

Validity of DFT+ U band gaps in all its known functional forms

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(Received 29 April 2026; revised 18 August 2026; accepted 9 September 2026; published 26 October 2026)

The density functional theory plus Hubbard U (DFT+ U) technique is one of the most widely used tools by condensed matter physicists and solid-state chemists for the simulation of transition-metal and lanthanide-bearing crystals, and increasingly of much more diverse chemistries. Although often synonymous with the corrective functionals of Dudarev *et al.* [Phys. Rev. B **57**, 1505 (1998)] and Liechtenstein *et al.* [Phys. Rev. B **52**, R5467 (1995)], there exists a wide variety of DFT+ U -type functionals ready to be utilized, and no doubt yet to be developed. Since the earliest days, the gap in the DFT+ U single-particle eigenspectrum has been associated with the fundamental band gap, and the method has typically found more success for spectra than for total-energy derived properties. There has been some doubt, however, as to the conceptual validity of this association. Here, extending findings from recent years regarding local, semilocal, and hybrid functionals within the generalized Kohn-Sham framework, we prove and numerically demonstrate that the DFT+ U eigenspectrum gap is conceptually valid, in the specific sense that it matches its own fundamental gap calculated using total-energy differences. We emphasize that this does not imply its agreement with experimental values, and indeed our argument is independent of the Hubbard U parameter. The result holds for pristine periodic systems with converged k -point sampling but not, however, for defective ones, isolated systems, or systems in which added charges exhibit spontaneous localization. We show that band-gap validity for pristine solids holds in the presence of pseudopotentials and PAW potentials, when using hybrid functionals, and in DFT+ U (+ J) irrespective of the level of subspace projection onto the band-edge states. We survey every collinear-spin DFT+ U -type functional known to have been published to date, within a unified notation. We verify analytically under which conditions the eigenvalue gap equals its fundamental gap, for each functional. Returning to the related but different question of band-gap correction efficiency, we offer fresh analysis of DFT+ U band-gap projection dependence, and each functional's effect on energies and gaps for the hydrogen lattice in the Mott-Hubbard limit.

DOI: [10.1103/9snx-cp83](https://doi.org/10.1103/9snx-cp83)

I. BACKGROUND

Kohn-Sham density functional theory (DFT) [1–4] is and has been, for several decades, the most popular tool for predicting the electronic structure of molecules, materials, nano-structures, surfaces and interfaces. It enjoys widespread use across the fields of physics, chemistry, and materials science [5,6]. Central to every Kohn-Sham DFT calculation is the selection of an appropriate exchange-correlation approximation. Following many years of sustained research on developing explicit approximate functionals for the total energies of condensed matter systems, no consensus has yet emerged within the electronic structure theory community as to the level of theoretical complexity that is most efficient for use in calculating such energies, their differences, and derivatives. Even at a given level of theory, there are

significant differences between different implementations [7]. The situation is particularly challenging for materials that exhibit significant correlation effects [8]. While qualitative agreement with experimental trends can often be sufficient for progress in solid-state physics [9], very high precision is needed, e.g., to calculate chemical reaction rates [10].

At present, there remains insufficient theoretical understanding available for this otherwise mature, impactful [11–13] field to assess whether it is best to focus on developing improved functionals of the electronic density alone, since DFT is exact in principle, or to focus attention on another specific quantity such as the kinetic energy density, the potential, the occupied, or even unoccupied Kohn-Sham orbitals [14], in pursuit of accuracy. Beyond DFT, there now exist sophisticated but typically very costly functionals of the one-body density matrix [15], the pair-density [16], the density response function [17], the Green's function [18,19], and the many-body wave-function (either in its entirety with appropriate restrictions [20], or for predefined subspaces within a mean-field embedding [21]). The diversity of this interdisciplinary field is a strength, and it reflects the differing requirements in its key areas of application. In the present work, we will focus on functionals of the occupied Kohn-Sham orbitals, giving rise to nonlocal (implicit) [22] orbital-dependent potentials

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[23,24]. These fall on functional “Rung 4,” i.e., the hybrid-functionals, although some that we will review have features not usually found in hybrids, such as explicit electron count dependence.

The situation, overall, is more optimistic if one looks at theoretical spectroscopy. It is now possible to predict the spectral functions of many materials, in excellent agreement with photoemission measurements, using first-principles theoretical methodologies which require no significant external parameters [25]. Often, progress has been made by means of the successful combination of electronic band-structure theory, e.g., periodic Kohn-Sham DFT and more recently many-body perturbation theory within the *GW* approximation [26,27], with algorithms for solving explicitly correlated discrete many-body Hamiltonians [21]. The latter are restricted to the selected subspaces deemed to be correlation-prone. The combination is usually made by means of self-consistent Green’s function embedding techniques such as dynamical mean-field theory, yielding DFT+DMFT [21,28–33] and *GW*+DMFT [34–36], and more recently increasingly on the basis of density-matrix rather than Green’s function embedding [37].

II. DFT+*U* IN CONTEXT

An alternative approach to employing such relatively costly methods is to supplement a standard, low-cost local or semilocal exchange-correlation (XC) functional [38–44] with a corrective functional such as Koopmans’ Compliant Functionals [45–48], self-interaction error (SIE) correction functionals [49,50] and van der Waals functionals [51–54]. In particular, the DFT plus Hubbard *U* (DFT+*U*) method [55–57] has been devised to treat systems with localized electronic states such as 3*d*-transition-metal oxides [58–73], 4*f*-lanthanide oxides [74–81], and transition-metal complexes [82–88]. Although originally developed for application with the Local Spin Density Approximation (LSDA) [89], it is now common practice to also apply this corrective functional with generalized Gradient Approximations (GGAs) [90–99], and more recent studies have investigated its application in conjunction with meta-GGAs [58,66,100,101]. One of the strengths of the DFT+*U* method is its ease of implementation as part of a broader DFT code package. Indeed, the method has been implemented in a wide variety of DFT codes, many of which have garnered a large, active community of users. The total number of Google Scholar [102] “hits” associated with the DFT+*U* method for a range of DFT packages [103–129] is presented in Fig. 1. The immense utility of the method is self-evident.

The DFT+*U* approach has also inspired the development of other advanced electronic structure methodologies such as the Koopmans’ Compliant (KC) Functionals [45–48]. The Koopmans’ Integer functional, for example, was explicitly developed to extend a DFT+*U*-type correction to each Kohn-Sham (KS) orbital separately, thus ensuring the retention of the base (i.e., underlying approximate) DFT total energy in the case of insulators. Within the frozen orbital approximation, the unscreened Koopmans’ correction $\{\Pi_{i\sigma}^u\}$ replaces the nonlinearity of the base DFT functional with a term that is linear with respect to orbital occupancy $f_{i\sigma}$. This term takes

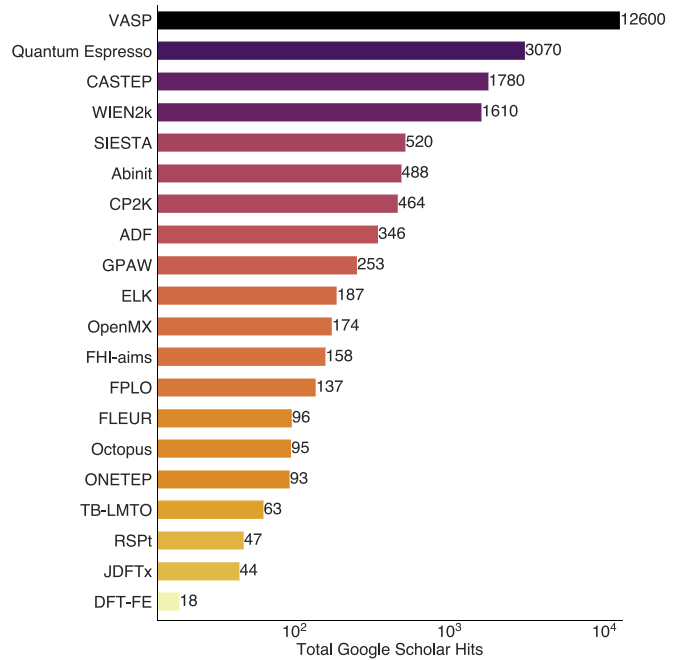


FIG. 1. The number of Google Scholar hits [102], on a logarithmic scale, for a range of DFT packages that implement DFT+*U* [103–129]. The search was conducted by searching the name of the DFT package in conjunction with DFT+*U*.

the form

$$\Pi_{i\sigma}^u(f_{i\sigma}) = f_{i\sigma} \eta_{i\sigma} - \int_0^{f_{i\sigma}} ds \langle \Psi_{i\sigma} | \hat{H}_{KS}(s) | \Psi_{i\sigma} \rangle. \quad (1)$$

Here, $\hat{H}_{KS}(s)$ is the approximate KS Hamiltonian where orbital $\Psi_{i\sigma}$ has occupation s . A number of methods have been devised for determining the slope of the linear term $\eta_{i\sigma}$, including the Koopmans’ Integer functional and the Koopmans’ Integer Perdew-Zunger self-interaction corrected functional. In practice, the orbitals relax with respect to occupancy so that the unscreened Koopmans’ correction $\{\Pi_{i\sigma}^u\}$ will not suffice to enforce linearity. Such orbital relaxation effects are accounted for through orbital-dependent screening parameters, which also need to be evaluated. Through rigorous benchmarking, KC functionals have been shown to significantly improve both the predicted band gaps and ionization potentials compared to the underlying (semi)local XC approximations [130–132].

In contrast, through the use of a set of fixed projection operators $\hat{P}$, conventional DFT+*U* corrective functionals act only on selected subspaces within the electronic system of interest. The suitability of various choices of projection operator have been investigated, including atomic orbitals, ortho-atomic orbitals [133–136], maximally localized Wannier functions [137,138] and molecular orbitals [139,140]. The strength of the DFT+*U* correction is also dependent on the value of the effective Hubbard parameter U_{eff} . Its value is often tuned to ensure agreement with some experimental property of interest [141,142], but numerous schemes have also been devised for the calculation of the necessary Hubbard *U* and Hund’s *J* interaction parameters [143,144]. More generally, low-energy model embedding or “down-folding” [145] has a long and successful record in the electronic

structure theory of strongly correlated materials [143,146–149]. A significant fundamental and practical breakthrough came with the invention of the Green-function-based constrained random phase approximation (cRPA) [147,150–157]. More recently, the resulting dynamical interaction parameters $U(\omega)$ and $J(\omega)$ have been physically interpreted [35,155,158] and applied within suitably adapted impurity solvers [159,160]. Within the SIE-correction interpretation of DFT+ U [86,143], the validity of which is numerically confirmed in [161], the targeted subspaces are effectively approximated as quantum systems in contact with a bath that provides screening and particle exchange. The Hubbard U is then calculated as a measure of the net self-interaction of the subspace, which is assumed to be spurious, together with the remainder of the system providing a screening environment [144,162].

While DFT+ U is routinely applied to calculate diverse electronic structure properties, of both total-energy derived and spectroscopic types, its success has been arguably weighted more towards the latter; for examples see Refs. [57,163]. This is due to the extraordinary cost-benefit ratio that it provides when the principal drawback of the underlying approximate functional is a greatly underestimated, or absent, fundamental gap, when calculated on the basis of the single-particle eigenvalues. Notwithstanding, for just a moment, the validity of such calculation, DFT+ U can often improve such a band-gap prediction on an almost cost-free basis, due to the implicit derivative discontinuity that it introduces, which manifests in a potential that depends on the occupancy of the bands. This is done on an empirical basis or, when the necessary parameters are calculated in situ, an effectively semi-empirical basis. Semi-empiricism arises because, even when self-consistent projector functions are used [138,164–167], there remains some empiricism related to their means of construction, albeit arguably at a level no worse than that of the typical underlying functional.

This brings us to the main topic of the present work. Throughout the history of DFT+ U , it may be said that there has remained some doubt concerning the validity in principle of using the eigenvalue gap as the basis for calculating the fundamental band gap [55,58]. DFT+ U has, in this regard, been sometimes viewed as a further layer of pragmatism on top of an already pragmatic practice, or something that might be analyzed as an approximation to a hybrid functional [168] or as an approximation to a many-body perturbation theory applied on top of the Kohn-Sham system [56].

The aim of the present work is to rigorously establish the validity in principle of calculating fundamental gaps from the DFT+ U (family of corrections) eigenvalue gap, for the case of pristine crystals, only where the added electron or hole delocalizes over the bulk system, and then only when treated with very well-converged k -point grids (i.e., in the so-called thermodynamic limit). This result does not apply to crystals simulated with insufficiently dense k -point sampling, however. Neither does it apply to molecules, defective solids, or pristine systems with spontaneous charge carrier localization, and so the fundamental gaps of such systems may be more reliably calculated using explicit (spin-polarized, for the avoidance of doubt) electron addition and removal energies.

One needs to proceed with caution in this context, as the question of whether such a gap should recover the fundamental gap is one that depends not only on the functional type, but equally on the domain over which it is minimized (e.g., whether the total energy is a functional of the density), and not just the nature of the system under scrutiny [23,169,170]. The result of band-gap validity, as we will discuss, holds for the standard widespread practice of DFT+ U for crystals, but not pure Kohn-Sham DFT settings as in optimized effective potential (OEP) DFT+ U [171,172].

It is a well-known and long-standing result that only the frontier occupied KS eigenvalue generally corresponds to a total energy difference, i.e., minus the ionization potential, in exact Kohn-Sham DFT [173]. Why this does not generally hold also for the unoccupied KS eigenvalue, i.e., it is not minus the electron affinity, is due to the absence of the exchange-correlation derivative discontinuity in the exact Kohn-Sham eigenspectrum [174]. In approximate KS DFT with an absent exchange-correlation derivative discontinuity (such as conventional local and semilocal functionals), both levels are valid for bulk systems under the aforementioned preconditions [170], and in all other cases, both KS eigenvalues are invalid.

