(\zeta, \xi)$ is designed to make $E_{xc}^{\text{TPSS}}[n_\uparrow, n_\downarrow]$ properly independent of ζ ($0 \leq |\zeta| \leq 0.7$) in the low-density limit.³² The $\max()$ function appears in Eq. (12) to ensure that $\epsilon_c^{\text{revPKZB}}$ is strictly negative everywhere.

As shown in Table I, the two meta-GGA functionals generally satisfy more constraints than their predecessors. The breakthrough in performance from PKZB to TPSS has been attributed²² to the satisfaction of the constraint “ $v_x(\mathbf{r})$ finite at the nucleus.” Note that PBE, PKZB, and TPSS all reduce to LSDA for a uniform density (this is one of the most basic requirements for approximate density functionals in applications to solids), while such common functionals as BLYP,^{14,15} B3LYP,³³ and VSXC²⁵ do not. Besides, in the low-density (strong-interaction) limit, TPSS recovers³² PKZB which is very accurate³⁴ for a spin-unpolarized density, while LSDA and PBE are severely wrong because of their self-interaction error in the correlation part.

III. BULK SOLIDS

A. Methodology

Our test set includes four basic types of crystalline systems: 4 main group metals (Li, Na, K, Al), 5 semiconductors (diamond, Si, β -SiC, Ge, GaAs), 5 ionic solids (NaCl, NaF, LiCl, LiF, MgO), and 4 transition metals (Cu, Rh, Pd, Ag). All 18 solids were calculated in their normal crystal structures (as indicated in Table II) and non-magnetic states.

The electron density in a crystal is approximately a superposition of atomic or ionic densities, so localized Gaussian-type orbitals (GTO) centered at the nuclei are well suited for such systems. The problem with GTO basis sets developed for atomic and molecular calculations is that they have diffuse functions (by which we mean GTOs with exponents of less than 0.05–0.10, depending on the structure type and lattice constant). Such functions decay very slowly with distance and thereby slow down dramatically the evaluation of Coulomb contributions to the total energy. Normally, diffuse functions have to be removed and the exponents of the remaining valence functions reoptimized. For many non-metals, molecular basis sets do not have diffuse functions and are already adapted for the crystalline phase. In particular, we found that the standard 6-31G* basis remains practical for C (diamond), Si, and SiC, while Ge can be calculated with an even larger 6-311G* basis.⁵⁰ No relativistic effects were included in the all-electron calculations. For Rh, Pd, and Ag we used the LANL effective core potentials⁴⁸ (ECP), which replace 28 core electrons ([Ar]3d¹⁰), in combination

TABLE I. Satisfaction (Yes/No) of selected exact constraints by approximate exchange–correlation functionals.

Constraint	LSDA	PBE	PKZB	TPSS
Global properties				
$E_x < 0$	Y	Y	Y	Y
$E_c \leq 0$	Y	Y	N	Y
$E_c = 0$ if $\int n(\mathbf{r}) d^3 r = 1$	N	N	Y	Y
$E_{xc} \geq -D \int n^{4/3}(\mathbf{r}) d^3 r^a$	Y	Y	YN ^b	Y
$E_{xc} = E_{xc}^{\text{LSDA}}, n_\uparrow, n_\downarrow = \text{const}$	Y	Y	Y	Y
$E_x = -U[n]$ if $\int n(\mathbf{r}) d^3 r = 1^c$	N	N	N	YN ^d
Highest order in ∇ for E_x^{GEA}	0	0	2 ^f	4
Highest order in ∇ for E_c^{GEA}	0	2	2	2
Spin and density scaling ^g				
$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} \sum_{\sigma=\uparrow, \downarrow} E_x[2n_\sigma]^h$	Y	Y	Y	Y
$E_x[n_\lambda] = \lambda E_x[n]^i$	Y	Y	Y	Y
$E_c[n_\lambda] > \lambda E_c[n], \lambda > 1^i$	Y	Y	Y	Y
$\lim_{\lambda \rightarrow \infty} E_c[n_\lambda] > -\infty^j$	N	Y	Y	Y
$\lim_{\lambda \rightarrow 0} \lambda^{-1} E_c[n_\lambda] > -\infty^j$	Y	Y	Y	Y
$\lim_{\lambda \rightarrow \infty} E_x[n_\lambda^x] > -\infty^j$	N	N	N	N
$\lim_{\lambda \rightarrow 0} E_x[n_\lambda^x] > -\infty^j$	Y	Y	Y	Y
$\lim_{\lambda \rightarrow \infty} E_c[n_\lambda^x] > -\infty^j$	N	Y	Y	Y
Asymptotic behavior				
$v_x(\mathbf{r}) \rightarrow -1/r, r \rightarrow \infty$	N	N	N	N
$v_x(\mathbf{r})$ finite at the nucleus	Y	N	N	YN ^k
$v_c(\mathbf{r})$ finite at the nucleus	Y	N	YN ^l	YN ^l

^aThe Lieb–Oxford bound (Refs. 17, 35). $1.44 < D < 1.68$ (or < 1.6358 —Ref. 36).

