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Rapid Communications

Microhartree precision in density functional theory calculations

Andris Gulans,[1] Anton Kozhevnikov,[2] and Claudia Draxl[1]

[1]*Department of Physics, IRIS Adlershof, Humboldt-Universität zu Berlin, Zum Großen Windkanal 6, 12489 Berlin, Germany*

[2]*Swiss National Supercomputing Center, Lugano, Switzerland*

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To address ultimate precision in density functional theory calculations we employ the full-potential linearized augmented plane-wave + local-orbital (LAPW + lo) method and justify its usage as a benchmark method. LAPW + lo and two completely unrelated numerical approaches, the multiresolution analysis (MRA) and the linear combination of atomic orbitals, yield total energies of atoms with mean deviations of 0.9 and 0.2 μHa, respectively. Spectacular agreement with the MRA is reached also for total and atomization energies of the G2-1 set consisting of 55 molecules. With the example of α iron we demonstrate the capability of LAPW + lo to reach μHa/atom precision also for periodic systems, which allows also for the distinction between the numerical precision and the accuracy of a given functional.

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Density functional theory (DFT) [1,2] is the most widely used method in modern computational condensed-matter physics and chemistry as reflected by the existence of dozens of implementations, employing diverse numerical schemes. Although each of these implementations may be most suitable for a specific type of application, in essence, all of them solve the Kohn-Sham (KS) equation [2]. Given the diversity of computational tools, it is natural to ask whether they indeed provide the same answers. This question, i.e., how reproducible DFT results are, was recently discussed in the context of a community effort where the equation of state of 71 elemental solids was calculated using a variety of DFT implementations [3]. It turned out that, after a period of fine-tuning, different DFT codes are now in good overall agreement. Despite the deviations between codes being small on average, discrepancies obtained for certain elements are much more substantial. Moreover, it is not clear or even not expected that such agreement would be preserved beyond bulk elemental materials. As a matter of fact, the work to be performed to explore and guarantee the precision of electronic-structure codes is certainly far from being finished.

Efforts on the improvement of computational methods are immensely alleviated if reliable reference data or reference tools are available. The gold standard for solving the same KS equation of DFT for condensed matter are full-potential all-electron methods, especially those employing (linearized) augmented plane waves with local orbitals (LAPW + lo) [4–6] as basis functions. LAPW + lo is often *trusted blindly* as the ultimate reference method for validating pseudopotentials or data sets of projector-augmented waves [7–10]. Yet, it has never been shown how precise this method can be in practice. Even more, arguing that the method would depend on parameters which "can influence the results in a more or less erratic way," it was even questioned recently [11] whether LAPW + lo can provide benchmark quality at all.

In this Rapid Communication, we use our LAPW + lo implementation in the full-potential all-electron package EXCITING [12] to show that for absolute total energies outstanding 1-μHa/atom precision can be obtained. In order to validate this statement, we first turn to atoms and molecules since for finite systems one can find other methods that, in principle, are capable of yielding an *exact* numerical solution of the KS equation. In the second step, we exploit the duality of the LAPW + lo basis for verifying the numerical performance of plane waves using atomic orbitals and vice versa. Making use of this concept, we demonstrate that microhartree precision is achievable also for periodic systems. Clearly, we can thus distinguish between the accuracy of a DFT functional and the numerical precision of the actual implementation.

Let us recall the Kohn-Sham equation of DFT,

$$\left[-\frac{\nabla^2}{2}+v_{\mathrm{eff}}(\mathbf{r})\right]\psi(\mathbf{r})=\varepsilon_{\mathrm{KS}}\psi(\mathbf{r}). \quad (1)$$

The major source of numerical issues in solving it is the behavior of the effective potential $v_{\mathrm{eff}}(\mathbf{r})$. Although it is very smooth in most of the space, its shape is dominated by the electrostatic contribution in the proximity of nuclei where it varies rapidly with a divergence at the nuclear sites. As a result, the otherwise well-behaved KS orbitals $\psi(\mathbf{r})$ exhibit cusps at the atomic positions and a nodal structure in their vicinity.

