ABSTRACT: Electron transfer with changing occupation in the 4f subshell poses a considerable challenge for quantitative predictions in quantum chemistry. Using the example of cerium oxide, we identify the main deficiencies of common parameter-dependent one-electron approaches, such as density functional theory (DFT) with a Hubbard correction, or hybrid functionals. As a response, we present the first benchmark of ab initio many-electron theory for electron transfer energies and lattice parameters under periodic boundary conditions. We show that the direct random phase approximation clearly outperforms all DFT variations. From this foundation, we, then, systematically improve even further. Periodic second-order Möller–Plesset perturbation theory meanwhile manages to recover standard hybrid functional values. Using these approaches to eliminate parameter bias allows for highly accurate benchmarks of strongly correlated materials, the reliable assessment of various density functionals, and functional fitting via machine-learning.
range-separation parameter of 0.3 Å⁻¹ (HSE03). Additionally, we demonstrate and discuss the performance of a systematic step beyond the RPA. In ME theories, the electron–electron interaction can be expressed as a sum over one-electron mean-field spin–orbitals

\[
\frac{1}{2} \sum_{q} \left[ (ij|q) - (qi|j) \right] + \frac{1}{2} \sum_{q} \sum_{ab} \left( (ij|ab) [t_{ij}^a - t_{ij}^b] \right)
\]

(1)

where \( t_{ij}^{ab} \) are double excitation amplitudes and the two-electron integrals read

\[
\langle pq|rs \rangle = \int dx \int dx' \langle x_p(x) \chi(x_p(x)) \chi(x) \rangle / |x - x'| \]

(2)

The double excitation amplitudes \( t_{ij}^{ab} \) define the approximation level for the correlation energy (second term in eq 1). The practical computations follow highly optimized formulations and are performed using recent low-scaling MP230 and RPA29 algorithms. The MP2 correlation energy can be defined by

\[
t_{ij}^{ab} = \langle abij \rangle / (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) \]

with Hartree–Fock spin–orbitals \( \chi \) and orbital energies \( \epsilon \). The direct RPA correlation energy can be defined by neglecting the exchange-like correlation in eq 1, that is, \( t_{ij}^{ab} = t_{ij}^{bb} \), with amplitudes implicitly defined by

\[
t_{ij}^{ab} = \langle abij \rangle + \langle aklic \rangle t_{ij}^{bb} + t_{ik}^{ac} (k\ell cl) + t_{ak}^{ac} (k\ell cl) t_{ij}^{bb}
\]

where a sum over occupied \( k \), \( l \) and unoccupied \( c \), \( d \) spin–orbitals is understood. The solution of eq 3 can analytically be expressed as an infinite sum over all possible ring-like Goldstone diagrams, that is, a summation of solely two-electron integrals and orbital energies, as we illustrate in the Supporting Information (SI). The Kohn–Sham spin–orbitals \( \chi \) and orbital energies \( \epsilon \) are provided by the HSE03 functional here.

We model the solid state as primitive bulk unit cells, shown in Figure 1, imposing Born–von Karman periodic boundary conditions and Brillouin zone sampling. Our calculations are carried out using the plane-wave based Vienna ab initio simulation package (VASP).38 Frozen-core potentials in combination with the projector augmented-wave (PAW)39 method are used. The cerium atom in particular requires a norm-conserving (nc) PAW potential to ensure proper convergence of the high-energy mean-field orbitals and orbital energies essential for correlation calculations.40 In combination with extrapolation techniques, the complete basis set and thermodynamic limit of the electron correlation were reached. The SI contains further details and in-depth explanations.