^bY for exchange, N for exchange–correlation.

^cCancellation of spurious electrostatic self-interaction energy in one-electron systems: $U[n] = \frac{1}{2} \int d^3 r \int d^3 r' n(\mathbf{r}) n(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d^3 r'$.

^dY for a one-electron exponential density.

^eThe highest correct order in the gradient expansion approximation (GEA) for slowly-varying densities. The true GEA is known to fourth order in ∇ for exchange (Ref. 37) and to second order for correlation (Ref. 38).

^fTwo of the three fourth-order terms are also reproduced (Ref. 19).

^gUniform scaling of the density: $n_\lambda(\mathbf{r}) = \lambda^3 n(\lambda \mathbf{r})$; non-uniform scaling: $n_\lambda^x(x, y, z) = \lambda n(\lambda x, y, z)$. See Ref. 39 for a review.

^hDerived in Ref. 31.

ⁱDerived in Ref. 40.

^jDerived in Ref. 41.

^kY for one- and spin-compensated two-electron densities.

^lY for one-electron densities.

with double-zeta quality GTO valence basis sets optimized for bulk metals.⁴⁹ Note that the ECPs absorb some relativistic effects. Our final selection of basis sets is documented in Table II. No auxiliary basis sets for the charge density were used.

All calculations on solids were performed self-consistently using a development version of the GAUSSIAN program.⁵¹ The implementation of periodic boundary conditions (PBC) in the GAUSSIAN program has been described in detail before.⁵² In this approach, all terms contributing to the KS Hamiltonian are evaluated in real space, including the infinite Coulomb summations, which are calculated with the

TABLE II. Gaussian-type basis sets used for calculations of the bulk solids. The number of contracted GTOs of each type is indicated in square brackets. Cartesian basis sets use all six components of d -functions; “pure” basis sets exclude s -type combinations ($d_{x^2} + d_{y^2} + d_{z^2}$).

Solid	Structure type	Basis set
Li	A2 (bcc)	[4s, 3p, 1d] (pure) ^a
Na	A2 (bcc)	[5s, 3p, 1d] (Cartesian) ^b
K	A2 (bcc)	[6s, 4p, 1d] (Cartesian) ^b
Al	A1 (fcc)	[6s, 3p, 1d] (Cartesian) ^c
C	A4 (diamond)	6-31G* (Cartesian)
Si	A4 (diamond)	6-31G* (Cartesian)
SiC	B3 (zincblende)	6-31G* (Cartesian)
Ge	A4 (diamond)	6-311G* (pure)
GaAs	B3 (zincblende)	[6s, 5p, 2d]/6-311G* (pure) ^d
NaCl	B1 (cubic)	[6s, 4p, 1d]/6-311G* (pure) ^e
NaF	B1 (cubic)	[6s, 4p, 1d]/6-311G* (pure) ^e
LiCl	B1 (cubic)	[4s, 3p, 1d]/6-311G* (pure) ^f
LiF	B1 (cubic)	[4s, 3p, 1d]/6-311G* (pure) ^f
MgO	B1 (cubic)	[4s, 3p, 1d]/[4s, 3p, 1d] (pure) ^g
Cu	A1 (fcc)	[6s, 5p, 2d] (pure) ^h
Rh	A1 (fcc)	ECP-[4s, 4p, 2d] (pure) ⁱ
Pd	A1 (fcc)	ECP-[4s, 4p, 2d] (pure) ⁱ
Ag	A1 (fcc)	ECP-[4s, 4p, 2d] (pure) ⁱ

^aReference 42.

^bReference 43.

^cReference 44.

^dThe basis set for Ga is from Ref. 45.

^e6-311G* basis with modifications for Na: exponents of the two outer primitive s functions were multiplied by 6, the contraction of two p functions was resolved into primitives, and the two outer p functions were eliminated.

^f6-311G* basis with modifications for Li: exponents of the two outer sp functions were multiplied by 6.

^gReference 46.

^hAll-electron basis of Ref. 47. The second from last sp exponent is 0.610 for LSDA, 0.596 for all other methods.

ⁱLANL effective core potential (Ref. 48) with the GTO basis of Ref. 49.

aid of the fast multipole method,⁵³ expanded and implemented for Gaussian orbitals⁵⁴ and periodic systems⁵⁵ with arbitrary unit cells.⁵⁶ Reciprocal space integration for metals takes advantage of a recently developed methodology for these cases.⁵⁷ The number of \mathbf{k} points employed is sufficiently large to achieve convergence in all types of solids, typically ranging from 500 (for semiconductors) to as many as 6300 (for metals).

Both LSDA and GGA are explicit functionals of the density. The meta-GGA makes use of the kinetic energy density $\tau_\sigma(\mathbf{r})$ and, therefore, is only an implicit functional of $n_\sigma(\mathbf{r})$. The implicit dependence poses no fundamental problem and can be treated strictly within the KS scheme by the optimized effective potential method.^{58,59} Alternatively, self-consistent calculations with τ -dependent functionals can use the approach of Neumann *et al.*,⁶⁰ which we have followed

here. In our experience, a self-consistent PBC meta-GGA calculation requires about the same computer time as GGA on most machines.

