

# Accurate and Numerically Efficient rSCAN meta-Generalized Gradient Approximation

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The recently proposed rSCAN functional [J. Chem. Phys. 150, 161101 (2019)] is a regularized form of the SCAN functional [Phys. Rev. Lett. 115, 036402 (2015)] that improves SCAN’s numerical performance at the expense of breaking constraints known from the exact exchange-correlation functional. We construct a new meta-generalized gradient approximation by restoring exact constraint adherence to rSCAN. The resulting functional maintains rSCAN’s numerical performance while restoring the transferable accuracy of SCAN.

**Introduction** There is a fundamental trade-off at the heart of all large scale chemical and material computational studies between prediction accuracy and computational efficiency. The level of theory used must simultaneously make accurate and efficient material property predictions. For many projects, Kohn–Sham density functional theory (KS-DFT) presents an appealing compromise, delivering useful accuracy and favorable algorithmic complexity.

The Materials Project database presents a case study of finding such a balance[1], stating an ambitious mission of “removing the guesswork from materials design by computing properties of all known materials”[2]. At the time of writing, the database lists 125,000 inorganic structures calculated from KS-DFT using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation (XC) functional [3]. While GGA functionals can be impressively accurate for many properties, they cannot be systemically accurate for all properties [4–6], and the last 10 years have shown that meta-GGA functionals can improve predictions for similar computational cost.

Meta-GGAs are commonly designed around constraints known for the exact XC functional while minimizing the number of free parameters that must be fit. Functionals derived in this way are termed “non-empirical,” and we refer the reader to the supplemental material of Ref. 7 for precise definitions of all the exact constraints known for meta-GGAs. Alternatively, the functional can be built from a more flexible form that allows some exact constraints to be broken, so that free parameters can be tuned for accuracy to reference data sets. Functionals taking the latter route, termed “empirical” functionals, tend to be less reliable for systems outside their fitting sets, making a non-empirical functional desirable for large scale applications.

The strongly constrained and appropriately normed (SCAN) functional [7] recovers all 17 exact constraints

presently known for meta-GGA functionals and has shown good transferable accuracy, even for systems challenging for DFT methods. Examples include predicting accurate geometries and energetics for diverse ice and silicon phases [8], and for polymorphs of MnO<sub>2</sub> [9]. SCAN accurately reproduces the complex doping driven metal-insulator transition, magnetic structure, and charge-spin stripe phases of cuprate [10–12] high-temperature superconductors and iridates [13]. It is one of the few functionals that predicts ice as less dense than liquid water under standard conditions [14], and its description of intermediate range van der Waals interactions has been used to study the dynamics of liquid water [14, 15]. Combination of SCAN with beyond DFT techniques such as van der-Waals functionals and the Hubbard *U* self-interaction correction have proven effective for modelling the ionic and electronic structures of transition metal oxides[16–18].

Despite these successes, SCAN’s utility for large scale projects is limited by its sensitivity to the density of the numerical integration grid used during calculation. This poor numerical performance in many codes mandates the use of dense integration grids which reduces SCAN’s computational efficiency [19, 20], and divergence in the associated XC potential has hindered the generation of SCAN pseudo-potentials [21, 22]. Neither limitation is inherent to the meta-GGA level or SCAN-like functionals, as we will show.

Some modifications to SCAN have been proposed to improve its accuracy for specific systems. The revSCAN functional is a simple modification to the slowly-varying limit of SCAN’s correlation energy to eliminate the fourth-order term in SCAN’s correlation energy density-gradient expansion [23]. The TASK functional is a complete revision of SCAN designed to accurately predict band gaps while retaining the exact constraints placed on the exchange energy [24], though TASK uses a local spin-density approximation (LSDA) to model correlation. It is not expected that these modifications address the numerical inefficiencies of the parent functional.

In recent work, Bartók and Yates propose a regularized SCAN termed “rSCAN” that aims to control SCAN’s

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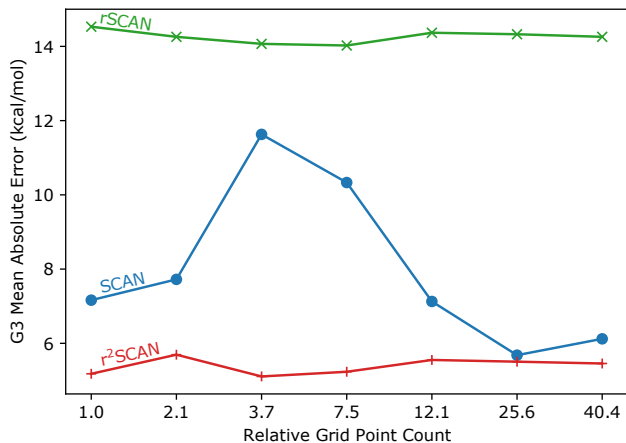


FIG. 1. Mean absolute error (MAE) of atomization energies (kcal/mol) for the G3 set of 226 molecules[28] as a function of increasing numerical integration grid density expressed relative to the smallest grid. The grids were chosen from TURBOMOLE [29, 30] grid levels 1-7.

numerical challenges while changing as little as possible from the parent functional [22]. The resulting functional shows greatly improved numerical stability and enables pseudo-potential generation. While initial testing suggested that rSCAN maintained the accuracy and transferability of SCAN, expanded testing by Mejía-Rodríguez and Trickey [25, 26] shows that some transferability is lost, with accuracy for atomization energies [27] particularly degraded.

The need for a computationally-efficient revision of SCAN is made plain in Fig. 1. This figure shows three meta-GGAs: SCAN and rSCAN, which have already been introduced, and a novel meta-GGA, r<sup>2</sup>SCAN, that is the topic of this paper. It illustrates a grid problem that arises for SCAN in codes with localized basis functions. The horizontal axis shows increasing integration grid density, and the vertical axis shows the mean absolute error (MAE) of the G3 test set [28] of 226 atomization energies. It would be difficult to assert that any of the grid settings present a converged SCAN energy, with SCAN errors varying unpredictably by a factor of 2. While rSCAN stabilizes SCAN numerically, its error offers little improvement over GGAs (e.g., PBE has a MAE of 22.2 kcal/mol [7] for the G3 set). The need for a meta-GGA that retains the accuracy of SCAN, with the grid efficiency of rSCAN, is evident. (No such grid problem is found for SCAN in the plane-wave code VASP, as shown in the Supplementary Material. However, in VASP, r<sup>2</sup>SCAN seems to converge with fewer iterations than SCAN does.)

**Summary of Changes** The SCAN functional is constructed using a dimensionless kinetic energy variable,

$$\alpha(\mathbf{r}) = \frac{\tau(\mathbf{r}) - \tau_W(\mathbf{r})}{\tau_{\text{unif}}(\mathbf{r})}, \quad (1)$$

where,  $\tau = \sum_i |\nabla \phi_i|^2 \Theta(\mu - \varepsilon_i)/2$  is the positive kinetic energy density,  $\phi_i(\mathbf{r})$  are the Kohn-Sham orbitals,  $\Theta(\mu - \varepsilon_i)$  is the orbital occupation,  $\tau_W = |\nabla n|^2/(8n)$  is the von Weizsäcker kinetic energy density, and  $\tau_{\text{unif}} = 3(3\pi^2)^{2/3}n^{5/3}/10$  is the kinetic energy density of a uniform electron gas,  $\mu$  is the chemical potential, and  $\varepsilon_i$  are the orbital energies. SCAN uses  $\alpha$  to tune functional performance for the local chemical environment [31]. While  $\alpha$  allows SCAN to satisfy exact constraints that would be contradictory at the GGA level [32],  $\alpha$  can introduce numerical sensitivity and divergences in the XC potential [33, 34].

The design of rSCAN prioritizes numerical efficiency over satisfaction of exact constraints, and instead uses a regularized  $\alpha'$ ,

$$\tilde{\alpha}(\mathbf{r}) = \frac{\tau(\mathbf{r}) - \tau_W(\mathbf{r})}{\tau_{\text{unif}}(\mathbf{r}) + \tau_r}, \quad (2)$$

$$\alpha'(\mathbf{r}) = \frac{\tilde{\alpha}(\mathbf{r})^3}{\tilde{\alpha}(\mathbf{r})^2 + \alpha_r}, \quad (3)$$

where  $\tau_r = 10^{-4}$  and  $\alpha_r = 10^{-3}$  are regularization constants. While the choice of a constant  $\tau_r$  eliminates numerical instability as  $\alpha \rightarrow 0$ ,  $\alpha'$  does not retain the correct uniform and non-uniform scaling properties of  $\alpha$ , nor the correct uniform density limit.

For a uniform electron gas,  $\alpha \rightarrow 1$ , which SCAN uses to recover the LSDA exactly. In rSCAN,  $\tilde{\alpha} \rightarrow 1/(1 + \tau_r/\tau_{\text{unif}})$  which varies with the density, losing the correct uniform electron gas description. It has been shown that recovery of the uniform gas limit is critical for an accurate description of solids, atoms and molecules [35, 36].

For a slowly-varying electron gas, the exchange and correlation energies have well-known expansions in powers of the gradient of the density. Let  $s = |\nabla n|/(2k_F n)$ , a dimensionless density-gradient on the scale of the Fermi wavevector  $k_F = (3\pi^2 n)^{1/3}$ , and  $q = \nabla^2 n/(4k_F^2 n)$  a dimensionless density-Laplacian. The gradient expansion for the exchange energy per particle  $\varepsilon_x(\mathbf{r})$  is [37],

$$\varepsilon_x = \varepsilon_x^{\text{LDA}} \left[ 1 + \mu_{\text{AK}} p + \frac{146}{2025} \left( q^2 - \frac{5}{2} p q \right) \right] + \mathcal{O}[(\nabla n)^6], \quad (4)$$

where  $\varepsilon_x^{\text{LDA}} = -3k_F/(4\pi)$ ,  $p = s^2$  and  $\mu_{\text{AK}} = 10/81$ . For the correlation energy, following Ref. 3, we define an additional dimensionless density-gradient  $t = |\nabla n|/[2k_s \phi(\zeta)n]$  on the scale of the Thomas-Fermi screening wavevector  $k_s = \sqrt{4k_F/\pi}$ . Here  $\phi(\zeta) = [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}]/2$  is a spin-scaling function of the spin-polarization  $\zeta = (n_\uparrow - n_\downarrow)/n$ . Then the density-gradient expansion of the correlation energy per particle  $\varepsilon_c(\mathbf{r})$  is [3, 7, 38],

$$\varepsilon_c = \varepsilon_c^{\text{LSDA}} + \phi(\zeta)^3 \beta(r_s) t^2, \quad (5)$$

where  $\beta(r_s)$  is a weakly-varying function of the Wigner-Seitz radius  $r_s = (4\pi n/3)^{-1/3}$ , with a maximum  $\beta(0) \approx 0.066725$ . The kinetic energy density  $\tau$  has an analogous but unwieldy density-gradient expansion [39]. It is

generally understood that recovering the exact density-gradient expansion is relevant for solids [40]. These terms also affect the asymptotic behavior of  $E_{xc}$  for atoms [41], as the asymptotic limit for atoms of large- $Z$  is a semi-classical limit that is described exactly by the LSDA at lowest-order, with the density-gradient terms modulating the higher-order terms (known accurately) [41]. Thus the uniform and slowly-varying density limits are relevant to both solid state and atomic systems.

SCAN eliminates erroneous contributions from  $\alpha$  to the second- and fourth-order slowly-varying density-gradient expansion (GE2 and GE4 respectively) of  $E_{xc}$  by using a non-analytic switching function whose value and derivatives of all orders are zero at  $\alpha = 1$ . Whilst theoretically convenient, constraining the interpolation function to have zero derivatives at  $\alpha = 1$  results in a twisted function that harms numerical performance. The SCAN interpolation function was replaced with a smooth polynomial in rSCAN (see Fig. 2) to remove this source of numeric instability, at the expense of introducing second- and fourth-order contributions from  $\alpha$  to the density-gradient expansion of  $E_{xc}$ .

It is clear then that rSCAN makes wide-ranging sacrifices in exact constraint adherence in order to make a numerically-efficient meta-GGA. Here, we will show definitively that such sacrifices are needless and derive revisions to the rSCAN functional to restore exact constraint adherence without harming numerical efficiency. We apply these revisions to build a regularized-restored SCAN functional, r<sup>2</sup>SCAN, which recovers the most important exact constraints of SCAN. Table I summarizes the constraint satisfaction of the functionals concerned and we stress that as only appropriate norm systems [7] were used to set the free parameters, all three functionals (SCAN, rSCAN, and r<sup>2</sup>SCAN) may be considered non-empirical. For brevity we only show parts of the functional that are modified in this work, and direct the reader to Section S2 of the Supplemental Materials for a full definition of the relevant equations.

TABLE I. Summary of exact constraint adherence for a subset of the 17 known exact constraints applicable to meta-GGA functionals. Here, GE2 denotes the second-order slowly-varying density-gradient expansion, and GE4X denotes the 4<sup>th</sup> order GE for exchange.

	SCAN	rSCAN	r <sup>2</sup> SCAN
Uniform Density	✓	–	✓
Coordinate Scaling	✓	–	✓
GE2	✓	–	✓
GE4X	✓	–	–

There are many situations where the exact exchange-correlation potential and energy density can be expected to be reasonably smooth (see, e.g., the plots of highly accurate exchange-correlation potentials and energy densities of simple hydrides in Ref. 42). In general, the exact Kohn-Sham exchange-correlation potential need not be smooth, as demonstrated by the Perdew-Parr-Levy-

Balduz theorem [43]: the exchange-correlation potential, as a function of the number of electrons  $N$ , exhibits discontinuities across integer values of  $N$ , with steps and peaks in the low-density region between two separated dissimilar systems. However, a semilocal functional cannot recover the precise behaviors of the exact exchange-correlation energy and potential, and instead averages over them. Therefore we consider smoothness of the energy density and potential to be a necessary construction principle of semilocal approximate density functionals. A construction principle is any physically- or mathematically-motivated principle that can supplement the design of a first-principles density functional approximation.

The correct uniform- and non-uniform- scaling properties of  $\alpha$ , as well as the correct uniform density limit of  $E_{xc}$ , are recovered in r<sup>2</sup>SCAN by regularizing  $\alpha$  as

$$\bar{\alpha} = \frac{\tau - \tau_W}{\tau_{\text{unif}} + \eta\tau_W}, \quad (6)$$

where  $\eta = 10^{-3}$  is a simple regularization parameter. Note that because  $\tau \geq \tau_W$ ,  $\bar{\alpha}$  has the same range as  $\alpha$ ,  $0 \leq \bar{\alpha} < \infty$ . This is distinct from the dimensionless kinetic energy variable suggested by Ref. 34,

$$\beta = \frac{\tau - \tau_W}{\tau + \tau_{\text{unif}}}, \quad (7)$$

which ranges between  $0 \leq \beta < 1$ , and has less rapidly-varying derivatives than  $\alpha$ . As this work seeks revisions to SCAN, we will not consider  $\beta$  or related iso-orbital indicators here and adopt  $\bar{\alpha}$  as the iso-orbital indicator used throughout r<sup>2</sup>SCAN.

SCAN uses the iso-orbital indicator variable  $\alpha$  to drive interpolation functions  $f_{x/c}(\alpha)$  for exchange and correlation. The rSCAN functional replaces the original SCAN interpolation functions with a polynomial function of  $\alpha'$  when  $\alpha' < 2.5$  that smooths out the plateau-like behavior of the original near  $\alpha = 1$ . The r<sup>2</sup>SCAN functional adopts the rSCAN interpolation function but uses  $\bar{\alpha}$  as the indicator variable. Both the SCAN and rSCAN interpolation functions are shown in Figure 2 as functions of a generic indicator.

The SCAN interpolation function was designed to have vanishing derivatives at  $\alpha = 1$ , but the rSCAN replacements go linearly through zero at this point. As a result of these non-vanishing derivatives, the interpolation function makes spurious contributions to the slowly-varying density-gradient expansions that break the corresponding exact constraints. The r<sup>2</sup>SCAN functional recovers the gradient expansions through  $\mathcal{O}[(\nabla n)^2]$  while using the rSCAN polynomial interpolation by directly canceling spurious terms in the slowly-varying energy densities.

For exchange we recover the gradient expansion by replacing the  $x(p, \alpha')$  function of SCAN and rSCAN with,

$$x(p) = \{C_\eta C_{2x} \exp[-p^2/d_{p2}^4] + \mu_{AK}\}p. \quad (8)$$

Here, the constants  $C_\eta = 20/27 + 5\eta/3$ , depending on the regularization parameter  $\eta = 10^{-3}$ , and

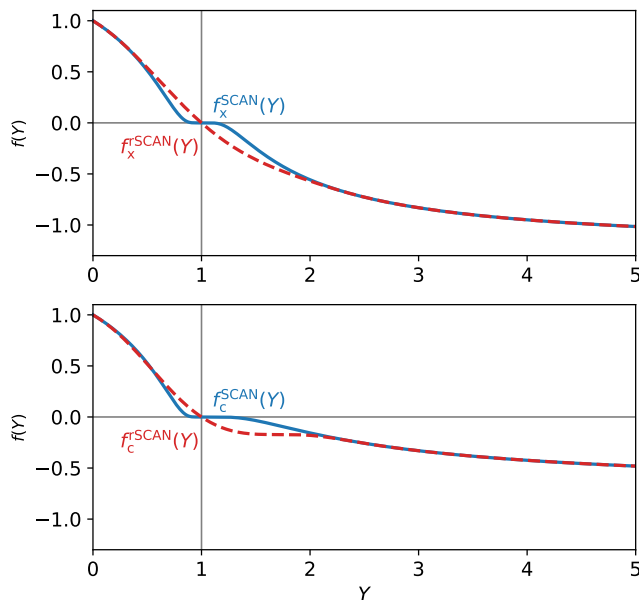


FIG. 2. SCAN (blue, solid) and rSCAN (red, dashed) interpolation functions plotted for a generic stand-in iso-orbital indicator “Y” ( $\alpha$  for SCAN,  $\alpha'$  for rSCAN,  $\bar{\alpha}$  for r<sup>2</sup>SCAN). The functions mix  $Y = 0$  (single orbital) and  $Y = 1$  (uniform density limit for  $\alpha$  and  $\alpha'$ ) energy densities. The derivatives of the SCAN interpolation functions vanish to all orders in  $Y$  at  $Y \rightarrow 1$ , allowing SCAN to recover the appropriate density-gradient expansions exactly in the slowly-varying limit. The rSCAN interpolation functions are used with  $Y = \bar{\alpha}$  in r<sup>2</sup>SCAN and their smooth, non-vanishing first derivatives at  $Y = 1$  necessitate changes from SCAN to r<sup>2</sup>SCAN in the  $Y = 1$  energy densities.

$$g(At^2, \Delta y) = [1 + 4(At^2 - \Delta y)]^{-1/4}, \quad (9)$$

$$\Delta y = \frac{\Delta f_{c2}}{27\gamma d_s \phi^3 w_1} \left\{ 20r_s \left[ \frac{\partial \epsilon_c^{\text{LSDA0}}}{\partial r_s} - \frac{\partial \epsilon_c^{\text{LSDA1}}}{\partial r_s} \right] - 45\eta [\epsilon_c^{\text{LSDA0}} - \epsilon_c^{\text{LSDA1}}] \right\} p \exp[-p^2/d_{p2}^4]. \quad (10)$$

Here  $\Delta y$  is the new term introduced in r<sup>2</sup>SCAN that eliminates erroneous contributions from  $df_c(\bar{\alpha})/d\bar{\alpha}$  at  $\bar{\alpha} \rightarrow 1$ . Replacing  $\alpha'$  with  $\bar{\alpha}$  and  $g(At^2)$  with Eqs. 9 and 10 in rSCAN correlation defines r<sup>2</sup>SCAN correlation and approximately recovers GE2C. In Eq. 10,  $\Delta f_{c2} \approx -0.711402$  and  $\gamma = (1 - \ln 2)/\pi^2 \approx 0.031091$  are constants; all other quantities are functions defined in the Supplemental Materials. The correlation gradient expansion of r<sup>2</sup>SCAN becomes exact whenever  $|\nabla\zeta| = 0$ , and approximately recovers GE2C for all other values of  $\nabla\zeta$ . Thus r<sup>2</sup>SCAN recovers GE2C exactly for spin-unpolarized systems, where the correlation energy is likely most negative, and for fully spin-polarized systems, where the correlation energy is likely least negative. Between these limits, the r<sup>2</sup>SCAN correlation gradient expansion is a reasonable approximation to the true gradi-

$C_{2x} \approx -0.162742$  eliminate erroneous contributions from  $df_x(\bar{\alpha})/d\bar{\alpha}$  at  $\bar{\alpha} \rightarrow 1$ , and  $d_{p2} = 0.316$  is a damping parameter determined as the maximal value (therefore least damped) required to recover SCAN’s error for the rare gas atom and jellium surface appropriate norms described in Ref. 7. Replacing  $\alpha'$  with  $\bar{\alpha}$  and  $x(p, \alpha')$  with Eq. 8 in the rSCAN functional defines r<sup>2</sup>SCAN exchange, and restores the uniform density limit, correct scaling properties, and GE2 for exchange (GE2X). As in Ref. 7 and earlier work, we employ the exact spin-scaling equality for the exchange energy [44], thus only formulas for spin-unpolarized exchange need to be displayed.

From Eq. 4, we see that a meta-GGA recovering GE4X must either explicitly include the Laplacian of the density as an ingredient, or recover  $q$ -dependent terms via integration by parts on  $\tau$ . The latter method, used in SCAN, is theoretically sound but likely introduces further numerical instabilities due to an increased sensitivity to  $\alpha$ . Furthermore, the gradient expansion for the correlation energy is known only to second order, and the relevance of GE4X (beyond GE2X terms) to real systems has not been established. To ensure that our functional is numerically stable we only consider GE2X here and defer further discussion of GE4X and its difficulties to a further publication in the near future.

The gradient expansion for correlation is only known to second order, and we recover it by replacing the  $g(At^2)$  function which appears in the slowly-varying correlation energy density of rSCAN and SCAN with,

ent expansion.

**Enhancement Factors and Derivatives** These modifications should not degrade the good numerical performance of rSCAN. Their effect can be seen in Figure 3 which compares the XC enhancement factor and XC potential components of SCAN and r<sup>2</sup>SCAN for the xenon atom. The implicit orbital dependence of  $\tau$  dependent meta-GGA functionals prevents direct evaluation of a multiplicative KS potential, and such functionals are more commonly implemented using derivatives with respect to individual orbitals in a generalized Kohn–Sham scheme [45–47]. Let  $\epsilon_{xc} = n\epsilon_{xc}$  be the XC energy density. We can identify a multiplicative component of the

potential,

$$v_{xc}^{sl}(\mathbf{r}) = \frac{\partial \epsilon_{xc}(\mathbf{r})}{\partial n(\mathbf{r})} - \nabla \cdot \left[ \frac{\partial \epsilon_{xc}(\mathbf{r})}{\partial |\nabla n(\mathbf{r})|} \frac{\nabla n(\mathbf{r})}{|\nabla n(\mathbf{r})|} \right], \quad (11)$$

and summarize the non-multiplicative component as the derivative of the energy density with respect to  $\tau$ . Both are shown in Figure 3.

While the overall inter-shell features of the  $F_{xc}$  are similar between the two functionals, SCAN shows plateaus where  $\alpha = 1$ , while  $r^2$ SCAN is smooth throughout. This behavior is echoed as sharp oscillations in both the multiplicative potential component and non-multiplicative  $\tau$  derivative for SCAN, which contrasts with the smooth equivalents for  $r^2$ SCAN. We suggest that  $r^2$ SCAN may make generation of meta-GGA pseudopotentials feasible. Note that on the scale of Figure 3 both  $\alpha$  and  $\bar{\alpha}$  appear to diverge. While it is true that  $\alpha$  diverges, the  $\eta$  regularization parameter ensures  $\bar{\alpha}$  remains finite, with a final maxima occurring around 8 Bohr after which it asymptotically approaches 0. Larger values of  $\eta$  cause the asymptotic return to occur closer to the nuclei, but cause the regularization to have a greater impact on predicted energies. We defer detailed discussion of  $\eta$  and single orbital system potential divergence to Supplemental Material Section S3.

**Atomization Energies** Reference 25 shows that atomization energies are particularly problematic for  $r$ SCAN, with its error being roughly twice that of SCAN’s. As such, we take the G3 set of 226 atomization energies [28] as a primary means of assessing the effect of constraint restoration. Table II summarizes the accuracy of the functionals for the G3 set using the most dense grid available. We find that the error for  $r$ SCAN is roughly twice that of SCAN, consistent with other studies. The new  $r^2$ SCAN functional shows similar accuracy to SCAN, supporting the importance of exact constraint adherence.

We restate that the improved numerical efficiency of  $r^2$ SCAN is immediately apparent from Figure 1, which shows accuracy for the G3 test set as a function of integration grid density.  $r^2$ SCAN shows consistent error with grid density, similar to  $r$ SCAN and in sharp contrast to SCAN. This figure should stand as a stark warning that studies comparing total energies from SCAN must carefully test for grid convergence, and shows the utility of the new regularized-restored functional which achieves consistently-good accuracy with even the smallest grids.

**Further Testing** The transferability of the new functionals was further tested for 76 reaction barrier heights [54], 22 weak interaction energies [55], and 20 lattice constants [56], with error statistics summarized in Table II. All functionals show similar performance across the test sets, with the exception of the G3 atomization energy set as discussed above. The LC20 set was assessed by fitting the stabilized jellium equation of state (SJEOS) [57, 58] to single point energies at a range of lattice volumes around equilibrium.

TABLE II. Mean error (ME) and mean absolute error (MAE) of TPSS[59], SCAN[7],  $r$ SCAN[22], and  $r^2$ SCAN for the the G3 set of 226 molecular atomization energies [28], the BH76 set of 76 chemical barrier heights [54], the S22 set of 22 interaction energies between closed shell complexes [55], and the LC20 set of 20 solid lattice constants [56]. Errors for G3, BH76, and S22 sets are in kcal/mol while errors for LC20 are in Å. We did not make corrections for basis set superposition error for the S22 set which used the aug-cc-pVTZ basis set[60]. All calculations for G3 and BH76 used the 6-311++G(3df,3pd) basis set [28, 61]. Details of the computational methods are included in Section S1 of the Supplemental Materials.

	G3		BH76		S22		LC20	
	ME	MAE	ME	MAE	ME	MAE	ME	MAE
TPSS	-5.2	5.8	-8.6	8.6	-3.4	3.4	0.033	0.041
SCAN	-5.0	6.1	-7.7	7.7	-0.5	0.8	0.009	0.015
$r$ SCAN	-14.0	14.3	-7.4	7.4	-1.2	1.3	0.020	0.025
$r^2$ SCAN	-4.5	5.5	-7.1	7.2	-0.9	1.1	0.022	0.027

**Conclusions** We recently learned of a “de-orbitalization” [62–64] of our  $r^2$ SCAN that replaces the exact orbital dependent Kohn-Sham kinetic energy density  $\tau$  by an posited function of  $n$ ,  $\nabla n$ , and  $\nabla^2 n$ , called “ $r^2$ SCAN-L”[65]. This speeds up computations while somewhat reducing overall accuracy, though interestingly the accuracy of the magnetic moment of metallic Fe is restored by the de-orbitalization to the good level of LSDA and PBE. As a possible explanation, we note that the exact  $\tau$  has a fully nonlocal dependence upon the electron density  $n$  that is needed to satisfy some exact constraints and is probably needed for optimal accuracy in atoms, molecules, and insulators. This full nonlocality may however be somewhat harmful for metals, where metallic screening can favor truly semi-local approximations to the valence-valence exchange-correlation energy.