The LAPW + lo method meets these properties of $\psi(\mathbf{r})$. The unit cell is partitioned into nonoverlapping atomic spheres (or muffin-tin spheres MT_α), centered at the nuclear positions with index α and the interstitial region (I). KS wave functions are expanded in terms of atomlike functions $f_\nu^\alpha(\mathbf{r}_\alpha)=u_\nu(r_\alpha)Y_{\ell m}(\hat{\mathbf{r}}_\alpha)$ and plane waves, respectively,

$$\phi_{\mathbf{G+k}}(\mathbf{r})=\begin{cases}\sum_\nu A^\alpha_{\mathbf{G+k},\nu}f^\alpha_\nu(\mathbf{r}_\alpha), & \mathbf{r}\in MT_\alpha,\\ \frac{1}{\sqrt{\Omega}}e^{i(\mathbf{G+k})\mathbf{r}}, & \mathbf{r}\in I.\end{cases} \quad (2)$$

The coefficients $A^\alpha_{\mathbf{G+k},\nu}$ are determined to ensure smoothness of the basis functions at the sphere boundaries. These augmented plane waves are typically complemented by local

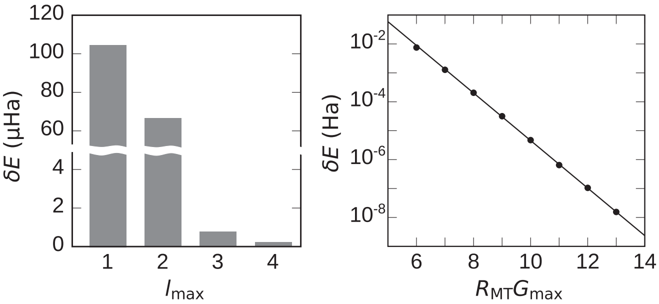

FIG. 1. The error in the total LSDA energy of an oxygen atom when using local orbitals with angular momenta up to ℓ_{max} (left) and as a function of a plane-wave cutoff $R_{\mathrm{MT}}G_{\mathrm{max}}$ (right). The limit of the total energy is estimated by using $\ell_{\mathrm{max}} = 6$ and by extrapolating its dependence on $R_{\mathrm{MT}}G_{\mathrm{max}}$.

orbitals,

$$\phi_\mu(\mathbf{r}) = \begin{cases} f_\mu^\alpha(\mathbf{r}), & \mathbf{r} \in MT_\alpha, \\ 0, & \mathbf{r} \in I. \end{cases} \tag{3}$$

That way the flexibility of the basis is improved which, indeed, has a major impact on results as we demonstrate below. Local orbitals are crucial also for reaching benchmark quality in GW calculations as was pointed out recently [13,14]. A more detailed introduction to the LAPW + lo method is available in Refs. [12,15]. The overall size of the basis and the quality in the interstitial region are controlled by the dimensionless parameter $R_{\mathrm{MT}}G_{\mathrm{max}}$, where G_{max} is the maximum length of wave-vectors $\mathbf{G} + \mathbf{k}$ used in the LAPW basis. In other words, $R_{\mathrm{MT}}G_{\mathrm{max}}$ can be freely adjusted to make the expansion of wave functions in the interstitial region as precise as necessary. In the atomic spheres, the quality of the wave functions is governed by the choice of the atomiclike functions [Eqs. (2) and (3)].

