Reformulation of DFT+\(U\) as a pseudo-hybrid Hubbard density functional

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The accurate prediction of the electronic properties of materials at a low computational cost has been the holy grail of computational materials science from the first applications of density functional theory (DFT) in the early 80’s to the current advanced high-throughput frameworks. Recent years have seen two competing approaches unfold to address these problems: DFT+\(U\) and hybrid exact exchange functionals. However, while the first one suffers of an ambiguity in the computation of critical parameters, the second allows for some empiricism and is computationally very expensive.

In this article we introduce ACBN0, a pseudo-hybrid Hubbard density functional that is a fast, accurate and parameter-free alternative to traditional DFT+\(U\) and hybrid methods and yields the proper description of Mott insulators and strongly correlated systems, as shown for the electronic properties of TiO\(_2\), MnO, NiO and ZnO, which display a remarkable agreement with experimental results at a negligible computational cost.

I. INTRODUCTION

Despite the enormous success of DFT in describing many physical properties of real systems, the method is hampered by the presence of an unknown correlation term that represents the difference between the true energy of the many-body system of the electrons and the approximate energy that we can compute. Notwithstanding the enormous efforts in improving the inevitable approximations to this term not a single method has emerged as the final solution to this problem. In recent years, two competing approaches have unfold: DFT+\(U\) and hybrid functionals. However, while the first one suffers of an ambiguity in the computation of critical parameters, the second allows for some empiricism and is computationally very expensive.

The DFT+\(U\) method introduced by Liechtenstein and Anisimov\(^{[2]}\) aims at compensating for the simplified, nearly-homogeneous-electron-gas treatment of the electron density by local-density (LDA) or generalized-gradient approximation (GGA). The success of DFT+\(U\) corroborates the fact that preserving the information of orbital localization from being averaged out is paramount for the correct prediction of the electronic structure for compounds with localized states, such as Mott insulators and other strongly correlated systems, and for an effective accelerated materials development\(^{[3]}\).

Within the DFT+\(U\) ansatz, the localized states \(\varphi_i\) largely retain their atomic nature and, therefore, can be expanded in term of atomic-orbital basis sets \(\{m\}\). The Coulomb and exchange interactions are explicitly evaluated using the Hartree-Fock (HF) framework via electron repulsion integrals (ERI), also known as two-electron integrals, with a screened (renormalized) Coulomb interaction \(V_{ee}\). The HF Coulomb and exchange energy of the localized states is given by\(^{[4]}\)

\[
E_{\text{HF}}^{(m)} = \frac{1}{2} \sum_{\{m\},\sigma} \{\langle mm''|V_{ee}|m'm''\rangle n^\sigma_m n^\sigma_{m''} n^\sigma_{m'} n^\sigma_{m'''}
+ \langle mm''|V_{ee}|m'm''\rangle - \langle mm'|V_{ee}|m'm'\rangle \}
\times n^\sigma_m n^\sigma_{m''} n^\sigma_{m'} n^\sigma_{m'''}\},
\]

where \(n^\sigma\) is the spin density matrix \(n^\sigma\) of the atomic orbitals \(\phi_m\). This equation can be simplified via the introduction of the phenomenological parameters \(\bar{U}\) and \(\bar{J}\) that describe the on-site Hubbard-like interactions as expressed by Dudarev et al\(^{[5]}\)

\[
E_{\text{HF}}^{(m)} \approx \frac{\bar{U}}{2} \sum_{\{m\},\sigma} N^\sigma_m N^\sigma_{m'} + \frac{\bar{U} - \bar{J}}{2} \sum_{m \neq m',\sigma} N^\sigma_m N^\sigma_{m'}
\]

Here, \(N^\sigma_m\) is the spin occupation number of the atomic orbital \(\phi_m\).

From the equations above, it clearly follows that the new parameters, \(\bar{U}\) and \(\bar{J}\), contain the information of all the ERIs in an averaged scenario. In physical terms, \(\bar{U}\) is the strong correlation experienced between localized electrons — only subtly coupled to the sea of extended states in which they live. Thus, the most akin definition of \(\bar{U}\) (for the non-spin-polarized case) is the average\(^{[6]}\)

\[
\bar{U} = \frac{1}{(2l + 1)^2} \sum_{i,j} \langle \varphi_i | \varphi_j | V_{ee} | \varphi_i \varphi_j \rangle,
\]

where \((2l + 1)^2\) is the total number of localized states \(\varphi_i\), and \(l = 2, 3\) for \(d, f\) orbitals, respectively. The exchange contribution, \(\bar{J}\), is given by a similar average\(^{[7]}\).

Although the physical picture is clear, an unambiguous procedure for computing \(\{\bar{U}, \bar{J}\}\) from \textit{ab-initio} does not exist. Two factors need to be further clarified: \(i\) the screened (renormalized) Coulomb interaction \(V_{ee}\) arising from the “subtle coupling” to the background extended states; and \(ii\) the actual orbitals \(\varphi_i\) used to represent the “localized electrons”.

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Amongst the most common ab-initio methods to compute \( \bar{U} \) are the constrained random-phase approximation (cRPA) and the linear-response constrained DFT (or cLDA). The former computes the screened Coulomb interaction as the bare Coulomb potential renormalized by the inverse dielectric function, which is calculated using the random phase approximation. The latter circumvents the ambiguity of \( V_{cc} \) by indirectly determining \( \bar{U} \) as the second derivative of the total energy with respect to constrained variations of the atomic charge \( q_i \) of the chosen Hubbard center \( I \), \( \bar{U} = \partial^2 E / \partial q_i ^2 \). \( E \) is the total energy of a supercell large enough to converge to the bulk environment for the atom \( I \). It is assumed that the charge perturbation on atom \( I \) does not disturb the local environment. In DFT with linear-combination-of-atomic-orbital (LCAO) basis, this is enforced by suppressing the hopping integrals to prevent charge rehybridization or transfer with its environment and in the case of plane-wave DFT by subtracting a correcting term from \( \partial^2 E / \partial q_i ^2 \) as given in Ref. [8]. This method has been widely used for open-shell systems; nonetheless, the numerical reliability becomes challenging for closed-shell systems where the localized bands are completely full, thus exhibiting very small response to the linear perturbation.

Regarding the representation of the \( \varphi_i \) states, i.e. the \( d \) or \( f \) states of transition metals, localized orbitals —obtained either from the linear-muffin-tin-orbital (LMTO) method or from the \( N^{th} \) order muffin-tin-orbital (NMTO) method— can be used with both the cLDA and cRPA to obtain \( \bar{U} \). Recently, maximally localized Wannier functions (MLWF), an invariant choice suitable for plane-wave calculations, have also been employed. By construction, these functions are associated with a given angular momentum \((l, m)\) and the direct correspondence makes them convenient to represent the localized \( d \) or \( f \) states. Ultimately, pinpointing a single localized state within the solid is arbitrary — any of these options are equally valid. In principle, the options should be equivalent for very localized states; nonetheless, the physical significance and construction becomes more ambiguous when bands corresponding to localized states are not fully disentangled. Despite attempting the computation of the same physical entity, the cLDA and cRPA methods do not yield the same value of \( \bar{U} \). Considering the number of assumptions taken in numerical implementations, the outcome is unsurprising.