To showcase our concerns with the \( U \) and \( \alpha \) dependence, we performed a sampling for the electronic structure of Ce₂O₃ in Figure 2. The typical interpretation of Dudarev’s implementation is that it localizes the electron density in order to minimize the off-diagonal energy penalty.41,42 Such a minimum is then reached at integer subshell occupation. In our scan, PBE starts out in a metallic ground state, so that as \( U \) increases the more noisy subshells depopulate. Electron density is displaced to outside the \( f \)-band rather than filling the \( f_2^- \) from \( f_1' \)–\( f_3' \) hybridization,43,44 which mostly remains unaltered. At around \( U = 0.4 \) eV, a metal-to-insulator transition (MIT) occurs and a bandgap appears. These findings were also recuperated in ref 43. While note that bulk Ce₂O₃ passes through a MIT rather early on, defect sites at the CeO₂ surface take up to \( U = 2.2 \) eV for the MIT.21 Even so, the Hubbard energy penalty remains nonvanishing under the hybridization and instead attains a linear dependence as observed both in this work and others.21,26 We postulate then that the varying responses at different reaction coordinates in Figure 2 of ref 21 can be traced back to the total filling of the hybridized \( f \)-orbitals. We further develop a hypothesis for its persistence in the SI.

While the effect of \( \alpha \) in HSE03(\( \alpha \)) starts off in a similar fashion to PBE+\( U \), the hybridization largely becomes undone in the \( \alpha \to 1 \) limit. The electron thus starts properly localizing onto \( f_2^- \) as was the aim of Dudarev’s method. This comes at the price though of severely overestimating the O\( (2p) \)–Ce\( 4f \) gap at 9.45 eV compared to experimental value of 2.4 eV.19 As such, neither PBE + \( U \) nor HSE provide even a qualitatively correct picture of the electronic structure. Recently, Jiang46 presented with success the first basis set converged, ME correction to the electronic structure of one-electron approaches by using the GW method. By contrast, we target the ground state energy as an integral over the electronic structure. We employ MP2, RPA, as well as corrections beyond RPA, and compare their performance with respect to the one-electron methods on geometry and reaction energy in the following:

Figure 1. Ceria bulk geometries. Panel 1: CeO₂ phase exhibiting a fluorite structure (fcc cubic, \( Pm\bar{3}m \)), of which we show the cubic supercell cell with the primitive cell enclosed in the shaded region. Panel 2: Ce₂O₃ is a sesquioxide A-type (hexagonal, \( P3m1 \)) described by two lattice parameters \( (a_0 \) and \( c_0 \). The values of all primitive cell parameters can be found in Table 1. Color code: cerium (yellow), oxygen (red).
strong response in \(a_0\) and \(c_0\) to the parameter \(\alpha\), as was observed in ref 23. MP2 greatly improves upon the HF lattice constants for both oxides. The residual underestimation is in fact a general trend of MP2 for solids and goes back to a systemic overestimation of attractive dispersion forces at this level of theory. As a finite-order ME correlation method, the accuracy of MP2 however is limited to the simplest double-excitation effects from the underlying HF Slater determinants. In the language of time-dependent perturbation theory, this in itself excludes electron–hole pair interactions. As such, MP2 cannot adequately account for the correlation effect of electron screening and its quality decreases with increasing polarizability of the material. Note that the static dielectric constant of both cerium oxide phases is quite high, roughly in the order of 25 times the vacuum permittivity.

The RPA markedly provides even more accurate lattice constants for Ce\(_2\)O\(_3\). The remaining overestimation is well-known and may be attributed to the missing exchange-like correlation. The common effect of exchange-like correlation can be well observed when comparing dMP2 (neglecting \(-t_{ji}^{ab}\) in eq 1) with MP2 (including \(-t_{ji}^{ab}\)). By adding exchange-like correlation, the lattice constants are reduced and the bulk modulus grows. A similar effect is observed, when we correct for the exchange-like correlation missing from the RPA. To this end we reintroduce \(-t_{ji}^{ab}\) by a renormalized second-order amplitude \(\Delta_{ji}^{ab} = \langle \epsilon_j - \epsilon_i - \epsilon_a - \epsilon_b \rangle\).

