



## Is the error on first-principles volume predictions absolute or relative?



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### ABSTRACT

Many benchmarks of density-functional theory with respect to experiment suggest the error on predicted equilibrium volumes to scale with the volume. Relative volume errors are therefore often used as a decisive argument to select one exchange–correlation functional over another. We show that the error on the volume (after correcting for systematic deviations) is only approximately relative. A simple analytic model, validated by rigorous Monte Carlo simulations, reveals that a more accurate error estimate can be derived from the inverse of the bulk modulus. This insight is not only instrumental for the selection or design of suitable functionals. It also calls for a new attitude towards computational errors: to report computational errors on electronic-structure calculations, identify systematic deviations and distinguish between relative and absolute effects.

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### 1. Introduction

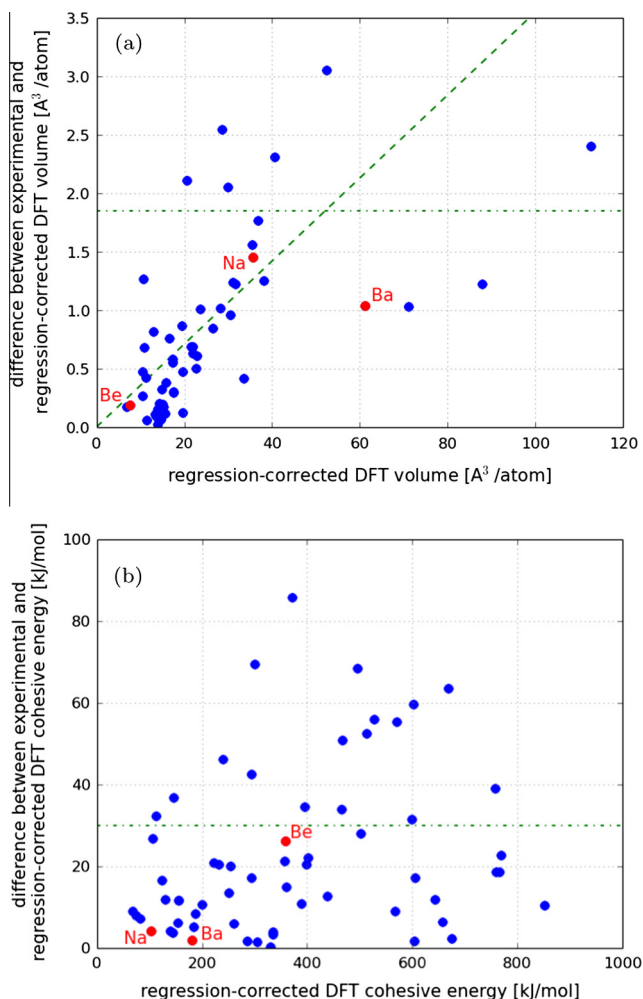
Over the last few decades, powerful computers and advanced computational approaches have revolutionized materials science. Whereas first-principles methods were originally limited to *a posteriori* analyses of experimentally studied compounds, they now make it possible to investigate materials prior to experiment and at significantly lower costs. As a result, computational materials design has become a research discipline in its own right. However, a compromise between accuracy and available resources is inevitable. Applied methods vary from very approximate yet cheap (e.g. classical force fields [1,2]) to nearly exact yet terribly expensive (e.g. full configuration interaction [3]). A popular middle ground is density-functional theory (DFT) [4,5], which produces qualitatively acceptable predictions at a reasonable cost for many systems, provided a good choice is made for the so-called exchange–correlation functional. Nevertheless, the obtained results are still approximate, and the accuracy of the DFT calculations is determined by the selected functional. Understanding the expected deviations between DFT and experimental values is therefore essential to assess the reliability of a prediction and choose an appropriate functional correspondingly.

Several benchmark studies in the literature seek to evaluate the differences between DFT predictions and experimental results. Although these kind of studies are mainly limited to molecular sys-

tems [7–11], a number of exhaustive solid-state tests are available as well [11–16]. However, conclusions drawn in these works may be significantly affected by the choice of the error model [17]. This is nicely illustrated by the equilibrium volume, or equivalently the lattice parameter. Most benchmarks list both absolute (mean error, mean absolute error) and relative differences with respect to experiment (mean relative error, mean absolute relative error) [12–15], while other articles express the community intuition that errors should scale in a relative way (i.e. smaller errors on smaller volumes) and only mention the latter [11,16]. The volume of beryllium ( $7.8 \text{ \AA}^3/\text{atom}$  experimentally), for example, is thus expected to be predicted more accurately with DFT than that of sodium ( $37.2 \text{ \AA}^3/\text{atom}$ ) or barium ( $62.3 \text{ \AA}^3/\text{atom}$ ) [6]. In addition to these relatively simple approaches, some authors also assessed DFT errors more rigorously. Some of the present authors [6,18], for example, applied a linear regression between experimental and DFT results to distinguish between systematic and residual deviations. In the current article, a systematic error denotes the predictable over- or underestimation of DFT compared to experiment, which can be corrected for by means of a regression analysis. The remaining unpredictable (yet deterministic) fluctuation is denoted as residual error. In Refs. [6,18], we did not observe the residual errors on the volume to behave in a purely absolute or relative way (see Fig. 1(a)). Pernot et al. [19] applied a more general Bayesian Model Selection to determine the most appropriate polynomial degree to describe the systematic bias between predictions with several functionals and experiment. They also found a linear relationship to be most suitable, and expressed the remaining