Our work does not revisit KS DFT and has no bearing upon it, as it takes place instead within the different context of generalized Kohn-Sham theory (GKS) [23], and moreover an approximated form with an implicit rather than explicit derivative discontinuity. GKS is, in a nutshell, where the orbitals but not the resulting density provide the functional dependence of the total energy, and it is the practical, commonplace formalism of DFT+ U . In GKS theory, unlike KS, any implicit derivative discontinuities (i.e., where the energy remains differentiable with respect to the density matrix) are automatically included in the eigenspectrum [169], and it is this type that arises almost universally in DFT+ U (we will later discuss some recently introduced exceptions).

The excluded case of spontaneous charge carrier localization [175], i.e., where the added electron or hole localizes in space despite the absence of defects or lattice distortions has, to the best of the authors' knowledge, never been reported to date in DFT+ U studies but could conceivably occur for sufficiently large values of the applied Hubbard U parameter. Such symmetry breaking is, however, suppressed in conventional DFT+ U calculations where a pristine periodic system is modeled using a primitive unit cell with converged k -point sampling.

Importantly and reassuringly, in connection with the choice of projection operators $\hat{P}$ that define a DFT+ U calculation, we find that the validity in principle of the resulting eigenvalue gap holds independently of such choice. The numerical value of the calculated band gap does, of course, generally depend on $\hat{P}$. Its validity in principle holds even for very poor or unphysical choices of $\hat{P}$ and/or the Hubbard U and related parameters, reinforcing the point that we are primarily addressing in the present work a different aspect from that of comparing DFT+ U band gaps with experimental ones.

Notwithstanding, we will return in Secs. X and XI to shed new light on the functional and projection dependence, respectively, of the DFT+ U band gap. We prove, in passing, that hybrid functional eigenvalue-based band gaps

are perfectly valid for crystals (under the aforementioned restrictions). We further show, in Appendixes C and D, that this GKS eigenvalue-based band-gap validity is generally preserved by the use of pseudopotentials or the projector-augmented wave (PAW) construction. Validity in the case of local and semilocal functionals, which was addressed in Ref. [170] using a somewhat different derivation, is automatically included in our proof by setting the Hubbard parameters or exact exchange hybrid mixing parameter to zero.

III. NUMERICAL TEST FOR BAND-GAP VALIDITY

In order to provide a minimal and motivating test for the numerical equivalence of the Dudarev *et al.* [176] functional DFT+*U* fundamental gap and its own single-particle eigenvalue-based gap, we performed such calculations on an antiferromagnetic two-dimensional hydrogen square lattice with a large lattice constant. The Hubbard *U* parameter and projectors were kept fixed. Computational details are provided in Appendix A, and the main findings are shown in Fig. 2. Using QUANTUM ESPRESSO [105], we reached a *k*-point sampling density equivalent to a supercell of $\gtrsim 1.7 \times 10^4$ atoms, i.e., not at the thermodynamic limit required for exact equality of the gaps, but sufficiently close to make a reasonable extrapolation.

In this system, neither the valence nor conduction band edge is degenerate, and no spontaneous localization of surplus charges is permitted by the two-atom unit cell used. We found that, with a sufficiently small cold smearing parameter, an acceptable balance between convergence and smearing errors could be found in the more numerically challenging regime of charged systems sampled with high *k*-point density. Some evidence of remaining $\sim$ meV numerical errors is seen in the top-left corner of Fig. 2(a), which shows the isolated explicit DFT+*U* energy contribution to the fundamental gap (i.e., based on DFT+*U* energy differences). Some of this noise cancels, however, when the other terms in the total gap are added. Figure 2(a) shows that the finite-size error of the DFT+*U* gap contribution scales almost perfectly inversely with respect to the effective volume of this system, i.e., like N_k^{-1} .

Moving to Fig. 2(b), we see that, in this system, the band gap as judged from the (commonplace) GKS eigenvalue spectrum of the neutral lattice is almost perfectly constant with respect to *k*-point density. This is because the band edges are included in the sampling in all cases, and because the density contribution is near-constant across the Brillouin zone in this Mott-Hubbard system with very flat bands. A constant line, with a value E_g^{eigen} , shows the numerically best available estimate of the eigenvalue-based band gap.

The fundamental gap directly calculated using charged systems (one electron added or removed per effective supercell), as we can see shown with squares in Fig. 2(b), instead converges relatively slowly with respect to *k*-point sampling. The power-law behavior of the finite-size error in the energy-based fundamental gap is known to be rather involved [177] when kinetic and XC contributions are included. The antiferromagnetic order may further complicate the finite-size exponents, and their detailed study is beyond the scope of the present work. We include the points shown in a fit to this data,

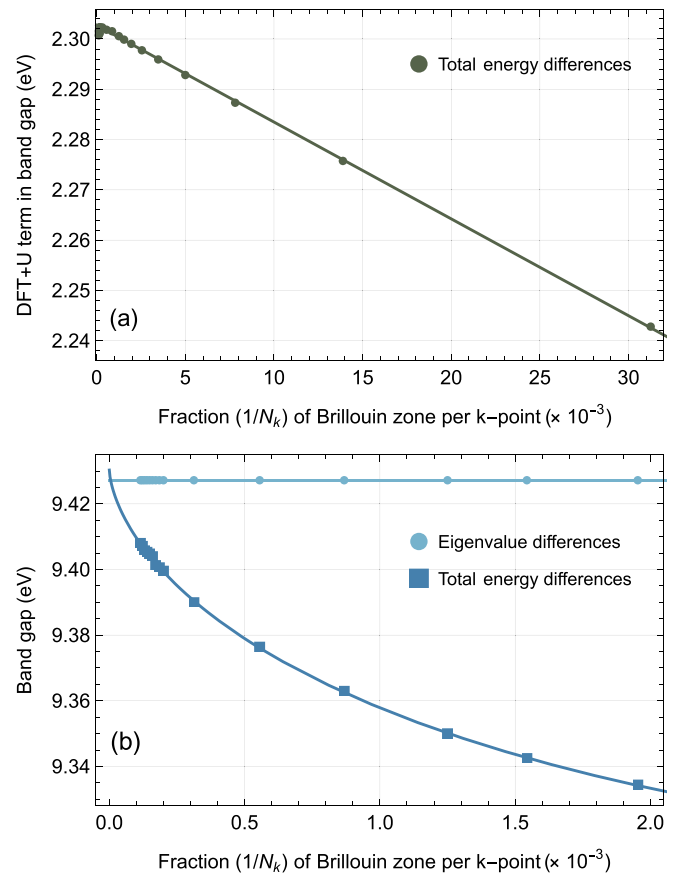


FIG. 2. Panel (a), above, shows the dependence of the explicit DFT+*U* contribution to the fundamental band gap of an antiferromagnetic two-dimensional square hydrogen lattice, with respect to the inverse of the effective number of two-atom unit cells that is implemented using Brillouin zone sampling. DFT+*U* projectors and the Hubbard *U* parameter are kept fixed. The largest calculation, with data points furthest to the left, corresponds to an effective supercell size $\gtrsim 1.7 \times 10^4$ atoms. In panel (b), below (enlarging by $15\times$ towards the converged limit), total band gaps based on frontier eigenvalue differences and total-energy differences are compared. Fitted curves, described in the main text, suggest that near-identical values will be reached in the thermodynamic limit.

while excluding those from coarser samplings. Supposing a N_k^{-1} behavior of the aforementioned term, and permitting a variable exponent for a second one yields an (electrostatics dominated) exponent very close to $-2/3$, echoing the early analysis of Ref. [178], noting that the precise value and that of the intercept depend somewhat on the points included. As a guide to the eye, therefore, we show the best fit of the form $a + bN_k^{-2/3} + cN_k^{-1}$. This, for example, yields an intercept error of $a - E_g^{\text{eigen}} = 3$ meV.

We anticipate that the extrapolated finite-size error would vanish with yet more *k*-point data towards the thermodynamic limit, increasing out-of-plane cell dimension, and a more sophisticated, multi-exponent extrapolation formula. Overall, this test strongly suggests that the DFT+*U* eigenvalue gap agrees with the corresponding fundamental gap in the thermodynamic limit. It further suggests that the eigenvalue

gap converges much faster to this limit, at least when the band-edge k -points are kept included in the sampling. In a system with more band dispersion, we would expect this convergence to be slower, of course, but for the eigenvalue gap to still be by far the more efficient estimator for the fundamental gap of periodic systems within the GKS formalism.

IV. THE FUNDAMENTAL BAND GAP FROM DFT+ U AND HYBRID FUNCTIONALS

In this section, we provide the main result of this work. We prove that the fundamental band gap as calculated from the generalized Kohn-Sham (GKS) eigenvalues [23] (that is to say, within commonplace practical DFT), in DFT+ U and hybrid functionals, is entirely valid for pristine periodic systems. This has previously been shown for local and semilocal functionals and numerically for conventional hybrid functionals [170], and our proof includes such cases, and indeed almost all functionals in current use, while modifying the logical argument somewhat. By “valid,” we mean that this gap *exactly* matches what would be calculated from explicit electron removal and addition energies, for pristine periodic systems that remain periodic under charging. This is not to say that the result must agree well with experiment, not by any means, but only that it is a proper and well-founded procedure to predict a fundamental band gap based on the gap in the conventional single-particle eigenvalues.

As previously mentioned, but still very worth acknowledging, this may at first seem contrary to the received, often repeated statement that only the highest occupied eigenvalue has physical meaning in DFT. That statement is indeed true in the case of exact DFT applied generally (and also for approximate, yet exchange-correlation derivative discontinuity exhibiting, functionals when they are applied to well-converged pristine bulk systems) within a strict Kohn-Sham DFT setting. There, the density provides the functional dependence of the total energy.

In the in-practice conventional formalism of GKS, it is the orbitals but not the resulting density that provide the functional dependence for the total energy, and this is the key difference. The KS or GKS distinction only becomes very relevant in the presence of a nonmultiplicative potential, e.g., due to its orbital dependence [179], as when the potential is purely local and orbital-independent there is no practical distinction and crystalline GKS eigenvalue-based band gaps have already been shown to be valid in that regime [170].

Our result implies that the lowest unoccupied eigenvalue is as valid as the highest occupied one, in the standard practice of DFT+ U . While this is only the case for defect-free periodic systems (and only with infinitely dense $\mathbf{k}$ -point sampling, strictly speaking), we will also provide expressions for the leading-order corrections to the GKS (i.e., usual, familiar eigenspectrum) gap needed to recover the fundamental gap, e.g., for defective solids or molecules. However, such corrections will typically be more demanding to compute than direct explicit electron (along with their spin) removal and addition calculations for the fundamental gap. In the following, we mirror the proof provided in Ref. [170]; however, we instead

invoke as our starting point the underpinning total-energy construction and logical procedure regarding its variation following the Ph.D. thesis of Poilvert [180].

A. Establishing the variationally optimized constrained energy

We begin by considering the total energy constructed using the Generalized Kohn-Sham system of N electrons, with orbitals $\{\psi_i\}$ and their complex conjugates as variables. We allow for possibly noninteger N values, representing a statistical ensemble of integer-electron-count states. We suppress the spin-index for simplicity, as the extension to spin-DFT is at least procedurally trivial (as discussed in Appendix E), and we focus on zero temperature. The real-valued orbital occupancies f^i will also be seen as variational variables. These are defined, for possibly nonorthogonal $\{\psi_i\}$, as the matrix elements that construct the generalized Kohn-Sham density matrix according to $\hat{\rho} = \sum_i |\psi_i\rangle f_i \langle\psi_j|$, noting that this only represents a valid ensemble state when the orbitals are orthonormal.

The total energy, including orthonormality and orbital filling constraints, in atomic units and with fixed external potential v , reads

$$E_v = - \sum_i f_i \frac{\langle\psi_i|\nabla^2|\psi_i\rangle}{2} + E_{v\text{Hxc}+U}[\{\psi_i\}, \{f_i\}] + \sum_{ij} \lambda_{ij} (\delta_{ji} - \langle\psi_j|\psi_i\rangle) + \epsilon_F \left(N - \sum_i f_i \langle\psi_i|\psi_i\rangle \right). \quad (2)$$

Here $E_{v\text{Hxc}+U}$ is the approximated energy due to the Coulomb interaction, the beyond-independent-particle kinetic energy, and the external potential. The potential contribution represented as U here could also be an exact exchange term, for the purposes of the present construction. The Lagrange multipliers λ_{ij} , as well as their complex conjugates and the real-valued Fermi energy ϵ_F , a final Lagrange multiplier, are promoted as independent variables.

The energy E_v is simultaneously extremized with respect to each degree of freedom, which includes the Lagrange multipliers. First applying $|0\rangle = \partial E_v / \partial \langle\psi_j|$, noting that the derivatives are partial, we find the generalized eigenequation

$$\left(-\frac{\nabla^2}{2} + \hat{v}_{v\text{Hxc}+U} - \epsilon_F \right) |\psi_j\rangle f_j = \sum_i |\psi_i\rangle \lambda_{ij}. \quad (3)$$

Here, $\hat{v}_{v\text{Hxc}+U}$ is the functional derivative of $E_{v\text{Hxc}+U}$ with respect to the density matrix $\hat{\rho}$. Before going further, we can apply $0 = \partial E_v / \lambda_{ij}$, from which we deduce that the $\delta_{ji} - \langle\psi_j|\psi_i\rangle = 0$, i.e., that the orbitals are orthonormalized at the minimum of E_v . Applying next $\langle 0| = \partial E_v / \partial |\psi_j\rangle$, we find a very similar equation,

$$f_j \langle\psi_j| \left(-\frac{\nabla^2}{2} + \hat{v}_{v\text{Hxc}+U} - \epsilon_F \right) = \sum_i \lambda_{ji} \langle\psi_i|. \quad (4)$$

Comparing this with the complex conjugate of Eq. (3), we deduce that $\lambda_{ji}^* = \lambda_{ij}$. Here, we have invoked the Hermitian property of $\hat{v}_{v\text{Hxc}+U}$ for the now assuredly valid

(due to orthonormality) GKS density matrix, noting that while both DFT+ U and hybrid functionals introduce an implicitly orbital-dependent Hamiltonian, they do not introduce an *explicit* orbital dependence, which might jeopardize the self-adjoint property of the potential. As an aside, it is preserved for KC functionals by their satisfaction of the Pederson condition [48,181].