In this article, we introduce an alternative ab-initio method to compute \( \bar{U} \) and \( \bar{J} \), which parallels the calculation of the HF energy for molecules and solids and follows closely the original definition of Anisimov et al. (Eq. [1]): the Agapito-Curtarolo-Buongiorno Nardelli (ACBN0) pseudo-hybrid Hubbard density functional. In ACBN0 the Hubbard energy of DFT+\( U \) is calculated via the direct evaluation of the local Coulomb (\( U \)) and exchange (\( J \)) integrals in which the screening of the bare Coulomb potential is accounted for by a renormalization of the density matrix. Through this procedure, the values of \( U \) and \( J \) are thus functionals of the electron density and depend directly on the chemical environment and crystalline field, introducing an effective procedure of giving the proper description of Mott insulators and other strongly correlated systems. As a first application, we discuss the electronic properties of a series of transition metal oxides that show good agreement with hybrid functionals, the GW approximation and experimental results at a fraction of the computational cost. In particular, we will demonstrate that the ACBN0 functional satisfies the rather ambitious criteria outlined by Pickett et al. in one of the first seminal articles on LDA+U. i) ACBN0 reduces to (LDA)PBE when (LDA)PBE is known to be good; ii) the energy is given as a functional of the density; iii) the method specifies how to obtain the local orbital in question; iv) the definition of \( \bar{U} \) and \( \bar{J} \) is provided unambiguously; and v) the method predicts antiferromagnetic insulators when appropriate and improves the description of highly correlated metals.

The article is organized as follows: the methodology is discussed in Section II. The application of the method for four prototypical transition-metal oxides is presented in Section III, and the results are compared against available experimental and theoretical data. Section IV discusses the important features of the method and suggests extensions of potential significance to the goal of discovering novel functional materials. Conclusions are summarized in Section V.

II. METHODOLOGY

The foundations of the approach for evaluating the on-site Coulomb and exchange parameters are:

i) \( \bar{U} \) and \( \bar{J} \) are obtained from the corresponding on-site HF Coulomb and exchange energies where the screened potential \( V_{cc} \) is not explicitly computed. In this regard, we follow the ansatz of Mosey and Carter, in which the screening of the bare Coulomb potential is accounted for by a renormalization in the density matrix;

ii) no localized orbitals \( \varphi_i \) need to be explicitly computed. As in the Hartree-Fock method, all the molecular orbitals (MO), or crystalline wavefunctions for the case of solids, are used. This eliminates the indeterminacy in finding the subset of MOs that better corresponds to the localized states, which can lead to a wide fluctuations of the calculated \( \bar{J} \). During the calculation of the on-site HF energies, the localized orbitals are implicitly taken as a linear combinations the basis functions of interest, \( \phi_m \), with the expansion coefficients included in the renormalized density matrix coming directly from the solution of the Kohn-Sham equations projected onto the localized basis of choice (see below);

iii) a plane-wave basis set is the natural choice for DFT calculations of periodic systems, but on-site HF energies are more efficiently computed in a localized basis set. Electron-repulsion integrals are evaluated using pseudo-atom-orbitals (PAO) expressed as linear combination of Gaussian-type functions, that we define as the PAO-3G.
minimal basis set. This is possible by the projection procedure that we have recently developed, which seamlessly maps the plane-wave electronic structure onto a localized atomic-orbital basis set (see Appendix A). However, it is important to note that the construction of $\mathcal{U}$ and $\mathcal{J}$ outlined below is completely general and can be applied to any choice of basis, localized or otherwise.

iv) $E_{19}^{\text{mol}}$ is a true functional of the electron density in the spirit of the Hohenberg-Kohn theorems. This leads to the definition of the ACBN0 pseudo-hybrid Hubbard density functional.

### A. Calculation of the Electron Repulsion Integrals

The enormous quantity of Electron Repulsion Integrals, ERIs, needed in the calculation of the HF exchange energy is the fundamental bottleneck in the use of hybrid DFT functionals. In DFT calculations based on LCAO (PAO) basis sets, the problem is made more tractable when the PAOs are expressed as linear combinations of Gaussian-type functions, as it is commonly done in commercial packages such as Gaussian09 and Crystal06.

The electron repulsion integrals used in Eq. 1 are defined as four PAOs interacting under the bare Coulomb interaction $V = |\mathbf{r}_12|^{-1}$ as:

$$
\text{ERI} \equiv \langle mm'|mm''m''' \rangle = \langle mm''|V|mm'\rangle \\
= \int dr_1dr_2\phi_m^*(\mathbf{r}_1)\phi_m(\mathbf{r}_1)V\phi_{m''}(\mathbf{r}_2)\phi_{m'}(\mathbf{r}_2).
$$

The real-space evaluation of these integrals is not directly possible when using a plane-wave basis set, which is the preferred choice for periodic systems. For this reason, we employ the auxiliary space of PAOs naturally included in the definition of the pseudo-potentials. Given that the radial and angular part of the PAO basis functions, $\phi_m(\mathbf{r}) \equiv R(\mathbf{r})r^{m\ell}(e,s)(\theta, \phi)$, are separable, they can be directly fitted using linear combinations of spherical-harmonic Gaussian functions. For efficiency, the latter functions are then further expanded as linear combination of Cartesian Gaussians defining the PAO-3G minimal basis set. (see Appendix A for more technical details on these transformations). Once expressed in the PAO-3G basis set, the ERIs can be efficiently evaluated using any optimized quantum-chemistry library. We use the C routines included in the open-source quantum-chemistry package PyQuante.

### B. Hartree-Fock Coulomb and exchange energies

The knowledge of the ERIs and the molecular (or crystal) orbitals allows the calculation of the HF Coulomb and exchange energies $E_{\text{HF}}$. For isolated systems (molecules or clusters) and in the restricted case:

$$
E_{\text{mol}}^{\text{HFC}} = \sum_{i,j} N_{\psi_i} N_{\psi_j} [2(\psi_i\psi_j|\psi_j\psi_j) - (\psi_i\psi_j|\psi_j\psi_i)]
= \sum_{\mu\nu\kappa\lambda} P_{\mu\nu} P_{\kappa\lambda} [2(\mu\nu|\kappa\lambda) - (\mu\lambda|\kappa\nu)].
$$

Here $\psi_\alpha(\mathbf{r}) = \sum_{i,\mu} c_{\mu i}^\alpha \phi_\mu(\mathbf{r})$ are occupied molecular orbitals/crystalline wavefunctions expanded in the PAO's basis: $N_{\psi_\alpha}^2 = \sum_{i,\mu} c_{\mu i}^{\alpha*} S_{\mu\nu} c_{\nu i}^{\alpha} = 1$ is the charge of $\psi_\alpha$ and $S_{\mu\nu}$ is the overlap integral between the PAOs $\phi_\mu$ and $\phi_\nu$.