To illustrate how the LAPW + lo basis can be exploited to reach essentially exact total energies for a given exchange-correlation functional, we consider the oxygen atom. We restrict ourselves to using the local spin-density approximation (LSDA). Still, the same procedure works for any other functional for which a local KS potential is available, and we present a similar discussion for the generalized-gradient approximation (GGA) in the Supplemental Material [16]. According to the Aufbau principle, the $2p$ shell is partially filled with one p orbital doubly occupied and two others singly occupied. Consequently, this atom is not only magnetic, but also its effective potential and hence the electron density are not spherically symmetric. Thus, radial and angular degrees of freedom are entangled, and all wave functions formally contain contributions from all angular momenta. We take it into account by introducing local orbitals not only with angular momenta of $\ell = 0$ and 1, that are the dominating contributions to the $1s$, $2s$, and $2p$ states, but also consider higher values of ℓ. Their impact on the total energy is shown in Fig. 1. In the classical LAPW formalism, $f_\nu^\alpha(\mathbf{r})$ combines strictly two functions per spherical harmonic for each atom. Local orbitals allow us to correct for all missing features in the pure LAPW representation and are not limited in number. A calculation using local orbitals with ℓ up to 1 yields the total energy within an error of $\sim$100 μHa. Adding basis functions with higher angular momenta gradually improves the result, and, at $\ell_{\mathrm{max}} = 4$, this quantity differs from the estimated exact limit by less than 10^{-7} Ha. Likewise, we show how the total energy converges with increasing $R_{\mathrm{MT}}G_{\mathrm{max}}$. In this case, we observe an exponential decay of the error similarly as in Ref. [12]. Note that the errors due to missing angular degrees of freedom depend on the atomic-sphere radius; the magnitudes shown in Fig. 1 are obtained for $R_{\mathrm{MT}} = 1.2a_0$. It is possible to reduce R_{MT} so far that already at $\ell_{\mathrm{max}} = 1$ the errors are negligible. We find that, at $R_{\mathrm{MT}} = 0.5a_0$, this error is only 2 μHa. However, a reduction of R_{MT} to such a small value leads to an enormous increase in the number of LAPWs, making the calculations very expensive.

At this point, it is already clear that the quality of the basis in the atomic spheres is essential for highly accurate results, and the discussed example reflects how to handle systems with substantially asymmetric potentials in the atomic spheres. Such potentials not only occur in a range of spin-polarized systems, but also occur in systems with short bonds.

To show that the converged limit in LAPW + lo corresponds to the exact numerical solution we compare them to two other all-electron methods that are expected to deliver highly precise results. The first one is the multiresolution analysis (MRA) [17] that also has been used as a reference method in Ref. [11]. It recasts the KS equation in the Lippmann-Schwinger integral equation form and solves it iteratively by applying local and nonlocal operators on trial wave functions numerous times. The wave functions are stored in an adaptive multiscale representation, whereas the integral kernels of the nonlocal operators are represented in a separable form. Such a numerical approach allows for solving the KS equation efficiently with a guaranteed precision. The MRA is implemented in the MADNESS code [17], which is currently restricted to finite systems. The other alternative method is the linear combination of atomic orbitals (LCAO) for which we use the NWCHEM package [18]. Although, in the general case, where the precision of the LCAO for absolute total energies is limited, it was shown how Gaussian-type orbitals can be used for reaching the complete-basis limit for atoms [19] which we employ in this Rapid Communication. In the calculations of molecules, we resort to the augmented correlation-consistent polarized quadruple- and quintuple-ζ basis sets known also by their acronyms aug-cc-pVQZ and aug-cc-pV5Z [20–22], respectively. These basis sets were used by Willand *et al.* [23] for generating all-electron reference data for benchmarking newly generated pseudopotentials. The so-obtained atomization energies turned out to be converged to at least 1 kcal/mol ($\approx$1.6 × 10^{-3} Ha), which is commonly referred to as chemical accuracy.

The MRA and LCAO are designed for calculating finite systems, and thus we make use of them first for comparison with our total energies of atoms and further below for molecules. We employ nonrelativistic theory and the LSDA [24]. This choice, however, does not influence the overall conclusions from our Rapid Communication. The total energies of atoms obtained with the three codes are compared in Fig. 2. In all cases, we observe outstanding agreement between the LAPW + lo and the MRA (LCAO) with a mean absolute deviation of 0.9 μHa (0.2 μHa). (Computational details and the total energies are provided in the Supplemental Material [16].)