We estimated the equilibrium lattice constants a_0 and bulk moduli B_0 at $T=0$ K by calculating the total energy per unit cell at 7–10 points in the range $V_0 \pm 5\%$ (where V_0 is the equilibrium unit cell volume), fitting the data to an analytic equation of state (EOS) $E(V)$, and differentiating the latter. Unit cell volumes are related to the lattice constants as follows: $V=a^3/4$ (fcc, cubic, diamond, and zincblende structures); $V=a^3/2$ (bcc). The equilibrium bulk modulus is given by

$$B_0 = B|_{V=V_0} = -V \left. \frac{dP}{dV} \right|_{V=V_0} = V \left. \frac{d^2E}{dV^2} \right|_{V=V_0}. \quad (13)$$

Also of interest is the first pressure derivative of the bulk modulus at equilibrium

$$B_1 = \left. \frac{dB}{dP} \right|_{V=V_0}. \quad (14)$$

We compared two forms of the $E(V)$ function: the traditional Murnaghan EOS⁶¹ and the “stabilized jellium” (SJ) EOS.^{62,63} Unlike the Murnaghan EOS, the SJEOS is theoretically motivated (by the picture of a weak local electron-ion pseudopotential). It is also realistic over a larger range of V than prior equations of state.⁶² The SJEOS has been applied not only to metals^{62,64} but even to actinide oxides.⁶⁵

For present purposes, it is convenient to cast the Murnaghan EOS in the form

$$E(V) = \frac{B_0 V}{B_1(B_1 - 1)} \left[B_1 \left(1 - \frac{V_0}{V} \right) + \left(\frac{V_0}{V} \right)^{B_1} - 1 \right] + E_0, \quad (15)$$

where $E_0 = E(V_0)$. A nonlinear fit to Eq. (15) produces parameters V_0 , B_0 , B_1 , and E_0 directly.

The stabilized jellium equation of state (SJEOS) is

$$E(V) = \alpha \left(\frac{V_0}{V} \right) + \beta \left(\frac{V_0}{V} \right)^{2/3} + \gamma \left(\frac{V_0}{V} \right)^{1/3} + \omega. \quad (16)$$

Equation (16) has a very physical form. For a uniform electron gas, the $V^{-2/3}$ term mimics the kinetic energy, the $V^{-1/3}$ term the exchange energy (and the Madelung energy, if any), and the V^0 term the correlation energy. The V^{-1} term mimics the first-order effect of the pseudopotential core repulsion in a simple metal. A linear fit to the SJEOS yields parameters $\alpha_s = \alpha V_0$, $\beta_s = \beta V_0^{2/3}$, $\gamma_s = \gamma V_0^{1/3}$, and ω , from which

$$V_0 = \left(-\frac{\beta_s + \sqrt{\beta_s^2 - 3\alpha_s\gamma_s}}{\gamma_s} \right)^3, \quad (17a)$$

$$B_0 = \frac{18\alpha + 10\beta + 4\gamma}{9V_0}, \quad (17b)$$

$$B_1 = \frac{108\alpha + 50\beta + 16\gamma}{27B_0V_0}, \quad (17c)$$

$$E_0 = \alpha + \beta + \gamma + \omega. \quad (17d)$$

Cohesive energies ε_0 were evaluated as the difference between the total lattice energy per atom at the equilibrium lattice constant (using the SJEOS) and the spin-unrestricted (i.e., spin-polarized) ground-state energy of the isolated atom(s). The difference was corrected for zero-point motion effects by subtracting the zero-point energy (ZPE) estimated from the Debye temperature Θ_D of the solid ($\varepsilon_{\text{ZPE}} = \frac{9}{8} k_B \Theta_D$).⁶² Experimental values of Θ_D were taken from Ref. 66; for SiC, we used the theoretical estimate $\Theta_D = 1232$ K (at 0 K) of Ref. 67.

B. Results

1. Lattice constants

The equilibrium lattice constants calculated by fitting $E(V)$ to the SJEOS were found to agree with the corresponding Murnaghan EOS values at least to the third decimal place. As seen from the mean error (m.e.) in Table III, LSDA underestimates and PKZB overestimates equilibrium lattice constants for all 18 solids without exception. PBE and TPSS produce mixed result, but clearly tend toward overestimation. Judging by either the mean absolute error (m.a.e.) or the mean absolute relative error (m.a.r.e.), PKZB is the worst performer for the lattice structure, while TPSS is the best. For LSDA and PBE, our GTO results are in a very good agreement with the linearized augmented plane-wave calculations of the equilibrium unit cell volumes reported by Kurth *et al.*¹¹ For PKZB, the agreement is not so perfect (the largest deviation of 0.2 Å is observed for NaCl), possibly because the PKZB values of Kurth *et al.* are based on PBE orbitals and densities, while our PKZB calculations are fully self-consistent.