The last line of Eq. 4 is expressed in the basis of atomic orbitals $\phi_\mu$ with the density matrix $P_{\mu\nu} = \sum_{c,s} N_{\psi_c}^\mu c_{\mu i}^{\alpha*} c_{\nu i}^{\beta}$. The expression of the Coulomb and exchange HF energies for a periodic system is analogous to the molecular case (see Pisani et al.):

$$
E_{\text{HF}}^{\text{solid}} = \sum_{\mu\nu\kappa\lambda} g_{\mu\nu\kappa\lambda} [2(\mu^{0,\mathbf{g}}|\kappa^m\lambda^{m+1}) - (\mu^{0,\mathbf{g}}|\kappa^m\lambda^{m+1})],
$$

where $\mathbf{g}$, $\mathbf{m}$ and $\mathbf{l}$ are lattice vectors and $\mathbf{0}$ refers to the primitive unit cell. However, the mapping of the crystalline wavefunctions in a local basis (i.e. the expansion coefficients $c_{\mu i}^\alpha$) is not readily available when using a plane-wave basis to solve for the electronic structure of the material as it is common for solids. We circumvent this problem by projecting the plane-wave solution into the chosen auxiliary space of PAOs following the method described in Ref. [19]. This projection procedure is a noniterative scheme to represent the electronic ground state of a periodic system using an atomic-orbital basis, up to a predictable number of electronic states, and with controllable accuracy by filtering out high-kinetic-energy plane waves components. See Appendix B for a summary of this procedure to calculate the expansion coefficients $c_{\mu i}^\alpha$ and the real-space density matrices of the solid, $P_{\mu\nu}^\mathbf{R}$.

### C. $\mathcal{U}$ and $\mathcal{J}$ as functional of the density: the ACBN0 functional

The energy functional for the DFT+$U$ method is given by:

$$
E_{\text{DFT}+U} = E_{\text{DFT}} + E_U
$$

where $E_{\text{DFT}}$ is the DFT energy calculated using a LDA or GGA functional. The energy correction $E_U$ is given either in the original Anisimov-Liechtenstein formulation or in the simplified Dudarev formulation as:

$$
E_U^{\text{Anisimov}} = \left[ \sum_i E_{\text{HF}}^{(m) i} \right] - E_{\text{DC}}, \quad (7a)
$$

$$
E_U^{\text{Dudarev}} = \bar{U} - \bar{J}/2 - \frac{1}{2} \sum_{i,m} \left[ n_{i\sigma} - \sum_{m'} n_{i\sigma} n_{i\sigma'} n_{i\sigma'} m' \right]. \quad (7b)
$$
with $E_{\text{DC}}^{(m)},I$ defined in Eq. 1 for a given atom $I$. $E_{\text{DC}}$ corrects for a possible double counting of the localized-states interaction energy already captured (in an averaged way) in $E_{\text{DFT}}$. The second formulation defines an effective on-site Coulomb interaction $U_{\text{eff}} = \bar{U} - \bar{J}$ (henceforth referred simply as $U$). It should be noticed that numerical implementations of the Anisimov DFT+U functional (Eq. 1), for instance in Quantum Espresso\textsuperscript{22} or VASP\textsuperscript{23} do not compute the ERIs explicitly. They are evaluated from tabulated Slater integrals, which ultimately depend on the provided values of $\bar{U}$ and $\bar{J}$, or from phenomenological considerations (e.g. Ref. [26] and [27]).

On the contrary, we evaluate $\bar{U}$ and $\bar{J}$ by computing directly the on-site Coulomb and exchange energies on the chosen Hubbard center, from the Coulomb and exchange Hartree-Fock energies of the solid. The following assumptions are used.

(i) We follow a central ansatz, introduced by Mosey et al.\textsuperscript{16,17} for the case of cluster calculations, that defines a “renormalized” occupation number $\bar{N}_{\psi_i} \neq 1$ for each MO or crystalline wavefunction $\psi_i$:

$$\bar{N}_{\psi_i} = \sum_{\mu \in \{\overline{m}\}} \sum_{\nu} c_{\mu \psi_i}^* c_{\nu \psi_i},$$

which is the Mulliken charge of the basis $\{\overline{m}\} = \bigcup_{R} \{m_R\}$. The set $\{\overline{m}\}$ includes the basis of localized orbitals $\{m\}$ not only on the Hubbard center of interest but also on all the atoms within the cluster or the periodic unit cell that are equivalent to it by symmetry (same Wyckoff positions).

Correspondingly, we define a renormalized density matrix as:

$$\bar{P}_{\mu \nu} = \sum_i \bar{N}_{\psi_i} c_{\mu \psi_i}^* c_{\nu \psi_i},$$

The renormalized occupations can be interpreted as weighting factors that specify the on-site occupation of each electronic state.

The expressions in Eqs. 8 and 9 are applicable to isolated systems (molecules and clusters). Solid-state systems are calculated in reciprocal $k$-space that inherently apply periodic-boundary conditions, thus, surface effects are avoided. Periodic plane waves are the basis of choice for the solution of solid-state systems. The $k$-space electronic-structure information of the material can be projected into a PAO basis directly from the plane-wave DFT solution. We take advantage of this to compute the reduced density matrices and occupation number, needed to calculate $\bar{U}$ and $\bar{J}$, as follows

$$\bar{P}_{\mu \nu} = \bar{P}_{\mu \nu}^{0,\sigma} = \frac{1}{\sqrt{N_k}} \sum_{k} \bar{N}_{\psi_i}^{k \sigma} c_{\mu \psi_i}^* c_{\nu \psi_i}$$  \hspace{1cm} (10a)

$$\bar{N}_{\psi_i}^{k \sigma} = \sum_{\kappa \in \{\overline{m}\}} \sum_{i, \lambda} c_{\kappa \psi_i}^* s_{\kappa \lambda} c_{\lambda \psi_i}$$  \hspace{1cm} (10b)

$$\bar{N}_{m}^{\sigma} = \frac{1}{\sqrt{N_k}} \sum_{k, i, \nu} c_{m \nu}^* s_{m \nu} c_{\nu}$$  \hspace{1cm} (10c)

Here, $N_k$ is the total number of $k$-vectors in the 1$^{st}$ Brillouin zone. See Appendix 5 for more details.