We have presented  $r^2$ SCAN as a functional combining SCAN’s transferable accuracy from exact constraint satisfaction with  $r$ SCAN’s numerical efficiency.  $r^2$ SCAN satisfies the most important exact constraints of SCAN. In our future work, we will assess the importance of the GE4X terms beyond GE2X (recovered by SCAN, but not by  $r^2$ SCAN) as an exact constraint. We draw this conclusion from the competitive accuracy shown for the diverse test sets of Table II and the rapid grid convergence of Figure 1. The XC potential analysis from Figure 3 suggests that  $r^2$ SCAN will be preferable when a smooth potential is critical. In particular, it should now be more practical to construct a pseudopotential, and to evaluate the second functional derivative which can play the role of an exchange-correlation kernel in time-dependent density functional applications. We expect the new regularized-restored SCAN functional to bridge the gap between accuracy and numerical efficiency and enable meta-GGA use in large-scale computational studies.

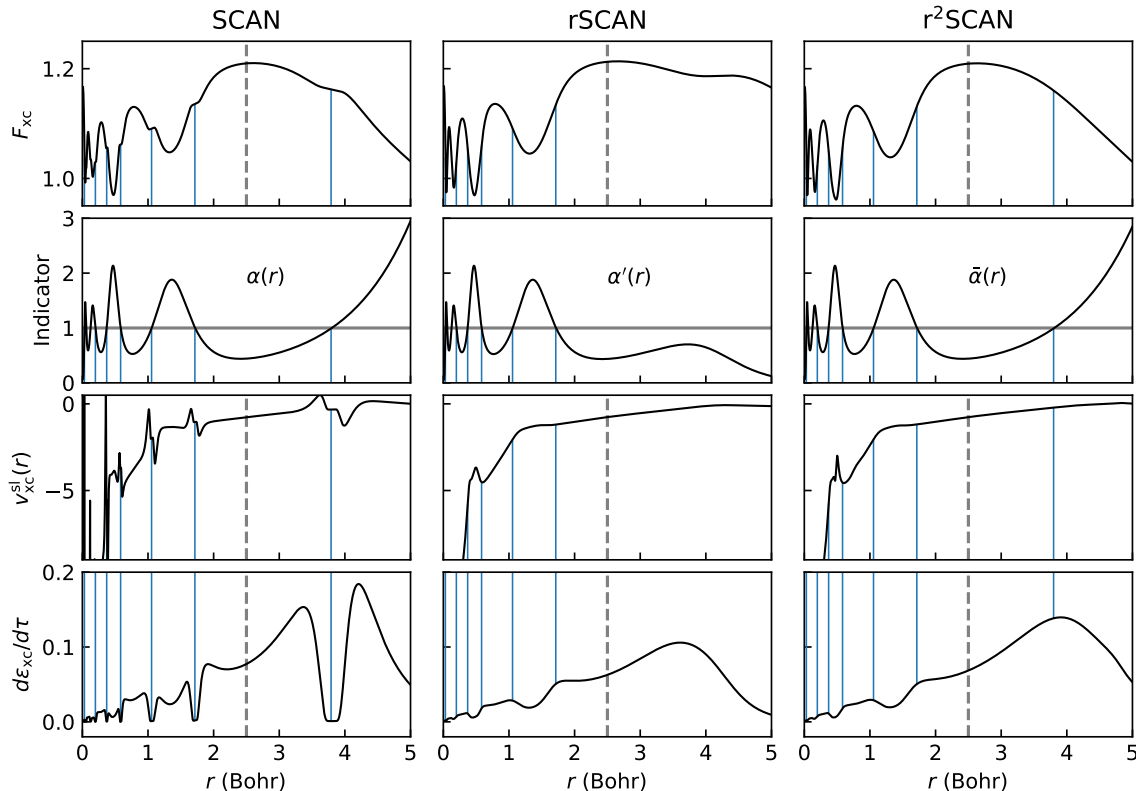


FIG. 3. (Top) Exchange-correlation enhancement factors, (middle-upper) iso-orbital indicator  $\alpha(r)$ ,  $\alpha'(r)$ , or  $\bar{\alpha}(r)$  as appropriate, (middle-lower) semi-local part of the exchange-correlation potential as in Eq. 11, and (bottom) derivative of exchange-correlation energy density with respect to kinetic energy density. Calculated for the xenon atom from accurate Hartree-Fock Slater orbitals [48] for the SCAN [7], rSCAN [22] and  $r^2$ SCAN functionals. The VASP [49–52] projector-augmented wave [53] pseudopotential cutoff radius (2.5 Bohr) is illustrated by a dashed vertical line. Solid vertical lines show where  $\alpha = 1$ .

## SUPPORTING INFORMATION

S1: Computational Methods and grid convergence in VASP, S2:  $r^2$ SCAN Working Equations, S3: Determining  $\eta$  regularization parameter and XC potential divergence, S4: reference atomic energies, S5: full test set data.

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[1] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, and K. a. Persson, The Materials Project: A materials genome approach to accelerating materials innovation, *APL Materials* **1**, 11002 (2013).

[2] K. Persson, About the Materials Project (2020).

[3] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple., *Physical Review Letters* **77**, 3865 (1996).

[4] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov,

- G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Generalized gradient approximation for solids and their surfaces, *Physical Review Letters* **100**, 136406 (2008).
- [5] A. Ruzsinszky, G. I. Csonka, and G. E. Scuseria, Regularized gradient expansion for atoms, molecules, and solids, *Journal of Chemical Theory and Computation* **5**, 763 (2009).
- [6] F. Tran, J. Stelzl, and P. Blaha, Rungs 1 to 4 of DFT Jacob's ladder: Extensive test on the lattice constant, bulk modulus, and cohesive energy of solids, *Journal of Chemical Physics* **144**, 204120 (2016).
- [7] J. Sun, A. Ruzsinszky, and J. P. Perdew, Strongly Constrained and Appropriately Normed Semilocal Density Functional, *Physical Review Letters* **115**, 036402 (2015).
- [8] J. Sun, R. C. Remsing, Y. Zhang, Z. Sun, A. Ruzsinszky, H. Peng, Z. Yang, A. Paul, U. Waghmare, X. Wu, M. L. Klein, and J. P. Perdew, Accurate first-principles structures and energies of diversely bonded systems from an efficient density functional, *Nature Chemistry* **8**, 831 (2016).
- [9] D. A. Kitchev, H. Peng, Y. Liu, J. Sun, J. P. Perdew, and G. Ceder, Energetics of MnO<sub>2</sub> polymorphs in density functional theory, *Physical Review B* **93**, 045132 (2016).
- [10] J. W. Furness, Y. Zhang, C. Lane, I. G. Buda, B. Barbiellini, R. S. Markiewicz, A. Bansil, and J. Sun, An accurate first-principles treatment of doping-dependent electronic structure of high-temperature cuprate superconductors, *Communications Physics* **1**, 1 (2018).
- [11] C. Lane, J. W. Furness, I. G. Buda, Y. Zhang, R. S. Markiewicz, B. Barbiellini, J. Sun, and A. Bansil, Antiferromagnetic ground state of La<sub>2</sub>CuO<sub>4</sub>: A parameter-free ab initio description, *Physical Review B* **98**, 125140 (2018).
- [12] Y. Zhang, C. Lane, J. W. Furness, B. Barbiellini, J. P. Perdew, R. S. Markiewicz, A. Bansil, and J. Sun, Competing stripe and magnetic phases in the cuprates from first principles, *Proceedings of the National Academy of Sciences* **117**, 68 (2019).
- [13] C. Lane, Y. Zhang, J. W. Furness, R. S. Markiewicz, B. Barbiellini, J. Sun, and A. Bansil, First-principles calculation of spin and orbital contributions to magnetically ordered moments in SrIrO<sub>4</sub>, *Physical Review B* **101**, 155110 (2020).
- [14] M. Chen, H. Y. Ko, R. C. Remsing, M. F. Calegari Andrade, B. Santra, Z. Sun, A. Selloni, R. Car, M. L. Klein, J. P. Perdew, and X. Wu, Ab initio theory and modeling of water, *Proceedings of the National Academy of Sciences of the United States of America* **114**, 10846 (2017), arXiv:1709.10493.
- [15] L. Zheng, M. Chen, Z. Sun, H. Y. Ko, B. Santra, P. Dhuvad, and X. Wu, Structural, electronic, and dynamical properties of liquid water by ab initio molecular dynamics based on SCAN functional within the canonical ensemble, *Journal of Chemical Physics* **148**, 10.1063/1.5023611 (2018).
- [16] H. Peng and J. P. Perdew, Synergy of van der Waals and self-interaction corrections in transition metal monoxides, *Physical Review B* **96**, 100101(R) (2017).
- [17] G. Sai Gautam and E. A. Carter, Evaluating transition metal oxides within DFT-SCAN and SCAN+U frameworks for solar thermochemical applications, *Physical Review Materials* **2**, 095401 (2018).
- [18] Y. Zhang, J. W. Furness, B. Xiao, and J. Sun, Subtlety of TiO<sub>2</sub> phase stability: Reliability of the density functional theory predictions and persistence of the self-interaction error, *The Journal of Chemical Physics* **150**, 014105 (2019).
- [19] Z.-h. Yang, H. Peng, J. Sun, and J. P. Perdew, More realistic band gaps from meta-generalized gradient approximations: Only in a generalized Kohn-Sham scheme, *Physical Review B* **93**, 205205 (2016).
- [20] Y. Yamamoto, C. M. Diaz, L. Basurto, K. A. Jackson, T. Baruah, and R. R. Zope, Fermi-Löwdin orbital self-interaction correction using the strongly constrained and appropriately normed meta-GGA functional, *Journal of Chemical Physics* **151**, 154105 (2019).
- [21] Y. Yao and Y. Kanai, Plane-wave pseudopotential implementation and performance of SCAN meta-GGA exchange-correlation functional for extended systems, *Journal of Chemical Physics* **146**, 224105 (2017).
- [22] A. P. Bartók and J. R. Yates, Regularized SCAN functional, *Journal of Chemical Physics* **150**, 161101 (2019).
- [23] P. D. Mezei, G. I. Csonka, and M. Kallay, Simple modifications of the SCAN meta-generalized gradient approximation functional, *Journal of Chemical Theory and Computation* 10.1021/acs.jctc.8b00072 (2018).
- [24] T. Aschbrock and S. Kümmel, Ultranonlocality and accurate band gaps from a meta-generalized gradient approximation, *Physical Review Research* **1**, 033082 (2019).
- [25] D. Mejia-Rodriguez and S. B. Trickey, Supplementary Material: Comment on Regularized SCAN functional, *The Journal of Chemical Physics* **151**, 207101 (2019).
- [26] A. P. Bartók and J. R. Yates, Response to Comment on Regularized SCAN functional” [J. Chem. Phys. 151, 207101 (2019)], *Journal of Chemical Physics* **151**, 207102 (2019).
- [27] Y. Yamamoto, A. Salcedo, C. M. Diaz, M. S. Alam, T. Baruah, and R. R. Zope, Comparison of regularized SCAN functional with SCAN functional with and without self-interaction for a wide-array of properties, (2020), arXiv:2004.13393.
- [28] L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, Assessment of Gaussian-3 and density functional theories for a larger experimental test set, *Journal of Chemical Physics* **112**, 7374 (2000).
- [29] O. Treutler and R. Ahlrichs, Efficient molecular numerical integration schemes, *The Journal of Chemical Physics* **102**, 346 (1995).
- [30] S. G. Balasubramani, G. P. Chen, S. Coriani, M. Diedenhofen, M. S. Frank, Y. J. Franzke, F. Furche, R. Grotjahn, M. E. Harding, C. Hättig, A. Hellweg, B. Helmich-Paris, C. Holzer, U. Huniar, M. Kaupp, A. Marefat Khah, S. Karbalaeei Khani, T. Müller, F. Mack, B. D. Nguyen, S. M. Parker, E. Perlt, D. Rappoport, K. Reiter, S. Roy, M. Rückert, G. Schmitz, M. Sierka, E. Tapavicza, D. P. Tew, C. van Wüllen, V. K. Voora, F. Weigend, A. Wodyński, and J. M. Yu, TURBOMOLE: Modular program suite for ab initio quantum-chemical and condensed-matter simulations, *The Journal of chemical physics* **152**, 184107 (2020).
- [31] 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, *Physical Review Letters* **111**, 106401 (2013).
- [32] J. Sun, J. P. Perdew, and A. Ruzsinszky, Semilocal density functional obeying a strongly tightened bound for exchange, *Proceedings of the National Academy of Sci-*

- ences **112**, 685 (2015).
- [33] N. Holzwarth, Private communication (2018).
- [34] J. W. Furness and J. Sun, Enhancing the efficiency of density functionals with an improved iso-orbital indicator, *Physical Review B* **99**, 041119 (2019).
- [35] R. R. Zope, Y. Yamamoto, C. M. Diaz, T. Baruah, J. E. Peralta, K. A. Jackson, B. Santra, and J. P. Perdew, A step in the direction of resolving the paradox of Perdew-Zunger self-interaction correction, *Journal of Chemical Physics* **151**, 214108 (2019), arXiv:1911.08659.
- [36] P. Bhattarai, K. Wagle, C. Shahi, Y. Yamamoto, S. Romero, B. Santra, R. R. Zope, J. E. Peralta, K. A. Jackson, and J. P. Perdew, A Step in the Direction of Resolving the Paradox of Perdew-Zunger Self-interaction Correction. II. Gauge Consistency of the Energy Density at Three Levels of Approximation, *The Journal of Chemical Physics* **152**, 214109 (2020), arXiv:2004.12233.
- [37] P. Svendsen and U. von Barth, Gradient expansion of the exchange energy from second-order density response theory, *Physical Review B* **54**, 17402 (1996).
- [38] S.-K. Ma and K. A. Brueckner, Correlation energy of an electron gas with a slowly varying high density, *Physical Review* **165**, 18 (1968).
- [39] M. Brack, B. K. Jennings, and Y. H. Chu, The kinetic energy density, *Physics Letters B* **65**, 1 (1976).
- [40] J. P. Perdew, L. A. Constantin, E. Sagvolden, and K. Burke, Relevance of the slowly varying electron gas to atoms, molecules, and solids, *Physical Review Letters* **97**, 223002 (2006).
- [41] P. Elliott, D. Lee, A. Cangi, and K. Burke, Semiclassical origins of density functionals, *Physical Review Letters* **100**, 10.1103/PhysRevLett.100.256406 (2008).
- [42] O. V. Gritsenko, R. Van Leeuwen, and E. J. Baerends, Molecular exchange-correlation Kohn-Sham potential and energy density from ab initio first- and second-order density matrices: Examples for XH (X=Li, B, F), *Journal of Chemical Physics* **104**, 8535 (1996).
- [43] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Density-functional theory for fractional particle number: Derivative discontinuities of the energy, *Physical Review Letters* **49**, 1691 (1982).
- [44] G. L. Oliver and J. P. Perdew, Spin-density gradient expansion for the kinetic energy, *Physical Review A* **20**, 397 (1979).
- [45] A. Seidl, A. Görling, P. Vogl, J. Majewski, and M. Levy, Generalized Kohn-Sham schemes and the band-gap problem, *Physical Review B* **53**, 3764 (1996).
- [46] R. Neumann, R. H. Nobes, and N. C. Handy, Exchange functionals and potentials, *Molecular Physics* **87**, 1 (1996).
- [47] C. Adamo, M. Ernzerhof, and G. E. Scuseria, The meta-GGA functional: Thermochemistry with a kinetic energy density dependent exchange-correlation functional, *Journal of Chemical Physics* **112**, 2643 (2000).
- [48] E. Clementi and C. Roetti, Roothaan-Hartree-Fock Atomic Wavefunctions, *Atomic Data and Nuclear Data Tables* **14**, 177 (1974).
- [49] G. Kresse and J. Hafner, Ab initio molecular dynamics for liquid metals, *Physical Review B* **47**, 558 (1993).
- [50] G. Kresse and J. Hafner, Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium, *Physical Review B* **49**, 14251 (1994).
- [51] G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Physical Review B - Condensed Matter and Materials Physics* **54**, 11169 (1996).
- [52] G. Kresse and J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Computational Materials Science* **6**, 15 (1996).
- [53] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Physical Review B* **59**, 1758 (1999).
- [54] Y. Zhao, N. González-Garda, and D. G. Truhlar, Benchmark database of barrier heights for heavy atom transfer, nucleophilic substitution, association, and unimolecular reactions and its use to test theoretical methods, *Journal of Physical Chemistry A* **109**, 2012 (2005).
- [55] P. Jurečka, J. Šponer, J. Černý, and P. Hobza, Benchmark database of accurate (MP2 and CCSD(T) complete basis set limit) interaction energies of small model complexes, DNA base pairs, and amino acid pairs, *Physical Chemistry Chemical Physics* **8**, 1985 (2006).
- [56] J. Sun, M. Marsman, G. I. Csonka, A. Ruzsinszky, P. Hao, Y. S. Kim, G. Kresse, and J. P. Perdew, Self-consistent meta-generalized gradient approximation within the projector-augmented-wave method, *Physical Review B* **84**, 035117 (2011).
- [57] V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, Tests of a ladder of density functionals for bulk solids and surfaces, *Physical Review B* **69**, 075102 (2004).
- [58] A. B. Alchagirov, J. P. Perdew, J. C. Boettger, R. C. Albers, and C. Fiolhais, Energy and pressure versus volume: Equations of state motivated by the stabilized jellium model, *Physical Review B - Condensed Matter and Materials Physics* **63**, 2241151 (2001).
- [59] 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, *Physical Review Letters* **91**, 146401 (2003).
- [60] T. H. Dunning, Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *The Journal of Chemical Physics* **90**, 1007 (1989).
- [61] T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. V. R. Schleyer, Efficient diffuse function augmented basis sets for anion calculations. III. The 321+G basis set for first row elements, LiF, *Journal of Computational Chemistry* **4**, 294 (1983).
- [62] S. Šmiga, S. Laricchia, L. A. Constantin, and F. Della Sala, Subsystem density functional theory with meta-generalized gradient approximation exchange-correlation functionals, *Journal of Chemical Physics* **142**, 154121 (2015).
- [63] S. Šmiga, E. Fabiano, L. A. Constantin, and F. Della Sala, Laplacian-dependent models of the kinetic energy density: Applications in subsystem density functional theory with meta-generalized gradient approximation functionals, *Journal of Chemical Physics* **146**, 064105 (2017).
- [64] D. Mejia-Rodriguez and S. B. Trickey, Deorbitalization strategies for meta-GGA exchange-correlation functionals, *Physical Review A* **96**, 052512 (2017).
- [65] D. Mejia-Rodriguez and S. B. Trickey, Meta-GGA Performance in Solids at Almost GGA Cost, (2020),



arXiv:2008.12420.

- [66] B. J. Lynch and D. G. Truhlar, Erratum: Small representative benchmarks for thermochemical calculations (J. Phys. Chem. A (2003) 107A, (8997)), Journal of Physical Chemistry A **108**, 1460 (2004).
- [67] D. E. Woon and T. H. Dunning, Gaussian basis sets for use in correlated molecular calculations. V. Core-valence basis sets for boron through neon, The Journal of Chemical Physics **103**, 4572 (1995).

**SUPPLEMENTAL MATERIALS FOR: “ACCURATE AND NUMERICALLY EFFICIENT R<sup>2</sup>SCAN  
META-GENERALIZED GRADIENT APPROXIMATION”**

**CONTENTS**

Section S1 provides essential input parameters needed to reproduce the calculations reported in the main text. Section S2 provides the equations of r<sup>2</sup>SCAN, with numeric parameters given. Section S4 tabulates reference atomic energies for the nitrogen and neon atoms. Section S5 tabulates all resultant data for the test sets in the main text. All data referenced in the main text is made available here. Machine-readable data will be made available at reasonable request.

Tables S5, S6, and S7 list all errors of SCAN, rSCAN, and r<sup>2</sup>SCAN, respectively for the G3 set. Table S8 lists all errors for the BH76 set; Table S9 does this for the S22 set, and Table S10 for the LC20 set.

**S1. COMPUTATIONAL METHODS**

Within TURBOMOLE [29, 30], all calculations used the following parameters:

- Gaussian basis set 6-311++G(3df,3pd), excepting the S22 set, which used aug-cc-pVTZ. [28, 61]
- self-consistent convergence at  $10^{-6}$  eV.

The G3 set of atomisation energies [28], the BH76 set of reaction barrier heights [54], and the S22 set of weakly-interacting molecular complex formation energies [55] were calculated in TURBOMOLE. The S22 calculation included no counterpoise correction, however it is evident from Table S9 that the scores are similar to that found in Ref. [7].

Within VASP [49–52], all calculations presented used the following parameters:

- ISMEAR function (controlling partial occupancy near the Fermi level) set to -5 (tetrahedron method with Blöchl corrections), except for Sr, where it was set to 1 (Methfessel–Paxton scheme)
- ENCUT set to 650 eV for plane wave cutoff energy (except for Na, where it was set to 1000 eV)
- $\Gamma$ -centered grid in  $\mathbf{k}$ -space, with KSPACING set to  $0.1 \text{ \AA}^{-1}$
- ADDGRID set to true (optional finer grid to calculate augmentation charge density)
- PREC set to “Accurate”.

The LC20 set of cubic lattice constants [56] was calculated in VASP. The ENCUT parameter in VASP controls the number of reciprocal space vectors included in the basis set. For  $\mathbf{G}$  a reciprocal lattice vector and  $\mathbf{k}$  the crystal momentum, VASP includes all reciprocal space vectors  $|\mathbf{G} + \mathbf{k}|^2/2 < \text{ENCUT}$ . We have selected values of ENCUT that are much larger than the minimal value required by the pseudopotential (these range between 119.552 eV for Al to 487.335 eV for F).

Note that the PBE pseudopotential for Na required a much larger cutoff (645.64 eV when including  $s$  semi-core states) than the corresponding GW pseudopotential (259.494 eV, also including  $s$  semi-core states). The GW pseudopotential for Na was used here. To ensure that our calculations could be adequately reproduced regardless of the pseudopotential parameters, we have set the Na cutoff much higher than the other elements.

VASP does not use basis sets for real-space integration; the fineness of the real-space mesh and the reciprocal-space mesh are controlled by the KSPACING parameter. Smaller values of KSPACING increase the fineness of both meshes, generally improving the quality of numeric integration, and allowing for more  $\mathbf{k}$ -states to be included in the Hamiltonian. We have selected a value of  $0.1 \text{ \AA}^{-1}$  much smaller than the recommended default,  $0.5 \text{ \AA}^{-1}$ .

We have also performed a convergence test of the mean absolute error (MAE) for AE6 test set [66] of six atomization energies (a subset of G3) with respect to the real-space grid in VASP. The size of the real-space grid in VASP is controlled by the precision (PREC, set to “accurate” here) and the energy cutoff (ENCUT). One may also specify the number of grid points per axis using the NGX, NGY, and NGZ tags. For this test, the “fine” grid settings NGXF, etc. were left to be automatically determined by the combination of PREC, ENCUT, and the grid points per axis. A default grid was selected by leaving ENCUT as the default from the pseudopotentials, and the grid points per axis unspecified. As is common for molecular and atomic calculations in VASP, only the  $\Gamma$  point was used to sample  $\mathbf{k}$  space. In Table S1, it can be seen that the default grid setting is completely sufficient to resolve the SCAN potential.

TABLE S1: Real-space grid convergence of the AE6 test set [66] of six atomization energies in VASP. Mean absolute errors are given in kcal/mol. For each setting besides “Default”, ENCUT was set to 1000 eV, and the number of grid points along each axis  $NGX=NGY=NGZ$  was set to the displayed number of points per axis. For the “Default” grid setting, ENCUT was left unspecified, as were  $NGX$ ,  $NGY$ , and  $NGZ$ . In all cases, only the  $\Gamma$  point was used for  $\mathbf{k}$ -space sampling. The authors were recently made aware of a long-standing bug affecting convergence of spin-polarized calculations ( $ISPIN=2$ ) using meta-GGAs in VASP. The routine used here was updated to correctly treat spin-polarization.

Points per axis	Default	60	80	100	120	140	150
SCAN	3.581	4.018	3.951	3.906	4.032	3.989	3.989
rSCAN	7.054	6.958	7.032	7.026	7.031	7.033	7.027
r <sup>2</sup> SCAN	3.491	3.866	3.767	3.765	3.765	3.765	3.765

## S2. $r^2$ SCAN EQUATIONS

The full equations required for implementing  $r^2$ SCAN are given below. Note that by construction  $\bar{\alpha} \geq 0$  (also  $\alpha$  and  $\alpha'$ ). In pseudopotential codes (e.g., VASP) or through rounding errors in regions of very small density,  $\bar{\alpha}$  (or  $\alpha$ ) can become negative, which can cause numerical problems for interpolation functions that do not consider this possibility. An additional condition was included to Eqs. S7 and S26 to consistently handle negative  $\bar{\alpha}$  regions. These provisions were essential to reliably converge calculations in VASP, as neither extending the polynomial interpolation nor setting a constant  $f(\bar{\alpha} < 0) = 1$  were sufficient.

The ultimate choice of regularization for the unphysical region  $\bar{\alpha} < 0$ , as shown in Eqs. S7 and S26, is consistent with the current implementation of SCAN in VASP. The current SCAN subroutines in VASP simply extend SCAN's interpolating functions,  $f_x(\alpha)$  and  $f_c(\alpha)$ , to  $\alpha < 0$ ; our implementation does the same. We do not ascribe a physical interpretation to these regions, nor to the numeric regularization chosen. They are necessary computational artifices.

An exchange functional for a density with arbitrary spin polarization,  $n_\uparrow$  and  $n_\downarrow$ , can be constructed from a spin-unpolarized functional via the spin-scaling relation [44]

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} \{E_x[2n_\uparrow] + E_x[2n_\downarrow]\}. \quad (\text{S1})$$

Thus we present equations only for spin-unpolarized exchange energy functionals.

All constants not defined here nor in the main text are unchanged from  $r$ SCAN.