The experimental lattice constants contain a small contribution from zero-point anharmonic expansion which is not included in our density functional calculations and is traditionally neglected in solid state studies. This effect may be estimated from Eq. (A6) of Ref. 62,

$$\frac{\Delta a_0}{a_0} = \frac{1}{3} \frac{\Delta V_0}{V_0} = \frac{3}{16} (B_1 - 1) \frac{k_B \Theta_D}{B_0 V_0}. \quad (18)$$

The experimental a_0 shown in parentheses in Table III have this estimate subtracted out. [In Eq. (18), we used experimental a_0 , B_0 , and Θ_D along with the theoretical $\tilde{B}_1^{\text{TPSS}}$ values from Table V]. The corresponding error statistics are also shown in parentheses. With this correction, the lattice constants of our test set of solids behave like the bond lengths of our test set of molecules³⁰ (which make the corresponding correction): LSDA and TPSS have about the same mean absolute error; PBE is slightly and PKZB is substantially less accurate than TPSS, with too-long lattice constants or bond lengths.

On the first three rungs of the density functional ladder, exchange–correlation interaction occurs only through density overlap. Thus these rungs are not expected to provide a good description of lattice constants in van der Waals-bound

TABLE III. Equilibrium lattice constants (Å) of the 18 test solids at 0 K calculated from the SJEOS of Eq. (16). The Murnaghan EOS of Eq. (15) yields identical results within the reported number of decimal places. Experimental a_0 values are from Ref. 68 (Li) and Ref. 69 (Na, K, Al, NaCl, NaF, LiCl, LiF, MgO). The rest are based on room temperature values corrected to the $T=0$ limit using linear thermal expansion coefficients from Ref. 70. The numbers in parentheses refer to experimental values with an estimate of the zero-point anharmonic expansion subtracted out. (The calculated values are precise to within 0.001 Å for the given basis sets, although basis-set incompleteness limits the accuracy to one less digit.)

Solid	a_0^{LSDA}	a_0^{PBE}	a_0^{PKZB}	a_0^{TPSS}	Expt.
Li	3.383	3.453	3.512	3.475	3.477(3.451)
Na	4.049	4.199	4.305	4.233	4.225(4.210)
K	5.093	5.308	5.494	5.362	5.225(5.212)
Al	4.008	4.063	4.040	4.035	4.032(4.020)
C	3.544	3.583	3.592	3.583	3.567(3.556)
Si	5.426	5.490	5.475	5.477	5.430(5.423)
SiC	4.351	4.401	4.404	4.392	4.358(4.349)
Ge	5.633	5.765	5.729	5.731	5.652(5.646)
GaAs	5.592	5.726	5.698	5.702	5.648(5.643)
NaCl	5.471	5.698	5.801	5.696	5.595(5.580)
NaF	4.505	4.700	4.764	4.706	4.609(4.594)
LiCl	4.968	5.148	5.220	5.113	5.106(5.090)
LiF	3.904	4.062	4.109	4.026	4.010(3.987)
MgO	4.156	4.242	4.265	4.224	4.207(4.197)
Cu	3.530	3.636	3.616	3.593	3.603(3.596)
Rh	3.791	3.871	3.844	3.846	3.798(3.793)
Pd	3.851	3.950	3.928	3.917	3.881(3.877)
Ag	3.997	4.130	4.101	4.076	4.069(4.064)
m.e.	−0.069	0.052	0.078	0.039	...
(Å)	(−0.058)	(0.063)	(0.089)	(0.050)	...
m.a.e.	0.069	0.057	0.078	0.040	...
(Å)	(0.058)	(0.064)	(0.089)	(0.050)	...
m.a.r.e.	1.55	1.25	1.65	0.83	...
(%)	(1.31)	(1.40)	(1.92)	(1.07)	...

layered solids like graphite,⁷¹ although they might be able to describe the equilibrium bond lengths of rare gas dimers.^{72,73}

2. Bulk moduli

The equilibrium bulk moduli estimated from fits to the Murnaghan EOS and SJEOS are summarized in Table IV. The SJEOS predicts slightly higher values than the Murnaghan equation, but regardless of which EOS was used, (i) PBE bulk moduli are roughly twice as accurate as those from LSDA; (ii) neither PKZB nor TPSS succeeds in improving upon PBE for B_0 values.

When assessing the performance of approximate density functionals for bulk moduli, one should keep in mind the following. According to Table III, theoretical equilibrium unit cell volumes can deviate from experiment by as much as 5%. Since the bulk modulus is evaluated at the theoretical V_0 , an error in V_0 translates into an even larger error in B_0 . Inasmuch as LSDA, PBE, PKZB, and TPSS are very good approximations for the exchange–correlation energy of the

TABLE IV. Equilibrium bulk moduli (GPa) of the 18 test solids at 0 K calculated from equations of state (15) and (16). The third section lists bulk moduli corrected by Eq. (21). Experimental values, also for 0 K, are from Ref. 74 (Li), Ref. 75 (Na, extrapolated to 0 K), Ref. 76 (K), Ref. 77 (Al), Ref. 78 (C), Ref. 69 (Si, Ge, GaAs), Ref. 79 (SiC, 298 K), Ref. 80 (NaCl, NaF, LiCl), Ref. 81 (LiF), Ref. 82 (MgO), Ref. 83 (Cu), Ref. 84 (Rh), Ref. 85 (Pd), and Ref. 86 (Ag).