Taking $0 = \partial E_v / \epsilon_F$, together with orbital orthonormality, provides simply that the f_i sum to the correct electron count N . To gain further insight into ϵ_F , we must apply the final condition available, $\partial E_v / \partial f_j = 0$. Technically, the f_i may be parametrized in terms of $\sin^2 \theta$ to ensure continuous variability and hence differentiability. This yields, for all states j with $0 < f_j < 1$, the condition

$$H_{jj}^{\text{GKS}} = \langle \psi_j | \left(-\frac{\nabla^2}{2} + \hat{v}_{\text{Hxc}+U} \right) | \psi_j \rangle = \epsilon_F. \quad (5)$$

Thus, ϵ_F is indeed the Fermi level as expected, i.e., the degenerate GKS eigenvalue of g partially filled states.

Let us explore the generalized eigensystem further. We premultiply Eq. (3) with $\langle \psi_k |$ and trace, to find

$$(h_{kj}^{\text{GKS}} - \epsilon_F) f_j = \sum_i \delta_{ki} \lambda_{ij} = \lambda_{kj}. \quad (6)$$

Consider the unitary matrix A that diagonalizes the matrix λ , such that $\Lambda_i = A_{ik}^\dagger \lambda_{kl} A_{li}$. The eigenvectors of $\hat{h}^{\text{GKS}}$ are the canonical GKS orbitals,

$$|\Psi_i\rangle = \sum_j |\psi_j\rangle A_{ji}. \quad (7)$$

Let us verify that unitary orbital transformations leave E_v unchanged. For the kinetic energy, for example,

$$\sum_i f_i \frac{\langle \Psi_i | \nabla^2 | \Psi_i \rangle}{2} = \sum_i f_i \frac{\langle \psi_k | \nabla^2 | \psi_l \rangle A_{li} A_{ik}^\dagger}{2}, \quad (8)$$

which is as in the original E_v by the property of unitary matrices. Similarly, it is straightforward to show that all other terms are unitary invariant, including the energy $E_{v\text{Hxc}+U}$, as this is comprised of density (and possibly its spatial derivatives) dependent terms, where the density is unitary invariant, or density-matrix dependent terms, as in the DFT+ U and/or exact exchange energies, which can also be readily shown to be invariant under unitary transformations of the GKS orbitals.

The matrix A may be expected to change as the total electron count N (an external parameter) is varied, as it shortly will be, and if A couples states of different occupancy, this would considerably complicate the analysis. It is necessary therefore to verify whether the f_i may validly be considered to be independent of A , e.g., for constructing the density matrix $\hat{\rho}$. Let us again consider, for this, the expression $\lambda_{ji}^* = \lambda_{ij}$. At the minimum of E_v , we have from Eq. (6), therefore

$$(h_{ji}^{\text{GKS}*} - \epsilon_F) f_i = (h_{ij}^{\text{GKS}} - \epsilon_F) f_j, \quad (9)$$

but noting that $\hat{h}^{\text{GKS}}$ itself is hermitian, this implies that either $f_i = f_j$ or $h_{ij}^{\text{GKS}} = 0$ for any pair of differing states i and j . Thus, somewhat remarkably, the GKS Hamiltonian is block-diagonal, with no coupling between fully filled, partially filled, or empty states. Without loss of generality, then, the unitary matrix A and hence the canonical eigensystem

retains the same block-diagonal structure. Even if there were multiple different noninteger f_i considered, it would not be necessary to consider the variation of the degeneracy pattern of the f_i with external parameters unless the parameters vary sufficiently to cause crossing of states and a rearrangement of the block-diagonal Hamiltonian structure. For sufficiently small variations of the external parameters (as we will see, adding or subtracting is a sufficiently small change in crystals), we conclude that the degeneracy grouping of the f_i remains constant as the ϵ_i and Ψ_i change.

Referring back, as a final preliminary observation with the latter result in hand, to Eq. (6), and considering the case $f_i = 1$, we find that the unitary transformation also diagonalizes h_{kj}^{GKS} . This, in terms of the eigenvalues ϵ_i of the GKS Hamiltonian for fully occupied eigenvalues, gives $\epsilon_i - \epsilon_F = \Lambda_i$. For the case $f_i = 0$, i.e., unoccupied orbitals, we deduce that $\Lambda_i = 0$. For the case of frontier orbitals, with $0 < f_i < 1$, let us suppose that there are g such degenerate GKS eigenstates with the same f_i , so that $g f_i = N - [N]$. This gives $(\epsilon_i - \epsilon_F)(N - [N])/g = \Lambda_i$. However, we already know that for such orbitals $H_{ii}^{\text{GKS}} = \epsilon_F$, and so also following diagonalization of this isolated Hamiltonian block (noting that rotation preserves the trace), we must have $\epsilon_i = \epsilon_F$ and hence also in this case $\Lambda_i = 0$.

B. Energy variations with respect to total electron count

We are now ready to consider the rate of change of the minimized total energy E_v with respect to the total electron count N , having set the problem up somewhat differently to Ref. [170] and instead as per Ref. [180]. This derivative is necessarily a total one; however, for all N we note that E_v is minimized with respect to its degrees of freedom $\{\psi_i\}$, $\{\psi_i^*\}$, f_i , λ_{ij} , λ_{ij}^* , and ϵ_F , and so the partial derivatives of E_v with respect to these vanish. We therefore have, when evaluated at all but points of eigenvalue cross-over or degeneracy change of the frontier orbitals, the great simplification

$$\frac{dE_v}{dN} = \frac{\partial E_v}{\partial N} = \epsilon_F. \quad (10)$$

This holds, in principle, even for infinite degeneracy g as in a solid. This result is the generalization of Janak's theorem to GKS in the presence of Hermitian, possibly density-matrix-dependent nonlocal potentials as in DFT+ U and hybrid functionals, with possibly degenerate frontier orbitals. From Eq. (10) and under the same conditions, it follows that the second derivative of the total energy with respect to total electron count may be expressed as

$$\frac{d^2 E_v}{dN^2} = \frac{d\epsilon_F}{dN} = \sum_i \frac{df_i}{dN} \frac{d\epsilon_F}{df_i} = g \frac{1}{g} \frac{d\epsilon_F}{df_i} = \frac{d\epsilon_F}{df_i}, \quad (11)$$

where the sum runs over all frontier (i.e., partially filled) orbitals. The k th derivative is similarly

$$\frac{d^k E_v}{dN^k} = \frac{d^{k-1} \epsilon_F}{df_i^{k-1}}. \quad (12)$$

Conventional DFT+ U and Hybrid functionals are explicit, infinitely differentiable functionals of the first-order reference-system reduced density matrix and as such will vary continuously with respect to the g frontier GKS orbital

occupancies, and hence with respect to N . Therefore, one may employ a Taylor expansion of the total energy functional, for example, around an integer electron count N_0 to yield the following expression for the total energy of the $N_0 + 1$ electron system,

$$E_v(N_0 + 1) = E_v(N_0) + \sum_{k=1}^{\infty} \frac{1}{k!} \frac{d^k E_v}{dN^k} \Big|_{N=N_0} (1 - 0)^k. \quad (13)$$

Combining Eqs. (12) and (13) with some rearranging yields the following expression for the electron affinity,

$$\begin{aligned} EA \equiv E_v(N_0) - E_v(N_0 + 1) &= -\epsilon_F - \sum_{k=2}^{\infty} \frac{1}{k!} \frac{d^{k-1} \epsilon_F}{df_F^{k-1}} \Big|_{f_F=0} \\ &= -\epsilon_L - \sum_{k=1}^{\infty} \frac{1}{k+1!} \frac{d^k \epsilon_L}{df_L^k} \Big|_{f_L=0}, \end{aligned} \quad (14)$$

where ϵ_L is the possibly degenerate lowest unoccupied GKS eigenvalue of the N_0 electron system, and f_L is its occupancy. Similarly, for the ionization potential, we can deploy a Taylor expansion considering electron removal, of the form

$$E_v(N_0 - 1) = E_v(N_0) + \sum_{k=1}^{\infty} \frac{1}{k!} \frac{d^k E_v}{dN^k} \Big|_{N=N_0} (0 - 1)^k. \quad (15)$$

Combining Eqs. (12) and (15) with some rearranging yields the following expression for the ionization potential,

$$\begin{aligned} IP \equiv E_v(N_0 - 1) - E_v(N_0) &= -\epsilon_F - \sum_{k=2}^{\infty} \frac{(-1)^{k-1}}{k!} \frac{d^{k-1} \epsilon_F}{df_F^{k-1}} \Big|_{f_F=1} \\ &= -\epsilon_H - \sum_{k=1}^{\infty} \frac{(-1)^k}{k+1!} \frac{d^k \epsilon_H}{df_H^k} \Big|_{f_H=1}, \end{aligned} \quad (16)$$

where ϵ_H is the possibly degenerate (with not necessarily the same degeneracy factor as ϵ_L) highest occupied GKS eigenvalue of the N_0 electron system, and f_H is its occupancy. Finally, the fundamental band gap is given as the difference between the electron affinity and ionization potential, and so may be expressed as

$$\begin{aligned} E_g \equiv IP - EA &= \epsilon_L - \epsilon_H \\ &+ \sum_{k=1}^{\infty} \frac{1}{k+1!} \left(\frac{d^k \epsilon_L}{df_L^k} \Big|_{f_L=0} - (-1)^k \frac{d^k \epsilon_H}{df_H^k} \Big|_{f_H=1} \right). \end{aligned} \quad (17)$$

This result accounts for the possibly different degeneracy of the lowest unoccupied and highest occupied GKS levels of an N_0 -electron insulator, the degeneracy factors having already canceled out in the expression. The result only holds straightforwardly if there is no degeneracy breaking or discrete orbital re-ordering of the lowest unoccupied GKS level as an electron is continuously added (or, separately, of the highest occupied GKS level as an electron is removed); however, this is assured in an infinite pristine solid with no spontaneous charge localization, as we go on to show in Sec. V.

First, however, we note that for many commonplace functionals in many systems, the quadratic term in the total energy

overwhelmingly dominates [182]. In the case we can write

$$E_g^{\text{quadratic}} = \epsilon_L - \epsilon_H + \frac{1}{2} \left(\frac{d\epsilon_L}{df_L} + \frac{d\epsilon_H}{df_H} \right), \quad (18)$$

albeit this is no easier to calculate than the energies of explicit electron addition and removal. For the case instead where a functional exhibits precise piecewise linearity with respect to electron count, which the exact functional should [183–185], then both ϵ_L and ϵ_H remain constant over the electron count intervals for which they serve, respectively, as the Fermi level. Then, all the derivative terms vanish in Eq. (17). In such a GKS approximation, therefore, an analog of Koopmans' theorem holds both for electron removal and attachment, and we simply have for the fundamental gap the result $E_g^{\text{linear}} = \epsilon_L^{\text{linear}} - \epsilon_H^{\text{linear}}$, for any system that it is applied to, not just pristine solids. We caution, however, that piecewise linearity does not imply that the exact functional is at hand, and in the exact functional there will be an explicit derivative discontinuity [186], as, unlike conventional DFT+*U* or hybrid functionals, the exact functional is not an explicit, differentiable functional of the first-order reference-system reduced density matrix.

The many-body generalization of the Burgess-Linscott-O'Regan (mBLOR) DFT+*U* functional [187] introduces such an explicit derivative discontinuity, while conventional DFT+*U* or hybrid functionals exhibit only an implicit derivative discontinuity. Unlike implicit derivative discontinuities, such explicit contributions are not incorporated within the GKS eigenspectrum gap [169], i.e., do not appear in Eq. (17), and require explicit addition to E_g . The need for the exact functional to exhibit such an explicit derivative discontinuity is discussed in Appendix B.

If DFT+*U* brings an approximate functional closer to agreement with global piecewise linearity, we can suppose that DFT+*U* makes it a better approximation to use $E_g \approx \epsilon_L - \epsilon_H$ in defective solids and molecules, but it will still be approximate. Even with the most sophisticated DFT+*U* correction or hybrid functional, the energy and its derivatives are not exact and beyond-quadratic, and hence we can expect nonvanishing noncancelling derivative contributions in Eq. (17). As a result, we might expect the GKS frontier eigenvalue difference $\epsilon_L - \epsilon_H$, i.e., the commonplace 'gap' extracted from the DFT+*U* density of states, to be an invalid value for the fundamental band gap. As we will see in the next section, however, its validity is perfectly recovered in extended systems under the preconditions often repeated here.

This does not mean to imply, of course, that the fundamental band gap calculated from $\epsilon_L - \epsilon_H$, or further corrections to this per Eq. (17) as may be necessary, will bear a good resemblance to the experimental fundamental gap (even leaving aside zero-point phonon renormalization effects, etc.). It only implies that such a quantity is valid, i.e., gives the same result as explicit gap calculation by electron addition and removal. In particular, if $E_v[N]$ lacks or severely underestimates the derivative discontinuity at N_0 , as it does so typically with LDA and GGA functionals, then the predicted fundamental gap will be zero or severely underestimated at best. It is part of the success of DFT+*U* and hybrids that they introduce such a derivative discontinuity, but we find here that their introduction (because it is an implicit and not an explicit

derivative discontinuity) does not affect the validity of the GKS eigenvalue-based band gap in principle.