(ii) $E_{\text{HF}}^{(m)}$, the on-site HF energy associated to the basis $\{m\}$, is obtained from Eq. 6 by restricting the summation indexes to $\{m\}$. In the periodic case, it is reduced from Eq. 5 considering the central unit cell only, i.e. lattice vectors $R = g = 1 = m = 0$. Combining (i) and (ii), we obtain in the general spin-unrestricted case:

$$E_{\text{HF}}^{(m)} = \frac{1}{2} \sum_{\{m\}} \bar{P}_{mm}^{\sigma} \bar{P}_{mm}^{\sigma} + \bar{P}_{mm}^{\bar{\alpha}} \bar{P}_{mm}^{\bar{\beta}}$$

$$+ \bar{P}_{mm}^{\alpha} \bar{P}_{mm}^{\bar{\beta}} \bar{P}_{mm}^{\bar{\alpha}} \bar{P}_{mm}^{\bar{\beta}} (m|mm')$$

$$+ \frac{1}{2} \sum_{\{m\}} \bar{P}_{mm}^{\sigma} \bar{P}_{mm}^{\sigma} + \bar{P}_{mm}^{\bar{\alpha}} \bar{P}_{mm}^{\bar{\beta}} \bar{P}_{mm}^{\bar{\alpha}} \bar{P}_{mm}^{\bar{\beta}} (m'|m'm')$$

$$+ \frac{1}{2} \sum_{\{m\}} \bar{P}_{mm}^{\sigma} \bar{P}_{mm}^{\sigma} + \bar{P}_{mm}^{\bar{\alpha}} \bar{P}_{mm}^{\bar{\beta}} \bar{P}_{mm}^{\bar{\alpha}} \bar{P}_{mm}^{\bar{\beta}} (m|mm')$$

(11)

Clearly, the above equation is equivalent to Anisimov’s original DFT+U functional (Eq. 1) once we replace $n_{mm'}^{\sigma}$ with the renormalized density matrix $\bar{P}_{mm'}^{\sigma}$. However, while Eq. 1 requires the knowledge of a subjective screened Coulomb potential $V_{ee}$, Eq. 11 uses the bare Coulomb interaction with the screening implicitly accounted for through the renormalization of the density matrix.

The comparison of Eqs. 2 with 11 leads to the definitions of $\bar{U}$ and $\bar{J}$ as density dependent quantities in the ACBN0 functional:

$$\bar{U} = \sum_{\{m\}} \frac{\bar{P}_{mm}^{\sigma} \bar{P}_{mm'}^{\sigma} + \bar{P}_{mm}^{\bar{\alpha}} \bar{P}_{mm'}^{\bar{\beta}} + \bar{P}_{mm}^{\bar{\alpha}} \bar{P}_{mm'}^{\bar{\beta}} + \bar{P}_{mm}^{\alpha} \bar{P}_{mm'}^{\bar{\beta}} + \bar{P}_{mm}^{\bar{\alpha}} \bar{P}_{mm'}^{\alpha}}{N_{m}^{\sigma} N_{m'}^{\sigma} + \sum_{\{m\}} N_{m}^{\alpha} N_{m'}^{\alpha} + \sum_{\{m\}} N_{m}^{\bar{\alpha}} N_{m'}^{\bar{\alpha}} + \sum_{m \neq m'} N_{m}^{\bar{\alpha}} N_{m'}^{\bar{\alpha}}},$$

$$\bar{J} = \sum_{\{m\}} \frac{\bar{P}_{mm}^{\sigma} \bar{P}_{mm'}^{\sigma} + \bar{P}_{mm}^{\bar{\alpha}} \bar{P}_{mm'}^{\bar{\beta}}}{N_{m}^{\sigma} N_{m'}^{\sigma} + \sum_{m \neq m'} N_{m}^{\sigma} N_{m'}^{\sigma}}$$

(12)

(13)

There are essential and relevant differences between Eqs. 12 and 13 and the similar framework of Mosey et
of Dudarev \(a_{12}\) i) our on-site energy requires the computation of a smaller number of electron-repulsion integrals, namely only those involving the \(\{m\}\) set (i.e. \(5^4\) integrals for the \(d\) shell). This directly parallels the original definition of Anisimov, in sharp contrast with the methodology of Mosey et al. requiring ERIs between all basis functions contained in the cluster; ii) we consider the larger set \(\{m\}\) of localized orbitals (instead of \(\{m\}\)) in the calculation of the reduced occupation number given in Eq. 8; iii) in the Mosey et al. \(a_{13}\) approach the atom of interest is embedded in a cluster of volume large enough to yield local convergence to bulk conditions, thus requiring calculations on clusters of increasing volume to ensure convergence, which can become extremely computationally expensive; iv) finally, we never solve the full Hartree-Fock problem for the solid (Roothaan’s equations) but project the DFT Kohn-Sham wavefunctions on the minimal PAO-3G basis set, thus implicitly including in the renormalized density matrix all the local screening effects that come from the mean field solution on the local set.

III. RESULTS

We selected four prototypical examples to benchmark the ACBN0 density functional: TiO\(_2\) (rutile), MnO, NiO, and ZnO (wurtzite) are technological important transition metal oxides (TMO) that have been extensively studied both theoretically and experimentally. These materials pose a methodological challenge to traditional energy functionals (LDA or GGA) due to the strong localization of the TM-3d electrons that results in significant errors in the description of their electronic structure\(^{28}\). The set of chosen TMOs covers a wide range of 3d shell fillings, namely, \(3d^2\), \(3d^5\), \(3d^8\), and \(3d^{10}\) in Ti, Mn, Ni and Zn, respectively.

All our calculations use the Perdew-Burke-Ernzerhoff (PBE)\(^{29}\) functional as a starting point and a plane wave energy cutoff of 350 Ry with a dense Monkhorst-Pack mesh to ensure good convergence of all quantities. All DFT+\(U\) calculations use the simplified rotational-invariant scheme of Dudarev\(^{4}\) and Cococcioni\(^{5}\) as implemented in the QUANTUM ESPRESSO package\(^{23}\). It is noticed that both the original DFT+\(U\) formulation of Anisimov and the simplified rotationally-invariant scheme are equivalent within numerical error for the same values of \(U\) and \(J\). For all elements, we used scalar-relativistic norm-conserving pseudopotential from the PSlibrary 1.0.0\(^{22}\).

Although the calculation of the effective values of \(\tilde{U}\) and \(\bar{J}\) should be performed concurrently within the general Kohn-Sham self-consistent loop for electronic convergence, in this work we follow a simplified scheme: the initial and objective guess for the first DFT+\(U\) calculation is \(U_{3d}^{\text{(0)}} = U_{2p}^{\text{(0)}} = 0\) eV. Then, the resulting electronic structure is used to compute \(U^{(1)}\) for the next DFT+\(U\) step (from Eqs. 12 and 13). The process is iterated simultaneously for both transition metal and oxygen atoms until the difference between two subsequent iterations is \(|U^{(n)} - U^{(n-1)}| < 10^{-4}\) eV. This self-consistent scheme ensures the internal consistency of the results while the true variational solution using the ACBN0 functional will be implemented in the near future. The converged effective values of \(U\) for the transition-metal oxides under study are reported in Table I. All the presented band structures follow the AFLOW standard integration path\(^{20}\).

A. Titanium dioxide (rutile)

Rutile, with space group \(P4_2/mnm\) (\#136) is the most common form of TiO\(_2\). We use the experimental lattice constants and internal ordering parameter of \(a = b = 4.594\) Å, \(c = 2.959\) Å, \(\mu = 0.305\)\(^{30}\).