The excellent agreement between the different methods is all the more remarkable in view of the very different ways the

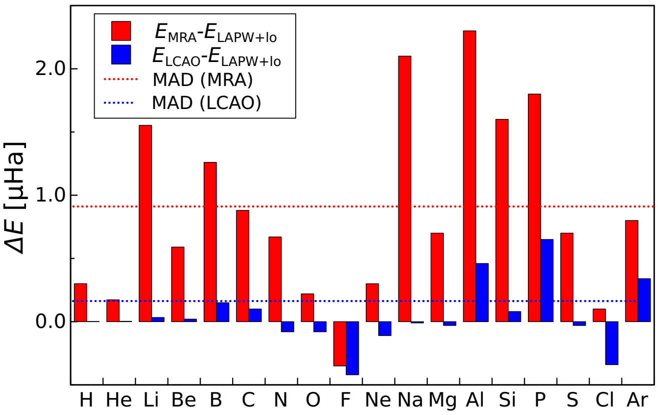

FIG. 2. LSDA energies of atoms obtained by MADNESS (MRA) and NWCHEM (LCAO) with EXCITING (LAPW + lo) results taken as a reference. Note the microhartree precision throughout.

KS equation is solved. In particular, it concerns the fact that EXCITING has been developed primarily for studying problems of condensed-matter theory, e.g., it considers electrons in periodic potentials. In other words, we compute isolated atoms and molecules employing periodic boundary conditions. It translates into a huge number of basis functions and, thus, requires an efficient way to diagonalize the Hamiltonian. To do so, we have implemented a different approach. It follows the block-Davidson algorithm [25] although with an important modification such that the initial subspace is particularly suitable for LAPW + lo. It consists of an initial guess for the KS wave functions, all local orbitals, and a number of eigenvectors of the overlap matrix. As a result, we obtain an algorithm that predictably converges even at high values of the cutoff parameter $R_{\mathrm{MT}}G_{\max}$ when the LAPWs become nearly linearly dependent. Our implementation of this algorithm follows the spirit of Ref. [26] and thus does not require the construction of the entire Hamiltonian and overlap matrices. Details of the implementation will be published elsewhere [27].

In order to reach the limit of an isolated molecule (or atom) in LAPW + lo calculations, it is necessary to ensure that there is no artificial interaction between the periodic images of molecules in neighboring unit cells. It is especially critical for polarizable molecules with permanent dipoles as their interaction energy scales as d^{-3} [28], where d is the distance between adjacent molecules. We eliminate this slow decay by truncating the Coulomb potential [29]. Such an approach is particularly important for molecules, such as LiH. The truncation of the Coulomb potential allows for a reduction of the unit-cell dimensions from 80 to 16 Å. Thus, the size of the LAPW + lo basis reduces from 10^8 to 10^6 making the total-energy calculation feasible. Note that even 10^6 basis functions are an unusually large problem size in comparison to typical LAPW + lo calculations.

Equipped with this methodology, we turn to the second benchmark, which is the G2-1 set [30]. This set contains 55 molecules, consisting of two to eight atoms for which a variety of experimental data is available. Thus it provides an excellent opportunity for benchmarking methods of DFT and quantum chemistry. Here, we use it for comparing different computational methods. We consider fixed geometries according to the data published in Refs. [31,32].

TABLE I. Mean deviation (MD), mean absolute deviation (MAD), and maximum absolute deviation (MaxD) of LAPW + lo total (left columns) and atomization energies (right columns) of the G2-1 molecules with respect to the results obtained with MADNESS (MRA) and NWCHEM (LCAO). All quantities (in Ha/atom) are obtained using the LSDA.