V. FRONTIER GKS EIGENVALUE DERIVATIVES

To understand why the GKS eigenvalue derivatives in Eq. (17) do not contribute to the fundamental band gap in the case of defect-free infinitely extended systems, we now derive an explicit expression for the first-order derivative of the frontier GKS eigenvalue ϵ_F with respect to its orbital occupancy f_F . Here, F can refer either to the highest occupied (H) or lowest unoccupied (L) GKS orbital, and it may be degenerate. Due to the orthogonality of wavefunctions with their derivatives, the derivative of the frontier GKS eigenvalue with respect to the frontier orbital occupancy simplifies to

$$\frac{d\epsilon_F}{df_F} = \langle \Psi_F | \frac{d\hat{H}^{\text{GKS}}}{df_F} | \Psi_F \rangle. \quad (19)$$

Here, total derivatives imply that all variational parameters are permitted to vary as needed to extremize the total energy. The GKS Hamiltonian operator in real space is given by

$$H^{\text{GKS}}(\mathbf{r}, \mathbf{r}') = -\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{Hxc}}(\mathbf{r}) + v_U(\mathbf{r}, \mathbf{r}'), \quad (20)$$

where $v_{\text{ext}}(\mathbf{r})$ is the external potential, which is kept fixed throughout this work. Additionally, $v_{\text{Hxc}}(\mathbf{r})$ is the Hartree plus base exchange-correlation potential of local or semilocal character, and $v_U(\mathbf{r}, \mathbf{r}')$ is the DFT+ U (+ J) potential. Aside from the latter nonlocal potential, the other two terms in the GKS potential include Dirac delta functions $\delta(\mathbf{r} - \mathbf{r}')$, which have been suppressed in Eq. (20) for brevity. The reference system kinetic energy operator and external potential exhibit no dependence on the GKS orbital occupancies. The Hartree plus exchange-correlation potential will contribute to the derivative via its explicit dependence on the ground-state electron density ρ_0 via

$$\frac{dv_{\text{Hxc}}(\mathbf{r})}{df_F} = \int d\mathbf{r}' \frac{\delta v_{\text{Hxc}}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \bigg|_{\rho_0} \left(\frac{d\rho_0(\mathbf{r}')}{df_F} \right). \quad (21)$$

The first term on the right-hand side is the Hartree plus base exchange-correlation kernel. In the case of the highest occupied or lowest unoccupied GKS orbital, i.e., $f_F = f_H$ or f_L , the final term in Eq. (21) is the right- or left-hand Fukui function $F_{\pm}(\mathbf{r}')$ [188–193], which is a quantity that incorporates screening effects. Therefore, Eq. (21) simplifies to

$$\frac{dv_{\text{Hxc}}(\mathbf{r})}{df_F} = \int d\mathbf{r}' f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') F_{\pm}(\mathbf{r}'), \quad (22)$$

where $f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}')$ is the Hxc kernel. In the frozen orbital approximation, the Fukui function is given by the frontier GKS orbital density; however, we do not make such an approximation. The Hxc kernel can be decomposed into a sum of Hartree and exchange-correlation components, where the Hartree kernel is given by the usual expression

$$f_H(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}, \quad (23)$$

while the base exchange-correlation kernel depends, of course, on the choice of exchange-correlation functional. For the Hubbard potential, we invoke here as a representative case the DFT+ U functional of Dudarev *et al.* [176], although we

emphasize that the same proof holds with caveats (that are always satisfied or overcome in practice) for all known DFT+ U functionals, a point which will be elaborated upon further in Sec. X. For concision, we denote the effective Hubbard parameter simply as U in this section. In real space within the spin-restricted formalism, the Hubbard potential of Dudarev *et al.* may be expressed as

$$v_U^{\sigma}(\mathbf{r}, \mathbf{r}') = \sum_I \frac{U^I}{2} \left\{ \langle \mathbf{r} | \hat{P}^I | \mathbf{r}' \rangle - \int d\mathbf{r}'' d\mathbf{r}''' \langle \mathbf{r} | \hat{P}^I | \mathbf{r}'' \rangle \times \rho(\mathbf{r}'', \mathbf{r}''') \langle \mathbf{r}''' | \hat{P}^I | \mathbf{r}' \rangle \right\}. \quad (24)$$

The derivative of the Hubbard potential with respect to frontier GKS orbital occupancy is given by

$$\frac{dv_U(\mathbf{r}, \mathbf{r}')}{df_F} = \int d\mathbf{r}'' d\mathbf{r}''' \frac{\delta v_U(\mathbf{r}, \mathbf{r}')}{\delta \rho(\mathbf{r}'', \mathbf{r}''')} \bigg|_{\rho_0} \left(\frac{d\rho_0(\mathbf{r}'', \mathbf{r}''')}{df_F} \right). \quad (25)$$

The latter derivative in Eq. (25) is the right- or left-hand Fukui matrix $F_{\pm}(\mathbf{r}'', \mathbf{r}''')$ [194–197], i.e., the screened rate of change of the ground-state (KS or, here, GKS) density matrix. This quantity is sometimes termed a “noninteracting” Fukui matrix since it applies to the Kohn-Sham reference density matrix. This term allows it to be distinguished from its counterpart in first-order reduced density matrix functional theory [198,199], but given both the GKS and DFT+ U context, and the risk that this might misleadingly imply “unscreened,” we do not use this term. The functional derivative of the Hubbard potential can be explicitly calculated from Eq. (24), to yield

$$\frac{dv_U(\mathbf{r}, \mathbf{r}')}{df_F} = - \sum_I \frac{U^I}{2} \int d\mathbf{r}'' d\mathbf{r}''' \times (\langle \mathbf{r} | \hat{P}^I | \mathbf{r}'' \rangle \langle \mathbf{r}''' | \hat{P}^I | \mathbf{r}' \rangle) F_{\pm}(\mathbf{r}'', \mathbf{r}'''). \quad (26)$$

Combining Eqs. (22) and (26) with Eq. (19) and given that the diagonal element of the Fukui matrix is equal to the Fukui function [200], we have

$$\begin{aligned} \frac{d\epsilon_F}{df_F} = \langle \Psi_F | \int d\mathbf{r} d\mathbf{r}' | \mathbf{r} \rangle \bigg\{ \int d\mathbf{r}'' f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}'') F_{\pm}(\mathbf{r}'', \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \\ - \sum_I \frac{U^I}{2} \int d\mathbf{r}'' d\mathbf{r}''' (\langle \mathbf{r} | \hat{P}^I | \mathbf{r}'' \rangle \langle \mathbf{r}''' | \hat{P}^I | \mathbf{r}' \rangle) \\ \times F_{\pm}(\mathbf{r}'', \mathbf{r}''') \bigg\} \langle \mathbf{r}' | \Psi_F \rangle. \end{aligned} \quad (27)$$

The Hxc contribution to the eigenvalue derivative consists of three integrals over real space, one of which is countered by the Dirac delta function $\delta(\mathbf{r} - \mathbf{r}')$, which is zero for all $|\mathbf{r} - \mathbf{r}'| > 0$. Assuming the added electron or hole delocalizes over the bulk system, the frontier orbital density $\rho_F(\mathbf{r}) = \langle \mathbf{r} | \Psi_F \rangle \langle \Psi_F | \mathbf{r} \rangle$ will tend to zero at any given point in space. Likewise, the Fukui function $F^{\pm}(\mathbf{r}'', \mathbf{r}''')$, which is defined as the derivative of the total electron density at the point $\mathbf{r}''$ with respect to the total electron count, will tend to zero, as the addition of a single electron or hole to the system will offer only an infinitesimal change in the total electron density at

any point in space. The vanishing frontier orbital density and Fukui function counter the remaining two spatial integrals. This, combined with the Hxc kernel $f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}')$ vanishing in the limit of large $|\mathbf{r} - \mathbf{r}'|$, ensures that the Hxc contribution to the eigenvalue derivative vanishes in the bulk limit (excluding cases of spontaneous localization of added electrons or holes, a caveat that we hereafter assume is satisfied).

In the case of the Hubbard contribution, there are four spatial integrals and a summation over the Hubbard sites. The $\langle \mathbf{r} | \hat{P}^I | \mathbf{r}'' \rangle \langle \mathbf{r}''' | \hat{P}^I | \mathbf{r}' \rangle$ term offers a negligible contribution for large values of $|\mathbf{R}_I - \mathbf{r}|$, where $\mathbf{R}_I$ is the position of the atomic site to which the localized projection operator $\hat{P}^I$ is assigned; the same goes for large values of $|\mathbf{R}_I - \mathbf{r}'|$, $|\mathbf{R}_I - \mathbf{r}''|$ and $|\mathbf{R}_I - \mathbf{r}'''|$. This counters the four spatial integrals. Analogous to the frontier orbital density and Fukui function, the frontier orbital density matrix $\rho_F(\mathbf{r}', \mathbf{r}) = \langle \mathbf{r}' | \Psi_F \rangle \langle \Psi_F | \mathbf{r} \rangle$ and Fukui matrix $F^\pm(\mathbf{r}'', \mathbf{r}''')$ will also tend to zero in the bulk limit. This ensures that, like the Hxc contribution, the Hubbard contribution to the eigenvalue derivative vanishes in the bulk limit.

The same argument can also be applied to all higher-order derivatives of the frontier GKS eigenvalue with respect to GKS occupancy, as these may also be expressed as integrals over real space of the Hxc kernel and $\langle \mathbf{r} | \hat{P}^I | \mathbf{r}'' \rangle \langle \mathbf{r}''' | \hat{P}^I | \mathbf{r}' \rangle$ Hubbard term, the frontier orbital density and frontier orbital density matrix, the Fukui function and Fukui matrix and derivatives thereof. Take, for example, the second derivative of the frontier GKS eigenvalue with respect to GKS occupancy,

$$\begin{aligned} \frac{d^2 \epsilon_F}{df_F^2} = & \int d\mathbf{r} d\mathbf{r}' [\rho_F^\pm(\mathbf{r}) F^\pm(\mathbf{r}') + \rho_F(\mathbf{r}) F'_\pm(\mathbf{r}')] f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \\ & + \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \rho_F(\mathbf{r}) F^\pm(\mathbf{r}') f'_{\text{xc}}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') F^\pm(\mathbf{r}'') \\ & - \sum_I \frac{U^I}{2} \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' [\rho_F^\pm(\mathbf{r}', \mathbf{r}) F^\pm(\mathbf{r}'', \mathbf{r}''') \\ & + \rho_F(\mathbf{r}', \mathbf{r}) F'_\pm(\mathbf{r}'', \mathbf{r}''')] \langle \mathbf{r} | \hat{P}^I | \mathbf{r}'' \rangle \langle \mathbf{r}''' | \hat{P}^I | \mathbf{r}' \rangle, \end{aligned} \quad (28)$$

where derivatives are denoted by a prime mark. Using the same arguments as before, each term will again vanish in the bulk limit. It is worth emphasizing that the exact same argument of the frontier GKS eigenvalue derivatives presented here for DFT+*U*-type functionals also applies to hybrid functionals, and of course (if $U = 0$) the underlying base local or semilocal functionals. By way of example, in the case of global hybrid functionals the first derivative of the GKS eigenvalue with respect to frontier occupancy in the spin-restricted formalism will instead be given by

$$\begin{aligned} \frac{d\epsilon_F}{df_F} = & \langle \Psi_F | \int d\mathbf{r} d\mathbf{r}' |\mathbf{r}\rangle \left\{ \int (f_{\text{Hc}}(\mathbf{r}, \mathbf{r}'') + (1 - a_{\text{HF}}) f_{\text{x}}(\mathbf{r}, \mathbf{r}'')) \right. \\ & \times F_\pm(\mathbf{r}'', \mathbf{r}'') \delta(\mathbf{r} - \mathbf{r}') d\mathbf{r}'' - \frac{a_{\text{HF}}}{2} \frac{F_\pm(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \left. \right\} |\mathbf{r}' \rangle | \Psi_F \rangle, \end{aligned} \quad (29)$$

where a_{HF} is the fraction of exact exchange, $f_{\text{Hc}}(\mathbf{r}, \mathbf{r}'')$ is the Hartree plus (semi)local correlation kernel, and $f_{\text{x}}(\mathbf{r}, \mathbf{r}'')$ is the (semi)local exchange kernel, which is diagonal in spatial coordinates. The exact exchange contribution consists of two spatial integrals. However, again there will be a negligible

contribution for large values of $|\mathbf{r} - \mathbf{r}'|$, and the frontier orbital density matrix and Fukui matrix both tend to zero. Thus, like all other terms, the exact exchange contribution to the GKS eigenvalue derivative vanishes in the bulk limit.

Therefore, in the specific case of an infinite pristine solid where the added electron or hole delocalizes over the bulk system, the first and all higher-order derivatives of the frontier GKS eigenvalues with respect to orbital occupancy can be neglected and Eqs. (14), (16), and (17) reduce to the simple expressions,

$$\text{IP} = -\epsilon_{\text{H}}, \quad (30)$$

$$\text{EA} = -\epsilon_{\text{L}}, \quad (31)$$

$$E_{\text{g}} = \epsilon_{\text{L}} - \epsilon_{\text{H}}. \quad (32)$$

In the case of a conventional DFT+*U* or hybrid functional, Eq. (32) demonstrates that the frontier GKS eigenvalue difference is a rigorous and formally exact approach to evaluating the fundamental band gap of a pristine solid. Furthermore, from Eqs. (30) and (31), the negative of the highest occupied and lowest unoccupied GKS eigenvalues are exactly equal to the ionization potential and electron affinity of the bulk system. Equation (30) is equivalent in form to the ionization potential theorem, also known as the DFT Koopmans' theorem, an exact condition in DFT which the above derivation demonstrates must always be satisfied by conventional DFT+*U* and hybrid functionals for pristine solids. Perhaps more surprisingly, no derivative discontinuity term appears in Eq. (31). This is a direct result of conventional DFT+*U* and hybrid functionals being explicit, differentiable functionals of the first-order reference-system reduced density matrix. Despite Eqs. (30), (31), and (32) being formally exact at this level of theory, it does not imply that such functionals will yield quantitatively accurate predictions. Rather, for a given functional, equating the negative of the frontier GKS eigenvalues to the functional's predicted ionization potential and electron affinity for the system is a correct and formally exact procedure at this level of theory.