The valence manifold is predominantly of O-2p character with small Ti-3d hybridization except at the top of the manifold at \(\Gamma\), where it takes almost exclusively an O-2p character. Conversely, the unoccupied manifold is predominantly of Ti-3d character; the conduction-band minimum (CBM) is at \(\Gamma\) but in practice it is degenerate with the minima at R and M. Two regions are distinguishable in the 3d projected density of states (PDOS) in the unoccupied manifold. The 2\(d\) states (lower energy).

The use of an increasing on-site Coulomb potential \(U_{3d}\) on Ti alone (without correcting the oxygen) has been shown to monotonically open the gap, which reaches satisfactory accord with the experimental value of 3.03 eV\(^{31}\) only at values of \(U_{3d} \sim 10\) eV\(^{32,33}\). However, Park et al.\(^{34}\) have found that large values of the Ti on-site Coulomb interaction (> 7) introduces unphysical defect states in the study of vacancies and suggested a concomitant use of \(U_{2p} = 7\) eV on oxygen is necessary to achieve both the experimental bandgap and a good treatment of vacancy states.

With small Löwdin charges of 0.29e–0.45e (out of 2e) per orbital\(^{35}\) the Ti-3d states can not be considered localized and therefore the use of large values of \(U_{3d}\) is understood as an \textit{ad hoc} fitting parameter without physical basis. Instead, each oxygen 2p orbital charge is 1.66e (out of 2e).

Our converged values for the rutile environment are Ti \(U_{3d} = 0.15\) eV and O \(U_{2p} = 7.34\) eV. These values yield a bandgap of 2.83 eV close to the experimental range of 2.8–3.8 eV (Table II), which improves the DFT prediction by 0.9 eV. Contrary to the predominant focus on the Ti-3d states, our results show that a correction on the oxygen 2p states can alone yield an equally satisfactory bandgap. More generally, it suggests that a correct treatment of oxygen 2p states may be more relevant to the correct modeling of TiO\(_2\) vacancies.

The occupied O-2p PDOS [red line in Fig. 1(a)] shows a split into two regions, upper 0–3 eV and lower 3.5–6 eV, which originates in the oxygen 2p crystal-field splitting. The \(2p_x\) and \(2p_y\) states form \(sp^2\)-like \(\sigma\) bonds contained in the planar Y-shaped OTi\(_3\) subunits whereas the \(2p_z\).
states remain as lone pairs perpendicular to the Y-shaped planes. The higher-energy 2p_x states correspond to the upper PDOS region. These nonbonding lone pairs have been explained with a simple empirical molecular-orbital model, whereby the octahedral O_h symmetry of the local environment of each Ti coordinated to six oxygen ligands (TiO_6)^8− frustrates the hybridization of the highest occupied orbitals.\cite{a}

Applying the on-site Coulomb potential U_{2p} on oxygen increases the localization of the 2p_x lone pairs, thus, increasing the splitting between the two 2p PDOS regions, cf. Figs. 1(a) and (b). The main peak of the lower PDOS region lowers by 1 eV, to ∼5.4 eV, consistent with the value of 5 eV reported by the full-frequency-dependent GW calculation of Khan and Hybertsen \cite{b,c} and X-ray photoelectron spectroscopy (XPS) measurements.\cite{d}

Examining the G_0 W_0@gGA band structure reported by Malashevich et al.,\cite{e} it is interesting to notice that besides a scissor-shift operation the main correction with respect to the DFT bands is a downward energy shift of the 2p_x,2p_y bands (lower region of the occupied manifold, -6 to -4 eV) whereas the upper region (-4 to 0 eV) remains mostly unchanged. A possible mechanism is that the GW approach implicitly applies a self-interaction correction that increases the splitting between the 2p_x and 2p_x,2p_y states by further localizing the 2p_x states, which can be captured in the ACBN0 calculation.

In this regard, ACBN0 bands closely follow the G_0 W_0@gGA bands of Ref. 11 in the range from -4 to 8 eV. The most significant difference happens in the remaining range of -7 to -4 eV, where our DFT+U bands are over downshifted with respect to the G_0 W_0@gGA results. This is expected from the explicit use of on-site Coulomb interaction on oxygen in the ACBN0 approach.

It is instructive to point out that comparisons between theory and photoemission spectra require GW quasiparticle energies (and more for excitonic effects) which go beyond DFT. Nonetheless, DFT+U has been shown to be formally equivalent to the GW approach, at least for localized states,\cite{f} thereby warranting basis for comparison to experimental data.

### B. Manganese and nickel oxides

For MnO (NiO), we use the ideal rocksalt structure with lattice constant a = 4.4315 Å (a = 4.1704 Å).\cite{g} The presence of type-II antiferromagnetic spin coupling along the [111] direction, below Néel temperature, effectively requires a rhombohedral primitive unit cell (RHL)\cite{h,i} a_RHL = a√3/2, α = 33.55° containing 4 atoms with space group R3m ( #166).

Our converged values for MnO are U_{3d} = 4.67 eV for Mn and U_{2p} = 2.68 eV for O. This value is in the range of other ab-initio Us reported for Mn (3.6–6.04 eV).\cite{i,j} From the different assumptions for the physical quantities (i.e. screening, localized states), ab-initio values of U should not be expected to the unique. A close empirical value of U_{3d} = 4.0 eV (albeit with no correction on oxygen) has been reported to reproduce well the experimental energy of formations of several manganese oxides.\cite{k,l}

Both PBE and ACBN0 band structures are shown in Fig. 2. The bottom of the conduction manifold is an itinerant sp band with noticeable parabolic dispersion and is predominantly of Mn-4s character at CBM at Γ. The set of low-dispersion bands located above the CBM are predominantly Mn-3d \ell_2g states. These bands are more narrowly resolved in the case of NiO.

In the occupied manifold, the PBE results (gray lines) distinctly show dispersionless Mn \epsilon_g bands (separated

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**FIG. 1.** Comparison between the band structures and projected density of states of TiO_2 without on-site interactions U = 0 (a) and with the converged effective values of U = 0.15 eV for Ti and 7.34 for O (b).

**TABLE I.** Converged values of the effective on-site Coulomb parameter U (in eV) for the transition metal (TM) 3d and the oxygen 2p states.

|          | TiO_2 | MnO | NiO   | ZnO |
|----------|-------|-----|-------|-----|
| TM-3d U  | 0.15  | 4.67| 7.63  | 12.8|
| Oxygen 2p U | 7.34 | 2.68| 3.0   | 5.29|

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In the occupied manifold, the PBE results (gray lines) distinctly show dispersionless Mn \epsilon_g bands (separated...
from the rest at the top of the manifold) centered at \(\sim -0.5\) eV and \(t_{2g}\) bands at \(\sim -1.5\) eV. These bands have minor oxygen hybridization whereas the bands below them (\(\lesssim -1.6\) eV) have a strong O-2p character. With the on-site repulsion correction in the ACBN0 results (black lines), the hybridization between Mn-3d and O-2p states increases. As a result the 3d bands are pushed down in energy while increasing their dispersion (more noticeably on the \(t_{2g}\) bands). This leads to: i) an increase of the bandwidth of the occupied manifold to \(\sim 7.5\) eV, in agreement with reported values of 7.6 eV (\(\text{GW} \oplus \text{LDA+U}\)) and 8 eV (sX-LDA)\(^{11}\), ii) an increase of the \(t_{2g}\) bonding-antibonding splitting across the bandgap and indirectly the separation of the 4s parabolic band (i.e. the energy difference between the parabolic CBM at Γ and the occupied \(t_{2g}\) bands) to 2.21 eV, which is close to the self-consistent \(\text{GW} \oplus \text{LDA+U}\) predictions of 2.42 eV and 2.27 eV, and iii) an increase of the energy difference between the CBM at Γ and the unoccupied \(e_g\) bands, i.e. the bandgap.