	Total energy		Atomization energy	
	$\Delta E^{\mathrm{tot}}_{\mathrm{MRA}}$	$\Delta E^{\mathrm{tot}}_{\mathrm{LCAO}}$	$\Delta E^{\mathrm{at}}_{\mathrm{MRA}}$	$\Delta E^{\mathrm{at}}_{\mathrm{LCAO}}$
MD	0.2×10^{-6}	1.2×10^{-3}	0.4×10^{-6}	6.1×10^{-5}
MAD	0.3×10^{-6}	1.2×10^{-3}	0.5×10^{-6}	9.9×10^{-5}
MaxD	1.1×10^{-6}	7.6×10^{-3}	1.5×10^{-6}	2.1×10^{-3}

Table I summarizes deviations of the MRA and LCAO energies from those obtained with EXCITING. The complete list of total energies can be found in the Supplemental Material [16]. The agreement between the LAPW + lo and the MRA is spectacular for both absolute total energies and atomization energies. The average and maximum deviations in total energy from the other methods amount to 0.3 and 1.1 μHa/atom, respectively, consistent with the results for atoms shown above. Similarly, we obtain 0.5 and 1.5 μHa/atom for the average and maximum deviations in atomization energies, respectively. The excellent agreement between the highly converged LAPW + lo and the MRA calculations allows us to argue that these two methods provide essentially exact answers. The obtained discrepancy, thus, can be considered as the error estimate of the two methods.

As argued above, the employed LCAO basis sets are not supposed to yield exact answers. Indeed, the average absolute deviations in the total (atomization) energies of LAPW + lo from LCAO calculations are three (two) orders of magnitude larger compared to those from the MRA. Still, with the only exception of the SO_2 molecule [error of 1.9×10^{-3} μHa (1.2 kcal/mol)], the LCAO atomization energies are within the chemical-accuracy limit of 1.0 kcal/mol.

The high precision of the LAPW + lo method obtained in calculations of atoms and molecules suggests a similar performance for solids. Although it would be desirable to benchmark against other methods also for periodic systems, we are not aware of implemented alternative approaches that are expected to be exact. On the other hand, the nature of the LAPW + lo method opens a door for "self-validation" through the partitioning of space that introduces two very different ways of representing wave functions. More specifically, if the atomic-sphere volume is reduced, a certain region that was previously described by atomiclike orbitals is now described by plane waves. We argue that, if such a rearrangement does not introduce a change in the total energy, the complete-basis limit has been reached.

We demonstrate the performance of the LAPW + lo method for periodic systems with the example of ferromagnetic α iron. This material presents numerical challenges as reflected in Ref. [3] where the corresponding results show scattering well above the average over the 71 elements of the Periodic Table. The need for a precise and thus unique result given

TABLE II. The equilibrium volume V_0 (in atomic units), bulk modulus B_0 (in gigapascals), and its pressure derivative B' for α iron as obtained from a fit of nonrelativistic LSDA results to the Birch-Murnaghan equation of state. ΔE^{tot} (in microhartrees) is relative to the value in the first row. All results above the separating line are fully converged.

R_{MT}	$R_{\mathrm{MT}}G_{\mathrm{max}}$	V_0	B_0	B'	ΔE^{tot}
1.4	14	71.3298	236.296	4.5992	0.0
1.8	14	71.3299	236.295	4.5994	0.4
2.1	14	71.3302	236.295	4.5994	0.8
2.1	12	71.3297	236.298	4.5998	3.8
2.1	10	71.3243	236.337	4.5968	95.0
2.1	8	71.1087	239.443	4.6320	2253.0

a certain functional is also motivated by the fact that all-electron calculations are commonly taken as a reference for benchmarking pseudopotentials as was performed in a recent DFT study of the thermoelastic properties of iron [46].