However, we emphasize that this proof only holds in the case of pristine periodic systems where the added electron or hole delocalizes over the bulk system. For finite electronic systems, nonpristine solids, or systems with spontaneous charge carrier localization, one can no longer assume that the added electron or hole delocalizes over the bulk system. By extension, one cannot assume that the frontier orbital density $\rho_F(\mathbf{r}) = \langle \mathbf{r} | \Psi_F \rangle \langle \Psi_F | \mathbf{r} \rangle$ will tend to zero at every point in space. Same too goes for the frontier orbital density matrix, the Fukui function and the Fukui matrix. Thus, the frontier eigenvalue derivatives of Eqs. (14), (16), and (17) must be accounted for, and the frontier GKS eigenvalue difference is not a valid measure of the fundamental band gap of such systems.

That said, for defective crystals with low lowest-energy singly ionized defect binding energies, i.e., "shallow" defect levels, the localization of the corresponding electron and hole may be relatively weak, i.e., long-ranged, compared to the case of "deep" defect levels. In such cases, it may be found that such DFT+*U* GKS eigenvalues match well, in practice, with the corresponding total-energy based transition Fermi

levels. As a consequence, the resulting GKS band-edges eigenvalue gap may be an acceptable estimate, in that case, of the true fundamental gap of the approximate DFT method being used. The magnitude of the corrective term describing localization, e.g., Eqs. (27) and (28) in such systems is worthy of future study.

Equations (30), (31), and (32) remain valid in the case of a pristine bulk system with frontier GKS eigenvalues evaluated using a conventional DFT+ U or hybrid functional. This is also the case with application of norm-conserving pseudopotentials, ultrasoft pseudopotentials, or the projector-augmented wave method, as detailed in Appendixes C and D. The results can also be readily generalized to spin-unrestricted GKS theory, as we briefly outline in Appendix E. In order to elaborate further on how the above proof of the validity of the GKS gap in the bulk limit applies not only to Dudarev's functional but to all other known DFT+ U functionals (subject only to caveats that are satisfied or accounted for in practice), we next provide a brief overview of the mathematical form and original derivation of every collinear-spin DFT+ U -type functional known by the present authors to have been published. We also discuss a representative noncollinear DFT+ U -type functional that is more than a generalization of one of the latter. We hope that the following section will provide a comprehensive, up-to-date compendium of collinear-spin DFT+ U functionals within a unified notation.

VI. THE ORIGINAL DFT+ U FUNCTIONALS

The DFT+ U method was originally developed by Anisimov *et al.* [89] to alleviate the shortcomings of the local spin density approximation (LSDA) in describing Mott insulators. In particular, Anisimov *et al.* noted the LSDA's severe underestimation of the band gap and local magnetic moments in 3d-transition-metal oxides, with the LSDA even predicting CoO and FeO as being metallic [201].

However, these systems are well described by the simple multiband Hubbard model. Anisimov *et al.* proposed supplementing the local density approximation (LDA) with an additional interaction energy term to treat the localized 3d states,

$$E_{\text{int}} = \frac{U}{2} \sum_{\sigma m m'} n_{mm}^{\sigma} n_{m'm'}^{\bar{\sigma}} + \frac{U-J}{2} \sum_{\substack{\sigma m m' \\ m \neq m'}} n_{mm}^{\sigma} n_{m'm'}^{\sigma}, \quad (33)$$

where U and J are the Hubbard U and Hund's rule exchange parameters and n_{mm}^{σ} is the spin- σ occupancy of orbital m , which can be defined as

$$n_{mm'}^{\sigma} = \langle \phi_m^I | \hat{\rho}^{\sigma} | \phi_{m'}^I \rangle, \quad (34)$$

where $\hat{\rho}^{\sigma}$ is the spin- σ Kohn-Sham density operator and $\{\phi_m^I\}$ are the set of atomically localized orbitals at atom I (the atomic site index is often suppressed for clarity). This interaction term is simply the expectation value of the Hubbard model Hamiltonian,

$$\hat{H}_{\text{mod}} = \frac{U}{2} \sum_{mm'\sigma} \hat{n}_{m\sigma} \hat{n}_{m'\bar{\sigma}} + \frac{U-J}{2} \sum_{\substack{\sigma m m' \\ m \neq m'}} \hat{n}_{m\sigma} \hat{n}_{m'\sigma}, \quad (35)$$

where only the on-site interaction term has been considered, i.e., the hopping term has been excluded. However, the inter-electron interactions described by Eq. (34) have already been accounted for to a less favorable extent by the LDA functional itself. This necessitates the use of a double-counting correction scheme. Anisimov *et al.* postulated that the on-site inter-electron interactions would be well described by the LDA in the homogeneous limit, i.e., when each of the $2(2l+1)$ orbitals is equally occupied, where l is the orbital angular momentum quantum number. The orbital occupancies in Eq. (33) are thus replaced by the deviation from the average occupancy n_0 . This is referred to as the around-mean-field double-counting correction scheme, where for completeness the average occupancy is given by

$$n_0 = \frac{\sum_{\sigma m} n_{mm}^{\sigma}}{2(2l+1)}. \quad (36)$$

Anisimov *et al.*'s DFT+ U -type functional can be written as

$$E_u^{\text{Anisimov-AMF}} = \frac{U-J}{2} \sum_{\substack{\sigma m m' \\ m \neq m'}} (n_{mm}^{\sigma} - n_0)(n_{m'm'}^{\sigma} - n_0) + \frac{U}{2} \sum_{\sigma m m'} (n_{mm}^{\sigma} - n_0)(n_{m'm'}^{\bar{\sigma}} - n_0). \quad (37)$$

To further develop the DFT+ U method, Anisimov *et al.* [202] devised an alternative double-counting correction scheme commonly referred to as the fully localized limit double-counting scheme. Anisimov *et al.* proposed treating the 3d subspace of the transition-metal site as an isolated system that exchanges electrons with the bath (the rest of the electronic system). In this case, the total subspace energy, which they assume is solely composed of the 3d inter-electron interaction energy, should obey the piecewise linearity condition with respect to electron count, originally developed by Perdew *et al.* [183].

Anisimov *et al.* argue that the LDA yields relatively accurate total energies, but by virtue of it being an explicit and differentiable functional of the electron density, it is a continuous function of the electron count N . They therefore approximate that the 3d inter-electron interaction energy within the LDA is given as

$$E_{\text{dc}} \approx \frac{U}{2} N(N-1), \quad (38)$$

where N is the total subspace occupancy and for now we have ignored the exchange interaction parameter J . Using Eq. (38) as our double-counting correction term, in combination with a simple Hubbard-like interaction term yields

$$E_u = \frac{U}{2} \sum_{\substack{\sigma \sigma' m m' \\ \sigma m \neq \sigma' m'}} n_{mm}^{\sigma} n_{m'm'}^{\sigma'} - \frac{U}{2} N(N-1). \quad (39)$$

For systems with integer orbital occupancies ($n_{mm}^{\sigma}=0$ or 1), whose valence and conduction bands project perfectly onto the 3d subspace, this corrective functional will, to first order in perturbation theory, open a gap of magnitude U between the occupied and unoccupied Generalized Kohn-Sham states, thus alleviating the LDA's significant underestimation of the quasi-particle band gap. This corrective functional introduces a discontinuity in the XC(+ U) potential within the

Kohn-Sham scheme but does not do so in the generalized Kohn-Sham scheme, as it is an explicit functional of the first-order reference (i.e., noninteracting or partially interacting, depending on perspective) reduced spin density matrix.

Anisimov *et al.* accounted for the nonsphericity of the Coulomb interactions by using orbitally resolved Coulomb interaction parameters $U_{mm'}$ within the Hubbard-like interaction term. Accounting also for the exchange interactions, they arrived at the following final expression for the DFT+ U -type functional,

$$E_u^{\text{Anisimov-FLL}} = \frac{1}{2} \sum_{\sigma mm'} U_{mm'} n_{mm}^{\sigma} n_{m'm'}^{\bar{\sigma}} + \frac{1}{2} \sum_{\substack{\sigma mm' \\ m \neq m'}} (U_{mm'} - J_{mm'}) n_{mm}^{\sigma} n_{m'm'}^{\sigma} - \frac{U}{2} N(N-1) + \frac{J}{4} N(N-2). \quad (40)$$

Motivated by Anisimov *et al.*'s seminal papers, several groups later developed DFT+ U -type functionals using either around-mean-field or fully localized limit double-counting schemes. We will explicate some of these functionals in the following three sections.

A. Around-mean-field double-counting schemes

Czyżyk *et al.* [203] proposed using the same orbitally resolved Hubbard-like interaction term

$$E_{\text{int}} = \frac{1}{2} \sum_{\sigma mm'} U_{mm'} n_{mm}^{\sigma} n_{m'm'}^{\bar{\sigma}} + \frac{1}{2} \sum_{\substack{\sigma mm' \\ m \neq m'}} (U_{mm'} - J_{mm'}) n_{mm}^{\sigma} n_{m'm'}^{\sigma} \quad (41)$$

used by Anisimov *et al.* [202] in their DFT+ U functional with a Fully localized Limit Double Counting Scheme, as given by Eq. (40). Instead of using the average occupancy n_0 in their around-mean-field double-counting scheme, Czyżyk *et al.* propose using the average spin-resolved occupancy n_0^{σ} ,

$$E_u^{\text{Czyżyk-AMF}} = \frac{1}{2} \sum_{\sigma mm'} U_{mm'} (n_{mm}^{\sigma} - n_0^{\sigma}) (n_{m'm'}^{\bar{\sigma}} - n_0^{\bar{\sigma}}) + \frac{1}{2} \sum_{\substack{\sigma mm' \\ m \neq m'}} (U_{mm'} - J_{mm'}) (n_{mm}^{\sigma} - n_0^{\sigma}) (n_{m'm'}^{\sigma} - n_0^{\sigma}). \quad (42)$$

Pickett *et al.* [148] proposed using the spin- and orbital-resolved LDA occupancies $n_0^{\sigma mm}$ as the reference occupancies as opposed to the average spin-resolved occupancies n_0^{σ} . This ensures that the LDA solution is a stationary solution of the LDA + U functional,

$$E_u^{\text{Pickett}} = \frac{1}{2} \sum_{\substack{\sigma mm' \\ m \neq m'}} (U_{mm'} - J_{mm'}) (n_{mm}^{\sigma} - n_0^{\sigma mm}) (n_{m'm'}^{\sigma} - n_0^{\sigma m'm'}) + \frac{1}{2} \sum_{\sigma mm'} U_{mm'} (n_{mm}^{\sigma} - n_0^{\sigma mm}) (n_{m'm'}^{\bar{\sigma}} - n_0^{\bar{\sigma} m'm'}). \quad (43)$$

Motivated by the failure of Czyżyk *et al.*'s [203] around-mean-field-type functional of Eq. (42) to provide a correction to fully spin-polarized systems at half occupancy, Seo developed a new DFT+ U -type functional with an around-mean-field double-counting scheme. Seo [204] rearranged the

orbitally resolved Hubbard-like interaction term of Eq. (41) to give

$$E_{\text{int}} = \frac{1}{2} \sum_{\sigma mm'} U_{mm'} (n_{mm}^{\sigma} n_{m'm'}^{\bar{\sigma}} + n_{mm}^{\sigma} n_{m'm'}^{\sigma}) - \frac{1}{2} \sum_{\sigma mm'} U_{mm'} n_{mm}^{\sigma} n_{m'm'}^{\sigma} + \frac{1}{2} \sum_{\substack{\sigma mm' \\ m \neq m'}} (U_{mm'} - J_{mm'}) n_{mm}^{\sigma} n_{m'm'}^{\sigma}. \quad (44)$$

Seo identified the first term as the Hartree energy component E_H and proposed using average Hubbard U and Hund's J parameters for the second two terms so that

$$E_{\text{int}} = E_H - \frac{U - J}{2} \sum_{\sigma m} n_{mm}^{\sigma} n_{mm}^{\sigma} - \frac{J}{2} \sum_{\sigma} N^{\sigma} N^{\sigma}, \quad (45)$$

where N^{σ} is the total spin- σ subspace occupancy. For the double-counting correction, Seo proposed replacing the spin-resolved orbital occupancies with the average spin-resolved occupancy n_0^{σ} and argued that $(U + 2IJ)/(2I + 1)$ should be replaced simply by the Hund's J parameter. The resulting double-counting correction is

$$E_{\text{dc}} = E_H - \frac{J}{2} \sum_{\sigma} N^{\sigma} N^{\sigma}. \quad (46)$$

Seo's DFT+ U -type functional is given by the combination of the interaction term of Eq. (45) and the double-counting term of Eq. (46), yielding

$$E_u^{\text{Seo}} = -\frac{U - J}{2} \sum_{\sigma m} n_{mm}^{\sigma} n_{mm}^{\sigma}. \quad (47)$$

B. Fully localized limit double-counting schemes

Czyżyk *et al.* [203] propose using the same orbitally resolved Hubbard interaction term of Eq. (41) that Anisimov *et al.* [202] used for the original DFT+ U functional with a Fully localized Limit Double-Counting Scheme. Czyżyk *et al.* correctly pointed out that the interaction term as given by Eq. (41) in the fully localized limit (with $n_{mm}^{\sigma} = 0$ or 1) and $U_{mm'}$ and $J_{mm'}$ replaced by the average Coulomb repulsion and exchange parameters U and J , is given by

$$E_{\text{dc}} = \frac{U}{2} N(N-1) - \sum_{\sigma} \frac{J}{2} N^{\sigma} (N^{\sigma} - 1), \quad (48)$$

which slightly differs from the double-counting scheme used by Anisimov *et al.* [202]. Combining the interaction energy term given by Eq. (41) with the double-counting term given by Eq. (48) yields the DFT+ U energy functional

$$E_u^{\text{Czyżyk-FLL}} = \frac{1}{2} \sum_{\sigma mm'} U_{mm'} n_{mm}^{\sigma} n_{m'm'}^{\bar{\sigma}} + \frac{1}{2} \sum_{\substack{\sigma mm' \\ m \neq m'}} (U_{mm'} - J_{mm'}) n_{mm}^{\sigma} n_{m'm'}^{\sigma} - \frac{U}{2} N(N-1) + \sum_{\sigma} \frac{J}{2} N^{\sigma} (N^{\sigma} - 1). \quad (49)$$

In Ref. [205], Solovyev *et al.* propose a DFT+ U functional with a fully localized limit double-counting scheme, but the proposed functional is equivalent to Anisimov *et al.*'s DFT+ U functional [202] as given by Eq. (40). It is worth emphasizing

that Anisimov and Solovyev are named authors on both papers, and the later paper should be regarded as a follow-up study rather than the introduction of a novel DFT+ U functional.