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**Fig. 1.** Absolute values of the difference between DFT predictions and thermally corrected experimental values for (a) the equilibrium volume, plotted as a function of the DFT volume and (b) the cohesive energy, plotted as a function of the DFT cohesive energy [6]. Three example materials are highlighted in red. All DFT quantities were corrected for systematic deviations from experiment by means of a linear regression, following the procedure described by Lejaeghere et al. [6]. For the volume no obvious absolute (dot-dashed line) or relative behaviour (dashed line) is observed, while the cohesive energy is characterized by an absolute error bar (dot-dashed line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

discrepancies in terms of method inadequacy and parametric uncertainty of the fit, using a virtual measurement framework [20]. In this way, they found the prediction uncertainty on lattice parameters to increase as a function of the lattice parameter itself. Finally, Mortensen et al. [21] extracted error estimates per element by varying the generalized-gradient approximation (GGA) functional itself according to a Gaussian distribution. This distribution was tuned to a least-squares fit of DFT-GGA cohesive energies to experimental results. Although the resulting error bars were found to scale nicely with the deviation from experiment, the study did not provide a definite answer on the nature of the volume error either.

It therefore remains unclear whether the error on  $V_0$  should be an absolute or a relative one. The error on the volume is indeed larger for Ba than for Be, for example, but not larger than for Na (Fig. 1 (a)). Nevertheless, insight in the error is critical for the comparison, ranking and construction of high-accuracy functionals. The present study aims to answer that question, based on the properties of a

solid-state equation of state. After formulating our primary ansatz, we will approach the problem from both an analytic and a numerical (Monte Carlo) point of view. In each case, we will assume that systematic deviations (such as the 4% volume overestimation [6] by the PBE functional) have been corrected for, allowing for a better stochastic description of the remaining errors.

## 2. Ansatz

Before dealing with the equilibrium volume, we first focus on the energy. Indeed, besides electron densities or wave functions, the basic quantities in first-principles methods are cohesive energies or, more precisely, cohesive energy differences. They are used to evaluate the relative stability of two configurations, such as in formation energies. In addition, many other properties are derived from energy differences. Think of elastic moduli, for example, which represent second derivatives of the total energy with respect to deformation. Since the equilibrium volume relates to the absolute minimum of the potential energy surface, this quantity too depends on energy differences.

The primary ansatz of this study is that after correcting for systematic deviations, *the error bar on cohesive energy (differences) per atom is absolute*, i.e. not proportional to the cohesive energy (difference) itself. Indeed, a relative error is unlikely, as small cohesive energy (differences) may arise from the cancellation of large energetic contributions, thus not necessarily giving rise to smaller errors. The assumption of an absolute error bar is also consistent with observed distributions of cohesive energies (see Fig. 1(b)) and formation energies [22,23]. When assessing a large and diverse set of materials, the errors may then be considered to assume a Gaussian distribution, and only the elimination of systematic deviations makes it possible to treat all materials on equal footing. Note that each type of cohesive energy difference is characterized by its own error bar. The energy difference between two almost identical structures will always be small, and hence the error will be too. This is the case for two slightly different volumes of the same material, for example. We account for this dependency of the error on the volume, as will be discussed later.

If the fundamental error is an error on energy differences, the errors on derived quantities, such as the volume, must depend on it. Whether the error on the volume should be absolute or relative hence follows from the absolute character of the energy error. The easiest way to determine the relation between the volume error and the energy error, is by looking at the inverse problem: rather than starting from a certain energy error and investigating what volume changes yield equations of state (EOS) within that error bar, it is more straightforward to directly evaluate the energy change associated with a change in equilibrium volume. We first treat this problem in an analytic yet approximate way, ascertaining the most important trends. Afterwards, we apply a more rigorous numerical method based on a Monte Carlo procedure.

## 3. Analytic approximation

To analytically assess the relation between errors on the energy and on the EOS parameters (such as the equilibrium volume), we examine how the shape of the EOS influences the energy difference between two fixed volumes,  $E(\alpha V'_0) - E(V'_0) \equiv \Delta E(\alpha)$ , with  $V'_0$  a volume close to the equilibrium volume and  $\alpha$  close to 1 (see<sup>1</sup> coloured vertical lines near the  $E$  axis in Fig. 2(a)). We use the Birch–Murnaghan EOS with zero reference energy:

<sup>1</sup> For interpretation of color in Fig. 2, the reader is referred to the web version of this article.

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