Solid	Murnaghan EOS				SJEOS				Corrected SJEOS				Expt.
	B_0^{LSDA}	B_0^{PBE}	B_0^{PKZB}	B_0^{TPSS}	B_0^{LSDA}	B_0^{PBE}	B_0^{PKZB}	B_0^{TPSS}	$\tilde{B}_0^{\text{LSDA}}$	\tilde{B}_0^{PBE}	$\tilde{B}_0^{\text{PKZB}}$	$\tilde{B}_0^{\text{TPSS}}$	
Li	14.7	13.6	13.2	13.2	14.7	13.7	13.2	13.2	13.2	13.3	13.8	13.2	13.0
Na	9.1	7.7	7.4	7.3	9.2	7.8	7.4	7.3	7.3	7.5	8.0	7.4	7.5
K	4.6	3.8	3.5	3.6	4.6	3.8	3.5	3.6	4.0	4.1	4.1	4.2	3.7
Al	81.8	76.2	88.9	84.7	82.5	76.8	89.4	85.2	78.9	81.4	90.6	85.7	79.4
C	454	422	418	417	458	426	422	421	443	436	438	431	443
Si	95.1	88.6	94.6	91.5	95.6	89.0	94.9	91.9	95.1	95.6	99.4	96.8	99.2
SiC	224	207	211	211	225	209	212	213	223	221	225	223	225
Ge	75.7	62.8	67.9	66.2	75.9	63.0	68.1	66.4	73.8	74.3	76.1	74.5	75.8
GaAs	81.1	68.0	71.6	70.0	81.3	68.1	71.8	70.1	75.4	75.3	76.7	75.1	75.6
NaCl	32.2	23.7	21.5	22.9	32.5	23.9	21.6	23.0	27.0	27.7	27.5	26.6	26.6
NaF	62.8	47.3	44.3	43.7	63.3	47.7	44.5	44.0	53.3	54.1	54.6	50.6	51.4
LiCl	41.8	32.7	29.8	34.1	42.0	32.9	30.0	34.3	34.6	34.8	34.7	34.6	35.4
LiF	86.8	65.4	65.0	66.5	87.5	65.9	65.4	67.2	72.4	71.7	76.4	69.1	69.8
MgO	182	161	159	168	183	162	160	169	171	170	172	173	165
Cu	188	150	161	171	192	153	163	173	161	164	167	170	142
Rh	303	239	248	257	309	243	253	262	304	289	284	294	269
Pd	235	177	184	200	240	180	187	203	222	215	211	223	195
Ag	149	106	115	127	153	107	117	129	126	125	126	131	109
m.e. (GPa)	13.1	-7.4	-4.5	-1.7	14.7	-6.3	-3.4	-0.5	5.5	4.1	5.5	5.4	...
m.a.e. (GPa)	13.7	8.4	8.4	8.4	15.1	7.6	7.8	8.2	6.6	6.0	6.2	7.7	...
m.a.r.e. (%)	15.2	7.1	8.0	7.6	16.2	6.8	7.8	7.5	5.1	5.0	6.3	5.9	...

valence electrons in most solids, errors in lattice constant and bulk moduli probably arise⁸⁷ from inadequacies of the description of core–valence exchange–correlation interaction. Alchagirov *et al.*⁶² reasoned that, since the core–valence interaction within a pseudopotential picture is built into the electron-ion pseudopotential represented by the first (V^{-1}) term of Eq. (16), the error in a_0 and B_0 can be reduced by modifying this term’s prefactor:

$$\tilde{E}(V) = \tilde{\alpha} \left(\frac{V_0}{V} \right) + \beta \left(\frac{V_0}{V} \right)^{2/3} + \gamma \left(\frac{V_0}{V} \right)^{1/3} + \tilde{\omega}, \quad (19)$$

where $\tilde{\alpha}$ is adjusted to make $\tilde{P} = -d\tilde{E}/dV$ vanish at the experimental equilibrium unit cell volume, $V = V_0^{\text{expt}}$. The latter condition gives

$$\tilde{\alpha} = -\frac{2\beta x_0 + \gamma x_0^2}{3}, \quad (20)$$

where $x_0 = (V_0^{\text{expt}}/V_0)^{1/3}$. Combining Eqs. (13), (14), (19), and (20), we obtain the corrected bulk modulus⁶²

$$\tilde{B}_0 = -\frac{2}{9V_0^{\text{expt}}} \left(\frac{\beta}{x_0^2} + \frac{\gamma}{x_0} \right) \quad (21)$$

and its pressure derivative

$$\tilde{B}_1 = \frac{11\beta + 10\gamma x_0}{3(\beta + \gamma x_0)}. \quad (22)$$