The aspherical density distribution due to the magnetic moment as discussed above requires particular care. In order to handle the anisotropy of the potential in the atomic spheres we introduce local orbitals with angular momenta ℓ up to six. Using this setup and a sufficiently high LAPW cutoff, we vary R_{MT} in the range of 1.4–2.1a_0. Note that such a variation of the atomic sphere corresponds to a change in its volume by a factor of 3. Remarkably, the total energy stays within the 1-μHa range. This is the case for any considered volume within a 10% deviation from the equilibrium volume of the primitive unit cell. Thus, we argue that the 1-μHa precision has been achieved also for this case. The outstanding agreement is obtained for the entire energy-versus-volume dependence as demonstrated by the Birch-Murnaghan equation of state based on 21 data points within ±5% of the volume change, shown in Table II. As soon as convergence is reached in terms of the plane-wave cutoff, we obtain extremely stable values of the equilibrium volume V_0, the bulk modulus B_0, and its pressure derivative B'. The former two fluctuate only in their sixth decimal places and the latter one in its fifth decimal place. A polynomial fit considering a wider range of volumes (±10%) exhibits the same stability (see the Supplemental Material [16]).

Using the same settings as above, we obtain also highly precise values for the equilibrium lattice constant and bulk modulus from scalar-relativistic Perdew-Burke-Ernzerhof (PBE) functional calculations, shown in Fig. 3 together with data from the literature. The scattering of the calculations (wider than the experimental ones) do not allow for conclusions about the *exact* result unless a highly reliable reference calculation is available. Strikingly, our reference value obtained in this Rapid Communication is located far from the middle of the *cloud* of the PBE functional data from Refs. [3,33] and farthest away from experiment. Note that our results also allow for comparing the performance of different functionals as we illustrate by comparing the PBE functional and PW91 [47] results. The spread of data obtained with these two GGAs implies that, without reference data, a distinction between the accuracy of a given functional and the numerical precision introduced by a specific implementation would not be possible. Indeed, besides a few exceptions [48], these two GGAs were often considered synonymous. Our calculations clearly show that PW91 yields a smaller lattice constant and a larger bulk modulus than the PBE functional.

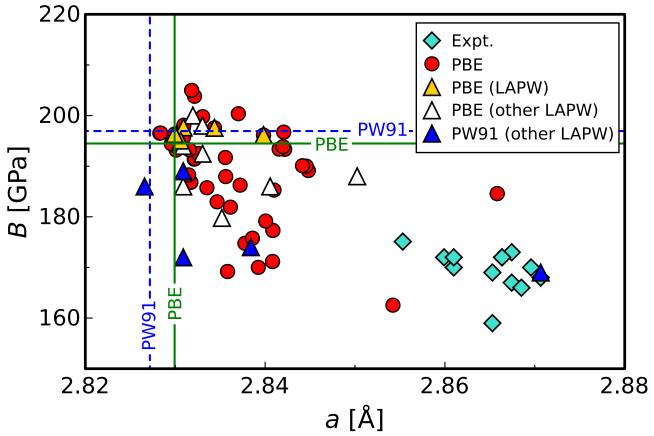

FIG. 3. Bulk moduli and lattice constants of α iron. The yellow triangles correspond LAPW + lo calculations, and the red circles correspond to results by other methods taken from Ref. [3]. The open and blue triangles represent older LAPW(+ lo) calculations [33]. The lines indicate results obtained in this Rapid Communication. The diamonds correspond to experimental data [33–45].

In conclusion, we have challenged the numerical accuracy of the LAPW + lo method. In order to demonstrate its capability, calculations for atoms and molecules have been benchmarked against two completely unrelated highly precise methods. The differences in absolute total energies are on average 1 μHa/atom. Furthermore, we have shown that we reach the same precision also for solids. The presented results allow us to claim that, once properly converged, LAPW + lo is an essentially exact method for DFT calculations. Overall, this Rapid Communication presents also a justification for using LAPW + lo as a reference method, backing up its reputation as the *gold-standard* method for DFT for condensed matter. The ability to reach the complete-basis limit will be indispensable for benchmarking less precise methods and for quality control of data collections. Furthermore, it opens perspectives towards reliably computing numerically sensitive quantities, such as magnetization anisotropy, weak noncovalent interactions, relative stabilities of isomers or polymorphs, etc., where high precision is crucial.

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The calculated data are available in the NOMAD repository [49,50].

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