The indirect bandgap improves from the PBE value of 0.98 eV to 2.31 eV; however, the experimental value of 3.6–4.1 eV (Table II) is still underestimated. On the other hand, the magnetic moment is evaluated to be 4.79 \(\mu_B\), which matches the experimental value (Fender et al.\(^{14}\)).

Franchini and coauthors\(^{72}\) have performed calculations with a larger value of \(U_{3d} = 6.0\) eV (without \(U\) on oxygen) yielding, however, a bandgap and magnetization (2.1 eV, 4.67\(\mu_B\)) smaller than our results. This evinces the importance of having the on-site Coulomb interaction not only on the TM but also on oxygen. Sakuma et al.\(^{13}\) have shown that O 2p orbitals are considerably localized (as measured by the spread of their MLWFs) in TMOs; correspondingly, cRPA ab-initio calculations find the Coulomb repulsion in oxygen \(\bar{U}_{2p} \approx 4\) eV\(^{69}\), independent of the TM.

ACBN0's bandgap is closer to the predictions of hybrid functionals (sX-LDA 2.5 eV, HSE03 2.6 eV); nonetheless, both \(G_0W_0\oplus\text{HSE03}\) and self-consistent GW yield results of 3.4 and 3.5 eV, much closer to the experimental range. This underperformance of the hybrid functionals suggests that correlation effects may be particularly predominant in the case of MnO and, therefore, beyond the Hartree-exchange correction of hybrid functionals.

![FIG. 2. Band structure (spin up) of manganese oxide. All energies are relative to the valence band maximum Ev. Effective values of \(U = 4.67\) eV for the Mn-3d states and 2.68 eV for the O-2p states are used in the DFT+\(U\) calculation.](image)

For NiO, PBE incorrectly locates the parabolic 4s band above the 3d ones, as seen in Fig. 5. With our values of \(U = 7.63\) and 3.0 eV for Ni and O, the 4s CBM is correctly positioned at the \(\Gamma\) point\(^{54}\), yielding an indirect bandgap (\(Z-\Gamma\)) of 3.8 eV and a direct gap of 4.29 eV. Considering that the 4s CBM has low spectral weight, the direct gap can well account for the dominant first peak at 4.3 eV observed with bremsstrahlung isochromat spectroscopy (BIS)\(^{59}\). Our value of Ni \(U_{3d} = 7.63\) eV is in the same range than the effective value reported by Anisimov et al. of 7.1 eV\(^{72}\), obtained with the cLDA method, widely used for ab-initio calculation of \(U\). Similar to the TiO\(_2\) case, the bands around the bottom region of the NiO occupied manifold are strongly of O-2p character and are noticeably downshifted by the use of O \(U_{2p}\) with respect.
to the p bands. The manifold bandwidth increases by 1.5 eV to 9 eV as seen in Fig. 3. Most band structures reported in the literature do not find an increase of the bandwidth; nonetheless, the same value of 9 eV is obtained with the self-consistent GW of Massidda et al.\(^\text{\[29\]}\) who argued that such a broad bandwidth accounts well for the presence of strong satellite structures observed experimentally in that range of energy.\(^{29,72}\) Admittedly, these satellites are not captured in other approximations such as the model GW of Massidda et al.\(^\text{\[29\]}\) As pointed by Gillen and Robertso\(^\text{\[11\]}\), a bandwidth of 9 eV in NiO is in agreement with experimental measurements of 8–8.5 eV (X-ray emission spectroscopy)\(^\text{\[72\]}\) and 8.5–9.5 eV (ultraviolet photoemission spectroscopy)\(^\text{\[5,6\]}\).\(^\text{\[11\]}\)

**C. Wurtzite zinc oxide**

We use a hexagonal lattice (space group \#186) with relaxed lattice constants \(a = b = 3.1995\ \text{Å}, c = 5.1330\ \text{Å}, \) \(\mu = 0.3816\), taken from the AFLOWLIB database.\(^\text{\[25\]}\) (Ref. \(\text{\[22\]}\), aid=aflow:b4819e0e63f994a8).

In the strongly ionic ZnO, the bands can be readily identified by their dominant orbital character. The bands in Fig. 4 (black lines) from 0 to -6 eV are mostly of O-2\(p\) character. The low-dispersion bands around -9 eV correspond to the Zn-3\(d\) states. The conduction bands are predominantly of Zn-4\(s\) character.

**TABLE III.** Local magnetic moments (in \(\mu_B\)) for the antiferromagnetic states of MnO and NiO.

|        | MnO | NiO |
|--------|-----|-----|
| PBE    | 4.58 | 1.49 |
| ACBN0  | 4.79 | 1.85 |
| HSE03  | 4.78 | 1.85 |
| GW@LDA | 4.91 | 1.94 |
| Experiment | 4.58, 4.79 | 1.77, 1.94 |

Within PBE, the 3\(d\) bands incorrectly overlap with the 2\(p\) manifold introducing spurious hybridizations, as shown in Fig. 4 with gray lines, which in turn leads to a strong underestimation of the bandgap. The PBE gap is 0.85 eV while the experimental gap is 3.3 eV\(^\text{\[83\]}\). Zinc oxide highlights the underlying failure of LDA or GGA in treating materials with localized electrons and thus constitutes a case study for the application of the DFT+U method.

Our converged values are Zn \(U_{3d} = 12.8\) eV and O \(U_{2p} = 5.29\) eV and yield a bandgap of 2.91 eV, which compares favorably to the experimental value. The bandwidth of the O-2\(p\) manifold shown in Fig. 4 is \(\sim 6\) eV, in accordance to the angle-resolved photoemission spectroscopy (ARPES) value of \(\sim 6.05\) eV\(^\text{\[84\]}\).

Although seemingly high, our parameters agree with values reported by Calzolari et al.\(^\text{\[85\]}\)\((U_{3d} = 12.0, U_{2p} = 6.5\) eV) and Ma et al.\(^\text{\[86\]}\)\((U_{3d} = 10, U_{2p} = 7\) eV), both of which were found by fitting to reproduce the experimental bandgap and position of the 3\(d\) bands.