### A. Exchange

$$E_x^{r^2\text{SCAN}}[n] = \int n(\mathbf{r}) \varepsilon_x^{r^2\text{SCAN}}(\mathbf{r}) d^3r \quad (\text{S2})$$

$$\varepsilon_x^{r^2\text{SCAN}} = \varepsilon_x^{\text{LDA}}(r_s) F_x^{r^2\text{SCAN}}(p, \bar{\alpha}) \quad (\text{S3})$$

$$\varepsilon_x^{\text{LDA}}(r_s) = -\frac{3}{4\pi} \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s} \quad (\text{S4})$$

$$F_x^{r^2\text{SCAN}}(p, \bar{\alpha}) = \{h_x^1(p) + f_x(\bar{\alpha}) [h_x^0 - h_x^1(p)]\} g_x(p) \quad (\text{S5})$$

$$\bar{\alpha}(p, \alpha) = \frac{\alpha}{1 + \eta \frac{5}{3} p} = \frac{\tau - \tau_W}{\tau_U + \eta \tau_W} \quad (\text{S6})$$

$$f_x(\bar{\alpha}) = \begin{cases} \exp\left[-\frac{c_{1x}^{\text{SCAN}} \bar{\alpha}}{1 - \bar{\alpha}}\right] & \bar{\alpha} < 0 \\ \sum_{i=0}^7 c_{xi} \bar{\alpha}^i & 0 \leq \bar{\alpha} \leq 2.5 \\ -d_x^{\text{SCAN}} \exp\left[\frac{c_{2x}^{\text{SCAN}}}{1 - \bar{\alpha}}\right] & \bar{\alpha} > 2.5 \end{cases} \quad (\text{S7})$$

$$h_x^0 = 1 + k_0 \quad (\text{S8})$$

$$h_x^1(p) = 1 + k_1 - \frac{k_1}{1 + \frac{x(p)}{k_1}} \quad (\text{S9})$$

$$x(p) = (C_\eta C_2 \exp[-p^2/d_{p2}^4] + \mu) p \quad (\text{S10})$$

$$C_\eta = \left[\frac{20}{27} + \eta \frac{5}{3}\right] \quad (\text{S11})$$

$$C_2 = -\sum_{i=1}^7 i c_{xi} [1 - h_x^0] \approx -0.162742 \quad (\text{S12})$$

$$g_x(p) = 1 - \exp\left[\frac{-a_1^{\text{SCAN}}}{p^{1/4}}\right] \quad (\text{S13})$$

The values of the new constants appearing in the previous equations are  $\eta = 0.001$  and  $d_{p2} = 0.361$ .

Some constants appearing here are unchanged from either SCAN or  $r$ SCAN. Note that for the  $r$ SCAN interpolating polynomial we take the convention of indexing the coefficient by the power of  $\alpha$  it multiplies, thus the vector  $\mathbf{c}_x$  begins

at  $c_0$ . These are:

$$\mathbf{c}_x = (1, -0.667, -0.4445555, -0.663086601049, 1.451297044490, \\ -0.887998041597, 0.234528941479, -0.023185843322) \quad (\text{S14})$$

$$c_{1x}^{\text{SCAN}} = 0.667 \quad (\text{S15})$$

$$c_{2x}^{\text{SCAN}} = 0.8 \quad (\text{S16})$$

$$d_x^{\text{SCAN}} = 1.24 \quad (\text{S17})$$

$$k_0 = 0.174 \quad (\text{S18})$$

$$k_1 = 0.065 \quad (\text{S19})$$

$$\mu = 10/81 \quad (\text{S20})$$

$$a_1^{\text{SCAN}} = 4.9479 \quad (\text{S21})$$

## B. Correlation

$$E_c^{r^2\text{SCAN}}[n_\uparrow, n_\downarrow] = \int n(\mathbf{r}) \varepsilon_c^{r^2\text{SCAN}}(\mathbf{r}) d^3r \quad (\text{S22})$$

$$\varepsilon_c^{r^2\text{SCAN}} = \varepsilon_c^1 + f_c(\bar{\alpha})(\varepsilon_c^0 - \varepsilon_c^1) \quad (\text{S23})$$

$$\varepsilon_c^1 = \varepsilon_c^{\text{LSDA}} + H_c^1 \quad (\text{S24})$$

$$\varepsilon_c^{\text{LDA0}} = -\frac{b_{1c}}{1 + b_{2c}\sqrt{r_s} + b_{3c}r_s} \quad (\text{S25})$$

$$f_c(\bar{\alpha}) = \begin{cases} \exp\left[-\frac{c_{1c}^{\text{SCAN}}\bar{\alpha}}{1-\bar{\alpha}}\right] & \bar{\alpha} < 0 \\ \sum_{i=0}^7 c_{ci}\bar{\alpha}^i & 0 \leq \bar{\alpha} \leq 2.5 \\ -d_c^{\text{SCAN}} \exp\left[\frac{c_{2c}^{\text{SCAN}}}{1-\bar{\alpha}}\right] & \bar{\alpha} > 2.5 \end{cases} \quad (\text{S26})$$

$$\Delta f_{c2} = \sum_{i=1}^7 i c_{ci} \quad (\text{S27})$$

$$d_s(\zeta) = \frac{(1+\zeta)^{5/3} + (1-\zeta)^{5/3}}{2} \quad (\text{S28})$$

$$H_c^1 = \gamma\phi^3 \ln[1 + w_1(1 - g(y, \Delta y))] \quad (\text{S29})$$

$$w_1 = \exp\left[-\frac{\varepsilon_c^{\text{LSDA}}}{\gamma\phi^3}\right] - 1 \quad (\text{S30})$$

$$g(y, \Delta y) = \frac{1}{(1 + 4(y - \Delta y))^{1/4}} \quad (\text{S31})$$

$$y = \frac{\beta(r_s)}{\gamma w_1} t^2 \quad (\text{S32})$$

$$\beta(r_s) = \beta_{\text{MB}} \frac{1 + 0.1r_s}{1 + 0.1778r_s} \quad (\text{S33})$$

$$\Delta y = \frac{\Delta f_{c2}}{27\gamma d_s(\zeta)\phi^3 w_1} \left\{ 20r_s \left[ \frac{\partial \varepsilon_c^{\text{LSDA0}}}{\partial r_s} - \frac{\partial \varepsilon_c^{\text{LSDA1}}}{\partial r_s} \right] - 45\eta[\varepsilon_c^{\text{LSDA0}} - \varepsilon_c^{\text{LSDA1}}] \right\} p \exp[-p^2/d_{p2}^4] \quad (\text{S34})$$

$$\varepsilon_c^0 = (\varepsilon_c^{\text{LDA0}} + H_0) G_c(\zeta) \quad (\text{S35})$$

$$H_0 = b_{1c} \ln[1 + w_0(1 - g_\infty(\zeta = 0, s))] \quad (\text{S36})$$

$$G_c(\zeta) = [1 - 2.3631(d_x(\zeta) - 1)](1 - \zeta^{12}) \quad (\text{S37})$$

$$d_x(\zeta) = [(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3}]/2 \quad (\text{S38})$$

$$g_\infty(\zeta = 0, s) = \frac{1}{(1 + 4\chi_\infty s^2)^{1/4}} \quad (\text{S39})$$

$$w_0 = \exp\left[-\frac{\varepsilon_c^{\text{LDA0}}}{b_{1c}}\right] - 1 \quad (\text{S40})$$

$$(\text{S41})$$

The values of the new constants appearing in the previous equations are the same as for exchange,  $\eta = 0.001$  and  $d_{p2} = 0.361$ .

Some constants appearing here are unchanged from either SCAN or rSCAN. Note that for the rSCAN interpolating polynomial we take the convention of indexing the coefficient by the power of  $\alpha$  it multiplies, thus the vector  $\mathbf{c}_c$  begins at  $c_0$ . These are:

$$\mathbf{c}_c = (1, -0.64, -0.4352, -1.535685604549, 3.061560252175, \\ -1.915710236206, 0.516884468372, -0.051848879792) \quad (\text{S42})$$

$$c_{1c}^{\text{SCAN}} = 0.64 \quad (\text{S43})$$

$$c_{2c}^{\text{SCAN}} = 1.5 \quad (\text{S44})$$

$$d_c^{\text{SCAN}} = 0.7 \quad (\text{S45})$$

$$b_1 = 0.0285764 \quad (\text{S46})$$

$$b_2 = 0.0889 \quad (\text{S47})$$

$$b_3 = 0.125541 \quad (\text{S48})$$

$$\beta_{\text{MB}} \approx 0.066725 \quad (\text{S49})$$

$$\chi_\infty = \left(\frac{3\pi^2}{16}\right)^{2/3} \frac{\beta_{\text{MB}}}{1.778\{0.9 - 3[3/(16\pi)]^{2/3}\}} \approx 0.128025 \quad (\text{S50})$$

S3. DETERMINING  $\eta$  REGULARIZATION PARAMETER

The effect of the  $\eta$  regularization parameter on the r<sup>2</sup>SCAN exchange and correlation functionals is illustrated in Figures S1 and S2. For all systems studied the r<sup>2</sup>SCAN total exchange, correlation, and exchange-correlation energies were monotonic functions of  $\eta$ , as expected. The value  $\eta = 10^{-3}$  was arbitrarily selected as sufficiently large to ensure that  $\bar{\alpha}$  remains finite at long ranges in practical calculations, while remaining small enough to have minimal impact on total energy.

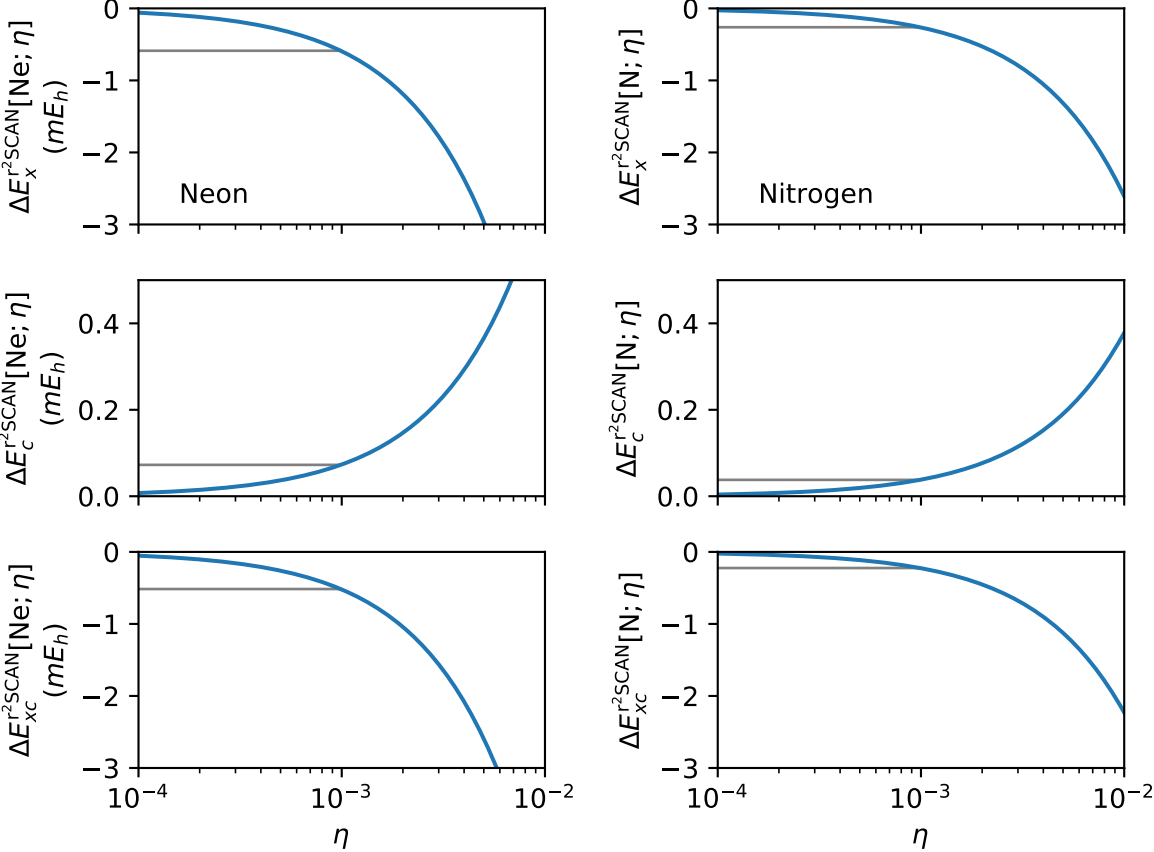


FIG. S1. Change in energy,  $\Delta E = E[\eta] - E[\eta = 0]$ , as a function of the  $\eta$  regularization parameter in r<sup>2</sup>SCAN for exchange (top), correlation (middle), and exchange-correlation (lower) calculated from fixed Hartree–Fock Slater orbitals[48] for the neon and nitrogen atoms. All energies are monotonic functions of the regularisation parameter. The selected  $\eta = 10^{-3}$  is shown by the horizontal line to the axis.

The exchange-correlation potential plots of Figure 3 in the main text are repeated here in Figure S3 to longer ranges and larger values of iso-orbital indicator, confirming that  $\alpha$  diverges, while  $\bar{\alpha}$  decays beyond  $\sim 8$  Bohr radii. The problematic divergence of SCAN potentials for single orbital systems is shown in Figure S4, where it is clear that the regularization introduced by r<sup>2</sup>SCAN (and rSCAN) prevents this divergence in both multiplicative and  $\tau$  dependent components.



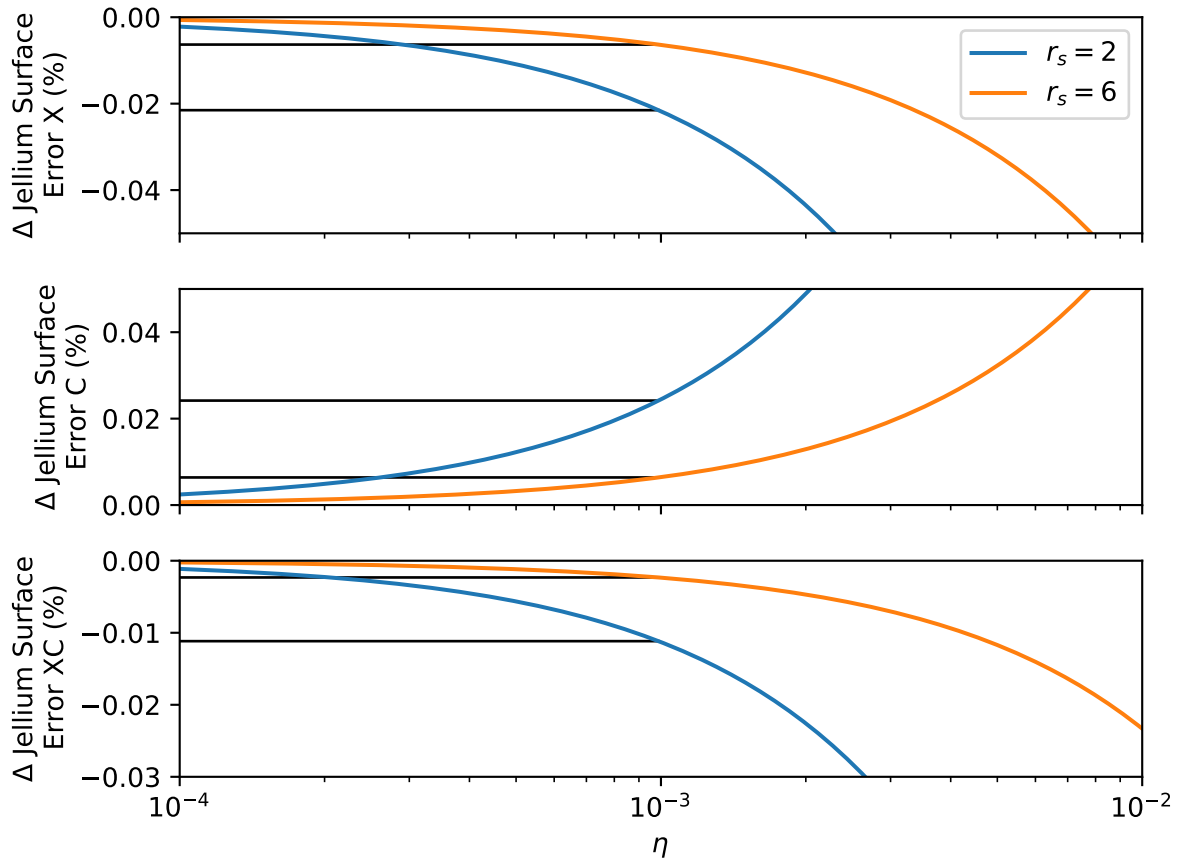


FIG. S2. Change in percentage error for jellium surface energy ( $r_s = 2, 6$ ),  $\Delta E = E[\eta] - E[\eta = 0]$ , as a function of the  $\eta$  regularisation parameter in  $r^2$ SCAN for exchange (top), correlation (middle), and exchange-correlation (lower). All energies are monotonic functions of the regularization parameter. The selected  $\eta = 10^{-3}$  is shown by the horizontal line to the axis.

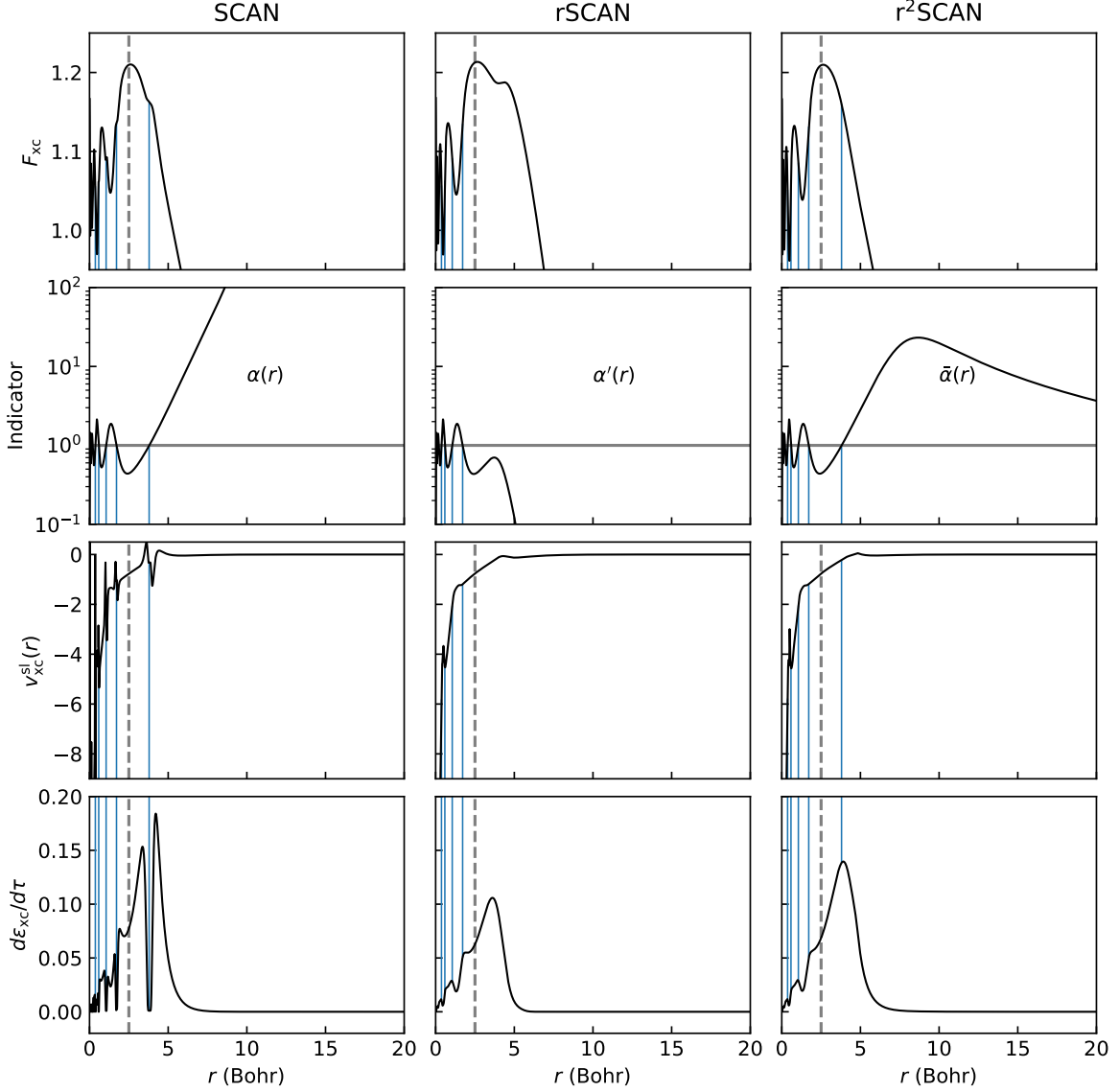


FIG. S3. (Top) Exchange-correlation enhancement factors, (middle-upper, logarithmic scale) iso-orbital indicator  $\alpha(r)$ ,  $\alpha'(r)$ , or  $\bar{\alpha}(r)$  as appropriate, (middle-lower) semi-local part of the exchange-correlation potential as in main text, and (bottom) derivative of exchange-correlation energy density with respect to kinetic energy density. Calculated for the xenon atom from accurate Hartree–Fock Slater orbitals [48] for the SCAN [7], rSCAN [22] and r<sup>2</sup>SCAN functionals. The VASP [49–52] projector-augmented wave [53] pseudopotential cutoff radius (2.5 Bohr) is illustrated by a dashed vertical line. Solid vertical lines show where  $\alpha = 1$ . This figure shows the same data as Figure 3 of the main text on a larger scale.

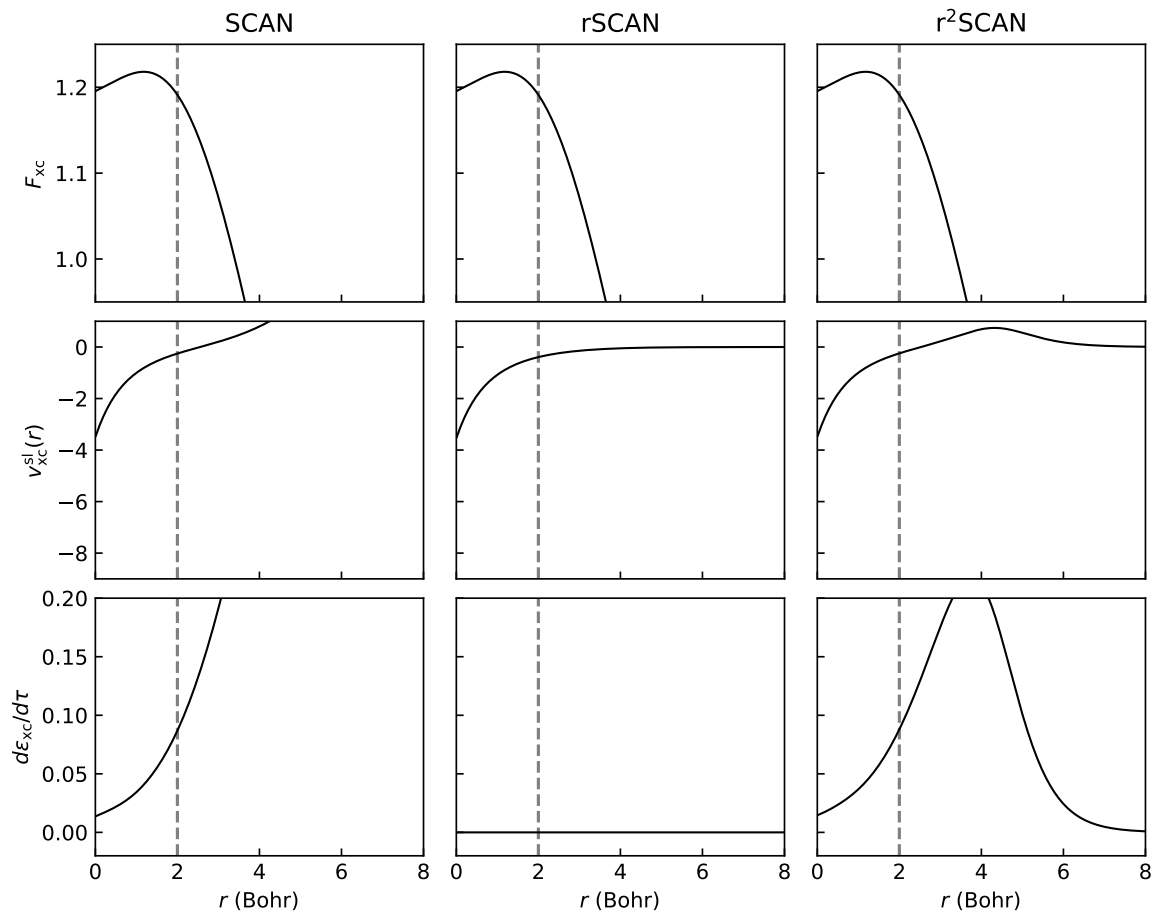


FIG. S4. (Top) Exchange-correlation enhancement factors, (middle-upper, all zero for single orbital system) iso-orbital indicator  $\alpha(r)$ ,  $\alpha'(r)$ , or  $\bar{\alpha}(r)$  as appropriate, (middle-lower) semi-local part of the exchange-correlation potential as in main text, and (bottom) derivative of exchange-correlation energy density with respect to kinetic energy density. Calculated for the helium atom from accurate Hartree–Fock Slater orbitals [48] for the SCAN [7], rSCAN [22] and r<sup>2</sup>SCAN functionals. The VASP [49–52] projector-augmented wave [53] pseudopotential cutoff radius (2 Bohr) is illustrated by a dashed vertical line. Note the divergence of SCAN potential components.

## S4. REFERENCE ATOMIC ENERGIES

We provide the total and exchange-correlation energies for the nitrogen and neon atoms from the common cc-pVTZ basis set [60, 67] as references for testing implementations of the functionals. The largest “reference” level TURBOMOLE grid was used with increased radial grid density specified as `radsize 100` in the `control` file, as commonly suggested for the SCAN functional.

TABLE S2: Reference self-consistent total atomic energies ( $E$ ) **using only the exchange part of the functional**, and corresponding exchange energies ( $E_x$ ) in Hartree. Calculated using the cc-pVTZ basis set [60, 67] and the “reference” level Turbomole grid.

		SCAN	rSCAN	r <sup>2</sup> SCAN
$E$	N	-54.40541174994	-54.41398626268	-54.39774875432
	Ne	-128.5891914977	-128.6082003154	-128.5698768302
$E_x$	N	-6.597139583375	-6.604261530513	-6.586631390511
	Ne	-12.143536468556	-12.160698876055	-12.11878636737

TABLE S3: Reference self-consistent total atomic energies ( $E$ ) and exchange-correlation energies ( $E_{xc}$ ) in Hartree calculated using the cc-pVTZ basis set [60, 67] and the “reference” level Turbomole grid.