As seen from Table IV, the spread of \tilde{B}_0 values predicted by various functionals is much smaller than the spread of B_0 values obtained from the original SJEOS for all solids except Al. As a result, the statistics of deviations is nearly the same for all four functionals. It should also be remembered that uncertainties in experimental bulk moduli are much greater than in lattice constants and can easily be as large as 10%. In fact, whenever the corrected functional-averaged \tilde{B}_0 value differs appreciably from experiment, the theoretical estimate may be more accurate. In Table IV, systematic deviations of \tilde{B}_0 from experiment are observed only for the transition metals (Cu, Rh, Pd, Ag). However, since the basis sets used for these metals are the least flexible in the group, the discrepancy is probably due to basis set effects rather than experimental errors. Another possibility is that the discrepancy between corrected SJEOS and experimental B_0 for the transition metals may arise from a failure of the underlying picture of a weak local electron–ion pseudopotential. If the four transition metals are excluded from the test set, the corresponding mean absolute errors of \tilde{B}_0 values fall to 1.5 (LSDA), 2.2 (PBE), 2.7 (PKZB), and 2.5 GPa (TPSS); the mean absolute relative errors become 2.5%, 3.0%, 4.7%, and 3.0%, respectively.

The pressure derivative of the bulk modulus at equilib-

TABLE V. Dimensionless pressure derivatives of the bulk moduli at equilibrium for the 18 test solids at 0 K calculated from fits to Eqs. (15) and (16). The third section lists B_1 values corrected by Eq. (22).

Solid	Murnaghan EOS				SJEOS				Corrected SJEOS			
	B_1^{LSDA}	B_1^{PBE}	B_1^{PKZB}	B_1^{TPSS}	B_1^{LSDA}	B_1^{PBE}	B_1^{PKZB}	B_1^{TPSS}	\bar{B}_1^{LSDA}	\bar{B}_1^{PBE}	\bar{B}_1^{PKZB}	\bar{B}_1^{TPSS}
Li	3.36	3.35	3.34	3.30	3.33	3.34	3.33	3.32	3.33	3.34	3.33	3.32
Na	3.79	3.61	3.32	3.49	3.80	3.62	3.32	3.53	3.80	3.62	3.32	3.53
K	3.88	3.38	3.15	3.75	3.88	3.40	3.14	3.76	3.89	3.40	3.13	3.75
Al	4.59	4.43	4.37	4.50	4.56	4.53	4.26	4.37	4.58	4.51	4.26	4.37
C	3.69	3.80	3.82	3.83	3.71	3.78	3.82	3.81	3.71	3.78	3.82	3.81
Si	4.13	4.18	3.82	3.93	4.09	4.18	3.89	4.00	4.09	4.16	3.89	4.00
SiC	3.81	3.95	3.94	4.00	3.84	3.98	3.98	4.01	3.84	3.97	3.97	4.01
Ge	4.73	4.77	4.79	4.78	4.76	4.81	4.80	4.80	4.77	4.72	4.73	4.74
GaAs	4.46	4.45	4.50	4.42	4.48	4.47	4.53	4.42	4.51	4.44	4.51	4.40
NaCl	4.80	4.74	4.22	4.82	4.71	4.76	4.24	4.73	4.82	4.68	4.19	4.65
NaF	4.44	4.17	4.16	4.21	4.49	4.19	4.07	4.25	4.56	4.16	4.04	4.22
LiCl	4.33	4.37	4.32	4.48	4.33	4.31	4.25	4.38	4.38	4.30	4.22	4.38
LiF	4.38	4.31	4.16	4.46	4.32	4.20	4.13	4.40	4.38	4.18	4.11	4.39
MgO	3.92	3.85	3.81	3.78	3.90	3.85	3.81	3.87	3.90	3.85	3.80	3.87
Cu	4.82	4.69	4.59	4.54	4.77	4.67	4.47	4.56	4.87	4.64	4.46	4.57
Rh	4.99	4.94	5.17	5.07	5.01	5.15	5.21	5.12	5.02	5.01	5.11	5.03
Pd	5.28	5.61	5.47	5.33	5.37	5.46	5.38	5.33	5.46	5.28	5.26	5.24
Ag	5.45	5.35	5.20	5.36	5.51	5.45	5.28	5.26	5.75	5.29	5.21	5.25

rium, B_1 , has also been calculated. The results are presented in Table V, not as a test of the ladder but for completeness. The table shows the differences among the functionals and among the equations of state. The reasonable agreement of B_1 between the Murnaghan EOS and SJEOS is a consequence of the fact that both have been fitted in a very narrow range of V about V_0 . The values in Table V can be used with the SJEOS to predict the pressure $P = -dE/dV$ over a wide range of volumes in these solids.