It is established that the 3\(d\) bands downshift monotonically with increasing values of \(U_{3d}\). As the 3\(d\) bands downshift, the \(p-d\) repulsion with the O-2\(p\) bands is decreased, which in turns lowers the energy of the valence-band maximum (VBM) and, thus, monotonically increases the gap.\(^\text{\[85\]}\) After the 3\(d\) bands have been fully disentangled from the 2\(p\) manifold, however, the 2\(p\) bands are well resolved and remain mostly insensitive to further increase of \(U_{3d}\). Consequently, the bandgap becomes progressively independent of \(U_{3d}\) and after the 3\(d\) bands are fully disentangled the application of on-site Coulomb interaction on oxygen becomes necessary to further reach the experimental bandgap.\(^\text{\[86\]}\)

For illustration, Fig. 5 shows a comparison of the band structure with different values of \(U_{3d}\) (12.8 and 9 eV), while the \(U_{2d}\) is kept fixed at the converged value 5.29 eV.
The unusual rigid shift of the $U_{3d}$ bands seen comparing Figs. 5(a) and (b) arises from a singularity particular to the case of the fully occupied 3$d^{10}$ bands of Zn in ZnO that is rooted in the definition of the Hubbard correction to the energy functional:

$$E_U = \frac{U}{2} \sum_{l,\sigma} \sum_m \left[ \lambda^l_{m\sigma} \left( 1 - \lambda^l_{m\sigma} \right) \right],$$

which is equivalent to Eq. (10) and the corresponding Hubbard potential is

$$V_U = \frac{U}{2} \sum_{l,\sigma} \sum_m (1 - 2\lambda^l_{m\sigma}) |\phi^l_m\rangle \langle \phi^l_m|,$$

where $0 \leq \lambda^l_{m\sigma} \leq 1$ is the occupation of the orbital $\phi_m$. For fully occupied orbitals such as Zn-3d in ZnO (Löwdin charge 9.97e out of 10e), i.e. $\lambda_m \approx 1$, the Hubbard energy reduces to $E_U \approx 0$, and the Hubbard potential becomes a rigid shift $V_U \approx -U/2$ applied to the localized orbitals. In principle, at this limit, the value of $U_{3d}$ does not change the energy of the material and becomes irrelevant in pinning the position of the 3d bands.

The experimental position of the center of the 3d bands is at -7.5 eV measured with respect to the VBM ($E_V$). Other experimental values have also been reported -8.81 eV, -6.6 eV, -7.8 eV. Our value of $U_{3d}$ underestimates the position of the 3d bands at ~9 eV. As discussed above, for fully disentangled and occupied 3d states, because a singularity of the DFT+$U$ energy functional, the energy of the system becomes almost independent of $U_{3d}$.

Similarly, the GW method and hybrid functionals, while correcting the bandgap and fully disentangling the 2p and 3p manifolds, consistently miss the position of the 3d bands by ~1 eV. Recently, Lim et al. proposed an assisted GW + $V_d$ approach in which the 3d bands are shifted by an ad hoc on-site potential $V_d = 1.5$ eV in the GW self-energy operator. Anallogously, the cLDA method fails in the case of Zn in ZnO. Because of the full occupancy of the 3d states, they become rather insensitive to small linear perturbations, yielding unreliable numerical values of $U$.

Lee and Kim have proposed an extension to cLDA method for systems with closed-shell localized electrons. They found $U_{3d} = 5.4$ eV for Zn by applying a large perturbation potential and correcting for the excess potential needed to reach the onset of the electron-density response.

IV. DISCUSSION

Indeed, the ACBN0 functional satisfies the rather ambitious criteria outlined by Pickett et al.

I. ACBN0 reduces to (LDA)PBE when (LDA)PBE is known to be good. The reduction of $U \rightarrow 0$, arises with the introduction of the “renormalized” density-matrix $P$ (instead of the regular density matrix $P$), which makes $U$ dependent on the degree of localization of the Bloch states.

A toy model with two basis functions $m$ and $m'$ reveals the scaling of Eq. 12 as $\hat{U} \sim \frac{1}{2} N_m N_{m'} (m|m'|m')$ in contrast to $\hat{U} \sim (m|m'|m')$ when using the regular density matrix instead. Delocalized Bloch states are assumed to be properly described at the LDA(PBE) level. The more delocalized a state, the lower the charge projected inside the atomic sphere ($N_m \approx N_{m'} \rightarrow 0$) and thereby $\hat{U}$ vanishes quadratically. See for instance the case of Ti $U_{3d}$ in TiO$_2$, or silicon where ACBN0 yields $U_{2p} \approx 0$ eV.

II. The energy is given as a functional of the density. The value of $U$ in ACBN0 depends only on the electron density. The ACBN0 functional can be considered a zeroth-order pseudo-hybrid density functional in the sense that it includes an on-site form of the Hartree-Fock exchange. The results for the test systems studied here follow closely the more established and far computationally more expensive $\sigma$X-LDA hybrid functional. Moreover, the methodology presented in this work can be immediately generalized to evaluate the nonlocal exchange energy for solids by computing the full set of required two-electron integrals. Thus, one could have a hybrid-functional plane-wave DFT calculation that is as fast as LCAO hybrid-functionals while still benefiting from the robust parallel fast-Fourier-transform algorithms and systematic basis-set convergence of plane waves.

III. The method specifies how to obtain the local orbital in question. ACBN0 directly parallels the original orbital-dependent DFT+$U$ functional of Anisimov that uses atomic orbitals $\{ \phi \}$. Conceptually, the localized states $\phi$ are linear combinations of $\{ \phi \}$ with the expansion coefficients obtained self-consistently, thus, they reflect the chemical environment of the site; however, the expansion coefficients need not be explicitly known. Even though the information of the coefficients is conceptually included in the renormalized density matrix, they are not individually resolved. Such LCAO expansion is more general and suitable for cases when the localized bands are not readily disentangled from other bands, which happens when the
IV. The method predicts antiferromagnetic insulators when appropriate. This is demonstrated by the results presented for TiO$_2$, MnO, NiO, and ZnO. The flexibility of ACBN0 is that it allows the calculation of $\bar{U}$ and $\bar{J}$ for any atom in the system of interest, yielding for instance non-negligible values for the 2$p$ lone-pair of Oxygen in transition metal oxides or for the $p$ states of the anion in transition metal chalcogenides. Through the inclusion of these terms, ACBN0 corrects both the bandgap and the relative position of the different bands, in particular the ones deriving from the $d$ orbitals of transition metal atoms. This characteristic of ACBN0 is crucial for the improved agreement with experimental results. Generally, the experimental bandgap can only be moderately improved when considering only the TM; Paudel and Lambrecht$^{[21]}$ have suggested a simultaneous use of $U$ on 3$d$ and 4$s$ only on zinc; however, a large value on Zn $U$$_{4s}$ = 43.5 eV is needed. Finally, our results predict the stability of the antiferromagnetic phases of both MnO and NiO. However, a more thorough discussion on the relative stability of different magnetic phases and the description of highly correlated metals will be the subject of a forthcoming publication.$^{[22]}$