		SCAN	rSCAN	r <sup>2</sup> SCAN
$E$	N	-54.58565736367	-54.59430112747	-54.57900797069
	Ne	-128.9340794821	-128.9541235246	-128.9168416529
$E_{xc}$	N	-6.782282570589	-6.790099568534	-6.773066377305
	Ne	-12.49701065638	-12.515767373154	-12.474955269761

## S5. TEST SET DATA

TABLE S4: Deviation of TPSS atomisation energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids. Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
LiH	-1.051	-1.089	-1.100	-1.098	-1.097	-1.097	-1.097
BeH	-10.159	-10.306	-10.192	-10.202	-10.205	-10.206	-10.206
CH	-3.306	-3.405	-3.397	-3.398	-3.402	-3.402	-3.402
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	-8.104	-8.205	-8.204	-8.200	-8.208	-8.208	-8.207
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	-0.341	-0.513	-0.503	-0.503	-0.507	-0.507	-0.507
CH <sub>3</sub>	-6.114	-6.322	-6.301	-6.300	-6.305	-6.305	-6.304
Methane (CH <sub>4</sub> )	-4.373	-4.618	-4.614	-4.607	-4.612	-4.612	-4.612
NH	-6.650	-6.739	-6.672	-6.698	-6.698	-6.698	-6.698
NH <sub>2</sub>	-5.967	-6.138	-6.074	-6.100	-6.100	-6.100	-6.100
Ammonia (NH <sub>3</sub> )	-1.466	-1.748	-1.689	-1.709	-1.709	-1.708	-1.708
OH	-0.734	-0.612	-0.602	-0.600	-0.601	-0.601	-0.601
Water (H <sub>2</sub> O)	3.351	3.471	3.488	3.493	3.492	3.492	3.492
Hydrogen fluoride (HF)	1.229	1.297	1.300	1.292	1.292	1.292	1.292
SiH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	-5.259	-5.277	-5.301	-5.306	-5.305	-5.306	-5.306
SiH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	-10.777	-10.694	-10.705	-10.706	-10.706	-10.706	-10.706
SiH <sub>3</sub>	-11.828	-11.786	-11.799	-11.802	-11.803	-11.803	-11.803
Silane (SiH <sub>4</sub> )	-11.656	-11.586	-11.602	-11.607	-11.607	-11.608	-11.608
PH <sub>2</sub>	-8.638	-8.754	-8.820	-8.804	-8.804	-8.804	-8.804
PH <sub>3</sub>	-7.869	-7.952	-8.022	-8.001	-8.002	-8.002	-8.002
Hydrogen sulfide (H <sub>2</sub> S)	-2.770	-3.000	-3.030	-3.004	-3.003	-3.004	-3.004
Hydrogen chloride (HCl)	-1.195	-1.065	-1.112	-1.108	-1.107	-1.107	-1.107
Li <sub>2</sub>	1.182	1.242	1.194	1.197	1.199	1.198	1.198
LiF	1.323	1.295	1.179	1.199	1.197	1.195	1.195
Acetylene (C <sub>2</sub> H <sub>2</sub> )	1.022	0.694	0.688	0.700	0.689	0.689	0.690
Ethylene (H <sub>2</sub> C=CH <sub>2</sub> )	-3.812	-4.318	-4.310	-4.299	-4.309	-4.309	-4.309
Ethane (H <sub>3</sub> C-CH <sub>3</sub> )	-5.674	-6.157	-6.121	-6.105	-6.115	-6.115	-6.115
CN	-1.290	-1.635	-1.594	-1.602	-1.607	-1.606	-1.606
Hydrogen cyanide (HCN)	-0.699	-1.039	-0.983	-0.998	-1.003	-1.002	-1.002
CO	4.247	4.159	4.191	4.202	4.196	4.196	4.196
HCO	-4.892	-4.931	-4.914	-4.903	-4.909	-4.908	-4.908
Formaldehyde (H <sub>2</sub> C=O)	-3.028	-3.132	-3.111	-3.099	-3.104	-3.104	-3.104
Methanol (CH <sub>3</sub> -OH)	-2.481	-2.658	-2.621	-2.609	-2.615	-2.615	-2.615
N <sub>2</sub>	1.224	0.813	0.929	0.893	0.894	0.894	0.894
Hydrazine (H <sub>2</sub> N-NH <sub>2</sub> )	-4.595	-5.124	-4.971	-5.013	-5.013	-5.012	-5.013
NO	-4.121	-4.180	-4.079	-4.099	-4.100	-4.100	-4.100
O <sub>2</sub>	-7.103	-6.817	-6.787	-6.797	-6.798	-6.798	-6.798
Hydrogen peroxide (HO-OH)	-0.505	-0.246	-0.204	-0.200	-0.202	-0.202	-0.202
F <sub>2</sub>	-6.615	-6.664	-6.695	-6.705	-6.705	-6.705	-6.705
Carbon dioxide (CO <sub>2</sub> )	-1.923	-1.832	-1.827	-1.802	-1.808	-1.808	-1.808
Na <sub>2</sub>	-2.374	-2.403	-2.399	-2.395	-2.395	-2.396	-2.396
Si <sub>2</sub>	-0.196	-0.054	-0.057	-0.067	-0.067	-0.067	-0.067
P <sub>2</sub>	0.217	0.072	-0.034	-0.002	-0.001	-0.001	-0.001
S <sub>2</sub>	-6.965	-7.101	-7.155	-7.107	-7.107	-7.107	-7.107
Cl <sub>2</sub>	-3.149	-3.157	-3.195	-3.208	-3.204	-3.205	-3.204
NaCl	0.893	0.873	0.805	0.796	0.795	0.799	0.799
Silicon monoxide (SiO)	5.344	5.552	5.592	5.594	5.594	5.594	5.594
CS	1.864	1.425	1.472	1.496	1.493	1.493	1.493
SO	-5.016	-4.913	-4.917	-4.897	-4.898	-4.898	-4.898
ClO	-7.751	-7.475	-7.501	-7.501	-7.503	-7.503	-7.503
Chlorine monofluoride (FCl)	-5.513	-5.447	-5.493	-5.500	-5.500	-5.501	-5.501
Si <sub>2</sub> H <sub>6</sub>	-18.040	-17.853	-17.895	-17.911	-17.911	-17.911	-17.911
Methyl chloride (CH <sub>3</sub> Cl)	-5.357	-5.481	-5.509	-5.498	-5.504	-5.504	-5.503
Methanethiol (H <sub>3</sub> CSH)	-4.915	-5.328	-5.338	-5.303	-5.306	-5.307	-5.306
Hypochlorous acid (HOCl)	-2.754	-2.499	-2.501	-2.502	-2.502	-2.502	-2.502

Continued on next page

TABLE S4: Deviation of TPSS atomisation energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids. Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
Sulfur dioxide (SO <sub>2</sub> )	1.174	1.433	1.455	1.488	1.492	1.491	1.491
BF <sub>3</sub>	3.743	3.940	3.948	3.890	3.897	3.893	3.893
BCl <sub>3</sub>	-2.440	-2.082	-2.078	-2.105	-2.108	-2.109	-2.110
AlF <sub>3</sub>	8.876	9.470	9.284	9.307	9.294	9.295	9.296
AlCl <sub>3</sub>	-1.367	0.035	-0.098	-0.099	-0.101	-0.093	-0.094
Carbon tetrafluoride (CF <sub>4</sub> )	-3.979	-4.157	-4.202	-4.200	-4.206	-4.208	-4.208
Carbon tetrachloride (CCl <sub>4</sub> )	-2.621	-2.413	-2.508	-2.485	-2.487	-2.487	-2.487
Carbon oxide sulfide (COS)	-5.779	-6.045	-6.046	-5.999	-6.002	-6.002	-6.002
Carbon bisulfide (CS <sub>2</sub> )	-7.952	-8.572	-8.572	-8.505	-8.505	-8.506	-8.506
Carbonic difluoride (COF <sub>2</sub> )	-0.129	-0.251	-0.295	-0.298	-0.308	-0.306	-0.306
Silicon tetrafluoride (SiF <sub>4</sub> )	16.260	16.254	16.211	16.183	16.188	16.186	16.185
Silicon tetrachloride (SiCl <sub>4</sub> )	3.067	3.600	3.391	3.387	3.396	3.396	3.396
Dinitrogen monoxide (N <sub>2</sub> O)	-11.848	-12.097	-11.974	-12.004	-12.005	-12.004	-12.004
Nitrogen chloride oxide (ClNO)	-13.506	-13.441	-13.399	-13.409	-13.409	-13.408	-13.409
Nitrogen trifluoride (NF <sub>3</sub> )	-19.185	-19.514	-19.361	-19.401	-19.401	-19.400	-19.400
PF <sub>3</sub>	1.872	1.865	1.768	1.796	1.794	1.793	1.793
O <sub>3</sub>	-9.542	-9.080	-9.004	-8.992	-8.996	-8.994	-8.995
F <sub>2</sub> O	-14.313	-14.281	-14.281	-14.297	-14.298	-14.298	-14.298
Chlorine trifluoride (ClF <sub>3</sub> )	-22.819	-22.848	-22.883	-22.905	-22.903	-22.901	-22.901
Tetrafluoro Ethene (F <sub>2</sub> C=CF <sub>2</sub> )	-14.342	-14.612	-14.772	-14.794	-14.807	-14.809	-14.809
Tetrachloro Ethene (C <sub>2</sub> Cl <sub>4</sub> )	-6.714	-6.391	-6.522	-6.501	-6.506	-6.506	-6.506
Acetonitrile, trifluoro- (CF <sub>3</sub> CN)	-5.002	-5.525	-5.494	-5.504	-5.515	-5.516	-5.516
Propyne (C <sub>3</sub> H <sub>4</sub> )	-2.048	-2.619	-2.612	-2.593	-2.608	-2.608	-2.608
Allene (C <sub>3</sub> H <sub>4</sub> )	-6.328	-7.023	-7.010	-6.997	-7.012	-7.011	-7.011
Cyclopropene (C <sub>3</sub> H <sub>4</sub> )	-4.539	-5.232	-5.210	-5.193	-5.207	-5.207	-5.207
Propylene (C <sub>3</sub> H <sub>6</sub> )	-4.930	-5.624	-5.617	-5.597	-5.611	-5.611	-5.611
Cyclopropane (C <sub>3</sub> H <sub>6</sub> )	-6.753	-7.430	-7.422	-7.400	-7.415	-7.414	-7.414
Propane (C <sub>3</sub> H <sub>8</sub> )	-6.247	-6.614	-6.629	-6.602	-6.617	-6.617	-6.616
Trans-1,3-butadiene (C <sub>4</sub> H <sub>6</sub> )	-4.842	-5.834	-5.830	-5.802	-5.819	-5.820	-5.819
Dimethylacetylene (C <sub>4</sub> H <sub>6</sub> )	-4.034	-4.849	-4.828	-4.803	-4.823	-4.822	-4.822
Methylenecyclopropane (C <sub>4</sub> H <sub>6</sub> )	-9.950	-10.732	-10.725	-10.700	-10.720	-10.719	-10.719
Bicyclo[1.1.0]butane (C <sub>4</sub> H <sub>6</sub> )	-6.829	-7.788	-7.727	-7.696	-7.715	-7.714	-7.714
Cyclobutene (C <sub>4</sub> H <sub>6</sub> )	-4.433	-5.160	-5.130	-5.101	-5.120	-5.120	-5.120
Cyclobutane (C <sub>4</sub> H <sub>8</sub> )	-6.768	-7.174	-7.142	-7.108	-7.125	-7.125	-7.124
Isobutene (C <sub>4</sub> H <sub>8</sub> )	-5.019	-5.623	-5.629	-5.609	-5.625	-5.625	-5.625
Trans-butane(C <sub>4</sub> H <sub>10</sub> )	-6.130	-6.930	-6.831	-6.807	-6.826	-6.825	-6.825
Isobutane (C <sub>4</sub> H <sub>10</sub> )	-4.593	-5.635	-5.629	-5.603	-5.624	-5.623	-5.623
Spiropentane (C <sub>5</sub> H <sub>8</sub> )	-9.902	-10.844	-10.833	-10.797	-10.821	-10.821	-10.820
Benzene (C <sub>6</sub> H <sub>6</sub> )	-4.370	-5.568	-5.543	-5.488	-5.521	-5.519	-5.518
Difluoromethane (CH <sub>2</sub> F <sub>2</sub> )	-6.953	-7.230	-7.292	-7.305	-7.311	-7.310	-7.310
Trifluoromethane(CHF <sub>3</sub> )	-5.903	-6.088	-6.108	-6.105	-6.110	-6.112	-6.112
CH <sub>2</sub> Cl <sub>2</sub>	-5.262	-5.159	-5.219	-5.205	-5.208	-5.209	-5.208
CHCl <sub>3</sub>	-4.043	-3.952	-4.015	-4.001	-4.005	-4.005	-4.005
Methylamine (H <sub>3</sub> C-NH <sub>2</sub> )	-4.692	-5.175	-5.087	-5.105	-5.109	-5.109	-5.109
Acetonitrile (CH <sub>3</sub> -CN)	-3.600	-4.165	-4.097	-4.105	-4.115	-4.114	-4.114
Nitromethane (CH <sub>3</sub> -NO <sub>2</sub> )	-13.374	-13.423	-13.302	-13.305	-13.311	-13.311	-13.311
Methyl nitrite (CH <sub>3</sub> -O-N=O)	-13.320	-13.446	-13.295	-13.307	-13.313	-13.313	-13.313
Methyl silane (CH <sub>3</sub> SiH <sub>3</sub> )	-9.852	-10.002	-10.011	-10.010	-10.015	-10.015	-10.015
Formic acid (HCOOH)	-0.871	-0.878	-0.835	-0.806	-0.813	-0.813	-0.813
Methyl formate (HCOOCH <sub>3</sub> )	-6.325	-6.493	-6.429	-6.409	-6.419	-6.419	-6.419
Acetamide (CH <sub>3</sub> CONH <sub>2</sub> )	-4.017	-4.412	-4.318	-4.309	-4.320	-4.320	-4.320
Aziridine (C <sub>2</sub> H <sub>4</sub> NH)	-8.683	-9.171	-9.099	-9.108	-9.116	-9.116	-9.116
Cyanogen (NCCN)	-2.917	-3.576	-3.471	-3.496	-3.506	-3.504	-3.505
Dimethylamine ((CH <sub>3</sub> ) <sub>2</sub> NH)	-7.097	-7.683	-7.596	-7.608	-7.616	-7.615	-7.615
Trans ethylamine (CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> )	-6.141	-6.728	-6.595	-6.607	-6.617	-6.616	-6.616
Ketene (CH <sub>2</sub> CO)	-5.739	-6.030	-6.018	-5.998	-6.009	-6.008	-6.008
Oxirane (C <sub>2</sub> H <sub>4</sub> O)	-8.055	-8.259	-8.221	-8.207	-8.215	-8.216	-8.216

Continued on next page

TABLE S4: Deviation of TPSS atomisation energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids. Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
Acetaldehyde (CH <sub>3</sub> CHO)	-4.137	-4.447	-4.423	-4.402	-4.412	-4.412	-4.412
Glyoxal (HCOCOH)	-2.834	-2.892	-2.835	-2.803	-2.815	-2.814	-2.814
Ethanol (CH <sub>3</sub> CH <sub>2</sub> OH)	-2.587	-2.977	-2.921	-2.903	-2.912	-2.913	-2.913
Dimethylether (CH <sub>3</sub> OCH <sub>3</sub> )	-6.928	-7.173	-7.117	-7.107	-7.117	-7.117	-7.116
Thiirane (C <sub>2</sub> H <sub>4</sub> S)	-7.902	-8.447	-8.449	-8.407	-8.416	-8.415	-8.415
Dimethyl sulfoxide ((CH <sub>3</sub> ) <sub>2</sub> SO)	-5.298	-5.666	-5.652	-5.605	-5.618	-5.620	-5.619
Ethaneithiol (C <sub>2</sub> H <sub>5</sub> SH)	-4.949	-5.555	-5.545	-5.502	-5.510	-5.510	-5.510
Dimethyl sulfide (CH <sub>3</sub> SCH <sub>3</sub> )	-6.578	-7.145	-7.141	-7.102	-7.111	-7.113	-7.112
Vinyl fluoride (CH <sub>2</sub> =CHF)	-6.832	-7.267	-7.299	-7.297	-7.307	-7.308	-7.308
Ethyl chloride (C <sub>2</sub> H <sub>5</sub> Cl)	-5.912	-6.223	-6.220	-6.203	-6.211	-6.211	-6.211
Vinyl chloride (CH <sub>2</sub> =CHCl)	-8.478	-8.783	-8.807	-8.796	-8.804	-8.804	-8.804
Acrylonitrile (CH <sub>2</sub> =CHCN)	-1.929	-2.756	-2.697	-2.700	-2.715	-2.714	-2.714
Acetone (CH <sub>3</sub> COCH <sub>3</sub> )	-4.541	-4.741	-4.737	-4.710	-4.724	-4.724	-4.723
Acetic acid (CH <sub>3</sub> COOH)	-0.910	-0.971	-0.934	-0.903	-0.915	-0.915	-0.915
Acetyl fluoride (CH <sub>3</sub> COF)	-4.529	-4.814	-4.820	-4.806	-4.816	-4.816	-4.816
CH <sub>3</sub> COCl (acetyl chloride)	-5.741	-5.931	-5.938	-5.909	-5.916	-5.916	-5.916
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl (propyl chloride)	-6.548	-6.782	-6.832	-6.802	-6.815	-6.815	-6.815
Isopropanol (CH <sub>3</sub> ) <sub>2</sub> CHOH)	-1.886	-2.605	-2.537	-2.509	-2.524	-2.524	-2.523
Methyl ethyl ether (C <sub>2</sub> H <sub>5</sub> OCH <sub>3</sub> )	-7.527	-7.918	-7.833	-7.811	-7.824	-7.824	-7.823
Trimethylamine ((CH <sub>3</sub> ) <sub>3</sub> N)	-8.749	-9.718	-9.609	-9.612	-9.627	-9.625	-9.625
Furan (C <sub>4</sub> H <sub>4</sub> O)	-4.949	-5.854	-5.833	-5.797	-5.818	-5.817	-5.817
C <sub>4</sub> H <sub>4</sub> S (thiophene)	-4.213	-5.182	-5.173	-5.104	-5.118	-5.118	-5.117
Pyrrrole (C <sub>4</sub> H <sub>5</sub> N)	-6.159	-7.365	-7.315	-7.300	-7.318	-7.317	-7.317
Pyridine (C <sub>5</sub> H <sub>5</sub> N)	-7.587	-8.813	-8.724	-8.693	-8.719	-8.717	-8.717
H <sub>2</sub>	-3.220	-3.203	-3.203	-3.203	-3.203	-3.203	-3.203
HS	-2.715	-2.806	-2.813	-2.798	-2.797	-2.797	-2.797
CCH	0.402	0.110	0.096	0.110	0.099	0.099	0.100
C <sub>2</sub> H <sub>3</sub> ( <sup>2</sup> A')	-7.121	-7.512	-7.498	-7.494	-7.504	-7.504	-7.504
CH <sub>3</sub> CO ( <sup>2</sup> A')	-6.845	-7.151	-7.119	-7.099	-7.110	-7.110	-7.109
H <sub>2</sub> COH ( <sup>2</sup> A)	-4.921	-5.045	-5.008	-5.000	-5.005	-5.005	-5.005
CH <sub>3</sub> O ( <sup>2</sup> A')	-8.022	-8.132	-8.117	-8.108	-8.113	-8.113	-8.113
CH <sub>3</sub> CH <sub>2</sub> O ( <sup>2</sup> A'')	-9.727	-9.942	-9.920	-9.902	-9.911	-9.912	-9.911
CH <sub>3</sub> S ( <sup>2</sup> A')	-6.613	-6.930	-6.923	-6.900	-6.904	-6.904	-6.904
C <sub>2</sub> H <sub>5</sub> ( <sup>2</sup> A')	-8.214	-8.630	-8.606	-8.598	-8.607	-8.607	-8.607
(CH <sub>3</sub> ) <sub>2</sub> CH ( <sup>2</sup> A')	-9.915	-10.324	-10.318	-10.307	-10.320	-10.320	-10.320
(CH <sub>3</sub> ) <sub>2</sub> CH ( <sup>2</sup> A')	-9.915	-10.324	-10.318	-10.307	-10.320	-10.320	-10.320
NO <sub>2</sub>	-14.368	-14.404	-14.288	-14.306	-14.307	-14.307	-14.307
Methyl allene (C <sub>4</sub> H <sub>6</sub> )	-7.350	-8.038	-8.018	-8.000	-8.018	-8.018	-8.018
Isoprene (C <sub>5</sub> H <sub>8</sub> )	-4.210	-5.341	-5.324	-5.296	-5.318	-5.317	-5.317
Cyclopentane (C <sub>5</sub> H <sub>10</sub> )	-3.826	-4.952	-4.944	-4.910	-4.935	-4.935	-4.935
n-Pentane (C <sub>5</sub> H <sub>12</sub> )	-6.689	-6.876	-6.964	-6.903	-6.927	-6.927	-6.926
Neo pentane (C <sub>5</sub> H <sub>12</sub> )	-2.566	-3.736	-3.721	-3.701	-3.728	-3.725	-3.725
1,4 Cyclohexadiene (C <sub>6</sub> H <sub>8</sub> )	-1.161	-2.257	-2.238	-2.198	-2.227	-2.226	-2.225
Cyclohexane (C <sub>6</sub> H <sub>12</sub> )	-1.366	-2.776	-2.733	-2.687	-2.724	-2.724	-2.723
n-Hexane (C <sub>6</sub> H <sub>14</sub> )	-6.460	-7.514	-7.351	-7.310	-7.336	-7.334	-7.334
3-Methyl pentane (C <sub>6</sub> H <sub>14</sub> )	-3.918	-5.320	-5.255	-5.203	-5.234	-5.232	-5.232
Toluene (C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )	-4.258	-5.732	-5.662	-5.599	-5.639	-5.636	-5.635
n-Heptane (C <sub>7</sub> H <sub>16</sub> )	-7.451	-7.438	-7.602	-7.506	-7.539	-7.539	-7.538
Cyclooctatetraene (C <sub>8</sub> H <sub>8</sub> )	-0.383	-2.015	-2.041	-1.992	-2.031	-2.031	-2.030
n-Octane (C <sub>8</sub> H <sub>18</sub> )	-6.872	-7.959	-7.781	-7.719	-7.745	-7.742	-7.742
Naphthalene (C <sub>10</sub> H <sub>8</sub> )	-3.624	-5.733	-5.675	-5.585	-5.643	-5.640	-5.639
Azulene (C <sub>10</sub> H <sub>8</sub> )	-6.308	-8.405	-8.408	-8.316	-8.362	-8.359	-8.358
Acetic acid methyl ester (CH <sub>3</sub> COOCH <sub>3</sub> )	-5.306	-5.480	-5.436	-5.402	-5.420	-5.420	-5.419
t-Butanol ((CH <sub>3</sub> ) <sub>3</sub> COH)	-0.046	-1.009	-0.937	-0.902	-0.927	-0.926	-0.926
Aniline (C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> )	-5.268	-6.628	-6.526	-6.494	-6.528	-6.525	-6.524
Phenol (C <sub>6</sub> H <sub>5</sub> OH)	-1.627	-2.723	-2.656	-2.595	-2.629	-2.627	-2.626
Divinyl ether (C <sub>4</sub> H <sub>6</sub> O)	-6.456	-7.064	-7.025	-6.997	-7.017	-7.017	-7.016

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TABLE S4: Deviation of TPSS atomisation energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids. Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
Tetrahydrofuran (C <sub>4</sub> H <sub>8</sub> O)	-3.946	-5.114	-5.041	-5.008	-5.025	-5.025	-5.025
Cyclopentanone (C <sub>5</sub> H <sub>8</sub> O)	-2.914	-4.119	-4.059	-4.009	-4.030	-4.030	-4.030
Benzoquinone(C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> )	-0.416	-1.418	-1.344	-1.304	-1.331	-1.330	-1.330
Pyrimidine (C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> )	-11.670	-12.845	-12.689	-12.699	-12.719	-12.717	-12.717
Dimethyl sulphone (C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> S)	0.137	0.135	0.132	0.182	0.178	0.177	0.177
Chlorobenzene (C <sub>6</sub> H <sub>5</sub> Cl)	-4.752	-5.845	-5.848	-5.792	-5.826	-5.823	-5.823
Butanedinitrile (NC-CH <sub>2</sub> -CH <sub>2</sub> -CN)	-1.404	-2.730	-2.587	-2.599	-2.620	-2.618	-2.618
Pyrazine (C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> )	-7.995	-9.268	-9.108	-9.102	-9.123	-9.122	-9.122
Acetyl acetylene (CH <sub>3</sub> -C(=O)-CCH)	0.891	0.158	0.171	0.205	0.183	0.184	0.185
Crotonaldehyde (CH <sub>3</sub> -CH=CH-CHO)	-6.650	-7.240	-7.221	-7.199	-7.218	-7.219	-7.218
Acetic anhydride (CH <sub>3</sub> -C(=O)-O-C(=O)-CH <sub>3</sub> )	-4.610	-5.113	-5.061	-5.004	-5.023	-5.023	-5.023
2,5-Dihydrothiophene (C <sub>4</sub> H <sub>6</sub> S)	-4.076	-5.176	-5.156	-5.099	-5.118	-5.118	-5.117
Isobutane nitrile ((CH <sub>3</sub> ) <sub>2</sub> CH-CN)	-1.882	-2.761	-2.705	-2.703	-2.722	-2.721	-2.721
Methyl ethyl ketone (CH <sub>3</sub> -CO-CH <sub>2</sub> -CH <sub>3</sub> )	-3.872	-5.065	-4.926	-4.904	-4.922	-4.922	-4.922
Isobutanal ((CH <sub>3</sub> ) <sub>2</sub> CH-CHO)	-2.871	-3.500	-3.436	-3.406	-3.424	-3.424	-3.423
1,4-Dioxane (C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	-4.454	-5.177	-5.060	-5.002	-5.024	-5.026	-5.025
Tetrahydrothiophene (C <sub>4</sub> H <sub>8</sub> S)	-3.195	-4.415	-4.368	-4.301	-4.321	-4.323	-4.322
t-Butyl chloride ((CH <sub>3</sub> ) <sub>3</sub> C-Cl)	-3.740	-4.713	-4.728	-4.700	-4.721	-4.719	-4.719
n-Butyl chloride (CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -Cl)	-6.045	-6.510	-6.534	-6.500	-6.522	-6.521	-6.521
Tetrahydropyrrole (C <sub>4</sub> H <sub>8</sub> NH)	-5.335	-6.397	-6.313	-6.303	-6.323	-6.322	-6.322
Nitro-s-butane (CH <sub>3</sub> -CH <sub>2</sub> -CH(CH <sub>3</sub> )-NO <sub>2</sub> )	-11.509	-12.410	-12.213	-12.204	-12.225	-12.223	-12.223
Diethyl ether (CH <sub>3</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>3</sub> )	-7.240	-7.671	-7.632	-7.602	-7.623	-7.623	-7.622
Dimethyl acetal (CH <sub>3</sub> -CH(OCH <sub>3</sub> ) <sub>2</sub> )	-6.312	-6.940	-6.839	-6.808	-6.830	-6.830	-6.829
t-Butanethiol ((CH <sub>3</sub> ) <sub>3</sub> C-SH)	-2.472	-3.672	-3.666	-3.605	-3.625	-3.624	-3.624
Diethyl disulfide (CH <sub>3</sub> -CH <sub>2</sub> -S-S-CH <sub>2</sub> -CH <sub>3</sub> )	-7.208	-8.158	-8.211	-8.106	-8.123	-8.124	-8.123
t-Butylamine ((CH <sub>3</sub> ) <sub>3</sub> C-NH <sub>2</sub> )	-2.737	-3.447	-3.330	-3.307	-3.323	-3.323	-3.323
Tetramethylsilane (Si(CH <sub>3</sub> ) <sub>4</sub> )	-2.377	-3.029	-3.014	-2.999	-3.016	-3.016	-3.016
2-Methyl thiophene (C <sub>5</sub> H <sub>6</sub> S)	-4.358	-5.764	-5.762	-5.694	-5.717	-5.717	-5.716
N-methyl pyrrole (cyc-C <sub>4</sub> H <sub>4</sub> N-CH <sub>3</sub> )	-7.722	-9.191	-9.118	-9.099	-9.120	-9.120	-9.119
Tetrahydropyran (C <sub>5</sub> H <sub>10</sub> O)	-2.726	-3.859	-3.728	-3.696	-3.725	-3.726	-3.725
Diethyl ketone (CH <sub>3</sub> -CH <sub>2</sub> -CO-CH <sub>2</sub> -CH <sub>3</sub> )	-5.423	-5.843	-5.859	-5.804	-5.831	-5.830	-5.830
Isopropyl acetate (CH <sub>3</sub> -C(=O)-O-CH(CH <sub>3</sub> ) <sub>2</sub> )	-4.269	-5.013	-4.948	-4.900	-4.927	-4.927	-4.926
Tetrahydrothiopyran (C <sub>5</sub> H <sub>10</sub> S)	-2.089	-3.441	-3.370	-3.298	-3.330	-3.329	-3.328
Piperidine (cyc-C <sub>5</sub> H <sub>10</sub> NH)	-2.731	-4.252	-4.131	-4.103	-4.130	-4.130	-4.129
t-Butyl methyl ether ((CH <sub>3</sub> ) <sub>3</sub> C-O-CH <sub>3</sub> )	-4.108	-4.701	-4.631	-4.613	-4.629	-4.630	-4.629
1,3-Difluorobenzene (C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> )	-7.514	-8.725	-8.711	-8.665	-8.700	-8.698	-8.697
1,4-Difluorobenzene (C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> )	-8.932	-10.017	-10.066	-10.021	-10.052	-10.052	-10.051
Fluorobenzene (C <sub>6</sub> H <sub>5</sub> F)	-6.057	-7.261	-7.242	-7.191	-7.225	-7.223	-7.222
Di-isopropyl ether ((CH <sub>3</sub> ) <sub>2</sub> CH-O-CH(CH <sub>3</sub> ) <sub>2</sub> )	-5.181	-5.738	-5.666	-5.605	-5.638	-5.637	-5.636
PF <sub>5</sub>	7.491	7.762	7.448	7.492	7.488	7.489	7.489
SF <sub>6</sub>	-3.769	-3.751	-3.941	-3.842	-3.824	-3.809	-3.808
P <sub>4</sub>	-9.532	-9.581	-9.984	-9.891	-9.900	-9.899	-9.899
SO <sub>3</sub>	1.283	1.821	1.854	1.887	1.892	1.891	1.891
SCL <sub>2</sub>	-5.422	-5.527	-5.635	-5.604	-5.604	-5.603	-5.603
POCl <sub>3</sub>	-0.272	0.893	0.760	0.788	0.798	0.795	0.795
PCL <sub>5</sub>	-8.252	-7.049	-7.341	-7.316	-7.307	-7.300	-7.299
Cl <sub>2</sub> O <sub>2</sub> S	-0.838	-0.594	-0.655	-0.616	-0.606	-0.609	-0.609
PCL <sub>3</sub>	-5.442	-4.562	-4.745	-4.707	-4.702	-4.702	-4.702
Cl <sub>2</sub> S <sub>2</sub>	-12.458	-12.744	-12.876	-12.800	-12.802	-12.801	-12.801
SiCl <sub>2</sub> singlet	-0.914	-0.820	-0.894	-0.903	-0.905	-0.904	-0.904
CF <sub>3</sub> Cl	-5.743	-5.841	-5.914	-5.901	-5.907	-5.909	-5.909
Hexafluoro ethane (C <sub>2</sub> F <sub>6</sub> )	-6.180	-6.507	-6.610	-6.598	-6.606	-6.610	-6.610
CF <sub>3</sub>	-10.578	-10.745	-10.790	-10.794	-10.803	-10.803	-10.803
C <sub>6</sub> H <sub>5</sub> (phenyl radical)	-8.446	-9.674	-9.639	-9.587	-9.619	-9.617	-9.617
Bicyclo[1.1.0]butane (C <sub>4</sub> H <sub>6</sub> )	-6.829	-7.788	-7.727	-7.696	-7.715	-7.714	-7.714
(CH <sub>3</sub> ) <sub>3</sub> C (t-butyl radical)	-9.278	-10.212	-10.131	-10.099	-10.120	-10.119	-10.119
Trans-butane(C <sub>4</sub> H <sub>10</sub> )	-6.130	-6.930	-6.831	-6.807	-6.826	-6.825	-6.825