Table 1. Bulk Properties of CeO\(_2\) (Left) and Antiferromagnetic Ce\(_2\)O\(_3\) (Right)*

| method            | \(a_0\) [Å] | % error | \(B_0\) [GPa] | \(a_0\) [Å] | % error | \(c_0\) [Å] | % error | \(B_0\) [GPa] | ref |
|-------------------|------------|--------|--------------|------------|--------|------------|--------|--------------|-----|
| RPA               | 5.421      | +0.5   | 202          | 3.883      | +0.0   | 6.070      | +0.4   | 145          |
| RPA+rSOX          | 5.381      | +0.2   | 216          | 3.892      | +1.2   | 6.259      | +3.5   | 141          |
| dMP2              | 5.454      | +1.1   | 229          | 3.929      | +0.2   | 6.082      | +0.6   | 143          |
| PBE+U = 4.5 eV    | 5.49       | +1.8   | 206          | 3.92       | +1.0   | 6.18       | +2.2   | 111          |
| PBE               | 5.47       | +1.4   | 180          | 3.85       | +0.8   | 6.10       | +0.9   | 101          |
| LDA+DMFT          | 5.394      | -1.9   | 172          | 3.81       | -1.9   | 6.047      | 50.51  |
| expt.             | 3.882      |        | 6.047        | 3.882      |        | 6.047      |        |              |

*These include the lattice constants \(a_0\) and \(c_0\), the relative error, and the bulk modulus \(B_0\). The experimental references are extrapolated to \(T \to 0\) K for CeO\(_2\) and at \(T = 3\) K for Ce\(_2\)O\(_3\). Zero-point vibrational effects are not taken into account. In the case of Ce\(_2\)O\(_3\), the Debye model estimates the experimental lattice constant at 99.7% \(a_0^{expt}\) so that the specified errors are slightly underestimated. For more detail, see the SI.
In contrast, pristine CeO$_2$ slabs exhibit no RPA in more detail. It is well-known that MP2 reaction with the latter contributing more to the energy (see SI). In one-electron theories, from systematic error cancellation. This effect is not present in the molecules. For comparison, the MP2 exchange term ($-\varepsilon_{\alpha\beta}$) for instance contributes +0.86 eV to the reaction enthalpy $r_{1\alpha}$ indicating a strong contribution of exchange-like correlation. It is reasonably assumed that this contribution largely corrects the self-correlation error in dMP2. In fact, the simple rSOX correction for the RPA also accounts for a large portion of the self-correlation error, shifting the reaction enthalpy of $r_1$ by +0.45 eV into the experimentally reported region. Although the RPA+rSOX transfer energies for $r_1-r_3$ suggest near chemical accuracy, a reliable assessment of the accuracy is impeded by the large uncertainty of the experimental data.

There are plenty of further improvements available to correct the RPA.15,54,64–66 Alternatively, there is the coupled cluster (CC) method as well. In each case, the RPA acts as a reasonably sound starting point, since it is equivalent to the direct ring coupled cluster approach and thus poses as a proper subset of the CC singles and doubles (CCSD).66 Recently published methodological advancements70,71 allow for tuned, regional CC corrections to the RPA correlation energy. This paves the way for even more accurate benchmarks that could include oxygen defect formation or heterogeneous catalysis at the ceria surface.

In conclusion, we present a novel benchmark of many-electron theory on strongly correlated materials, using ceria as a specific test case. We demonstrate that MP2 and RPA overcome the limits of DFT+U and hybrid functionals in terms of parameter bias while providing robust geometries and energies. The RPA in particular provides unprecedented agreement with experimental values, outperforming all DFT flavors. Moreover, it forms the basis for additional corrections that systematically improve the accuracy. Here, we demonstrate that RPA+rSOX resides reliably within the experimentally measured results. Such enhanced accuracy likewise raises the bar on computational reference data. Benchmarking aside,
the same methods also have potential applications in machine-learned density functionals.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c01589.

Computational settings and pseudopotentials, (anti)-ferromagnetic ground states and metastable states of solid Ce₃O₉, impact of the electronic structure on the U dependence, theory behind the correlation methods, basis set convergence and thermodynamic limit of the reaction energies and lattice parameters, timings, treatment of isolated molecules in a periodic code, tables of reaction and atomization energies, and the experimental references (PDF)

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Notes

The authors declare no competing financial interest. VASP input and output files pertaining to the phase transition have been made available on the ioChem-BD database, ref 72.

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