Due to the neglect of off-diagonal terms in the occupancy matrix $n_{mm'}^\sigma$, the interaction energy of Eq. (41) is not rotationally invariant and, by extension, neither are the DFT+ U functionals derived from it, i.e., Eqs. (40), (42), (43), (47), and (49). Liechtenstein *et al.* [206] proposed using the full Hartree-Fock expression for the interaction energy, without neglecting the off-diagonal terms,

$$E_{\text{int}} = \frac{1}{2} \sum_{\{m\}\sigma} U_{mm''m'm'''} n_{mm'}^\sigma n_{m''m'''}^{\bar{\sigma}} + \sum_{\{m\}\sigma} (U_{mm''m'm'''} - U_{mm''m''m'}) n_{mm'}^\sigma n_{m''m'''}^\sigma, \quad (50)$$

where the real-valued $U_{mm''m'm'''}$ is defined as

$$U_{mm''m'm'''} = \langle m m'' | V_{\text{ee}} | m' m''' \rangle \quad (51)$$

and V_{ee} is the screened Coulomb kernel. Liechtenstein *et al.* [206] combined this term with the fully localized limit double-counting term given by Eq. (48) to create a rotationally invariant DFT+ U functional,

$$E_{\text{u}}^{\text{Liechtenstein}} = \frac{1}{2} \sum_{\{m\}\sigma} U_{mm''m'm'''} n_{mm'}^\sigma n_{m''m'''}^{\bar{\sigma}} + \frac{1}{2} \sum_{\{m\}\sigma} (U_{mm''m'm'''} - U_{mm''m''m'}) n_{mm'}^\sigma n_{m''m'''}^\sigma - \frac{U}{2} N(N-1) + \sum_{\sigma} \frac{J}{2} N^\sigma (N^\sigma - 1). \quad (52)$$

Dudarev *et al.* [176] later developed a rotationally invariant DFT+ U functional using only the orbital-independent U and J parameters. Combining Anisimov *et al.*'s interaction term of Eq. (33) with Czyżyk *et al.*'s fully localized limit double-counting correction of Eq. (48), Dudarev *et al.* arrived at the DFT+ U functional

$$E_{\text{u}} = \frac{U-J}{2} \sum_{m\sigma} n_{mm}^\sigma - n_{mm}^\sigma n_{mm}^\sigma. \quad (53)$$

However, this functional is not rotationally invariant. Dudarev *et al.* [176] proposed that this functional should be replaced by the following expression,

$$E_{\text{u}}^{\text{Dudarev}} = \frac{U-J}{2} \sum_{mm'\sigma} n_{mm'}^\sigma \delta_{mm'} - n_{mm'}^\sigma n_{m'm}^\sigma. \quad (54)$$

In the case of diagonal occupancy matrices, Eqs. (53) and (54) are equal. Crucially, Eq. (54) can also be written in terms of the trace over the product of spin-resolved occupancy matrices

$$E_{\text{u}}^{\text{Dudarev}} = \frac{U-J}{2} \sum_{\sigma} \text{Tr}[\mathbf{n}^\sigma] - \text{Tr}[\mathbf{n}^\sigma \mathbf{n}^\sigma] \quad (55)$$

and so, unlike Eq. (53), Eq. (54) is invariant under unitary transformations of the projector orbitals. Several modifications to the DFT+ U functional of Dudarev *et al.* [176] have also been explored in the literature. For example, Dabo [207] and Moynihan *et al.* [161] have explored the use of separate

corrective parameters for the linear and quadratic terms of Eq. (55). The latter method [161], dubbed DFT+ $U_1 + U_2$, was shown to be sufficient to simultaneously correct the total energy and frontier eigenvalue for self-interaction error in the prototypical system stretched H_2^+ . More recently, Macke *et al.* [208] have explored the use of an orbital-resolved corrective parameter, with encouraging results.

C. A hybrid double-counting scheme

Petukhov *et al.* [209] proposed using a linear interpolation between the around-mean-field and fully localized limit double-counting schemes. The authors use a parameter α , with $0 \leq \alpha \leq 1$, to interpolate between the two double-counting schemes. In the fully localized limit, where $\alpha = 1$, Dudarev *et al.*'s functional is used. This functional, as given in Eqs. (54) and (55), can also be written in the form

$$E_{\text{u}}^{\text{Dudarev}} = -\frac{U-J}{2} \left(\sum_{\sigma mm'} n_{mm'}^\sigma n_{m'm}^\sigma - \sum_{\sigma} n^\sigma (2l+1) \right). \quad (56)$$

For the $\alpha = 0$ limit, Petukhov *et al.* develop a novel DFT+ U functional with an around-mean-field double-counting scheme. The authors propose treating the first term of Eq. (56) as the interaction term,

$$E_{\text{int}} = -\frac{U-J}{2} \sum_{\sigma mm'} n_{mm'}^\sigma n_{m'm}^\sigma. \quad (57)$$

The underlying L(S)DA should yield the correct solution in the limit of uniform spin-resolved orbital occupancies, so, as before, Petukhov *et al.*'s around-mean-field (P-AMF) DFT+ U functional can be found by replacing the $n_{mm'}^\sigma$ elements with $n_{mm'}^\sigma - n^\sigma \delta_{mm'}$ so that

$$E_{\text{u}}^{\text{P-AMF}} = -\frac{U-J}{2} \sum_{\sigma mm'} (n_{mm'}^\sigma - n^\sigma \delta_{mm'}) (n_{m'm}^\sigma - n^\sigma \delta_{m'm}) = -\frac{U-J}{2} \left(\sum_{\sigma mm'} n_{mm'}^\sigma n_{m'm}^\sigma - \sum_{\sigma} (n^\sigma)^2 (2l+1) \right). \quad (58)$$

To interpolate between these two limits Petukhov *et al.* [209] proposed the double-counting correction term,

$$E_{\text{dc}} = -\frac{U-J}{2} \sum_{\sigma} (1-\alpha)(2l+1)(n^\sigma)^2 - \frac{U-J}{2} \sum_{\sigma} \alpha(2l+1)n^\sigma. \quad (59)$$

Combining the interaction and double-counting terms of Eqs. (57) and (59), Petukhov *et al.* [209] proposed the following functional with a hybrid double-counting scheme:

$$E_{\text{u}}^{\text{P-Hybrid}} = -\frac{U-J}{2} \sum_{\sigma mm'} n_{mm'}^\sigma n_{m'm}^\sigma + \frac{U-J}{2} \sum_{\sigma} (1-\alpha)(2l+1)(n^\sigma)^2 + \frac{U-J}{2} \sum_{\sigma} \alpha(2l+1)n^\sigma. \quad (60)$$

They proposed setting the value of the parameter α such that the DFT+ U functional of Eq. (60) corrects only the potential, i.e., offers no correction to the total energy. To satisfy this constraint, α is defined as

$$\alpha = \frac{\sum_{\sigma mm'} n_{mm'}^{\sigma} n_{m'm}^{\sigma} - \sum_{\sigma} (n^{\sigma})^2 (2l+1)}{(2l+1) \sum_{\sigma} n^{\sigma} (1 - n^{\sigma})}. \quad (61)$$

VII. EXTENDED DFT+ U FUNCTIONALS

A. DFT+ U + J

Himmetoglu *et al.* [149] developed an extended DFT+ U functional, nowadays often referred to as the DFT+ U + J functional, or sometimes DFT+ U + $J0$. They proposed that the full Hartree-Fock interaction term of Eq. (50) is dominated by the two-orbital Coulomb and exchange terms with interaction parameters of the form $U_{mm'mm'}$ and $U_{mm'm'm}$, respectively. Replacing these interaction parameters with their atomic averages,

$$U = \frac{1}{(2l+1)^2} \sum_{mm'} \langle m m' | V_{ee} | m m' \rangle, \quad (62)$$

and

$$J = \frac{1}{(2l+1)^2} \sum_{mm'} \langle m m' | V_{ee} | m' m \rangle, \quad (63)$$

Himmetoglu *et al.* [149] arrived at the interaction term

$$E_{\text{int}} = \frac{U}{2} \sum_{mm'\sigma} n_{mm'}^{\sigma} n_{m'm}^{\sigma} + n_{mm'}^{\sigma} n_{m'm}^{\bar{\sigma}} - n_{mm'}^{\sigma} n_{m'm}^{\sigma} + \frac{J}{2} \sum_{mm'\sigma} n_{mm'}^{\sigma} n_{m'm}^{\sigma} + n_{mm'}^{\sigma} n_{m'm}^{\bar{\sigma}} - n_{mm'}^{\sigma} n_{m'm}^{\sigma}. \quad (64)$$

This interaction term can also be written in the form

$$E_{\text{int}} = \frac{U}{2} \sum_{\sigma} \text{Tr}[\mathbf{n}^{\sigma}]^2 + \text{Tr}[\mathbf{n}^{\sigma}] \text{Tr}[\mathbf{n}^{\bar{\sigma}}] - \text{Tr}[\mathbf{n}^{\sigma} \mathbf{n}^{\sigma}] + \frac{J}{2} \sum_{\sigma} \text{Tr}[\mathbf{n}^{\sigma} \mathbf{n}^{\sigma}] + \text{Tr}[\mathbf{n}^{\sigma} \mathbf{n}^{\bar{\sigma}}] - \text{Tr}[\mathbf{n}^{\sigma}]^2. \quad (65)$$

Analogous to Dudarev's functional of Eq. (55), this interaction term is invariant under unitary transformations of the projector orbitals. Himmetoglu *et al.* choose to apply a fully localized limit double-counting scheme. Using the orbital representation that diagonalizes the occupation matrix and recalling that in the fully localized limit the orbital occupations (i.e., the diagonal elements of the occupation matrix) are equal to zero or one, one can readily show that in the fully localized limit the interaction term of Eq. (64) becomes

$$E_{\text{dc}} = \frac{U}{2} N(N-1) - \frac{J}{2} \sum_{\sigma} N^{\sigma} (N^{\sigma} - 1) + J N^{\sigma_{\text{min}}}. \quad (66)$$

Combining the interaction and double-counting terms of Eqs. (64) and (66), Himmetoglu *et al.* proposed the following

DFT+ U + J functional,

$$E_{\text{u}}^{\text{Himmetoglu}} = \frac{U-J}{2} \sum_{\sigma mm'} n_{mm'}^{\sigma} \delta_{mm'} - n_{mm'}^{\sigma} n_{m'm}^{\sigma} + \frac{J}{2} \sum_{\sigma mm'} n_{mm'}^{\sigma} n_{m'm}^{\bar{\sigma}} - J N^{\sigma_{\text{min}}}. \quad (67)$$

The final term on the right-hand side of Eq. (67) is referred to as the minority spin term and is almost always omitted in practical calculations to aid numerical convergence. Despite being derived by very distinct techniques, Eq. (67) bears a remarkable resemblance to Dudarev's functional of Eq. (54) but also contains an unlike spin interaction term.

B. DFT+ U + $U_{\uparrow\downarrow}$

Instead of using the Hartree-Fock interaction term of Eq. (64), Shishkin *et al.* used the Hubbard-like interaction term of Eq. (33) and applied the same arguments as Himmetoglu *et al.* in deriving their double-counting correction term to arrive at the following expression,

$$E_{\text{u}} = \frac{U-J}{2} \sum_{\sigma mm'} n_{mm'}^{\sigma} \delta_{mm'} - n_{mm'}^{\sigma} n_{m'm}^{\sigma} + \frac{U}{2} \sum_{\sigma mm'} n_{mm'}^{\sigma} n_{m'm}^{\bar{\sigma}} - U N^{\sigma_{\text{min}}}. \quad (68)$$

Finally, Shishkin *et al.* [210] chose to denote the like-spin interaction ($U-J$) simply by U and the unlike-spin interaction U by $U_{\uparrow\downarrow}$,

$$E_{\text{u}}^{\text{Shishkin}} = \frac{U}{2} \sum_{\sigma mm'} n_{mm'}^{\sigma} \delta_{mm'} - n_{mm'}^{\sigma} n_{m'm}^{\sigma} + \frac{U_{\uparrow\downarrow}}{2} \sum_{\sigma mm'} n_{mm'}^{\sigma} n_{m'm}^{\bar{\sigma}} - U_{\uparrow\downarrow} N^{\sigma_{\text{min}}}. \quad (69)$$

Shishkin *et al.*'s functional is equivalent to Himmetoglu *et al.*'s DFT+ U + J except that the unlike-spin interaction is of Coulomb type rather than exchange. Shishkin *et al.* proposed evaluating [211] the unlike-spin Hubbard U parameter per a formula

$$U_{\uparrow\downarrow} = -U \frac{\sum_{\sigma} \text{Tr}[\mathbf{n}_{\sigma} \mathbf{n}_{\bar{\sigma}}]}{\sum_{\sigma} \text{Tr}[\mathbf{n}_{\sigma} \mathbf{n}_{\sigma}]}, \quad (70)$$

yielding zero and $-U$ at the fully spin-polarized and non-spin-polarized limits, respectively.