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TABLE S4: Deviation of TPSS atomisation energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids. Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
1,3 Cyclohexadiene (C <sub>6</sub> H <sub>8</sub> )	-1.861	-3.194	-3.145	-3.094	-3.125	-3.125	-3.124
ME	-4.837	-5.262	-5.250	-5.230	-5.242	-5.241	-5.241
MAE	5.428	5.864	5.843	5.826	5.837	5.836	5.836

TABLE S5: Deviation from reference “exact” values of SCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
LiH	2.186	2.549	2.778	2.524	2.449	2.448	2.518
BeH	-10.520	-10.879	-11.005	-10.701	-10.472	-10.447	-10.508
CH	1.438	1.265	0.127	1.596	2.317	2.277	1.914
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	-6.715	-6.243	-7.581	-6.325	-5.790	-5.911	-6.400
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	4.207	4.836	2.635	4.362	5.416	5.626	5.269
CH <sub>3</sub>	-5.871	-5.316	-7.022	-5.373	-4.543	-4.490	-4.867
Methane (CH <sub>4</sub> )	0.207	-0.173	-1.744	-0.707	0.398	0.746	0.570
NH	-2.770	-3.772	-1.302	-1.004	-1.294	-1.994	-1.230
NH <sub>2</sub>	-4.177	-6.533	-4.185	-3.224	-2.816	-3.294	-2.677
Ammonia (NH <sub>3</sub> )	3.112	-1.255	1.896	2.334	3.021	2.795	3.564
OH	-0.045	-1.446	-3.032	-4.284	-3.519	-2.676	-2.609
Water (H <sub>2</sub> O)	6.827	3.341	1.985	0.484	1.594	2.886	2.971
Hydrogen fluoride (HF)	0.847	4.405	3.877	2.541	3.018	3.642	3.051
SiH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	3.181	3.272	2.264	2.696	2.471	2.316	2.179
SiH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	-5.900	-8.309	-6.847	-7.640	-7.529	-7.592	-7.717
SiH <sub>3</sub>	-3.738	-4.588	-4.814	-4.743	-4.794	-4.948	-5.102
Silane (SiH <sub>4</sub> )	-0.270	0.160	-1.469	-0.594	-0.809	-1.062	-1.248
PH <sub>2</sub>	-1.783	-5.033	-1.050	-4.662	-4.630	-4.332	-4.024
PH <sub>3</sub>	2.702	-1.543	3.158	-1.232	-1.054	-0.669	-0.227
Hydrogen sulfide (H <sub>2</sub> S)	3.024	-1.871	2.961	-1.635	-0.892	-0.288	-0.089
Hydrogen chloride (HCl)	-1.589	2.333	0.073	-0.551	-0.208	0.417	0.270
Li <sub>2</sub>	5.462	6.040	6.290	5.925	5.823	5.839	5.963
LiF	-0.790	6.242	3.731	2.530	3.046	3.713	3.052
Acetylene (C <sub>2</sub> H <sub>2</sub> )	1.980	3.157	-1.206	1.534	3.594	4.140	3.719
Ethylene (H <sub>2</sub> C=CH <sub>2</sub> )	-0.949	-0.497	-4.482	-1.982	0.149	0.781	0.412
Ethane (H <sub>3</sub> C-CH <sub>3</sub> )	-2.103	-2.564	-5.813	-3.641	-1.396	-0.705	-1.086
CN	2.446	-1.058	0.805	1.916	3.371	3.249	3.742
Hydrogen cyanide (HCN)	3.210	0.741	0.811	2.758	4.491	4.558	5.124
CO	7.760	2.989	1.109	0.178	2.614	4.290	4.095
HCO	-1.365	-4.601	-7.396	-7.510	-5.389	-3.973	-4.253
Formaldehyde (H <sub>2</sub> C=O)	2.472	-0.627	-4.063	-4.200	-1.969	-0.340	-0.491
Methanol (CH <sub>3</sub> -OH)	2.170	-1.072	-4.520	-4.598	-2.383	-0.781	-0.914
N <sub>2</sub>	7.481	1.813	5.958	6.966	8.419	8.119	9.743
Hydrazine (H <sub>2</sub> N-NH <sub>2</sub> )	2.081	-5.216	0.374	1.449	2.909	2.434	3.919
NO	3.410	-2.254	-1.072	-1.984	-0.192	0.678	1.374
O <sub>2</sub>	-5.548	-2.950	-8.604	-10.389	-9.051	-7.782	-7.366
Hydrogen peroxide (HO-OH)	8.488	2.977	-0.946	-3.916	-1.679	0.915	1.153
F <sub>2</sub>	3.598	1.020	2.414	0.247	1.739	2.998	1.675
Carbon dioxide (CO <sub>2</sub> )	3.055	-6.629	-8.421	-11.459	-7.974	-5.192	-5.299
Na <sub>2</sub>	3.816	2.868	2.944	2.635	2.673	2.742	2.715
Si <sub>2</sub>	1.930	3.159	1.059	1.916	1.488	1.153	0.909
P <sub>2</sub>	11.197	2.794	12.012	2.790	3.048	3.876	4.847
S <sub>2</sub>	-1.598	-8.305	-2.055	-8.723	-8.039	-7.419	-7.062
Cl <sub>2</sub>	-2.926	2.723	-1.299	-0.482	-0.361	0.330	0.242
NaCl	-0.624	3.843	1.340	-1.178	-0.257	0.736	0.409
Silicon monoxide (SiO)	11.761	6.310	5.488	3.433	4.601	5.804	5.689
CS	6.628	1.874	4.535	0.883	2.809	3.779	3.781
SO	-1.665	-5.249	-4.847	-8.817	-7.946	-6.717	-6.318
ClO	-5.100	-2.966	-6.684	-7.039	-6.647	-5.100	-5.015
Chlorine monofluoride (FCl)	-2.146	1.092	-0.103	-0.486	-0.330	0.607	0.001
Si <sub>2</sub> H <sub>6</sub>	-3.243	-1.993	-5.529	-3.635	-4.149	-4.672	-5.078
Methyl chloride (CH <sub>3</sub> Cl)	-4.787	-0.833	-4.970	-4.038	-2.637	-1.778	-2.122
Methanethiol (H <sub>3</sub> CSH)	0.963	-3.920	-0.991	-4.221	-2.401	-1.510	-1.517
Hypochlorous acid (HOCl)	2.196	1.714	-1.983	-2.735	-1.745	-0.095	-0.010
Sulfur dioxide (SO <sub>2</sub> )	11.258	-3.155	1.681	-7.031	-3.987	-0.835	-0.505
BF <sub>3</sub>	-13.344	3.819	-0.202	-3.545	-2.246	-0.998	-2.619

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TABLE S5: Deviation from reference “exact” values of SCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
BCl <sub>3</sub>	-18.533	-4.845	-10.795	-14.932	-13.937	-11.983	-12.188
AlF <sub>3</sub>	-5.436	13.042	6.542	3.670	5.393	7.154	5.023
AlCl <sub>3</sub>	-13.365	-0.538	-7.735	-12.913	-10.628	-7.882	-8.833
Carbon tetrafluoride (CF <sub>4</sub> )	-16.947	-4.795	-7.932	-12.136	-8.825	-6.169	-8.845
Carbon tetrachloride (CCl <sub>4</sub> )	-15.690	-2.150	-12.259	-11.791	-9.380	-7.114	-7.830
Carbon oxide sulfide (COS)	-0.318	-10.165	-7.227	-13.138	-9.944	-7.652	-7.564
Carbon bisulfide (CS <sub>2</sub> )	-1.992	-12.356	-4.487	-13.602	-10.788	-9.010	-8.666
Carbonic difluoride (COF <sub>2</sub> )	-4.111	-1.675	-5.331	-8.262	-4.952	-2.230	-3.699
Silicon tetrafluoride (SiF <sub>4</sub> )	-2.075	20.933	12.645	8.344	10.686	12.757	9.832
Silicon tetrachloride (SiCl <sub>4</sub> )	-12.793	5.713	-6.801	-11.262	-8.975	-5.948	-7.288
Dinitrogen monoxide (N <sub>2</sub> O)	1.907	-11.626	-5.341	-6.886	-4.318	-3.535	-1.796
Nitrogen chloride oxide (ClNO)	-4.239	-7.362	-8.386	-10.665	-8.118	-6.275	-5.736
Nitrogen trifluoride (NF <sub>3</sub> )	-13.166	-11.202	-7.881	-11.179	-9.032	-7.592	-8.806
PF <sub>3</sub>	-3.745	9.737	9.021	1.565	3.328	5.379	3.662
O <sub>3</sub>	8.819	1.429	-4.593	-9.460	-5.877	-1.907	-1.540
F <sub>2</sub> O	-2.175	-3.190	-3.783	-8.446	-6.101	-3.631	-4.739
Chlorine trifluoride (ClF <sub>3</sub> )	-21.279	-9.913	-12.221	-15.243	-14.225	-11.733	-13.726
Tetrafluoro Ethene (F <sub>2</sub> C=CF <sub>2</sub> )	-26.836	-13.667	-18.805	-21.367	-17.449	-14.483	-17.353
Tetrachloro Ethene (C <sub>2</sub> Cl <sub>4</sub> )	-22.264	-7.569	-20.098	-18.276	-14.972	-12.303	-13.199
Acetonitrile, trifluoro- (CF <sub>3</sub> CN)	-14.441	-7.706	-10.425	-11.188	-6.724	-4.573	-6.107
Propyne (C <sub>3</sub> H <sub>4</sub> )	-1.947	-1.162	-7.008	-3.257	-0.066	0.829	0.218
Allene (C <sub>3</sub> H <sub>4</sub> )	-5.655	-5.047	-10.969	-7.274	-4.113	-3.157	-3.693
Cyclopropene (C <sub>3</sub> H <sub>4</sub> )	-1.682	-2.244	-7.391	-3.737	-0.512	0.418	-0.168
Propylene (C <sub>3</sub> H <sub>6</sub> )	-3.717	-3.562	-9.116	-5.572	-2.309	-1.329	-1.886
Cyclopropane (C <sub>3</sub> H <sub>6</sub> )	-4.806	-6.203	-10.831	-7.431	-4.119	-3.136	-3.715
Propane (C <sub>3</sub> H <sub>8</sub> )	-4.377	-4.826	-9.806	-6.533	-3.143	-2.107	-2.683
Trans-1,3-butadiene (C <sub>4</sub> H <sub>6</sub> )	-6.072	-5.055	-12.979	-8.057	-3.778	-2.499	-3.232
Dimethylacetylene (C <sub>4</sub> H <sub>6</sub> )	-4.579	-4.214	-11.520	-6.764	-2.429	-1.187	-1.994
Methylenecyclopropane (C <sub>4</sub> H <sub>6</sub> )	-9.776	-10.506	-17.299	-12.681	-8.321	-7.016	-7.777
Bicyclo[1.1.0]butane (C <sub>4</sub> H <sub>6</sub> )	-6.294	-8.637	-14.492	-10.004	-5.592	-4.284	-5.068
Cyclobutene (C <sub>4</sub> H <sub>6</sub> )	-5.894	-5.804	-12.923	-8.197	-3.758	-2.441	-3.221
Cyclobutane (C <sub>4</sub> H <sub>8</sub> )	-8.111	-8.449	-14.936	-10.455	-5.924	-4.546	-5.345
Isobutene (C <sub>4</sub> H <sub>8</sub> )	-6.141	-6.059	-13.169	-8.595	-4.202	-2.872	-3.619
Trans-butane(C <sub>4</sub> H <sub>10</sub> )	-6.083	-7.065	-13.471	-9.148	-4.620	-3.230	-4.005
Isobutane (C <sub>4</sub> H <sub>10</sub> )	-5.313	-6.576	-13.083	-8.769	-4.244	-2.856	-3.623
Spiropentane (C <sub>5</sub> H <sub>8</sub> )	-10.924	-13.199	-20.757	-15.223	-9.674	-8.010	-8.983
Benzene (C <sub>6</sub> H <sub>6</sub> )	-15.017	-12.995	-25.133	-17.774	-11.333	-9.378	-10.432
Difluoromethane (CH <sub>2</sub> F <sub>2</sub> )	-8.938	-2.334	-5.281	-6.285	-4.207	-2.740	-4.218
Trifluoromethane(CHF <sub>3</sub> )	-13.277	-3.304	-6.503	-9.068	-6.385	-4.307	-6.428
CH <sub>2</sub> Cl <sub>2</sub>	-8.892	-1.098	-7.560	-6.777	-5.080	-3.688	-4.201
CHCl <sub>3</sub>	-12.121	-1.528	-9.932	-9.342	-7.287	-5.413	-6.055
Methylamine (H <sub>3</sub> C-NH <sub>2</sub> )	0.146	-4.125	-2.783	-1.053	0.790	0.878	1.427
Acetonitrile (CH <sub>3</sub> -CN)	-0.621	-3.511	-4.898	-1.901	0.943	1.337	1.719
Nitromethane (CH <sub>3</sub> -NO <sub>2</sub> )	-1.237	-13.405	-14.233	-15.988	-11.686	-8.940	-8.265
Methyl nitrite (CH <sub>3</sub> -O-N=O)	-0.797	-10.986	-13.084	-14.070	-9.969	-7.280	-6.659
Methyl silane (CH <sub>3</sub> SiH <sub>3</sub> )	-0.794	-0.749	-3.827	-1.938	-1.058	-0.956	-1.329
Formic acid (HCOOH)	3.336	-4.913	-8.475	-10.566	-7.098	-4.202	-4.308
Methyl formate (HCOOCH <sub>3</sub> )	-1.889	-9.602	-15.235	-15.937	-11.404	-8.210	-8.531
Acetamide (CH <sub>3</sub> CONH <sub>2</sub> )	-2.839	-11.631	-11.952	-11.514	-7.305	-5.526	-5.086
Aziridine (C <sub>2</sub> H <sub>4</sub> NH)	-4.200	-8.135	-8.862	-5.701	-2.832	-2.429	-2.077
Cyanogen (NCCN)	0.979	-4.074	-3.793	0.056	3.558	3.670	4.761
Dimethylamine ((CH <sub>3</sub> ) <sub>2</sub> NH)	-2.847	-7.189	-7.529	-4.657	-1.668	-1.242	-0.903
Trans ethylamine (CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> )	-3.063	-7.742	-7.872	-5.088	-2.110	-1.670	-1.314
Ketene (CH <sub>2</sub> CO)	-3.098	-7.970	-11.729	-11.340	-8.040	-6.158	-6.457
Oxirane (C <sub>2</sub> H <sub>4</sub> O)	-2.841	-6.122	-11.132	-10.172	-6.793	-4.861	-5.194
Acetaldehyde (CH <sub>3</sub> CHO)	-0.739	-4.341	-9.162	-8.325	-4.977	-2.999	-3.327

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TABLE S5: Deviation from reference “exact” values of SCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
Glyoxal (HCOCOH)	1.424	-4.682	-11.485	-11.814	-7.378	-4.102	-4.379
Ethanol (CH <sub>3</sub> CH <sub>2</sub> OH)	0.084	-3.551	-8.409	-7.498	-4.123	-2.176	-2.506
Dimethylether (CH <sub>3</sub> OCH <sub>3</sub> )	-2.158	-5.078	-10.447	-9.185	-5.872	-3.941	-4.279
Thiirane (C <sub>2</sub> H <sub>4</sub> S)	-3.180	-7.754	-6.951	-8.929	-6.041	-4.826	-5.047
Dimethyl sulfoxide ((CH <sub>3</sub> ) <sub>2</sub> SO)	0.834	-9.436	-7.573	-12.238	-8.226	-5.714	-5.753
Ethaneithiol (C <sub>2</sub> H <sub>5</sub> SH)	-0.864	-5.927	-4.626	-6.788	-3.826	-2.580	-2.784
Dimethyl sulfide (CH <sub>3</sub> SCH <sub>3</sub> )	-1.565	-6.376	-5.183	-7.159	-4.269	-3.076	-3.276
Vinyl fluoride (CH <sub>2</sub> =CHF)	-8.324	-4.326	-8.855	-7.468	-4.903	-3.702	-4.729
Ethyl chloride (C <sub>2</sub> H <sub>5</sub> Cl)	-7.345	-3.430	-9.191	-7.307	-4.729	-3.488	-4.054
Vinyl chloride (CH <sub>2</sub> =CHCl)	-10.376	-5.774	-12.217	-9.983	-7.539	-6.344	-6.896
Acrylonitrile (CH <sub>2</sub> =CHCN)	-0.797	-2.889	-6.695	-2.279	1.600	2.293	2.492
Acetone (CH <sub>3</sub> COCH <sub>3</sub> )	-3.776	-7.361	-13.726	-11.859	-7.382	-5.050	-5.563
Acetic acid (CH <sub>3</sub> COOH)	0.568	-7.639	-12.837	-13.850	-9.272	-6.034	-6.328
Acetyl fluoride (CH <sub>3</sub> COF)	-6.596	-6.380	-11.830	-12.278	-8.352	-5.850	-6.876
CH <sub>3</sub> COCl (acetyl chloride)	-7.092	-7.391	-14.071	-14.207	-10.353	-7.735	-8.329
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl (propyl chloride)	-9.587	-5.784	-13.263	-10.222	-6.519	-4.937	-5.700
Isopropanol (CH <sub>3</sub> ) <sub>2</sub> CHOH)	-1.932	-5.921	-12.449	-10.441	-5.955	-3.651	-4.163
Methyl ethyl ether (C <sub>2</sub> H <sub>5</sub> OCH <sub>3</sub> )	-4.759	-7.910	-14.820	-12.496	-8.033	-5.753	-6.285
Trimethylamine ((CH <sub>3</sub> ) <sub>3</sub> N)	-5.909	-10.460	-12.649	-8.570	-4.487	-3.721	-3.584
Furan (C <sub>4</sub> H <sub>4</sub> O)	-8.459	-11.623	-20.469	-17.107	-11.695	-9.109	-9.780
C <sub>4</sub> H <sub>4</sub> S (thiophene)	-7.629	-12.230	-15.052	-14.851	-9.797	-7.860	-8.393
Pyrrrole (C <sub>4</sub> H <sub>5</sub> N)	-10.190	-14.989	-18.490	-13.809	-8.686	-7.556	-7.517
Pyridine (C <sub>5</sub> H <sub>5</sub> N)	-14.824	-16.824	-24.095	-17.380	-11.314	-9.932	-10.057
H <sub>2</sub>	2.072	2.088	2.088	2.089	2.088	2.088	2.088
HS	-0.164	-3.056	-0.181	-2.786	-2.409	-2.111	-2.052
CCH	-1.141	-0.784	-3.802	-1.578	0.092	0.360	-0.195
C <sub>2</sub> H <sub>3</sub> ( <sup>2</sup> A')	-7.439	-7.003	-10.391	-7.823	-5.980	-5.577	-6.114
CH <sub>3</sub> CO ( <sup>2</sup> A')	-4.740	-8.392	-12.771	-11.763	-8.559	-6.823	-7.308
H <sub>2</sub> COH ( <sup>2</sup> A)	-2.919	-5.761	-9.061	-8.986	-6.965	-5.578	-5.881
CH <sub>3</sub> O ( <sup>2</sup> A')	-5.613	-7.371	-10.746	-10.875	-8.922	-7.689	-7.802
CH <sub>3</sub> CH <sub>2</sub> O ( <sup>2</sup> A'')	-8.731	-11.190	-15.918	-15.059	-11.956	-10.346	-10.638
CH <sub>3</sub> S ( <sup>2</sup> A')	-3.660	-6.737	-5.552	-7.008	-5.548	-4.925	-5.043
C <sub>2</sub> H <sub>5</sub> ( <sup>2</sup> A')	-8.630	-8.437	-11.686	-8.989	-7.019	-6.628	-7.192
(CH <sub>3</sub> ) <sub>2</sub> CH ( <sup>2</sup> A')	-11.700	-11.662	-16.422	-12.663	-9.581	-8.837	-9.589
(CH <sub>3</sub> ) <sub>2</sub> CH ( <sup>2</sup> A')	-11.700	-11.662	-16.422	-12.663	-9.581	-8.837	-9.589
NO <sub>2</sub>	-1.476	-13.635	-11.987	-14.997	-11.989	-9.855	-9.083
Methyl allene (C <sub>4</sub> H <sub>6</sub> )	-7.918	-7.192	-14.781	-10.023	-5.709	-4.410	-5.143
Isoprene (C <sub>5</sub> H <sub>8</sub> )	-7.995	-7.242	-16.749	-10.749	-5.338	-3.710	-4.634
Cyclopentane (C <sub>5</sub> H <sub>10</sub> )	-8.610	-10.140	-18.250	-12.753	-7.052	-5.323	-6.317
n-Pentane (C <sub>5</sub> H <sub>12</sub> )	-8.313	-8.787	-17.092	-11.642	-5.966	-4.239	-5.209
Neo pentane (C <sub>5</sub> H <sub>12</sub> )	-6.580	-8.076	-16.122	-10.787	-5.128	-3.394	-4.351
1,4 Cyclohexadiene (C <sub>6</sub> H <sub>8</sub> )	-10.463	-9.852	-20.989	-13.911	-7.327	-5.359	-6.498
Cyclohexane (C <sub>6</sub> H <sub>12</sub> )	-10.149	-11.918	-21.759	-15.174	-8.329	-6.243	-7.431
n-Hexane (C <sub>6</sub> H <sub>14</sub> )	-9.910	-11.385	-20.937	-14.457	-7.642	-5.551	-6.723
3-Methyl pentane (C <sub>6</sub> H <sub>14</sub> )	-8.395	-10.349	-19.805	-13.332	-6.513	-4.435	-5.606
Toluene (C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )	-17.063	-15.427	-29.048	-20.665	-13.085	-10.779	-12.027
n-Heptane (C <sub>7</sub> H <sub>16</sub> )	-12.561	-13.046	-24.678	-17.051	-9.087	-6.669	-8.033
Cyclooctatetraene (C <sub>8</sub> H <sub>8</sub> )	-14.861	-12.822	-28.540	-18.724	-10.108	-7.537	-9.015
n-Octane (C <sub>8</sub> H <sub>18</sub> )	-13.713	-15.598	-28.310	-19.684	-10.565	-7.775	-9.341
Naphthalene (C <sub>10</sub> H <sub>8</sub> )	-28.554	-25.405	-45.599	-33.372	-22.624	-19.318	-21.089
Azulene (C <sub>10</sub> H <sub>8</sub> )	-28.941	-26.523	-46.202	-34.044	-23.255	-19.963	-21.741
Acetic acid methyl ester (CH <sub>3</sub> COOCH <sub>3</sub> )	-3.630	-11.300	-18.500	-18.123	-12.484	-8.931	-9.434
t-Butanol ((CH <sub>3</sub> ) <sub>3</sub> COH)	-3.363	-7.715	-15.843	-12.782	-7.177	-4.522	-5.219
Aniline (C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> )	-17.440	-20.168	-28.714	-21.139	-13.912	-12.146	-12.472
Phenol (C <sub>6</sub> H <sub>5</sub> OH)	-13.912	-15.660	-28.981	-23.054	-15.506	-12.277	-13.284
Divinyl ether (C <sub>4</sub> H <sub>6</sub> O)	-6.711	-9.115	-18.479	-14.763	-9.381	-6.880	-7.601