V. CONCLUSIONS

In conclusion, we have introduced ACBN0, a pseudo-hybrid density functional that incorporates the Hubbard correction of DFT+$U$ as a natural function of the electron density and chemical environment. The values of $\bar{U}$ and $\bar{J}$ are functionals of the electron density and provide a variational way of obtaining the proper description of Mott insulators and other strongly correlated systems. Although a more extensive validation of this functional is needed, the first results of our tests show good agreement with hybrid functionals, the $GW$ approximation and experimental measurements for the electronic properties of TMOs at a fraction of the computational cost. This is an essential requirement for the design efficient algorithms for electronic structure simulations of realistic material systems and massive high-throughput investigations.$^{[1]}$

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Appendix A: The PAO-3G minimal basis set

The PAO basis functions $\phi_{lm}(r) \equiv R_l(r) Y_{m|\{c,s}\}(\theta, \varphi)$ are in fact obtained by solving the pseudopotential Kohn-Sham equation for a given atomic reference configuration, where $Y_{m|\{c,s\}}$ are real-valued spherical harmonics$^{[93]}$. Given that the radial and angular part are separable, they can be directly fitted using linear combinations of spherical-harmonic Gaussian functions $G_{s}(r, l, m, \zeta) = r^l e^{-\zeta r^2} Y_{m|\{c,s\}}(\theta, \varphi)$. Then, $\phi(r) = \sum_{l,m=1}^{N_G} a_l G_s(r, l, m, \zeta)$. The expansion coefficients $\{a_l\}$ and exponents $\{\zeta\}$ are found by fitting to $R_l(r_n)$, which is performed by using the non-linear least-square Levenberg–Marquardt algorithm to minimize the deviation

$$\left( \sum_{r_n} \left[ \left( \sum_{l=1}^{N_G} a_l r_n^{l+1} e^{-\zeta r_n^2} - R_l(r_n) \right) \right]^2 \right)$$

$R_l(r)$ is evaluated at a logarithmic radial mesh $\{r_n\}$ and provided in the atomic pseudopotential files taken from the PSLibrary 1.0.$^{[92]}$ We only use norm-conserving pseudopotentials since they guarantee the charge conservation for $\phi$. The initial guess for the coefficients and exponents are taken from the STO-3G$^{[95,96]}$ basis-set, which associates three Gaussian functions per orbital ($N_G = 3$), from the EMSL library.$^{[97]}$

Traditionally, Cartesian Gaussian functions of the type $G_c(r, l_x, l_y, l_z, \zeta) = x^{l_x} y^{l_y} z^{l_z} e^{-\zeta r^2}$ are held as the most efficient basis to compute the staggering number of two-electron integrals needed in quantum chemistry calculations. We follow the procedure by Mathar$^{[93,94]}$ to further convert each spherical-harmonic Gaussian into a linear combination of Cartesian Gaussians. Then, the Cartesian expansion of the PAOs is

$$\phi_{lm}(r) = \frac{1}{4} \frac{(2l + 1)!}{\pi N_{lm}} f_{l,m}(x, y, z) \sum_{i=1}^{N_G} a_l e^{-\zeta_i r^2}$$

where $f_{l,m}(x, y, z)$ is given in Table $\bar{\text{IV}}$.

An example of this fitting procedure is shown in Figure $\bar{\text{C}}$ for Zn-3$d$ and O-2$p$ PAO. Having the PAOs expressed as linear combination of Gaussian-type orbitals in Eq. $\bar{\text{A2}}$ is largely advantageous, since it allows computation of the ERIs in a straightforward and analytical way. Furthermore Gaussians allow filtering out ERIs with negligible energy contribution$^{[95]}$ further speeding up calculations, as implemented in the Heyd-Scuseria-Ernzerhof HSE03$^{[100]}$ hybrid functional.
The solid is efficiently calculated using plane-wave DFT on a unit cell with periodic boundary conditions. The plane-wave basis allows a systematic convergence of the basis-set energy error, which is controlled by a single energy-cutoff parameter. Periodic-boundary conditions are implicit to the plane-wave basis, thus avoiding the presence of surface effects intrinsic to molecular cluster calculations. Moreover, plane waves allow the use robust and scalable Fourier-transform algorithms. We follow the method described in Ref. [19] to project the k-space electronic structure of the solid onto an atomic-orbital space by filtering out high-kinetic-energy plane waves. The resulting reciprocal-space Hamiltonian $H^{\sigma, \mathbf{k}}$ and overlap $S^{\mathbf{k}}$ matrices are then Fourier-transformed into real space resulting in:

$$H^{\sigma, 0\mathbf{R}} = \frac{1}{\sqrt{N_k}} \sum_{\mathbf{k}} e^{-i \mathbf{R} \cdot \mathbf{k}} S^{\mathbf{k}} H^{\sigma, \mathbf{k}}(\mathbf{k}, N) S^{\mathbf{k}}^\dagger,$$

$$S^{0\mathbf{R}} = \frac{1}{\sqrt{N_k}} \sum_{\mathbf{k}} e^{-i \mathbf{R} \cdot \mathbf{k}}.$$

The parameters $\kappa$ and $N$, defined in Ref. [19] determine the shifting and filtering for the projection procedure. The overlap integral between a basis function $\phi_{\mu}$ located inside the primitive unit cell (lattice vector $0$) and the periodic translation of $\phi_{\nu}$ to lattice vector $\mathbf{R}$ is the matrix element $S^{\mu\nu}_{\mu\nu} = \langle \mu^0 | \nu^R \rangle$.

The real-space density matrix is then computed as:

$$P^{\mu\nu}_{\mu\nu} = \frac{1}{\sqrt{N_k}} \sum_{\mathbf{k}} e^{-i \mathbf{R} \cdot \mathbf{k}} N^{k\sigma}_{\mu\nu} \psi_{\mu}^{k\sigma} \psi_{\nu}^{\dagger}.$$

where $N^{k\sigma}_{\mu\nu} = 1$ for all occupied states $\psi_{\mu}^{k\sigma}$. The expansion coefficients $c_{\mu\nu}^{k\sigma}$ are the components of the generalized eigenvectors of $H^{\sigma, \mathbf{k}}$ and $S^{\mathbf{k}}$.

TABLE IV. Cartesian expansion of $f_{l,m}$

| $(l, m)$ | $N_{l,m}$ | $f_{l,m}(x, y, z)$ |
|---------|-----------|------------------|
| $(0, 0)$ | 0.25      | 1                |
| $(1,-1)$ | 0.25      | $y$              |
| $(1, 0)$ | 0.25      | $z$              |
| $(1, 1)$ | 0.25      | $x$              |
| $(2,-2)$ | 0.25      | $xy$             |
| $(2,-1)$ | 0.25      | $yz$             |
| $(2, 0)$ | 3         | $2z^2 - x^2 - y^2$ |
| $(2, 1)$ | 0.25      | $xz$             |
| $(2, 2)$ | 1         | $x^2 - y^2$      |

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