C. DFT+ U + V

Campo *et al.* [212] proposed using an extended DFT+ U functional typically referred to as the DFT+ U + V method to treat both on-site and intersite interactions. Accounting for both on-site and intersite interactions, Campo *et al.* [212] started with the Hartree-Fock interaction energy,

$$E_{\text{int}} = \frac{1}{2} \sum_{\{I\}\{m\}\sigma} U_{mm'm'm'}^{I I'' I' I'''} n_{mm'}^{\sigma} n_{m'm}^{\bar{\sigma}} + \frac{1}{2} \sum_{\{I\}\{m\}\sigma} (U_{mm'm'm'}^{I I'' I' I'''} - U_{mm'm'm'}^{I I'' I'' I'}) n_{mm'}^{\sigma} n_{m'm}^{\sigma}, \quad (71)$$

where the real-valued interaction matrix elements

$$U_{mm'n'm''}^{II'I'I''} = \langle \phi_m^I \phi_{n''}^{I'} | V_{ee} | \phi_{m'}^{I'} \phi_{n''}^{I''} \rangle \quad (72)$$

have both site and orbital indices, and the occupancy matrix elements are given by

$$n_{mm'}^{\sigma II'} = \langle \phi_m^I | \hat{\rho}^\sigma | \phi_{m'}^{I'} \rangle. \quad (73)$$

Campo *et al.* neglected all but the two-orbital Coulomb terms with interaction parameters of the form $U_{mm'mm'}^{II'I'I'}$ and replaced these parameters with orbital averages

$$V^{II'} = \frac{\sum_{ij} \langle \phi_i^I \phi_j^{I'} | V_{ee} | \phi_i^I \phi_j^{I'} \rangle}{(2I_I + 1)(2I_{I'} + 1)}. \quad (74)$$

They arrived at the interaction energy expression

$$E_{\text{int}} = \sum_{II'} \frac{V^{II'}}{2} n^I n^{I'} - \sum_{II'\sigma mm'} \frac{V^{II'}}{2} n_{mm'}^{\sigma II'} n_{m'm}^{\sigma I'I}. \quad (75)$$

The interaction energy expression of Eq. (75) can also be written in terms of the trace over the product of occupancy matrices

$$E_{\text{int}} = \sum_{II'\sigma\sigma'} \frac{V^{II'}}{2} \text{Tr}[\mathbf{n}^{I\sigma}] \text{Tr}[\mathbf{n}^{I'\sigma'}] - \sum_{II'\sigma} \frac{V^{II'}}{2} \text{Tr}[\mathbf{n}^{\sigma II'} \mathbf{n}^{\sigma I'I}], \quad (76)$$

and so is invariant under unitary transformations of the projector orbitals. Campo *et al.* proposed that in the fully localized limit, the off-diagonal terms $\text{Tr}[\mathbf{n}^{\sigma II'} \mathbf{n}^{\sigma I'I}]$, where $I \neq I'$, are equal to zero. The on-diagonal terms $\text{Tr}[\mathbf{n}^{\sigma II'} \mathbf{n}^{\sigma I'I}]$ are approximated by $\text{Tr}[\mathbf{n}^{\sigma II}]$, as discussed in the derivation of Himmetoglu *et al.*'s DFT+ U + J functional. The fully localized limit double-counting correction is

$$E_{\text{dc}} = \sum_{II'} \frac{V^{II'}}{2} n^I n^{I'} - \sum_I \frac{V^{II}}{2} n^I. \quad (77)$$

Subtracting the double-counting term of Eq. (77) from the interaction term of Eq. (75), Campo *et al.* arrived at the DFT+ U functional

$$E_{\text{u}}^{\text{Campo}} = \sum_{II'\sigma mm'} \frac{U^{II'}}{2} n_{mm'}^{\sigma II'} \delta_{mm'} \delta_{II'} - \sum_{II'\sigma mm'} \frac{U^{II'}}{2} n_{mm'}^{\sigma II'} n_{m'm}^{\sigma I'I}, \quad (78)$$

where all but the same site $U^I = U^{II}$ is usually denoted by $V^{II'}$.

D. DFT+ U + F

Soler-Polo *et al.* [213] proposed using a Kanamori-like Hamiltonian for the on-site interaction,

$$\begin{aligned} \hat{H}_{\text{int}} = & \sum_{m\sigma} \epsilon_m^\sigma \hat{n}_{mm}^\sigma + U \sum_m \hat{n}_{mm}^\dagger \hat{n}_{mm}^\dagger \\ & + \frac{U-J}{2} \sum_{m \neq m', \sigma} \hat{n}_{mm}^\sigma \hat{n}_{m'm'}^\sigma + \frac{U-2J}{2} \sum_{m \neq m', \sigma} \hat{n}_{mm}^\sigma \hat{n}_{m'm'}^\sigma \\ & - \frac{J}{2} \sum_{m \neq m', \sigma} \hat{c}_{m'\sigma}^\dagger \hat{c}_{m'\sigma} \hat{c}_{m\sigma}^\dagger \hat{c}_{m\sigma}, \end{aligned} \quad (79)$$

where the last term in Eq. (79) is the spin-flip term, which is expressed in terms of creation and annihilation operators. At integer occupancy, the expectation value of Eq. (79) can be expressed as

$$E_{\text{int}} = \begin{cases} \frac{U-2J}{2} N(N-1), & N \leq \text{Tr}[\hat{P}], \\ \frac{U-2J}{2} N(N-1) \\ + J(\text{Tr}[\hat{P}] + 1)(N - \text{Tr}[\hat{P}]), & N > \text{Tr}[\hat{P}], \end{cases} \quad (80)$$

where the one-electron contribution has been omitted and it is assumed that Hund's First rule is satisfied. At noninteger occupancy, Soler-Polo *et al.* argued that the total energy should be expressed as a linear combination of the N_0 and $N_0 + 1$ energies, where $N_0 = \lfloor N \rfloor$, which yields the interaction energy

$$E_{\text{int}} = \begin{cases} \frac{U-2J}{2} N_0(2N - N_0 - 1), & N \leq \text{Tr}[\hat{P}], \\ \frac{U-2J}{2} N_0(2N - N_0 - 1) \\ + J(\text{Tr}[\hat{P}] + 1)(N - \text{Tr}[\hat{P}]), & N > \text{Tr}[\hat{P}]. \end{cases} \quad (81)$$

Like many other DFT+ U functionals, the above expression for the total energy was derived by explicitly ignoring the hopping term of the model Hamiltonian, i.e., the expressions were derived in the $U/T \rightarrow \infty$ limit. By explicitly solving the Kanamori-Hamiltonian-like model system, for a range of values of U/T and analyzing the corresponding potential, Soler-Polo *et al.* argue that the interaction term of Eq. (81) should be modified using a set of four fitting parameters $\{F_i\}$ to better model systems beyond the $U/T \rightarrow \infty$ limit. Soler-Polo *et al.* split the interaction energy of Eq. (81) into a mean-field Hartree contribution and a correlation contribution. The fitting parameters $\{F_i\}$ were then set as prefactors for each of the four terms in the correlation energy expression so that

$$\begin{aligned} E_{\text{int}} = & \frac{U-2J}{2} (N - N_0)(1 + N_0 - N) F_2 \\ & - \frac{U-2J}{2} \sum_{m\sigma} n_{mm}^\sigma (1 - n_{mm}^\sigma) F_1 \\ & - J F_3 \left(N^\dagger N^\dagger + \sum_m n_{mm}^\dagger n_{mm}^\dagger \right) \\ & + J F_4 (\text{Tr}[\hat{P}] + 1)(N - \text{Tr}[\hat{P}]) + \frac{U-2J}{2} N(N-1) \\ & + \frac{U-2J}{2} \sum_{m\sigma} n_{mm}^\sigma (1 - n_{mm}^\sigma) + J N^\dagger N^\dagger + J \sum_m n_{mm}^\dagger n_{mm}^\dagger. \end{aligned} \quad (82)$$

Finally, Soler-Polo *et al.* employed the non-spin-polarized, fully localized limit double-counting scheme of Anisimov *et al.* (with the U parameter replaced by $U - J$) to arrive at

the following expression for their DFT+ U -type functional,

$$\begin{aligned}
 E_{\text{u}}^{\text{Soler-Polo}} = & (1 - F_1) \frac{U - 2J}{2} \sum_{m\sigma} n_{mm}^{\sigma} (1 - n_{mm}^{\sigma}) \\
 & + \frac{U - 2J}{2} (N - N_0)(1 + N_0 - N) F_2 \\
 & + (1 - F_3) J \left(N^{\uparrow} N^{\downarrow} + \sum_m n_{mm}^{\uparrow} n_{mm}^{\downarrow} \right) \\
 & + J F_4 (\text{Tr}[\hat{P}] + 1)(N - \text{Tr}[\hat{P}]) - \frac{J}{4} N^2. \quad (83)
 \end{aligned}$$

VIII. DFT+ U FUNCTIONALS FROM THE FLAT-PLANE CONDITION

It has long been argued in the literature that the success of the widely used DFT+ U functional of Dudarev *et al.* can be attributed to its ability to correct for the many-electron self-interaction error. Ignoring off-diagonal occupancy matrix elements $n_{mm'}^{\sigma}$ where $m \neq m'$, Dudarev's functional,

$$\frac{U_{\text{eff}}}{2} \sum_{\sigma m} n_{mm}^{\sigma} - n_{mm}^{\sigma} n_{mm}^{\sigma}, \quad (84)$$

will enforce a linearity condition in the total energy with respect to orbital occupancy, assuming that the total energy at the bare DFT level is quadratic with respect to orbital occupancy with a curvature of U_{eff} . There is, of course, a serious caveat to this: many-electron self-interaction error is

defined as the energetic deviation from the piecewise linearity condition of Perdew *et al.*, which pertains to the total electron count rather than to the subspace orbital occupancy. Hence, enforcing a linearity condition on the total energy with respect to orbital occupancy is not rigorously justified.

However, in the case of highly localized subspaces such as that of the $3d$ transition-metal atomic sites where DFT+ U functionals are traditionally applied, the neglect of subspace-bath interactions for the purpose of deriving improved DFT+ U -type functionals may be justified. By neglecting such interactions, the subspace can be treated as an isolated electronic system and many of the exact conditions which are often used to motivate approximate XC functional expressions can then be leveraged. Once a DFT+ U -type functional has been derived, subspace-bath interaction effects can then be re-accounted for during corrective parameter evaluation, by ensuring that they are appropriately screened (we emphasize, however, that this is very much a topic of active research).

Several modern DFT+ U -type functionals have been developed to enforce exact conditions on localized subspaces, most notably the flat-plane condition [184,186,214–216] and its generalization, the tilted plane condition [217]. The flat-plane condition defines the shape of the total energy surface of a finite electron system with respect to electron count N and spin magnetization M . In the case of an electronic system with $N \leq 2$, the $E_v[N, M]$ surface will typically be composed of two triangular-shaped planes with a derivative discontinuity along the $N = 1$ line,

$$E_v[N, M] = \begin{cases} \frac{1}{2}(N + M)E_v[1, 1] + \frac{1}{2}(N - M)E_v[1, -1], & N \leq 1, \\ \frac{1}{2}(2 - N + M)E_v[1, 1] + \frac{1}{2}(2 - N - M)E_v[1, -1] + (N - 1)E_v[2, 0], & N > 1, \end{cases} \quad (85)$$

where, for simplicity, we have ignored the highly magnetized $M = \pm 2$ triplet states. Standard local and semilocal XC approximations fail to reproduce this planar energy surface and instead exhibit a spurious curvature in the total energy with respect to electron count, resulting in many-electron self-interaction error, and a spurious curvature with respect to magnetization, resulting in static correlation error.

A. Judiciously modified DFT

Bajaj *et al.* [218,219] were the first to develop a DFT+ U -type functional from the flat-plane condition. They proposed that the unlike-spin interaction term of the DFT+ U + J functional can help mitigate static correlation error, in the same spirit that Dudarev's functional acts as a corrector for many-electron self-interaction error. They asserted that the standard DFT+ U + J functional of Himmetoglu *et al.* [149] can be used to enforce the flat-plane condition in s -valence species when the s subshell is less than half filled ($N < 1$). Bajaj *et al.* argued that the unlike-spin interaction term should be modified for cases when $N > 1$ as the term increases with increased filling of the subshell, while the subspace analog of strictly correlated electrons vanishes at full occupancy. Upon assessing several functional forms, Bajaj *et al.* [218,219] arrived at the following modified DFT+ U + J functional, which they refer to as judiciously modified DFT (jmDFT),

$$E_{\text{u}}^{\text{Bajaj}} = \begin{cases} \frac{U - J}{2} \sum_{\sigma} \text{Tr}[\mathbf{n}^{\sigma} (1 - \mathbf{n}^{\sigma})] + \frac{J}{2} \sum_{\sigma} \text{Tr}[\mathbf{n}^{\sigma} \mathbf{n}^{\bar{\sigma}}], & N \leq 1, \\ \frac{U - J}{2} \sum_{\sigma} \text{Tr}[\mathbf{n}^{\sigma} (1 - \mathbf{n}^{\sigma})] + \frac{J}{2} \sum_{\sigma} \text{Tr}[(\mathbf{n}^{\sigma} - 1)(\mathbf{n}^{\bar{\sigma}} - 1)], & N > 1. \end{cases} \quad (86)$$

Bajaj *et al.* successfully employed their functional to correct for energetic errors in finite atomic and molecular test systems at fractional values of electron count and magnetization.