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TABLE S5: Deviation from reference “exact” values of SCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
Tetrahydrofuran (C <sub>4</sub> H <sub>8</sub> O)	-6.330	-9.966	-18.595	-15.193	-9.616	-6.984	-7.725
Cyclopentanone (C <sub>5</sub> H <sub>8</sub> O)	-8.899	-13.800	-23.265	-19.266	-12.461	-9.446	-10.372
Benzoquinone(C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> )	-10.968	-15.618	-30.342	-25.829	-17.068	-12.508	-13.508
Pyrimidine (C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> )	-15.751	-21.928	-24.133	-18.160	-12.418	-11.610	-10.809
Dimethyl sulphone (C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> S)	3.463	-12.938	-9.818	-17.113	-11.673	-7.872	-7.966
Chlorobenzene (C <sub>6</sub> H <sub>5</sub> Cl)	-20.608	-14.758	-29.157	-22.071	-15.324	-12.823	-14.051
Butanedinitrile (NC-CH <sub>2</sub> -CH <sub>2</sub> -CN)	-1.686	-7.626	-10.457	-4.331	1.391	2.179	2.912
Pyrazine (C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> )	-11.835	-17.633	-20.043	-14.107	-8.373	-7.554	-6.750
Acetyl acetylene (CH <sub>3</sub> -C(=O)-CCH)	-1.078	-3.609	-12.737	-9.221	-3.798	-1.262	-2.011
Crotonaldehyde (CH <sub>3</sub> -CH=CH-CHO)	-7.116	-10.095	-18.902	-15.618	-10.124	-7.515	-8.209
Acetic anhydride (CH <sub>3</sub> -C(=O)-O-C(=O)-CH <sub>3</sub> )	-5.758	-17.770	-27.541	-27.625	-19.664	-14.520	-15.218
2,5-Dihydrothiophene (C <sub>4</sub> H <sub>6</sub> S)	-6.530	-11.083	-13.869	-13.387	-8.290	-6.445	-7.042
Isobutane nitrile ((CH <sub>3</sub> ) <sub>2</sub> CH-CN)	-2.600	-5.850	-10.605	-5.349	-0.240	0.847	0.834
Methyl ethyl ketone (CH <sub>3</sub> -CO-CH <sub>2</sub> -CH <sub>3</sub> )	-4.851	-9.790	-17.530	-14.594	-8.966	-6.308	-7.018
Isobutanal ((CH <sub>3</sub> ) <sub>2</sub> CH-CHO)	-3.491	-7.429	-15.446	-12.399	-6.780	-4.116	-4.841
1,4-Dioxane (C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	-7.722	-13.501	-24.367	-21.747	-15.137	-11.294	-11.990
Tetrahydrothiophene (C <sub>4</sub> H <sub>8</sub> S)	-5.412	-11.001	-13.130	-12.856	-7.645	-5.739	-6.356
t-Butyl chloride ((CH <sub>3</sub> ) <sub>3</sub> C-Cl)	-10.951	-7.866	-16.965	-13.150	-8.259	-6.272	-7.248
n-Butyl chloride (CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -Cl)	-10.998	-7.263	-16.371	-12.296	-7.447	-5.500	-6.465
Tetrahydropyrrole (C <sub>4</sub> H <sub>8</sub> NH)	-7.881	-12.829	-16.487	-11.367	-6.079	-4.961	-5.034
Nitro-s-butane (CH <sub>3</sub> -CH <sub>2</sub> -CH(CH <sub>3</sub> )-NO <sub>2</sub> )	-6.746	-19.152	-24.951	-23.295	-15.614	-11.837	-11.744
Diethyl ether (CH <sub>3</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>3</sub> )	-6.372	-9.716	-18.134	-14.838	-9.288	-6.655	-7.383
Dimethyl acetal (CH <sub>3</sub> -CH(OCH <sub>3</sub> ) <sub>2</sub> )	-5.465	-12.006	-22.312	-19.966	-13.303	-9.451	-10.155
t-Butanethiol ((CH <sub>3</sub> ) <sub>3</sub> C-SH)	-4.121	-10.102	-11.961	-12.030	-6.781	-4.825	-5.410
Diethyl disulfide (CH <sub>3</sub> -CH <sub>2</sub> -S-S-CH <sub>2</sub> -CH <sub>3</sub> )	-4.171	-13.478	-11.127	-15.218	-9.381	-6.937	-7.351
t-Butylamine ((CH <sub>3</sub> ) <sub>3</sub> C-NH <sub>2</sub> )	-5.990	-10.652	-14.043	-9.150	-3.906	-2.772	-2.793
Tetramethylsilane (Si(CH <sub>3</sub> ) <sub>4</sub> )	-1.480	-3.070	-10.369	-5.434	-1.203	-0.081	-1.012
2-Methyl thiophene (C <sub>5</sub> H <sub>6</sub> S)	-9.649	-14.844	-19.194	-17.923	-11.735	-9.438	-10.172
N-methyl pyrrole (cyc-C <sub>4</sub> H <sub>4</sub> N-CH <sub>3</sub> )	-12.581	-17.459	-22.724	-16.768	-10.540	-9.095	-9.263
Tetrahydropyran (C <sub>5</sub> H <sub>10</sub> O)	-8.531	-12.726	-22.798	-18.361	-11.596	-8.631	-9.575
Diethyl ketone (CH <sub>3</sub> -CH <sub>2</sub> -CO-CH <sub>2</sub> -CH <sub>3</sub> )	-8.520	-12.429	-22.133	-18.044	-11.274	-8.252	-9.160
Isopropyl acetate (CH <sub>3</sub> -C(=O)-O-CH(CH <sub>3</sub> ) <sub>2</sub> )	-7.322	-15.758	-25.982	-23.582	-15.662	-11.402	-12.295
Tetrahydrothiopyran (C <sub>5</sub> H <sub>10</sub> S)	-7.886	-13.641	-17.255	-15.960	-9.612	-7.344	-8.160
Piperidine (cyc-C <sub>5</sub> H <sub>10</sub> NH)	-9.139	-14.607	-19.990	-13.751	-7.346	-5.872	-6.137
t-Butyl methyl ether ((CH <sub>3</sub> ) <sub>3</sub> C-O-CH <sub>3</sub> )	-7.749	-10.985	-21.069	-16.686	-9.973	-7.014	-7.924
1,3-Difluorobenzene (C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> )	-26.828	-18.559	-31.747	-26.671	-19.341	-16.268	-18.599
1,4-Difluorobenzene (C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> )	-29.211	-20.326	-33.327	-28.316	-20.931	-17.859	-20.201
Fluorobenzene (C <sub>6</sub> H <sub>5</sub> F)	-21.105	-15.943	-28.640	-22.411	-15.520	-13.002	-14.701
Di-isopropyl ether ((CH <sub>3</sub> ) <sub>2</sub> CH-O-CH(CH <sub>3</sub> ) <sub>2</sub> )	-9.489	-13.343	-25.129	-19.624	-11.750	-8.438	-9.541
PF <sub>5</sub>	-8.813	11.946	10.607	0.199	2.993	6.248	3.395
SF <sub>6</sub>	-22.844	-5.833	-1.148	-15.502	-12.046	-7.569	-10.782
P <sub>4</sub>	9.473	-6.849	12.287	-6.669	-6.414	-4.838	-2.888
SO <sub>3</sub>	11.684	-8.353	-3.105	-13.902	-9.538	-5.168	-4.853
SCL <sub>2</sub>	-4.313	-1.222	-1.535	-6.203	-5.103	-3.556	-3.575
POCl <sub>3</sub>	-6.586	-2.209	-4.906	-14.150	-11.245	-7.602	-7.849
PCL <sub>5</sub>	-23.160	-5.207	-12.969	-21.000	-18.722	-15.170	-15.684
Cl <sub>2</sub> O <sub>2</sub> S	-0.053	-8.993	-7.301	-17.982	-13.944	-9.699	-9.699
PCL <sub>3</sub>	-9.514	0.586	-2.869	-10.274	-8.500	-5.956	-6.296
Cl <sub>2</sub> S <sub>2</sub>	-9.472	-10.981	-6.376	-16.255	-14.098	-11.853	-11.807
SiCl <sub>2</sub> singlet	-4.249	5.245	-1.715	-4.714	-3.319	-1.749	-2.522
CF <sub>3</sub> Cl	-18.823	-6.193	-11.021	-14.235	-11.093	-8.492	-10.708
Hexafluoro ethane (C <sub>2</sub> F <sub>6</sub> )	-30.675	-11.656	-17.534	-22.828	-17.454	-13.298	-17.477
CF <sub>3</sub>	-19.471	-9.337	-12.250	-14.651	-12.340	-10.553	-12.775
C <sub>6</sub> H <sub>5</sub> (phenyl radical)	-21.391	-19.805	-31.271	-23.846	-17.749	-16.048	-17.300
Bicyclo[1.1.0]butane (C <sub>4</sub> H <sub>6</sub> )	-6.294	-8.637	-14.492	-10.004	-5.592	-4.284	-5.068
(CH <sub>3</sub> ) <sub>3</sub> C (t-butyl radical)	-12.936	-13.437	-19.718	-14.970	-10.755	-9.663	-10.598

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TABLE S5: Deviation from reference “exact” values of SCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
Trans-butane(C <sub>4</sub> H <sub>10</sub> )	-6.083	-7.065	-13.471	-9.148	-4.620	-3.230	-4.005
1,3 Cyclohexadiene (C <sub>6</sub> H <sub>8</sub> )	-11.085	-10.597	-21.739	-14.606	-8.023	-6.048	-7.186
ME	-5.613	-6.418	-10.524	-9.736	-6.209	-4.533	-5.035
MAE	7.163	7.723	11.629	10.332	7.128	5.681	6.121

TABLE S6: Deviation from reference “exact” values of rSCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
LiH	2.022	2.093	2.080	2.144	2.139	2.125	2.130
BeH	-11.229	-11.179	-10.945	-11.018	-11.011	-10.996	-11.004
CH	1.522	1.462	1.516	1.492	1.388	1.407	1.427
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	-8.619	-8.969	-8.713	-8.713	-8.797	-8.788	-8.767
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	3.672	3.601	3.784	3.737	3.597	3.612	3.645
CH <sub>3</sub>	-7.133	-7.526	-7.234	-7.322	-7.427	-7.407	-7.384
Methane (CH <sub>4</sub> )	-3.787	-3.666	-3.561	-3.535	-3.678	-3.666	-3.633
NH	-1.620	-1.739	-1.829	-2.047	-1.987	-1.930	-1.959
NH <sub>2</sub>	-4.129	-4.008	-4.056	-4.354	-4.334	-4.257	-4.290
Ammonia (NH <sub>3</sub> )	-0.658	-0.103	-0.319	-0.541	-0.549	-0.470	-0.499
OH	-3.765	-3.568	-3.749	-3.809	-3.838	-3.855	-3.866
Water (H <sub>2</sub> O)	-0.888	-0.754	-1.161	-1.223	-1.256	-1.274	-1.287
Hydrogen fluoride (HF)	-0.289	-0.392	-0.261	-0.122	-0.132	-0.136	-0.131
SiH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	1.266	1.069	1.122	1.132	1.162	1.135	1.138
SiH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	-8.894	-8.624	-8.712	-8.642	-8.604	-8.613	-8.618
SiH <sub>3</sub>	-6.446	-6.391	-6.399	-6.365	-6.328	-6.349	-6.351
Silane (SiH <sub>4</sub> )	-2.237	-2.299	-2.224	-2.224	-2.191	-2.224	-2.219
PH <sub>2</sub>	-5.468	-5.023	-5.022	-4.832	-4.851	-4.819	-4.814
PH <sub>3</sub>	-2.222	-1.643	-1.638	-1.397	-1.406	-1.360	-1.364
Hydrogen sulfide (H <sub>2</sub> S)	-3.161	-2.411	-2.395	-2.392	-2.410	-2.358	-2.352
Hydrogen chloride (HCl)	-1.186	-1.933	-1.823	-1.731	-1.701	-1.699	-1.689
Li <sub>2</sub>	4.837	5.126	5.107	5.227	5.215	5.188	5.198
LiF	-0.270	-0.674	-0.695	-0.398	-0.413	-0.431	-0.422
Acetylene (C <sub>2</sub> H <sub>2</sub> )	-3.159	-3.106	-2.700	-2.679	-2.956	-2.938	-2.874
Ethylene (H <sub>2</sub> C=CH <sub>2</sub> )	-6.537	-6.454	-6.122	-6.104	-6.388	-6.367	-6.301
Ethane (H <sub>3</sub> C-CH <sub>3</sub> )	-8.066	-7.840	-7.618	-7.569	-7.859	-7.833	-7.768
CN	-0.680	-0.254	-0.244	-0.430	-0.543	-0.464	-0.461
Hydrogen cyanide (HCN)	-0.593	-0.011	0.044	-0.158	-0.312	-0.227	-0.222
CO	0.028	0.200	-0.089	-0.153	-0.338	-0.357	-0.330
HCO	-8.357	-8.390	-8.619	-8.688	-8.841	-8.850	-8.834
Formaldehyde (H <sub>2</sub> C=O)	-5.321	-5.199	-5.400	-5.474	-5.655	-5.664	-5.643
Methanol (CH <sub>3</sub> -OH)	-6.036	-5.952	-6.187	-6.254	-6.430	-6.434	-6.415
N <sub>2</sub>	5.224	6.343	6.074	5.646	5.600	5.751	5.699
Hydrazine (H <sub>2</sub> N-NH <sub>2</sub> )	-2.190	-1.189	-1.536	-2.013	-2.025	-1.869	-1.926
NO	-2.138	-1.810	-2.376	-2.658	-2.688	-2.630	-2.672
O <sub>2</sub>	-11.014	-11.905	-12.028	-12.096	-12.153	-12.187	-12.202
Hydrogen peroxide (HO-OH)	-3.601	-3.444	-4.062	-4.215	-4.285	-4.326	-4.353
F <sub>2</sub>	-1.198	-1.191	-0.927	-0.758	-0.786	-0.799	-0.795
Carbon dioxide (CO <sub>2</sub> )	-12.833	-12.419	-13.130	-13.260	-13.484	-13.510	-13.500
Na <sub>2</sub>	1.811	1.979	1.836	1.862	1.882	1.886	1.886
Si <sub>2</sub>	-1.757	-1.861	-1.689	-1.543	-1.481	-1.528	-1.533
P <sub>2</sub>	0.194	1.278	1.270	1.801	1.775	1.864	1.856
S <sub>2</sub>	-11.350	-10.627	-10.637	-10.412	-10.421	-10.365	-10.369
Cl <sub>2</sub>	-0.924	-2.314	-2.172	-2.036	-2.000	-1.987	-1.969
NaCl	-1.192	-1.928	-1.933	-1.817	-1.761	-1.763	-1.752
Silicon monoxide (SiO)	2.559	2.820	2.351	2.316	2.306	2.255	2.250
CS	-0.835	-0.151	0.074	0.037	-0.136	-0.077	-0.032
SO	-9.437	-9.339	-9.467	-9.399	-9.457	-9.429	-9.448
ClO	-6.582	-7.029	-7.265	-7.224	-7.273	-7.272	-7.280
Chlorine monofluoride (FCl)	-1.580	-2.205	-2.053	-1.889	-1.890	-1.886	-1.876
Si <sub>2</sub> H <sub>6</sub>	-6.670	-6.756	-6.628	-6.625	-6.556	-6.625	-6.615
Methyl chloride (CH <sub>3</sub> Cl)	-5.686	-6.446	-6.173	-6.100	-6.212	-6.195	-6.154
Methanethiol (H <sub>3</sub> CSH)	-7.287	-6.494	-6.353	-6.332	-6.493	-6.429	-6.392
Hypochlorous acid (HOCl)	-3.076	-3.441	-3.733	-3.741	-3.763	-3.776	-3.780
Sulfur dioxide (SO <sub>2</sub> )	-6.978	-5.724	-6.710	-6.791	-6.885	-6.875	-6.895
BF <sub>3</sub>	-10.502	-10.948	-10.978	-10.599	-10.561	-10.552	-10.552

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TABLE S6: Deviation from reference “exact” values of rSCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
BCl <sub>3</sub>	-14.722	-16.930	-16.720	-16.546	-16.353	-16.345	-16.325
AlF <sub>3</sub>	-3.286	-3.647	-3.414	-2.866	-2.915	-2.924	-2.908
AlCl <sub>3</sub>	-12.659	-13.925	-13.563	-13.285	-13.172	-13.174	-13.145
Carbon tetrafluoride (CF <sub>4</sub> )	-17.248	-18.022	-17.475	-16.945	-17.137	-17.128	-17.079
Carbon tetrachloride (CCl <sub>4</sub> )	-11.679	-14.411	-13.971	-13.631	-13.683	-13.648	-13.578
Carbon oxide sulfide (COS)	-15.482	-14.466	-14.712	-14.778	-14.982	-14.939	-14.910
Carbon bisulfide (CS <sub>2</sub> )	-17.106	-15.486	-15.234	-15.245	-15.436	-15.320	-15.273
Carbonic difluoride (COF <sub>2</sub> )	-10.907	-11.227	-11.333	-11.128	-11.325	-11.335	-11.309
Silicon tetrafluoride (SiF <sub>4</sub> )	1.164	-0.277	0.253	0.914	0.899	0.858	0.883
Silicon tetrachloride (SiCl <sub>4</sub> )	-9.057	-12.371	-11.751	-11.377	-11.202	-11.242	-11.191
Dinitrogen monoxide (N <sub>2</sub> O)	-10.784	-9.268	-10.018	-10.548	-10.612	-10.474	-10.544
Nitrogen chloride oxide (ClNO)	-10.876	-10.907	-11.376	-11.586	-11.609	-11.552	-11.580
Nitrogen trifluoride (NF <sub>3</sub> )	-16.005	-16.370	-15.988	-15.869	-15.911	-15.849	-15.865
PF <sub>3</sub>	-1.806	-2.283	-1.931	-1.140	-1.179	-1.148	-1.141
O <sub>3</sub>	-8.913	-8.661	-9.768	-9.934	-10.035	-10.101	-10.143
F <sub>2</sub> O	-9.367	-9.540	-9.518	-9.373	-9.435	-9.468	-9.479
Chlorine trifluoride (ClF <sub>3</sub> )	-18.647	-19.853	-19.489	-18.965	-19.001	-19.003	-18.983
Tetrafluoro Ethene (F <sub>2</sub> C=CF <sub>2</sub> )	-26.875	-27.521	-26.895	-26.378	-26.694	-26.680	-26.603
Tetrachloro Ethene (C <sub>2</sub> Cl <sub>4</sub> )	-20.245	-22.548	-21.912	-21.563	-21.745	-21.702	-21.601
Acetonitrile, trifluoro- (CF <sub>3</sub> CN)	-17.258	-17.274	-16.782	-16.578	-16.912	-16.817	-16.768
Propyne (C <sub>3</sub> H <sub>4</sub> )	-9.743	-9.539	-9.041	-8.993	-9.413	-9.382	-9.285
Allene (C <sub>3</sub> H <sub>4</sub> )	-13.909	-13.736	-13.244	-13.195	-13.620	-13.593	-13.493
Cyclopropene (C <sub>3</sub> H <sub>4</sub> )	-10.750	-10.451	-10.063	-10.010	-10.437	-10.403	-10.306
Propylene (C <sub>3</sub> H <sub>6</sub> )	-11.794	-11.484	-11.069	-11.019	-11.448	-11.415	-11.316
Cyclopropane (C <sub>3</sub> H <sub>6</sub> )	-13.764	-13.253	-12.982	-12.901	-13.335	-13.296	-13.200
Propane (C <sub>3</sub> H <sub>8</sub> )	-12.733	-12.021	-11.741	-11.666	-12.101	-12.062	-11.964
Trans-1,3-butadiene (C <sub>4</sub> H <sub>6</sub> )	-15.999	-15.721	-15.085	-15.040	-15.609	-15.569	-15.436
Dimethylacetylene (C <sub>4</sub> H <sub>6</sub> )	-14.978	-14.623	-14.034	-13.960	-14.524	-14.479	-14.351
Methylenecyclopropane (C <sub>4</sub> H <sub>6</sub> )	-20.860	-20.242	-19.762	-19.679	-20.252	-20.205	-20.075
Bicyclo[1.1.0]butane (C <sub>4</sub> H <sub>6</sub> )	-17.807	-17.183	-16.811	-16.691	-17.271	-17.222	-17.091
Cyclobutene (C <sub>4</sub> H <sub>6</sub> )	-14.721	-14.136	-13.625	-13.548	-14.125	-14.079	-13.947
Cyclobutane (C <sub>4</sub> H <sub>8</sub> )	-17.244	-16.054	-15.674	-15.583	-16.162	-16.111	-15.980
Isobutene (C <sub>4</sub> H <sub>8</sub> )	-16.729	-15.914	-15.422	-15.344	-15.918	-15.872	-15.741
Trans-butane(C <sub>4</sub> H <sub>10</sub> )	-16.606	-16.059	-15.593	-15.504	-16.087	-16.034	-15.904
Isobutane (C <sub>4</sub> H <sub>10</sub> )	-16.029	-15.630	-15.256	-15.165	-15.747	-15.695	-15.565
Spiropentane (C <sub>5</sub> H <sub>8</sub> )	-24.960	-23.948	-23.497	-23.360	-24.082	-24.019	-23.857
Benzene (C <sub>6</sub> H <sub>6</sub> )	-28.752	-28.137	-27.161	-27.094	-27.950	-27.890	-27.691
Difluoromethane (CH <sub>2</sub> F <sub>2</sub> )	-9.046	-9.595	-9.253	-8.993	-9.156	-9.147	-9.107
Trifluoromethane(CHF <sub>3</sub> )	-12.910	-13.604	-13.130	-12.717	-12.895	-12.887	-12.842
CH <sub>2</sub> Cl <sub>2</sub>	-7.863	-9.202	-8.849	-8.688	-8.774	-8.753	-8.702
CHCl <sub>3</sub>	-9.720	-11.843	-11.434	-11.182	-11.248	-11.221	-11.160
Methylamine (H <sub>3</sub> C-NH <sub>2</sub> )	-4.872	-4.210	-4.297	-4.509	-4.661	-4.570	-4.566
Acetonitrile (CH <sub>3</sub> -CN)	-7.131	-6.400	-6.244	-6.423	-6.720	-6.621	-6.585
Nitromethane (CH <sub>3</sub> -NO <sub>2</sub> )	-19.368	-18.184	-19.023	-19.383	-19.609	-19.556	-19.580
Methyl nitrite (CH <sub>3</sub> -O-N=O)	-15.934	-14.997	-15.818	-16.184	-16.412	-16.362	-16.383
Methyl silane (CH <sub>3</sub> SiH <sub>3</sub> )	-5.973	-5.868	-5.697	-5.664	-5.775	-5.797	-5.759
Formic acid (HCOOH)	-11.162	-10.848	-11.561	-11.690	-11.902	-11.929	-11.920
Methyl formate (HCOOCH <sub>3</sub> )	-16.823	-16.448	-16.966	-17.112	-17.465	-17.478	-17.438
Acetamide (CH <sub>3</sub> CONH <sub>2</sub> )	-15.987	-14.850	-15.200	-15.472	-15.801	-15.717	-15.693
Aziridine (C <sub>2</sub> H <sub>4</sub> NH)	-11.221	-10.191	-10.176	-10.367	-10.664	-10.560	-10.525
Cyanogen (NCCN)	-5.811	-4.593	-4.510	-4.913	-5.221	-5.047	-5.040
Dimethylamine ((CH <sub>3</sub> ) <sub>2</sub> NH)	-9.567	-8.691	-8.665	-8.866	-9.162	-9.057	-9.022
Trans ethylamine (CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> )	-10.571	-9.691	-9.639	-9.830	-10.128	-10.023	-9.987
Ketene (CH <sub>2</sub> CO)	-15.127	-14.817	-14.954	-14.980	-15.301	-15.302	-15.246
Oxirane (C <sub>2</sub> H <sub>4</sub> O)	-12.332	-12.039	-12.154	-12.213	-12.536	-12.530	-12.478
Acetaldehyde (CH <sub>3</sub> CHO)	-11.382	-11.042	-11.154	-11.197	-11.521	-11.518	-11.464