3. Cohesive energies

Calculations of cohesive energies (ϵ_0) with GTO basis sets can be problematic. Diffuse functions, normally present in molecular basis sets, cause an enormous slowdown in the evaluation of Coulomb terms in periodic systems, and have to be removed. On the other hand, a basis set without diffuse functions is inadequate for isolated atoms. Thus, we can reliably report cohesive energies only for those solids that were computed with full molecular basis sets: C, Si, SiC, and Ge. It has been argued that since diffuse functions have a small effect on the total energy of the solid, they can be dispensed with in PBC calculations and then restored in the calculation of atomic energies. We believe that the use of different basis sets for atoms and solids is best avoided for metals and semiconductors, but is acceptable for the cations of ionic solids which are relatively insensitive to the presence of diffuse functions. In this manner, we have computed cohesive energies for the four alkali halides after restoring the Li and Na basis sets to the original 6-311G*.

As seen in Table VI, LSDA overbinds crystals by roughly 15%, which is nearly as large as the relative LSDA overbinding error reported for the G2 test set⁹⁰ of molecular atomiza-

tion energies.²² For Si, our ϵ_0^{LSDA} agrees with that of Ref. 91, while for Ge our nonrelativistic cohesive energy is 0.2 eV higher than the relativistic LSDA value of Ref. 91. PBE, PKZB, and TPSS are much more accurate with an error averaging 3%. Although the performance improves slightly in the order PKZB < TPSS < PBE, our test set is insufficient to pronounce this trend to be true in general.

IV. JELLIUM SURFACE ENERGY

Jellium, a system of electrons neutralized by a uniform positive background of density $\bar{n} = 3/4\pi r_s^3$, where r_s is the

TABLE VI. Cohesive energies (eV/atom) of 8 selected solids at 0 K, corrected for zero-temperature motion effects. Experimental values are based on zero-temperature enthalpies of formation ($\Delta_f H_0^\circ$) of the crystals and gaseous atoms taken from Ref. 88 (Ge) and Ref. 89 (all others).

Solid	ϵ_0^{LSDA}	ϵ_0^{PBE}	ϵ_0^{PKZB}	ϵ_0^{TPSS}	Expt.
C	8.83	7.62	7.14	7.12	7.37
Si	5.26	4.50	4.39	4.36	4.62
SiC	7.25	6.25	5.98	6.02	6.37
Ge	4.72	3.82	3.58	3.78	3.87
NaCl	3.58	3.16	3.15	3.18	3.31
NaF	4.50	3.96	3.81	3.87	3.93
LiCl	3.88	3.41	3.33	3.41	3.55
LiF	5.02	4.42	4.25	4.32	4.40
m.e. (eV/atom)	0.70	-0.04	-0.22	-0.17	...
m.a.e. (eV/atom)	0.70	0.11	0.22	0.17	...
m.a.e. (%)	14.4	2.4	4.9	3.5	...

TABLE VII. Surface exchange and exchange–correlation energies (erg/cm²) for jellium computed using LSDA-xc orbitals and densities. Non-TPSS values are from Ref. 11. Exact σ_x values are from Ref. 92. “Exact” xc values are from Ref. 93.

r_s (bohr)	Exchange					Exchange–correlation					
	σ_x^{LSDA}	σ_x^{PBE}	σ_x^{PKZB}	σ_x^{TPSS}	σ_x^{exact}	$\sigma_{xc}^{\text{LSDA}}$	σ_{xc}^{PBE}	$\sigma_{xc}^{\text{PKZB}}$	$\sigma_{xc}^{\text{TPSS}}$	$\sigma_{xc}^{\text{TPSSh}}$	$\sigma_{xc}^{\text{“exact”}}$
2.00	3037	2438	2578	2553	2624	3354	3265	3402	3380	3387	3413
2.07	2674	2127	2252	2231	2296	2961	2881	3002	2985	2992	3015
2.30	1809	1395	1484	1469	1521	2019	1962	2048	2035	2040	2060
2.66	1051	770	825	817	854	1188	1152	1205	1198	1202	1214
3.00	669	468	505	497	526	764	743	779	772	775	781
3.28	477	318	346	341	364	549	533	560	556	558	563
4.00	222	128	142	141	157	261	252	266	266	268	268
5.00	92	40	47	47	57	111	107	113	113	114	113
6.00	43	12	15	15	22	53	52	55	55	56	54
m.e. (erg/cm ²)	184	−81	−25	−34	...	−25	−59	−6	−13	−10	...
m.a.e. (erg/cm ²)	184	81	25	34	...	25	59	6	14	11	...
m.a.r.e. (%)	36.7	16.7	8.6	9.4	...	2.1	4.9	0.6	1.1	1.1	...

Seitz radius, is a simplified model for a bulk simple metal like Na or Al. Termination of the positive background at the plane $x=0$ defines the jellium model of a metal surface, with the background filling the half-space $x<0$. The surface energy σ is the energy per unit area needed to make such a cut through bulk jellium. The exchange–correlation contribu-

$$\sigma_{xc} = \int_{-\infty}^{\infty} n(x) [\epsilon_{xc}(x) - \epsilon_{xc}(-\infty)] dx, \quad (23)$$

is typically several times bigger than the total surface energy.