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TABLE S6: Deviation from reference “exact” values of rSCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
Glyoxal (HCOCOH)	-13.283	-12.894	-13.268	-13.413	-13.774	-13.795	-13.753
Ethanol (CH <sub>3</sub> CH <sub>2</sub> OH)	-10.518	-10.271	-10.404	-10.446	-10.767	-10.759	-10.707
Dimethylether (CH <sub>3</sub> OCH <sub>3</sub> )	-11.129	-10.842	-10.920	-10.992	-11.311	-11.302	-11.251
Thiirane (C <sub>2</sub> H <sub>4</sub> S)	-13.578	-12.609	-12.327	-12.299	-12.605	-12.528	-12.459
Dimethyl sulfoxide ((CH <sub>3</sub> ) <sub>2</sub> SO)	-16.752	-15.422	-15.638	-15.631	-15.977	-15.919	-15.862
Ethanethiol (C <sub>2</sub> H <sub>5</sub> SH)	-11.358	-10.381	-10.128	-10.086	-10.393	-10.316	-10.246
Dimethyl sulfide (CH <sub>3</sub> SCH <sub>3</sub> )	-12.083	-11.054	-10.822	-10.775	-11.082	-11.006	-10.937
Vinyl fluoride (CH <sub>2</sub> =CHF)	-11.724	-11.852	-11.437	-11.286	-11.576	-11.557	-11.489
Ethyl chloride (C <sub>2</sub> H <sub>5</sub> Cl)	-10.469	-11.007	-10.618	-10.520	-10.778	-10.748	-10.674
Vinyl chloride (CH <sub>2</sub> =CHCl)	-13.764	-14.323	-13.882	-13.784	-14.037	-14.012	-13.938
Acrylonitrile (CH <sub>2</sub> =CHCN)	-9.089	-8.314	-7.955	-8.128	-8.568	-8.462	-8.392
Acetone (CH <sub>3</sub> COCH <sub>3</sub> )	-17.046	-16.192	-16.225	-16.238	-16.705	-16.690	-16.604
Acetic acid (CH <sub>3</sub> COOH)	-16.410	-15.728	-16.340	-16.443	-16.800	-16.815	-16.774
Acetyl fluoride (CH <sub>3</sub> COF)	-15.726	-15.682	-15.732	-15.629	-15.961	-15.959	-15.903
CH <sub>3</sub> COCl (acetyl chloride)	-16.653	-17.133	-17.153	-17.115	-17.406	-17.400	-17.338
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl (propyl chloride)	-15.104	-15.268	-14.815	-14.686	-15.088	-15.045	-14.939
Isopropanol (CH <sub>3</sub> ) <sub>2</sub> CHOH)	-15.056	-14.727	-14.767	-14.779	-15.244	-15.224	-15.139
Methyl ethyl ether (C <sub>2</sub> H <sub>5</sub> OCH <sub>3</sub> )	-16.100	-15.603	-15.577	-15.619	-16.083	-16.061	-15.977
Trimethylamine ((CH <sub>3</sub> ) <sub>3</sub> N)	-14.468	-13.634	-13.509	-13.681	-14.123	-14.006	-13.938
Furan (C <sub>4</sub> H <sub>4</sub> O)	-22.554	-22.093	-21.970	-21.956	-22.560	-22.539	-22.419
C <sub>4</sub> H <sub>4</sub> S (thiophene)	-23.210	-21.990	-21.396	-21.311	-21.904	-21.811	-21.673
Pyrrrole (C <sub>4</sub> H <sub>5</sub> N)	-22.489	-21.345	-21.037	-21.183	-21.760	-21.639	-21.537
Pyridine (C <sub>5</sub> H <sub>5</sub> N)	-26.990	-25.882	-25.243	-25.417	-26.141	-26.014	-25.875
H <sub>2</sub>	2.073	2.089	2.089	2.089	2.089	2.089	2.089
HS	-3.432	-3.012	-3.031	-3.052	-3.058	-3.030	-3.027
CCH	-5.558	-5.688	-5.289	-5.231	-5.462	-5.449	-5.388
C <sub>2</sub> H <sub>3</sub> ( <sup>2</sup> A')	-11.705	-11.851	-11.455	-11.473	-11.717	-11.699	-11.639
CH <sub>3</sub> CO ( <sup>2</sup> A')	-14.344	-14.406	-14.461	-14.543	-14.834	-14.829	-14.781
H <sub>2</sub> COH ( <sup>2</sup> A)	-10.163	-10.345	-10.561	-10.652	-10.796	-10.799	-10.786
CH <sub>3</sub> O ( <sup>2</sup> A')	-10.977	-10.743	-10.820	-10.874	-11.047	-11.052	-11.031
CH <sub>3</sub> CH <sub>2</sub> O ( <sup>2</sup> A'')	-16.853	-16.401	-16.377	-16.412	-16.730	-16.722	-16.668
CH <sub>3</sub> S ( <sup>2</sup> A')	-9.508	-8.965	-8.869	-8.861	-9.011	-8.968	-8.934
C <sub>2</sub> H <sub>5</sub> ( <sup>2</sup> A')	-12.529	-12.720	-12.337	-12.395	-12.647	-12.614	-12.559
(CH <sub>3</sub> ) <sub>2</sub> CH ( <sup>2</sup> A')	-18.290	-18.012	-17.555	-17.588	-17.982	-17.938	-17.851
(CH <sub>3</sub> ) <sub>2</sub> CH ( <sup>2</sup> A')	-18.290	-18.012	-17.555	-17.588	-17.982	-17.938	-17.851
NO <sub>2</sub>	-16.419	-15.714	-16.733	-17.076	-17.143	-17.105	-17.161
Methyl allene (C <sub>4</sub> H <sub>6</sub> )	-18.360	-17.824	-17.244	-17.166	-17.738	-17.697	-17.565
Isoprene (C <sub>5</sub> H <sub>8</sub> )	-20.345	-19.818	-19.078	-19.002	-19.717	-19.663	-19.498
Cyclopentane (C <sub>5</sub> H <sub>10</sub> )	-20.612	-19.944	-19.473	-19.366	-20.096	-20.031	-19.868
n-Pentane (C <sub>5</sub> H <sub>12</sub> )	-21.279	-19.770	-19.356	-19.219	-19.944	-19.880	-19.717
Neo pentane (C <sub>5</sub> H <sub>12</sub> )	-19.653	-19.034	-18.554	-18.454	-19.183	-19.118	-18.954
1,4 Cyclohexadiene (C <sub>6</sub> H <sub>8</sub> )	-23.852	-23.031	-22.209	-22.091	-22.954	-22.886	-22.689
Cyclohexane (C <sub>6</sub> H <sub>12</sub> )	-24.008	-23.319	-22.766	-22.623	-23.501	-23.424	-23.228
n-Hexane (C <sub>6</sub> H <sub>14</sub> )	-25.018	-24.094	-23.377	-23.244	-24.117	-24.037	-23.841
3-Methyl pentane (C <sub>6</sub> H <sub>14</sub> )	-23.699	-23.005	-22.381	-22.230	-23.104	-23.026	-22.830
Toluene (C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )	-33.192	-32.450	-31.359	-31.258	-32.260	-32.187	-31.955
n-Heptane (C <sub>7</sub> H <sub>16</sub> )	-30.129	-27.810	-27.265	-27.064	-28.080	-27.990	-27.762
Cyclooctatetraene (C <sub>8</sub> H <sub>8</sub> )	-31.858	-31.014	-29.805	-29.687	-30.832	-30.749	-30.485
n-Octane (C <sub>8</sub> H <sub>18</sub> )	-33.502	-32.000	-31.073	-30.893	-32.050	-31.942	-31.681
Naphthalene (C <sub>10</sub> H <sub>8</sub> )	-50.065	-49.139	-47.551	-47.424	-48.853	-48.753	-48.420
Azulene (C <sub>10</sub> H <sub>8</sub> )	-50.697	-49.588	-48.015	-47.893	-49.324	-49.223	-48.890
Acetic acid methyl ester (CH <sub>3</sub> COOCH <sub>3</sub> )	-20.914	-20.199	-20.626	-20.742	-21.240	-21.241	-21.168
t-Butanol ((CH <sub>3</sub> ) <sub>3</sub> COH)	-18.992	-18.534	-18.475	-18.468	-19.081	-19.048	-18.930
Aniline (C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> )	-33.203	-31.822	-31.095	-31.239	-32.103	-31.962	-31.793
Phenol (C <sub>6</sub> H <sub>5</sub> OH)	-32.893	-32.135	-31.590	-31.575	-32.463	-32.421	-32.235
Divinyl ether (C <sub>4</sub> H <sub>6</sub> O)	-20.903	-20.350	-20.136	-20.144	-20.744	-20.719	-20.602

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TABLE S6: Deviation from reference “exact” values of rSCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
Tetrahydrofuran (C <sub>4</sub> H <sub>8</sub> O)	-18.881	-18.683	-18.576	-18.595	-19.203	-19.169	-19.052
Cyclopentanone (C <sub>5</sub> H <sub>8</sub> O)	-25.813	-25.273	-25.116	-25.079	-25.837	-25.795	-25.643
Benzoquinone(C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> )	-32.750	-32.014	-31.728	-31.814	-32.746	-32.727	-32.551
Pyrimidine (C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> )	-26.306	-24.741	-24.407	-24.834	-25.429	-25.232	-25.155
Dimethyl sulphone (C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> S)	-20.351	-18.470	-19.304	-19.349	-19.732	-19.690	-19.645
Chlorobenzene (C <sub>6</sub> H <sub>5</sub> Cl)	-31.943	-32.132	-31.047	-30.898	-31.723	-31.658	-31.451
Butanedinitrile (NC-CH <sub>2</sub> -CH <sub>2</sub> -CN)	-13.037	-11.649	-11.361	-11.708	-12.309	-12.111	-12.038
Pyrazine (C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> )	-22.327	-20.742	-20.447	-20.863	-21.456	-21.261	-21.184
Acetyl acetylene (CH <sub>3</sub> -C(=O)-CCH)	-15.580	-15.224	-14.975	-14.980	-15.584	-15.564	-15.446
Crotonaldehyde (CH <sub>3</sub> -CH=CH-CHO)	-21.909	-21.339	-21.149	-21.170	-21.780	-21.756	-21.636
Acetic anhydride (CH <sub>3</sub> -C(=O)-O-C(=O)-CH <sub>3</sub> )	-31.140	-30.387	-31.156	-31.307	-31.986	-31.995	-31.902
2,5-Dihydrothiophene (C <sub>4</sub> H <sub>6</sub> S)	-20.349	-19.277	-18.723	-18.647	-19.241	-19.143	-19.007
Isobutane nitrile ((CH <sub>3</sub> ) <sub>2</sub> CH-CN)	-13.531	-12.345	-12.005	-12.141	-12.731	-12.607	-12.506
Methyl ethyl ketone (CH <sub>3</sub> -CO-CH <sub>2</sub> -CH <sub>3</sub> )	-20.424	-20.285	-20.122	-20.128	-20.739	-20.712	-20.593
Isobutanal ((CH <sub>3</sub> ) <sub>2</sub> CH-CHO)	-18.480	-17.812	-17.709	-17.711	-18.324	-18.296	-18.177
1,4-Dioxane (C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	-23.212	-22.782	-22.952	-23.072	-23.713	-23.695	-23.593
Tetrahydrothiophene (C <sub>4</sub> H <sub>8</sub> S)	-19.297	-18.339	-17.863	-17.778	-18.378	-18.274	-18.139
t-Butyl chloride ((CH <sub>3</sub> ) <sub>3</sub> C-Cl)	-18.910	-19.433	-18.858	-18.721	-19.269	-19.214	-19.074
n-Butyl chloride (CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -Cl)	-18.628	-18.672	-18.094	-17.953	-18.502	-18.446	-18.307
Tetrahydropyrrole (C <sub>4</sub> H <sub>8</sub> NH)	-18.370	-17.146	-16.944	-17.094	-17.685	-17.554	-17.452
Nitro-s-butane (CH <sub>3</sub> -CH <sub>2</sub> -CH(CH <sub>3</sub> )-NO <sub>2</sub> )	-31.061	-29.649	-30.135	-30.432	-31.097	-31.004	-30.930
Diethyl ether (CH <sub>3</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>3</sub> )	-20.094	-19.398	-19.310	-19.324	-19.935	-19.900	-19.784
Dimethyl acetal (CH <sub>3</sub> -CH(OCH <sub>3</sub> ) <sub>2</sub> )	-23.106	-22.512	-22.732	-22.856	-23.500	-23.483	-23.380
t-Butanethiol ((CH <sub>3</sub> ) <sub>3</sub> C-SH)	-19.429	-18.306	-17.870	-17.783	-18.379	-18.277	-18.141
Diethyl disulfide (CH <sub>3</sub> -CH <sub>2</sub> -S-S-CH <sub>2</sub> -CH <sub>3</sub> )	-23.884	-21.625	-21.166	-21.059	-21.671	-21.516	-21.378
t-Butylamine ((CH <sub>3</sub> ) <sub>3</sub> C-NH <sub>2</sub> )	-18.205	-16.546	-16.331	-16.456	-17.040	-16.911	-16.809
Tetramethylsilane (Si(CH <sub>3</sub> ) <sub>4</sub> )	-16.911	-16.242	-15.803	-15.677	-16.223	-16.206	-16.071
2-Methyl thiophene (C <sub>5</sub> H <sub>6</sub> S)	-27.540	-26.349	-25.674	-25.572	-26.310	-26.204	-26.034
N-methyl pyrrole (cyc-C <sub>4</sub> H <sub>4</sub> N-CH <sub>3</sub> )	-26.401	-25.190	-24.755	-24.888	-25.608	-25.474	-25.340
Tetrahydropyran (C <sub>5</sub> H <sub>10</sub> O)	-23.513	-23.021	-22.763	-22.759	-23.520	-23.474	-23.324
Diethyl ketone (CH <sub>3</sub> -CH <sub>2</sub> -CO-CH <sub>2</sub> -CH <sub>3</sub> )	-26.145	-24.877	-24.744	-24.701	-25.461	-25.419	-25.268
Isopropyl acetate (CH <sub>3</sub> -C(=O)-O-CH(CH <sub>3</sub> ) <sub>2</sub> )	-29.429	-28.534	-28.777	-28.845	-29.633	-29.608	-29.470
Tetrahydrothiopyran (C <sub>5</sub> H <sub>10</sub> S)	-23.970	-22.598	-22.005	-21.896	-22.642	-22.525	-22.358
Piperidine (cyc-C <sub>5</sub> H <sub>10</sub> NH)	-21.658	-20.626	-20.342	-20.455	-21.192	-21.049	-20.915
t-Butyl methyl ether ((CH <sub>3</sub> ) <sub>3</sub> C-O-CH <sub>3</sub> )	-23.736	-22.757	-22.535	-22.543	-23.292	-23.246	-23.097
1,3-Difluorobenzene (C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> )	-36.912	-36.823	-35.593	-35.265	-36.133	-36.077	-35.874
1,4-Difluorobenzene (C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> )	-38.528	-38.332	-37.186	-36.851	-37.720	-37.663	-37.459
Fluorobenzene (C <sub>6</sub> H <sub>5</sub> F)	-33.020	-32.666	-31.567	-31.367	-32.229	-32.171	-31.970
Di-isopropyl ether ((CH <sub>3</sub> ) <sub>2</sub> CH-O-CH(CH <sub>3</sub> ) <sub>2</sub> )	-28.345	-27.146	-26.831	-26.783	-27.687	-27.627	-27.444
PF <sub>5</sub>	-6.771	-7.514	-7.009	-5.974	-6.028	-6.001	-5.988
SF <sub>6</sub>	-21.979	-21.950	-21.159	-20.272	-20.347	-20.316	-20.297
P <sub>4</sub>	-11.277	-9.098	-9.038	-7.958	-8.008	-7.823	-7.842
SO <sub>3</sub>	-13.929	-12.342	-13.787	-13.954	-14.087	-14.092	-14.127
SCl <sub>2</sub>	-6.121	-7.245	-7.011	-6.814	-6.772	-6.713	-6.693
POCl <sub>3</sub>	-12.118	-12.894	-12.982	-12.532	-12.471	-12.448	-12.438
PCl <sub>5</sub>	-17.783	-20.402	-19.767	-19.101	-18.932	-18.886	-18.848
Cl <sub>2</sub> O <sub>2</sub> S	-16.290	-16.646	-17.393	-17.310	-17.344	-17.319	-17.324
PCl <sub>3</sub>	-8.894	-10.161	-9.711	-9.207	-9.101	-9.060	-9.036
Cl <sub>2</sub> S <sub>2</sub>	-16.894	-17.323	-16.988	-16.799	-16.764	-16.659	-16.631
SiCl <sub>2</sub> singlet	-3.635	-5.578	-5.204	-5.020	-4.912	-4.947	-4.919
CF <sub>3</sub> Cl	-17.513	-18.885	-18.349	-17.865	-18.019	-18.005	-17.951
Hexafluoro ethane (C <sub>2</sub> F <sub>6</sub> )	-29.552	-30.836	-29.910	-29.096	-29.455	-29.439	-29.349
CF <sub>3</sub>	-19.082	-19.781	-19.391	-18.997	-19.129	-19.125	-19.087
C <sub>6</sub> H <sub>5</sub> (phenyl radical)	-34.216	-33.958	-32.913	-32.877	-33.696	-33.641	-33.446
Bicyclo[1.1.0]butane (C <sub>4</sub> H <sub>6</sub> )	-17.807	-17.183	-16.811	-16.691	-17.271	-17.222	-17.091
(CH <sub>3</sub> ) <sub>3</sub> C (t-butyl radical)	-22.144	-22.034	-21.441	-21.428	-21.970	-21.914	-21.793

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TABLE S6: Deviation from reference “exact” values of rSCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
Trans-butane(C <sub>4</sub> H <sub>10</sub> )	-16.606	-16.059	-15.593	-15.504	-16.087	-16.034	-15.904
1,3 Cyclohexadiene (C <sub>6</sub> H <sub>8</sub> )	-24.451	-23.904	-23.079	-22.962	-23.824	-23.756	-23.559
ME	-14.298	-14.010	-13.825	-13.774	-14.120	-14.079	-14.009
MAE	14.530	14.257	14.068	14.024	14.367	14.327	14.258

TABLE S7: Deviation from reference “exact” values of r<sup>2</sup>SCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
LiH	2.456	2.527	2.485	2.554	2.587	2.584	2.576
BeH	-10.429	-10.482	-10.241	-10.284	-10.263	-10.249	-10.258
CH	2.636	2.473	2.574	2.526	2.434	2.458	2.473
CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	-6.153	-6.572	-6.330	-6.329	-6.401	-6.386	-6.371
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	5.975	5.749	5.977	5.924	5.788	5.810	5.838
CH <sub>3</sub>	-3.492	-4.114	-3.772	-3.862	-3.961	-3.934	-3.917
Methane (CH <sub>4</sub> )	1.087	0.687	1.033	1.002	0.860	0.876	0.904
NH	-0.300	-0.680	-0.718	-0.906	-0.854	-0.805	-0.833
NH <sub>2</sub>	-1.429	-1.832	-1.706	-1.991	-1.990	-1.918	-1.951
Ammonia (NH <sub>3</sub> )	3.801	3.456	3.639	3.364	3.334	3.404	3.375
OH	-2.516	-2.324	-2.340	-2.477	-2.495	-2.518	-2.527
Water (H <sub>2</sub> O)	1.949	2.242	2.160	1.932	1.897	1.876	1.865
Hydrogen fluoride (HF)	1.855	1.876	1.848	1.928	1.929	1.918	1.923
SiH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	2.644	2.540	2.639	2.592	2.626	2.601	2.603
SiH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	-7.663	-7.399	-7.486	-7.435	-7.396	-7.399	-7.407
SiH <sub>3</sub>	-4.624	-4.542	-4.524	-4.518	-4.479	-4.494	-4.498
Silane (SiH <sub>4</sub> )	0.062	0.006	0.120	0.095	0.128	0.102	0.104
PH <sub>2</sub>	-3.792	-3.331	-3.628	-3.400	-3.453	-3.417	-3.413
PH <sub>3</sub>	0.290	0.948	0.619	0.842	0.811	0.858	0.851
Hydrogen sulfide (H <sub>2</sub> S)	-0.493	-0.193	-0.617	-0.295	-0.414	-0.320	-0.325
Hydrogen chloride (HCl)	-0.308	-0.395	-0.342	-0.366	-0.450	-0.411	-0.409
Li <sub>2</sub>	5.648	5.915	5.847	5.976	6.039	6.034	6.019
LiF	2.429	2.265	2.047	2.255	2.296	2.277	2.275
Acetylene (C <sub>2</sub> H <sub>2</sub> )	2.900	2.543	3.131	3.088	2.835	2.860	2.915
Ethylene (H <sub>2</sub> C=CH <sub>2</sub> )	0.766	0.168	0.770	0.725	0.459	0.489	0.544
Ethane (H <sub>3</sub> C-CH <sub>3</sub> )	0.459	-0.378	0.354	0.272	-0.013	0.019	0.075
CN	3.332	2.696	3.198	2.926	2.803	2.872	2.871
Hydrogen cyanide (HCN)	4.364	4.044	4.510	4.240	4.072	4.159	4.157
CO	2.874	2.901	3.127	2.845	2.674	2.656	2.680
HCO	-4.661	-4.709	-4.531	-4.793	-4.938	-4.947	-4.934
Formaldehyde (H <sub>2</sub> C=O)	-0.785	-0.728	-0.529	-0.788	-0.961	-0.969	-0.952
Methanol (CH <sub>3</sub> -OH)	-0.001	-0.126	0.113	-0.159	-0.331	-0.334	-0.319
N <sub>2</sub>	8.971	8.750	9.023	8.549	8.479	8.620	8.565
Hydrazine (H <sub>2</sub> N-NH <sub>2</sub> )	4.942	4.387	4.731	4.161	4.114	4.256	4.198
NO	0.185	0.285	0.197	-0.250	-0.305	-0.252	-0.293
O <sub>2</sub>	-9.386	-9.506	-9.575	-9.790	-9.839	-9.884	-9.896
Hydrogen peroxide (HO-OH)	-0.183	0.422	0.189	-0.205	-0.266	-0.317	-0.341
F <sub>2</sub>	0.539	0.302	0.344	0.557	0.529	0.509	0.513
Carbon dioxide (CO <sub>2</sub> )	-7.812	-7.389	-7.223	-7.751	-7.962	-7.991	-7.983
Na <sub>2</sub>	3.123	2.937	2.945	2.951	2.954	2.957	2.955
Si <sub>2</sub>	-0.271	-0.140	0.184	0.219	0.295	0.248	0.242
P <sub>2</sub>	2.306	3.656	3.027	3.397	3.352	3.433	3.425
S <sub>2</sub>	-9.324	-8.951	-9.479	-9.047	-9.136	-9.033	-9.052
Cl <sub>2</sub>	-0.837	-1.186	-0.928	-1.041	-1.147	-1.084	-1.076
NaCl	0.130	-0.012	-0.046	-0.074	-0.160	-0.117	-0.120
Silicon monoxide (SiO)	4.614	4.999	5.039	4.767	4.751	4.705	4.699
CS	2.296	2.398	2.246	2.477	2.228	2.317	2.352
SO	-7.572	-7.267	-7.449	-7.457	-7.545	-7.509	-7.530
ClO	-6.027	-5.786	-5.732	-5.949	-6.061	-6.027	-6.044
Chlorine monofluoride (FCl)	-0.577	-0.852	-0.688	-0.662	-0.691	-0.678	-0.671
Si <sub>2</sub> H <sub>6</sub>	-2.633	-2.647	-2.427	-2.500	-2.424	-2.484	-2.478
Methyl chloride (CH <sub>3</sub> Cl)	-1.570	-2.011	-1.627	-1.713	-1.927	-1.866	-1.838
Methanethiol (H <sub>3</sub> CSH)	-1.142	-1.231	-1.302	-1.042	-1.294	-1.185	-1.163
Hypochlorous acid (HOCl)	-1.335	-1.035	-1.000	-1.266	-1.342	-1.339	-1.346
Sulfur dioxide (SO <sub>2</sub> )	-2.768	-1.656	-2.154	-2.493	-2.640	-2.612	-2.637
BF <sub>3</sub>	-4.243	-4.154	-4.603	-4.504	-4.419	-4.444	-4.441

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TABLE S7: Deviation from reference “exact” values of r<sup>2</sup>SCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
BCl <sub>3</sub>	-12.144	-12.365	-12.385	-12.560	-12.755	-12.638	-12.643
AlF <sub>3</sub>	2.075	2.272	2.006	2.276	2.313	2.265	2.280
AlCl <sub>3</sub>	-10.796	-9.949	-9.946	-9.976	-10.254	-10.131	-10.130
Carbon tetrafluoride (CF <sub>4</sub> )	-9.477	-10.104	-9.977	-9.759	-9.899	-9.912	-9.868
Carbon tetrachloride (CCl <sub>4</sub> )	-9.093	-9.898	-9.229	-9.480	-9.934	-9.752	-9.720
Carbon oxide sulfide (COS)	-10.249	-9.881	-10.113	-10.025	-10.335	-10.246	-10.231
Carbon bisulfide (CS <sub>2</sub> )	-11.518	-11.173	-11.781	-11.121	-11.513	-11.318	-11.291
Carbonic difluoride (COF <sub>2</sub> )	-4.545	-4.733	-4.632	-4.788	-4.954	-4.978	-4.955
Silicon tetrafluoride (SiF <sub>4</sub> )	7.419	6.786	6.774	6.976	7.066	6.981	7.007
Silicon tetrachloride (SiCl <sub>4</sub> )	-7.608	-8.092	-7.821	-7.930	-8.278	-8.155	-8.138
Dinitrogen monoxide (N <sub>2</sub> O)	-5.063	-5.062	-4.890	-5.602	-5.703	-5.583	-5.651
Nitrogen chloride oxide (ClNO)	-7.766	-7.707	-7.584	-8.122	-8.284	-8.191	-8.229
Nitrogen trifluoride (NF <sub>3</sub> )	-10.751	-11.531	-11.327	-11.367	-11.394	-11.355	-11.371
PF <sub>3</sub>	2.810	3.111	2.791	3.261	3.248	3.255	3.261
O <sub>3</sub>	-5.980	-5.018	-5.342	-5.972	-6.085	-6.159	-6.198
F <sub>2</sub> O	-6.727	-6.642	-6.820	-6.779	-6.828	-6.877	-6.886
Chlorine trifluoride (ClF <sub>3</sub> )	-15.343	-15.665	-15.405	-15.286	-15.343	-15.329	-15.321
Tetrafluoro Ethene (F <sub>2</sub> C=CF <sub>2</sub> )	-16.733	-17.465	-17.198	-16.993	-17.243	-17.249	-17.181
Tetrachloro Ethene (C <sub>2</sub> Cl <sub>4</sub> )	-14.969	-15.556	-14.590	-14.887	-15.474	-15.269	-15.216
Acetonitrile, trifluoro- (CF <sub>3</sub> CN)	-6.494	-7.449	-6.786	-6.905	-7.214	-7.132	-7.094
Propyne (C <sub>3</sub> H <sub>4</sub> )	0.144	-0.624	0.319	0.237	-0.157	-0.116	-0.033
Allene (C <sub>3</sub> H <sub>4</sub> )	-3.860	-4.696	-3.794	-3.850	-4.245	-4.202	-4.120
Cyclopropene (C <sub>3</sub> H <sub>4</sub> )	-0.843	-1.801	-0.858	-0.950	-1.357	-1.309	-1.228
Propylene (C <sub>3</sub> H <sub>6</sub> )	-0.658	-1.608	-0.642	-0.727	-1.138	-1.091	-1.008
Cyclopropane (C <sub>3</sub> H <sub>6</sub> )	-2.489	-3.604	-2.548	-2.668	-3.095	-3.049	-2.966
Propane (C <sub>3</sub> H <sub>8</sub> )	-0.416	-1.343	-0.285	-0.409	-0.838	-0.790	-0.706
Trans-1,3-butadiene (C <sub>4</sub> H <sub>6</sub> )	-2.284	-3.422	-2.217	-2.307	-2.842	-2.780	-2.670
Dimethylacetylene (C <sub>4</sub> H <sub>6</sub> )	-1.312	-2.496	-1.196	-1.319	-1.854	-1.796	-1.686
Methylenecyclopropane (C <sub>4</sub> H <sub>6</sub> )	-7.019	-8.245	-6.933	-7.058	-7.610	-7.549	-7.438
Bicyclo[1.1.0]butane (C <sub>4</sub> H <sub>6</sub> )	-3.907	-5.483	-4.041	-4.192	-4.770	-4.711	-4.598
Cyclobutene (C <sub>4</sub> H <sub>6</sub> )	-0.824	-2.101	-0.737	-0.888	-1.443	-1.382	-1.270
Cyclobutane (C <sub>4</sub> H <sub>8</sub> )	-2.260	-3.252	-1.805	-1.997	-2.566	-2.503	-2.391
Isobutene (C <sub>4</sub> H <sub>8</sub> )	-1.712	-2.752	-1.429	-1.558	-2.112	-2.051	-1.939
Trans-butane(C <sub>4</sub> H <sub>10</sub> )	-0.548	-2.155	-0.639	-0.823	-1.398	-1.333	-1.221
Isobutane (C <sub>4</sub> H <sub>10</sub> )	0.095	-1.667	-0.243	-0.423	-0.997	-0.934	-0.821
Spiropentane (C <sub>5</sub> H <sub>8</sub> )	-7.290	-9.017	-7.246	-7.444	-8.159	-8.082	-7.942
Benzene (C <sub>6</sub> H <sub>6</sub> )	-9.500	-11.071	-9.244	-9.369	-10.184	-10.087	-9.922
Difluoromethane (CH <sub>2</sub> F <sub>2</sub> )	-3.174	-3.741	-3.580	-3.483	-3.615	-3.616	-3.581
Trifluoromethane(CHF <sub>3</sub> )	-6.092	-6.712	-6.528	-6.368	-6.503	-6.512	-6.472
CH <sub>2</sub> Cl <sub>2</sub>	-4.257	-4.646	-4.200	-4.334	-4.627	-4.524	-4.497
CHCl <sub>3</sub>	-6.612	-7.240	-6.690	-6.883	-7.258	-7.114	-7.085
Methylamine (H <sub>3</sub> C-NH <sub>2</sub> )	3.011	2.317	2.854	2.523	2.356	2.443	2.441
Acetonitrile (CH <sub>3</sub> -CN)	1.663	0.943	1.764	1.455	1.146	1.250	1.275
Nitromethane (CH <sub>3</sub> -NO <sub>2</sub> )	-10.326	-10.112	-9.773	-10.547	-10.791	-10.748	-10.774
Methyl nitrite (CH <sub>3</sub> -O-N=O)	-7.531	-7.372	-7.066	-7.848	-8.091	-8.043	-8.069
Methyl silane (CH <sub>3</sub> SiH <sub>3</sub> )	0.341	-0.122	0.376	0.309	0.198	0.185	0.216
Formic acid (HCOOH)	-4.761	-4.501	-4.357	-4.876	-5.081	-5.108	-5.102
Methyl formate (HCOOCH <sub>3</sub> )	-7.177	-7.166	-6.707	-7.271	-7.611	-7.619	-7.588
Acetamide (CH <sub>3</sub> CONH <sub>2</sub> )	-3.844	-4.311	-3.544	-4.124	-4.470	-4.391	-4.374
Aziridine (C <sub>2</sub> H <sub>4</sub> NH)	-0.930	-1.751	-0.874	-1.247	-1.554	-1.452	-1.427
Cyanogen (NCCN)	3.094	2.461	3.392	2.840	2.506	2.684	2.678
Dimethylamine ((CH <sub>3</sub> ) <sub>2</sub> NH)	1.935	0.971	1.857	1.474	1.167	1.271	1.297
Trans ethylamine (CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> )	1.114	0.084	1.032	0.652	0.340	0.443	0.470
Ketene (CH <sub>2</sub> CO)	-7.532	-7.782	-7.244	-7.527	-7.831	-7.826	-7.780
Oxirane (C <sub>2</sub> H <sub>4</sub> O)	-4.033	-4.426	-3.863	-4.175	-4.487	-4.477	-4.434
Acetaldehyde (CH <sub>3</sub> CHO)	-2.878	-3.175	-2.614	-2.905	-3.222	-3.215	-3.170

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TABLE S7: Deviation from reference “exact” values of r<sup>2</sup>SCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
Glyoxal (HCOCOH)	-5.050	-4.807	-4.371	-4.885	-5.229	-5.249	-5.215
Ethanol (CH <sub>3</sub> CH <sub>2</sub> OH)	-0.680	-1.187	-0.573	-0.888	-1.206	-1.192	-1.149
Dimethylether (CH <sub>3</sub> OCH <sub>3</sub> )	-1.670	-2.001	-1.425	-1.745	-2.059	-2.044	-2.002
Thiirane (C <sub>2</sub> H <sub>4</sub> S)	-4.914	-5.273	-5.039	-4.814	-5.208	-5.089	-5.036
Dimethyl sulfoxide ((CH <sub>3</sub> ) <sub>2</sub> SO)	-5.394	-5.360	-5.069	-5.193	-5.595	-5.507	-5.465
Ethaneethiol (C <sub>2</sub> H <sub>5</sub> SH)	-1.477	-1.926	-1.625	-1.408	-1.806	-1.680	-1.630
Dimethyl sulfide (CH <sub>3</sub> SCH <sub>3</sub> )	-2.303	-2.664	-2.390	-2.189	-2.579	-2.456	-2.408
Vinyl fluoride (CH <sub>2</sub> =CHF)	-3.740	-4.374	-3.854	-3.831	-4.090	-4.070	-4.013
Ethyl chloride (C <sub>2</sub> H <sub>5</sub> Cl)	-2.607	-3.351	-2.604	-2.731	-3.092	-3.015	-2.959
Vinyl chloride (CH <sub>2</sub> =CHCl)	-6.935	-7.497	-6.820	-6.922	-7.266	-7.192	-7.138
Acrylonitrile (CH <sub>2</sub> =CHCN)	2.187	1.326	2.389	2.077	1.642	1.760	1.812
Acetone (CH <sub>3</sub> COCH <sub>3</sub> )	-4.622	-4.986	-4.075	-4.404	-4.864	-4.841	-4.767
Acetic acid (CH <sub>3</sub> COOH)	-6.164	-6.065	-5.579	-6.130	-6.480	-6.490	-6.457
Acetyl fluoride (CH <sub>3</sub> COF)	-6.424	-6.864	-6.351	-6.592	-6.902	-6.904	-6.855
CH <sub>3</sub> COCl (acetyl chloride)	-8.557	-9.000	-8.358	-8.718	-9.117	-9.066	-9.021
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl (propyl chloride)	-3.464	-4.408	-3.328	-3.491	-3.994	-3.901	-3.817
Isopropanol (CH <sub>3</sub> ) <sub>2</sub> CHOH)	-1.351	-2.336	-1.359	-1.714	-2.176	-2.147	-2.075
Methyl ethyl ether (C <sub>2</sub> H <sub>5</sub> OCH <sub>3</sub> )	-2.835	-3.503	-2.554	-2.912	-3.369	-3.338	-3.267
Trimethylamine ((CH <sub>3</sub> ) <sub>3</sub> N)	0.782	-0.718	0.506	0.088	-0.362	-0.241	-0.188
Furan (C <sub>4</sub> H <sub>4</sub> O)	-8.366	-9.303	-8.167	-8.503	-9.075	-9.032	-8.934
C <sub>4</sub> H <sub>4</sub> S (thiophene)	-8.737	-9.683	-8.777	-8.580	-9.239	-9.085	-8.981
Pyrrrole (C <sub>4</sub> H <sub>5</sub> N)	-6.010	-7.455	-6.050	-6.414	-6.992	-6.853	-6.773
Pyridine (C <sub>5</sub> H <sub>5</sub> N)	-8.786	-10.249	-8.585	-8.951	-9.661	-9.507	-9.399
H <sub>2</sub>	2.073	2.089	2.088	2.088	2.089	2.088	2.088
HS	-2.162	-2.022	-2.250	-2.062	-2.134	-2.071	-2.078
CCH	-0.552	-1.104	-0.554	-0.533	-0.746	-0.727	-0.676
C <sub>2</sub> H <sub>3</sub> ( <sup>2</sup> A')	-5.424	-6.073	-5.500	-5.559	-5.783	-5.756	-5.707
CH <sub>3</sub> CO ( <sup>2</sup> A')	-6.741	-7.296	-6.727	-7.053	-7.333	-7.323	-7.284
H <sub>2</sub> COH ( <sup>2</sup> A)	-4.985	-5.226	-5.037	-5.319	-5.458	-5.457	-5.449
CH <sub>3</sub> O ( <sup>2</sup> A')	-6.122	-6.325	-6.012	-6.206	-6.366	-6.372	-6.353
CH <sub>3</sub> CH <sub>2</sub> O ( <sup>2</sup> A'')	-8.136	-8.690	-8.004	-8.245	-8.550	-8.540	-8.494
CH <sub>3</sub> S ( <sup>2</sup> A')	-4.543	-4.764	-4.659	-4.518	-4.728	-4.649	-4.629
C <sub>2</sub> H <sub>5</sub> ( <sup>2</sup> A')	-5.008	-5.985	-5.282	-5.411	-5.656	-5.613	-5.568
(CH <sub>3</sub> ) <sub>2</sub> CH ( <sup>2</sup> A')	-6.880	-7.958	-6.908	-7.082	-7.467	-7.411	-7.337
(CH <sub>3</sub> ) <sub>2</sub> CH ( <sup>2</sup> A')	-6.880	-7.958	-6.908	-7.082	-7.467	-7.411	-7.337
NO <sub>2</sub>	-11.949	-11.740	-11.840	-12.523	-12.605	-12.580	-12.632
Methyl allene (C <sub>4</sub> H <sub>6</sub> )	-4.574	-5.609	-4.346	-4.447	-4.984	-4.926	-4.815
Isoprene (C <sub>5</sub> H <sub>8</sub> )	-2.756	-4.236	-2.649	-2.780	-3.461	-3.382	-3.244
Cyclopentane (C <sub>5</sub> H <sub>10</sub> )	-1.937	-3.998	-2.169	-2.427	-3.143	-3.064	-2.923
n-Pentane (C <sub>5</sub> H <sub>12</sub> )	-1.398	-2.647	-0.918	-1.118	-1.835	-1.755	-1.615
Neo pentane (C <sub>5</sub> H <sub>12</sub> )	0.336	-1.762	0.040	-0.203	-0.922	-0.842	-0.701
1,4 Cyclohexadiene (C <sub>6</sub> H <sub>8</sub> )	-3.669	-5.460	-3.461	-3.639	-4.466	-4.375	-4.208
Cyclohexane (C <sub>6</sub> H <sub>12</sub> )	-1.516	-4.102	-1.930	-2.216	-3.082	-2.986	-2.819
n-Hexane (C <sub>6</sub> H <sub>14</sub> )	-1.430	-3.749	-1.445	-1.725	-2.587	-2.488	-2.320
3-Methyl pentane (C <sub>6</sub> H <sub>14</sub> )	0.038	-2.537	-0.324	-0.589	-1.450	-1.354	-1.185
Toluene (C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )	-10.116	-12.146	-9.920	-10.084	-11.045	-10.931	-10.739
n-Heptane (C <sub>7</sub> H <sub>16</sub> )	-2.690	-4.247	-1.848	-2.125	-3.129	-3.017	-2.821
Cyclooctatetraene (C <sub>8</sub> H <sub>8</sub> )	-6.519	-8.680	-6.222	-6.411	-7.492	-7.367	-7.146
n-Octane (C <sub>8</sub> H <sub>18</sub> )	-2.382	-5.214	-2.161	-2.536	-3.677	-3.545	-3.321
Naphthalene (C <sub>10</sub> H <sub>8</sub> )	-18.958	-21.765	-18.713	-18.916	-20.275	-20.113	-19.840
Azulene (C <sub>10</sub> H <sub>8</sub> )	-19.624	-22.283	-19.223	-19.436	-20.804	-20.641	-20.364
Acetic acid methyl ester (CH <sub>3</sub> COOCH <sub>3</sub> )	-7.399	-7.602	-6.811	-7.404	-7.890	-7.881	-7.822
t-Butanol ((CH <sub>3</sub> ) <sub>3</sub> COH)	-1.428	-2.845	-1.499	-1.904	-2.512	-2.467	-2.367
Aniline (C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> )	-10.492	-12.308	-10.264	-10.676	-11.521	-11.353	-11.219
Phenol (C <sub>6</sub> H <sub>5</sub> OH)	-12.036	-13.384	-11.609	-11.977	-12.824	-12.747	-12.595

Continued on next page

TABLE S7: Deviation from reference “exact” values of r<sup>2</sup>SCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
Divinyl ether (C <sub>4</sub> H <sub>6</sub> O)	-5.789	-6.516	-5.356	-5.702	-6.264	-6.223	-6.127
Tetrahydrofuran (C <sub>4</sub> H <sub>8</sub> O)	-3.068	-4.569	-3.257	-3.678	-4.273	-4.228	-4.130
Cyclopentanone (C <sub>5</sub> H <sub>8</sub> O)	-7.082	-8.858	-7.164	-7.608	-8.352	-8.298	-8.168
Benzoquinone(C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> )	-12.768	-13.628	-11.958	-12.542	-13.429	-13.385	-13.239
Pyrimidine (C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> )	-9.158	-10.545	-9.011	-9.630	-10.237	-10.028	-9.975
Dimethyl sulphone (C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> S)	-7.342	-6.669	-6.520	-6.931	-7.368	-7.297	-7.267
Chlorobenzene (C <sub>6</sub> H <sub>5</sub> Cl)	-13.248	-14.959	-13.051	-13.229	-14.120	-13.980	-13.817
Butanedinitrile (NC-CH <sub>2</sub> -CH <sub>2</sub> -CN)	3.363	1.841	3.489	2.860	2.237	2.446	2.497
Pyrazine (C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> )	-5.153	-6.524	-5.032	-5.644	-6.247	-6.037	-5.985
Acetyl acetylene (CH <sub>3</sub> -C(=O)-CCH)	-2.054	-2.788	-1.645	-1.978	-2.549	-2.516	-2.416
Crotonaldehyde (CH <sub>3</sub> -CH=CH-CHO)	-7.089	-7.851	-6.701	-7.039	-7.624	-7.585	-7.485
Acetic anhydride (CH <sub>3</sub> -C(=O)-O-C(=O)-CH <sub>3</sub> )	-13.700	-14.172	-13.111	-13.988	-14.649	-14.652	-14.575
2,5-Dihydrothiophene (C <sub>4</sub> H <sub>6</sub> S)	-5.355	-6.456	-5.530	-5.379	-6.041	-5.888	-5.782
Isobutane nitrile ((CH <sub>3</sub> ) <sub>2</sub> CH-CN)	2.692	1.331	2.871	2.461	1.865	2.000	2.082
Methyl ethyl ketone (CH <sub>3</sub> -CO-CH <sub>2</sub> -CH <sub>3</sub> )	-4.314	-5.899	-4.523	-4.920	-5.519	-5.481	-5.380
Isobutanal ((CH <sub>3</sub> ) <sub>2</sub> CH-CHO)	-2.490	-3.536	-2.220	-2.619	-3.218	-3.180	-3.078
1,4-Dioxane (C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	-6.285	-7.148	-5.976	-6.608	-7.235	-7.205	-7.121
Tetrahydrothiophene (C <sub>4</sub> H <sub>8</sub> S)	-3.159	-4.678	-3.630	-3.523	-4.208	-4.051	-3.945
t-Butyl chloride ((CH <sub>3</sub> ) <sub>3</sub> C-Cl)	-3.458	-5.254	-3.813	-4.027	-4.680	-4.572	-4.458
n-Butyl chloride (CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -Cl)	-3.222	-4.597	-3.122	-3.348	-3.997	-3.887	-3.775
Tetrahydropyrrole (C <sub>4</sub> H <sub>8</sub> NH)	-0.427	-2.200	-0.559	-1.053	-1.650	-1.513	-1.431
Nitro-s-butane (CH <sub>3</sub> -CH <sub>2</sub> -CH(CH <sub>3</sub> )-NO <sub>2</sub> )	-10.757	-11.927	-10.448	-11.366	-12.043	-11.950	-11.892
Diethyl ether (CH <sub>3</sub> -CH <sub>2</sub> -O-CH <sub>2</sub> -CH <sub>3</sub> )	-3.006	-4.039	-2.763	-3.162	-3.765	-3.718	-3.619
Dimethyl acetal (CH <sub>3</sub> -CH(OCH <sub>3</sub> ) <sub>2</sub> )	-4.976	-5.737	-4.565	-5.215	-5.846	-5.816	-5.731
t-Butanethiol ((CH <sub>3</sub> ) <sub>3</sub> C-SH)	-1.913	-3.317	-2.300	-2.171	-2.858	-2.699	-2.593
Diethyl disulfide (CH <sub>3</sub> -CH <sub>2</sub> -S-S-CH <sub>2</sub> -CH <sub>3</sub> )	-5.275	-5.864	-5.288	-4.880	-5.665	-5.421	-5.320
t-Butylamine ((CH <sub>3</sub> ) <sub>3</sub> C-NH <sub>2</sub> )	1.217	-0.166	1.486	1.033	0.436	0.570	0.653
Tetramethylsilane (Si(CH <sub>3</sub> ) <sub>4</sub> )	1.647	0.007	1.629	1.434	0.889	0.920	1.037
2-Methyl thiophene (C <sub>5</sub> H <sub>6</sub> S)	-9.360	-10.890	-9.633	-9.484	-10.292	-10.119	-9.987
N-methyl pyrrole (cyc-C <sub>4</sub> H <sub>4</sub> N-CH <sub>3</sub> )	-6.354	-8.208	-6.450	-6.863	-7.578	-7.423	-7.316
Tetrahydropyran (C <sub>5</sub> H <sub>10</sub> O)	-3.792	-5.582	-3.840	-4.305	-5.055	-4.993	-4.866
Diethyl ketone (CH <sub>3</sub> -CH <sub>2</sub> -CO-CH <sub>2</sub> -CH <sub>3</sub> )	-6.268	-7.321	-5.708	-6.121	-6.869	-6.813	-6.684
Isopropyl acetate (CH <sub>3</sub> -C(=O)-O-CH(CH <sub>3</sub> ) <sub>2</sub> )	-8.303	-9.411	-7.897	-8.579	-9.352	-9.312	-9.196
Tetrahydrothiopyran (C <sub>5</sub> H <sub>10</sub> S)	-3.977	-5.662	-4.210	-4.157	-4.984	-4.810	-4.677
Piperidine (cyc-C <sub>5</sub> H <sub>10</sub> NH)	0.076	-2.403	-0.421	-0.940	-1.682	-1.531	-1.421
t-Butyl methyl ether ((CH <sub>3</sub> ) <sub>3</sub> C-O-CH <sub>3</sub> )	-2.746	-4.039	-2.369	-2.832	-3.570	-3.508	-3.382
1,3-Difluorobenzene (C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> )	-16.314	-18.089	-16.343	-16.330	-17.130	-17.053	-16.884
1,4-Difluorobenzene (C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> )	-17.917	-19.598	-17.925	-17.907	-18.708	-18.631	-18.462
Fluorobenzene (C <sub>6</sub> H <sub>5</sub> F)	-13.089	-14.764	-12.977	-13.033	-13.840	-13.753	-13.587
Di-isopropyl ether ((CH <sub>3</sub> ) <sub>2</sub> CH-O-CH(CH <sub>3</sub> ) <sub>2</sub> )	-3.552	-5.180	-3.139	-3.618	-4.509	-4.431	-4.276
PF <sub>5</sub>	1.068	1.299	0.865	1.416	1.428	1.411	1.426
SF <sub>6</sub>	-12.356	-11.806	-12.357	-11.695	-11.769	-11.741	-11.733
P <sub>4</sub>	-7.181	-4.512	-5.961	-5.428	-5.414	-5.282	-5.301
SO <sub>3</sub>	-8.327	-6.681	-7.272	-7.898	-8.087	-8.074	-8.113
SCl <sub>2</sub>	-4.804	-4.882	-5.048	-4.934	-5.171	-5.011	-5.014
POCl <sub>3</sub>	-9.457	-8.027	-8.166	-8.293	-8.633	-8.493	-8.508
PCl <sub>5</sub>	-16.564	-15.681	-15.626	-15.619	-16.061	-15.822	-15.825
Cl <sub>2</sub> O <sub>2</sub> S	-11.846	-10.997	-11.394	-11.821	-12.136	-12.015	-12.041
PCl <sub>3</sub>	-7.692	-6.694	-6.785	-6.687	-6.975	-6.819	-6.821
Cl <sub>2</sub> S <sub>2</sub>	-13.950	-13.775	-14.369	-13.914	-14.287	-14.030	-14.038
SiCl <sub>2</sub> singlet	-2.391	-2.762	-2.550	-2.651	-2.801	-2.750	-2.744
CF <sub>3</sub> Cl	-11.068	-11.823	-11.571	-11.462	-11.684	-11.648	-11.607
Hexafluoro ethane (C <sub>2</sub> F <sub>6</sub> )	-16.825	-18.053	-17.687	-17.362	-17.640	-17.656	-17.574
CF <sub>3</sub>	-13.034	-13.634	-13.551	-13.396	-13.486	-13.498	-13.464
C <sub>6</sub> H <sub>5</sub> (phenyl radical)	-15.945	-17.754	-15.919	-16.065	-16.839	-16.747	-16.587
Bicyclo[1.1.0]butane (C <sub>4</sub> H <sub>6</sub> )	-3.907	-5.483	-4.041	-4.192	-4.770	-4.711	-4.598

Continued on next page

TABLE S7: Deviation from reference “exact” values of r<sup>2</sup>SCAN atomization energies (kcal/mol) for the G3 test set obtained with increasingly dense numerical grids (numbered from 1 to 7). Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	1	2	3	4	5	6	7
(CH <sub>3</sub> ) <sub>3</sub> C (t-butyl radical)	-6.846	-8.638	-7.180	-7.378	-7.912	-7.841	-7.738
Trans-butane(C <sub>4</sub> H <sub>10</sub> )	-0.548	-2.155	-0.639	-0.823	-1.398	-1.333	-1.221
1,3 Cyclohexadiene (C <sub>6</sub> H <sub>8</sub> )	-4.213	-6.276	-4.279	-4.460	-5.286	-5.192	-5.027
ME	-4.194	-4.831	-4.115	-4.286	-4.660	-4.599	-4.545
MAE	5.180	5.694	5.108	5.234	5.552	5.506	5.457



TABLE S8: Error in reaction barrier heights (kcal/mol) for the BH76 test set. Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	TPSS	SCAN	rSCAN	r <sup>2</sup> SCAN
0	-10.214	-8.791	-8.273	-7.781
1	-23.136	-18.390	-21.305	-20.121
2	-15.505	-13.497	-13.512	-13.044
3	-15.505	-13.497	-13.512	-13.044
4	-10.490	-8.797	-9.233	-8.601
5	-10.490	-8.797	-9.233	-8.601
6	-13.075	-10.468	-11.605	-11.038
7	-14.959	-10.804	-10.046	-10.149
8	-13.127	-13.704	-12.920	-12.261
9	-22.676	-16.482	-14.953	-15.065
10	-12.692	-12.131	-11.556	-11.402
11	-18.088	-15.415	-15.440	-15.448
12	-8.518	-7.986	-6.873	-7.131
13	-8.518	-7.986	-6.873	-7.131
14	-7.228	-5.314	-4.739	-4.886
15	-7.228	-5.314	-4.739	-4.886
16	-8.194	-8.027	-6.176	-6.558
17	-8.194	-8.027	-6.176	-6.558
18	-8.061	-6.536	-5.304	-5.543
19	-8.061	-6.536	-5.304	-5.543
20	-8.494	-9.200	-7.443	-7.723
21	-6.526	-5.157	-4.601	-4.936
22	-5.242	-4.379	-3.428	-3.603
23	-7.262	-4.722	-4.626	-4.813
24	-7.975	-7.495	-6.323	-6.592
25	-9.441	-8.043	-6.594	-6.913
26	-7.692	-5.832	-5.135	-5.373
27	-6.640	-3.076	-1.944	-2.358
28	-11.805	-10.529	-10.642	-10.129
29	-2.311	-0.959	-1.323	-1.411
30	-8.156	-6.871	-6.904	-6.456
31	0.928	1.453	1.574	1.126
32	-5.992	-6.209	-5.053	-4.880
33	-1.868	1.272	1.077	1.095
34	-3.692	-6.322	-4.408	-4.491
35	-5.025	-2.213	-1.624	-1.774
36	-0.783	-1.909	-1.600	-1.931
37	-1.219	-0.981	-1.217	-1.416
38	-10.108	-7.107	-5.951	-5.895
39	-7.799	-8.749	-9.552	-8.213
40	-6.895	-7.180	-8.073	-6.681
41	-13.798	-10.266	-8.153	-8.579
42	-4.935	-4.921	-5.684	-4.523
43	-10.009	-8.426	-7.503	-7.419
44	-7.977	-8.464	-8.399	-7.819
45	-9.807	-8.046	-6.660	-6.822
46	-8.954	-7.262	-7.834	-7.119
47	-8.954	-7.262	-7.834	-7.119
48	-10.913	-10.639	-10.641	-10.071
49	-10.202	-9.564	-9.015	-8.716
50	-5.477	-4.920	-4.845	-4.667
51	-8.243	-10.066	-10.265	-9.880
52	-7.874	-8.343	-8.513	-7.882
53	-8.720	-7.101	-5.577	-5.898
54	-10.710	-9.789	-10.369	-9.174
55	-15.498	-10.996	-8.393	-9.257
56	-9.025	-12.313	-11.802	-11.340

Continued on next page

TABLE S8: Error in reaction barrier heights (kcal/mol) for the BH76 test set. Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	TPSS	SCAN	rSCAN	r <sup>2</sup> SCAN
57	-7.396	-4.879	-4.797	-4.606
58	-7.990	-6.416	-6.726	-6.368
59	-3.427	-4.142	-4.791	-3.612
60	-12.258	-7.468	-7.637	-7.482
61	-8.813	-11.397	-12.823	-11.321
62	-8.048	-6.302	-6.444	-6.066
63	-4.780	-6.170	-7.599	-6.139
64	-13.302	-13.951	-14.410	-13.839
65	-14.439	-11.664	-12.825	-12.318
66	-5.274	-3.552	-3.700	-3.398
67	-6.307	-10.413	-9.764	-9.317
68	-2.813	-1.562	-1.598	-1.442
69	-4.828	-9.247	-8.860	-8.347
70	-4.198	-5.726	-5.726	-5.123
71	-5.756	-5.558	-4.416	-4.494
72	-5.620	-6.974	-6.714	-6.169
73	-8.061	-7.532	-6.501	-6.427
74	-3.728	-4.794	-5.678	-5.286
75	-3.728	-4.794	-5.678	-5.286
ME	-8.550	-7.653	-7.365	-7.125
MAE	8.574	7.724	7.434	7.182

TABLE S9: Error in dissociation energies (kcal/mol) for the S22 test set. Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	TPSS	SCAN	rSCAN	r <sup>2</sup> SCAN
0	-0.889	-0.032	-0.259	-0.236
1	-0.532	0.383	0.051	0.135
2	-0.915	2.157	1.332	1.248
3	-1.995	0.478	-0.181	-0.181
4	-2.728	0.025	-0.573	-0.640
5	-2.472	0.031	-0.434	-0.547
6	-3.268	-0.502	-1.045	-1.108
7	-0.652	-0.176	-0.298	-0.238
8	-1.845	-0.450	-0.618	-0.614
9	-1.890	-0.498	-0.862	-0.660
10	-5.488	-1.375	-2.431	-1.824
11	-6.015	-1.370	-2.379	-1.868
12	-8.413	-1.366	-2.605	-2.000
13	-8.215	-2.335	-3.678	-2.962
14	-12.093	-2.553	-4.153	-3.500
15	-0.588	-0.076	-0.276	-0.191
16	-1.800	0.075	-0.421	-0.108
17	-1.911	-0.235	-0.689	-0.406
18	-2.183	-0.348	-0.797	-0.580
19	-3.167	-1.012	-1.494	-1.262
20	-4.351	-1.344	-1.950	-1.619
21	-4.053	-1.017	-1.599	-1.454
ME	-3.430	-0.524	-1.153	-0.937
MAE	3.430	0.798	1.273	1.057

TABLE S10: Error in lattice constants ( $\text{\AA}$ ) for the LC20 test set. Mean error (ME) and Mean Absolute Error (MAE) are given at end of table.

	TPSS	SCAN	rSCAN	r <sup>2</sup> SCAN
Ag	0.019	0.012	0.028	0.034
Al	-0.011	-0.012	-0.027	-0.032
Ba	0.007	0.049	0.100	0.076
C	0.014	-0.004	-0.001	0.005
Ca	-0.032	-0.009	0.017	0.018
Cu	-0.016	-0.030	-0.023	-0.020
GaAs	0.075	0.020	0.031	0.029
Ge	0.083	0.029	0.043	0.039
Li	-0.014	0.011	0.021	0.016
LiCl	0.040	0.016	0.021	0.034
LiF	0.070	0.004	0.008	0.021
MgO	0.056	0.018	0.019	0.027
NaCl	0.129	0.010	0.025	0.036
NaF	0.133	0.006	0.015	0.028
Na	0.032	-0.007	0.024	0.004
Pd	0.025	0.016	0.026	0.032
Rh	0.011	-0.005	0.006	0.008
Si	0.033	0.005	0.012	0.018
SiC	0.019	0.002	-0.001	0.006
Sr	-0.014	0.039	0.064	0.056
ME	0.033	0.009	0.020	0.022
MAE	0.041	0.015	0.025	0.027