The first self-consistent calculations for the jellium surface were reported by Lang and Kohn⁹⁴ within the LSDA. However, since the exact solution for the jellium surface is not known, the magnitude of the exact σ_{xc} is still a matter of debate. Various methods have been applied, such as wave vector interpolation,⁹⁵ the Fermi hypernetted chain approximation,⁹⁶ and diffusion Monte Carlo.⁹⁷ More recently, Pitarke and Eguiluz⁹² calculated $\sigma_{xc} = \sigma_x + \sigma_c$ for jellium with the random phase approximation (RPA), which provided exact σ_x and approximate σ_c values. Yan, Perdew, and Kurth⁹³ estimated σ_{xc} beyond RPA by including a GGA “short-range” correction to RPA. We believe that this is the best estimate of σ_{xc} , and will take it to be “exact” here. This estimate agrees closely with several others, including a “long-range” wave vector interpolation correction to GGA,⁹⁸ surface energies extracted⁹⁹ from diffusion Monte Carlo calculations for jellium spheres of increasing radius,¹⁰⁰ and an exchange–correlation kernel correction to RPA.¹⁰¹ (For earlier studies of jellium spheres, see Ref. 102).

Using a modified jellium surface code,¹⁰³ we have evaluated LSDA, PBE, PKZB, and TPSS σ_x and σ_{xc} (see Table VII). Equation (15) of Ref. 99 can be used to interpolate or extrapolate the r_s dependence of σ_{xc} . All calculations in both tables use the LSDA-xc orbitals and densities, since self-consistency effects beyond LSDA are small.

Table VII shows that surface exchange energies σ_x are overestimated by LSDA, the error ranging from 16% at $r_s = 2$ bohr to almost 100% at $r_s = 6$ bohr (the typical range of valence–electron bulk densities). PBE values are better, but overshoot the needed correction to LSDA. PKZB and TPSS values are best.

Approximate surface exchange–correlation energies σ_{xc} are typically better due to a cancellation of error between exchange and correlation. LSDA values are accurate but tend to be a little too low. PBE produces still lower and less accurate values, while PKZB, and TPSS produce higher and more accurate values in comparison with LSDA. The too-low PBE values seem to arise^{11,98} from the use in PBE of a second-order gradient coefficient for the exchange energy that is too large in magnitude. This gradient coefficient is corrected in PKZB and TPSS. It is only at the meta-GGA rung of Jacob’s ladder that one can have the correct second-order gradient coefficient for exchange and also an accurate account of the linear response of a uniform density.^{12,104}

The hybrid TPSS (TPSSh) surface xc energy given in the penultimate column of Table VII is defined by

$$\sigma_{xc}^{\text{TPSSh}} = \sigma_{xc}^{\text{TPSS}} + a_x (\sigma_x^{\text{exact}} - \sigma_x^{\text{TPSS}}), \quad (24)$$

where $a_x = 0.10$ is an empirical parameter determined in Ref. 30 from a fit to atomization energies of molecules. The TPSSh σ_{xc} are only marginally better than the TPSS values. (Because of the difficulty of evaluating exact exchange for solid metals, we have not tested TPSSh for bulk solids.)

Surface energies for real metals¹⁰⁵ have been calculated and measured, but the measurements do not seem accurate enough to discriminate among the functionals tested here. The correction to the LSDA or PBE surface energy of jellium can be transferred^{106–108} to real surfaces, and is relevant to other properties such as vacancy formation^{107,109} and adhesion¹⁰⁸ energies. The TPSS functional should enable reliable direct calculations of such properties.

V. CONCLUSIONS

In agreement with earlier studies,¹¹ we find that the PBE GGA is a significant improvement over LSDA for most bulk solid properties. The progress from the PBE GGA to the TPSS meta-GGA is moderate. Among the four tested functionals of Jacob's ladder, TPSS has the best agreement with experiment for lattice constants. Although convergence with respect to basis set remains to be studied, neither PKZB nor TPSS appear to be more accurate than PBE for bulk moduli and cohesive energies. The TPSS functional corrects the main PKZB error—overestimation of lattice constants for ionic and, to a lesser extent, metallic crystals.

We have also supported the idea that most of the error of LSDA, PBE, PKZB and TPSS for bulk solids arises in the description of core–valence (not valence–valence) interaction,⁸⁷ by demonstrating that it can be removed through adjustment of the corresponding term in the equation of state. On the other hand, functionals that are not exact in the uniform-density limit, such as BLYP, can make sub-

stantial errors in the valence–valence interaction.

For the jellium surface energy, PBE is less accurate than LSDA, but PKZB and TPSS are more accurate. Overall, TPSS gives the best description of solids and surfaces, as it was found to do for molecules in earlier work.³⁰ In particular, we think that TPSS should be good for situations that are intermediate between molecules and solids (e.g., clusters) and for combinations of both (e.g., chemical reactions on a solid surface).

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