B. BLOR

In deriving the Burgess-Linscott-O'Regan (BLOR) DFT+ U -type functional from the flat-plane condition [220], the authors departed from the DFT+ U + J functional of Himmetoglu *et al.* and even dispensed with the Hubbard model. Instead, they specifically derived their DFT+ U -type functional based only on the principle of imposing the flat-plane (or, more generally, tilted-plane [217]) condition to DFT+ U subspaces. Specifically, they asserted that the corrective functional should satisfy four key conditions for a single orbital subspace, namely that it should (1) be a continuous function of the subspace occupancy N and spin-magnetization M . (2) Yield no correction at integer values of N and M . (3) Have a constant curvature of $-U^\sigma$ in order to mitigate the subspace analog of many-electron self-interaction error. (4) Have a constant curvature of J with respect to M in order to mitigate the subspace analog of static correlation error. BLOR is the unique simplified rotationally invariant (i.e., Dudarev-type) DFT+ U functional which satisfies these four conditions for a single orbital subspace. In the case of a multi-orbital subspace, it can be readily extended to enforce a helium-like flat-plane condition on each orbital of the localized subspace, which gives the following general expression for the BLOR functional,

$$E_{\text{BLOR}} = \begin{cases} \frac{U^\uparrow + U^\downarrow}{4} \text{Tr}[\mathbf{N} - \mathbf{N}^2] + \frac{J}{2} \text{Tr}[\mathbf{M}^2 - \mathbf{N}^2] + \frac{U^\uparrow - U^\downarrow}{4} \text{Tr}[\mathbf{M} - \mathbf{NM}], & \text{Tr}[\mathbf{N}] \leq \text{Tr}[\mathbf{P}], \\ \frac{U^\uparrow + U^\downarrow}{4} \text{Tr}[(\mathbf{N} - \mathbf{P}) - (\mathbf{N} - \mathbf{P})^2] + \frac{J}{2} \text{Tr}[\mathbf{M}^2 - (\mathbf{N} - 2\mathbf{P})^2] + \frac{U^\uparrow - U^\downarrow}{4} \text{Tr}[\mathbf{M} - \mathbf{NM}], & \text{Tr}[\mathbf{N}] > \text{Tr}[\mathbf{P}], \end{cases} \quad (87)$$

where $\mathbf{N} = \mathbf{n}^\uparrow + \mathbf{n}^\downarrow$ and $\mathbf{M} = \mathbf{n}^\uparrow - \mathbf{n}^\downarrow$ are the total subspace occupancy and magnetization matrices, respectively, and $\mathbf{P}$ is the subspace projection matrix (the identity matrix, in practice). In the case of multi-orbital subspaces, Eq. (88) corrects for the orbital analog of self-interaction error and static correlation error but, by construction, does not correct explicitly for inter-orbital errors.

As an alternative, multi-orbital generalization that includes inter-orbital many-electron self-interaction error and static correlation error corrections, Burgess *et al.* [187] proposed a DFT+ U -type functional that instead enforces a flat-plane condition once on the subspace as a whole, i.e., a neon-like flat-plane condition in the case of p orbitals, or a zinc-like flat-plane condition in the case of d orbitals. This alternative is known as the many-body generalization of the BLOR functional, or mBLOR for concision, and is given by

$$E_{\text{mBLOR}} = \begin{cases} \frac{U^\uparrow + U^\downarrow}{4} [(N - N_0) - (N - N_0)^2] + \frac{J}{2} [M^2 - N^2] + \frac{U^\uparrow - U^\downarrow}{4} F_{\text{AMSIE}}^{\text{early}}, & \text{Tr}[\mathbf{N}] \leq \text{Tr}[\mathbf{P}], \\ \frac{U^\uparrow + U^\downarrow}{4} [(N - N_0) - (N - N_0)^2] + \frac{J}{2} [M^2 - (N - 2\text{Tr}[\hat{P}])^2] + \frac{U^\uparrow - U^\downarrow}{4} F_{\text{AMSIE}}^{\text{late}}, & \text{Tr}[\mathbf{N}] > \text{Tr}[\mathbf{P}], \end{cases} \quad (88)$$

where F_{AMSIE} is known as the asymmetric many-electron self-interaction error function. The latter is a simple function of the subspace occupancy N and magnetization M , but it has eight different forms depending on occupancy conditions, and is irrelevant when $U^\uparrow = U^\downarrow$ or in practice when these are not separately calculated.

Due to their piecewise definition, the BLOR and mBLOR functionals exhibit an explicit derivative discontinuity with respect to subspace occupancy, which is a feature of the exact functional (see Appendix B). Explicit derivative discontinuities can contribute to the fundamental band gap but, unlike (and additional to) the usual implicit derivative discontinuity of DFT+ U , do not contribute to the generalized Kohn-Sham eigenvalue gap. Burgess *et al.* proposed, however, a computationally convenient scheme to “potentialize” this derivative discontinuity by adding a derivative discontinuity correction term $\hat{v}_{\Delta\text{xc}}^\sigma$ to the potential affecting only the unoccupied bands, to incorporate this contribution to the fundamental gap within the generalized Kohn-Sham gap. This correction is given by

$$\hat{v}_{\Delta\text{xc}}^\sigma = \tilde{\Delta}_{\text{xc}}[N](1 - \hat{\rho})\hat{P}(1 - \hat{\rho}), \quad (89)$$

where, for non-spin-polarized systems $\tilde{\Delta}_{\text{xc}} = U^\sigma = U - J$, except at half filling. The corresponding energy term $E_{\Delta\text{xc}}$, will yield a vanishing correction to the total energy in the case of insulators.

C. DFT+ U CI

Janesko [221] recently reported the development of an extended DFT+ U functional referred to as the DFT plus Hubbard U Configuration Interaction method (DFT+ U CI). Although its derivation is not explicitly motivated by the flat-plane condition, the functional has nevertheless been shown to reduce both many-electron self-interaction error and static correlation error in challenging molecular test systems and, as such, has been included within this section of the review. In deriving the DFT+ U CI functional, Janesko defines a partially interacting reference system through the use of the subspace projected electron interaction operator,

$$V_{\text{ee}}^{\hat{P}} = \sum_{i>j} \sum_{m\sigma\sigma'} |\phi_{m\sigma}(i)\phi_{m\sigma'}(j)\rangle U_m \langle \phi_{m\sigma}(i)\phi_{m\sigma'}(j)| \quad \text{and} \\ U_m = \langle \phi_m \phi_m | \hat{V}_{\text{ee}} | \phi_m \phi_m \rangle. \quad (90)$$

The exact total energy of the fully interacting system is given by

$$E[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{\text{ext}} + V_{\text{ee}}^{\hat{P}} | \Psi \rangle + E_{\text{H}}^{\hat{P}}[\rho] + E_{\text{xc}}^{\hat{P}}[\rho], \quad (91)$$

where here Ψ is a multideterminant wave function. The projected Hartree $E_{\text{H}}^{\hat{P}}[\rho]$ and Exchange-Correlation $E_{\text{xc}}^{\hat{P}}[\rho]$ functionals account for the remaining Hartree and Exchange-Correlation energies not incorporated within the partially

interacting reference system. Janesko argues that these two functionals can be approximated as

$$E_H^{\hat{P}}[\rho] = E_H[\rho] - \frac{1}{2} \sum_{m\sigma\sigma'} U_m n_m^\sigma n_m^{\sigma'} \quad \text{and} \quad E_{xc}^{\hat{P}}[\rho^\uparrow, \rho^\downarrow] = E_{xc}[\rho^\uparrow, \rho^\downarrow] - E_{xc}[\rho_m^\uparrow, \rho_m^\downarrow], \quad (92)$$

where ρ^σ is the total spin- σ density and ρ_m^σ is the projected spin- σ density,

$$\rho_m^\sigma(\mathbf{r}) = n_m^\sigma |\phi_m(\mathbf{r})|^2. \quad (93)$$

Equation (91) can be solved within the generalized Kohn-Sham scheme, to find the optimum ground-state single-determinant wave function Φ_0 . The total energy can be expressed as a standard DFT total energy plus a Hubbard-type corrective term,

$$E_u = \sum_m -\frac{U_m}{2} (n_m^\uparrow n_m^\uparrow + n_m^\downarrow n_m^\downarrow) - E_{xc}[\rho_m^\uparrow, \rho_m^\downarrow]. \quad (94)$$

The occupied and unoccupied GKS spin-resolved orbitals from the evaluation of Φ_0 can then be used to construct a multideterminant wavefunction, which Janesko uses as an approximation for the ground state wavefunction Ψ of the partially interacting system. Applying separate unitary transformations to the occupied and unoccupied GKS spin-resolved orbitals, Janesko showed that the Configuration Interaction Hamiltonian has an exceedingly simple structure and can be diagonalized exactly to yield a total energy which is the sum of a DFT total energy and a Hubbard-type corrective term and a non-self-consistent multiconfigurational correlation energy term,

$$E_{\text{DFT}} + \sum_m \left\{ -\frac{U_m}{2} (n_m^\uparrow n_m^\uparrow + n_m^\downarrow n_m^\downarrow) - E_{xc}[\rho_m^\uparrow, \rho_m^\downarrow] + \Delta_m - (\Delta_m^2 - 4U_m^2 n_m^\uparrow n_m^\downarrow n_{m(v)}^\uparrow n_{m(v)}^\downarrow)^{1/2} \right\}, \quad (95)$$

where $n_{m(v)}^\sigma$ is the occupancy of the unoccupied GKS orbital with spin- σ and orbital index m . Here, $2\Delta_m$ is the promotion energy associated with the doubly excited state configuration, which Janesko approximates using the GKS eigenvalues, Hubbard U_m parameters, and spin-resolved orbital occupancies.

Finally, Janesko used a weighting scheme in the multiconfigurational correlation energy term to account for the nonorthogonality between the projector states. Full exact exchange was introduced into the projector states by projecting $\hat{V}_{ee}$ onto the entire set of nonorthogonal projector states as opposed to projecting $\hat{V}_{ee}$ onto one state at a time, as specified by Eq. (90). The final expression for the DFT+*U*CI functional then becomes,

$$E_u^{\text{Janesko}} = -\frac{1}{2} \sum_{\sigma\{I\}\{m\}} U_{mm'm''m'''}^I I' I'' I''' n_{mm'}^{I'''} n_{mm''}^{I''} n_{m'm'''}^{I'} n_{m''m}^{I\sigma} - \sum_{Im} w_{Im} (\Delta_{Im}^2 - 4(U_m^I)^2 n_m^I n_m^I n_{m(v)}^I n_{m(v)}^I)^{1/2} + \sum_{Im} w_{Im} \Delta_{Im} - E_{xc}[\rho_{\hat{P}}^\uparrow, \rho_{\hat{P}}^\downarrow], \quad (96)$$

where $\rho_{\hat{P}}^\sigma$ is the total spin- σ subspace projected density and the summation on the first line runs over spins σ , orbitals $\{m\}$ and the combined shell and site indices $\{I\}$. Furthermore, we emphasize again that the multiconfigurational correlation energy contribution to Eq. (96), i.e., the terms with site- and orbital-indexed weights $\{w_{Im}\}$, is applied non-self-consistently.

IX. DFT+*U* FUNCTIONALS FOR NONCOLLINEAR SYSTEMS

Dudarev *et al.* developed a DFT+*U* functional to treat noncollinear magnetic systems [222]. They started with the on-site interaction operator used for cubic harmonic p orbitals, namely,

$$\hat{H} = \frac{1}{2} \left(U - \frac{J}{2} \right) (\hat{N}^2 - \hat{N}) - \frac{J}{4} (\hat{\mathbf{M}}^2 - 3\hat{N}) + \frac{J}{2} \sum_{mm'\sigma\sigma'} \hat{c}_{m\sigma}^\dagger \hat{c}_{m\sigma}^\dagger \hat{c}_{m'\sigma'} \hat{c}_{m'\sigma'}. \quad (97)$$

The operators $\hat{c}_{m\sigma}^\dagger$ and $\hat{c}_{m\sigma}$ are the orbital m , spin- σ creation and annihilation operators, while the total subspace electron count and magnetic moment vector operators,

$$\hat{N} = \sum_{m\sigma} \hat{c}_{m\sigma}^\dagger \hat{c}_{m\sigma} \quad \text{and} \quad \hat{\mathbf{M}} = \sum_{m\sigma\sigma'} \hat{c}_{m\sigma}^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} \hat{c}_{m\sigma'}, \quad (98)$$

and $\boldsymbol{\sigma}_{\sigma\sigma'}$ are the Pauli matrices. Focusing solely on terms in the Hamiltonian composed of two creation and two annihilation operators acting on the same electronic state, i.e., terms of the form $\hat{n}_{m\sigma} \hat{n}_{m\sigma}$, Dudarev *et al.* argued that with approximate DFT functionals such terms contribute an energy proportional to $n_{m\sigma}^2$, when they should contribute an energy proportional to $n_{m\sigma}$. In this case, the terms with a J prefactor cancel to yield the DFT+*U* functional

$$E_u = \frac{U}{2} \sum_{m\sigma} n_{mm}^\sigma - n_{mm}^\sigma n_{mm}^\sigma. \quad (99)$$

Dudarev *et al.* [222] propose modifying this functional, using the same technique applied to Eq. (53), so that the functional is invariant with respect to the choice of orbitals and spin quantization axis, specifically,

$$E_u^{\text{Dudarev-NC}} = \frac{U}{2} \sum_{\sigma\sigma'mm'} n_{mm'}^{\sigma\sigma'} \delta_{mm'} \delta_{\sigma\sigma'} - n_{mm'}^{\sigma\sigma'} n_{mm'}^{\sigma'\sigma'}, \quad (100)$$

where the occupancy matrix elements

$$n_{mm'}^{\sigma\sigma'} = \langle \phi_m^\sigma | \hat{\rho} | \phi_{m'}^{\sigma'} \rangle. \quad (101)$$

Interestingly, in the case of collinear spin systems, this functional reduces to Dudarev's standard functional of Eq. (54) except with an effective parameter $U_{\text{eff}} = U$ as opposed to $U - J$.

Several other DFT+*U* functionals have also been generalized to noncollinear spin systems, e.g., those discussed in Refs. [223–227]. A detailed exposition on these falls beyond the scope of the present study. However, while these may differ in their invariance with respect to the projection axes, no noncollinear DFT+*U* functional known to the authors exhibits an explicit derivative discontinuity or other additional cause for band-gap invalidity within the GKS bulk-limit context.

TABLE I. The DFT+ U functional checklist specifies which physical quantities must be kept fixed across the evaluation of the bulk total energies of the $N - 1$, N , and $N + 1$ electron systems to ensure agreement with the respective GKS gap.

DFT+ U functional	Hubbard parameters	Projection axes	Auxiliary parameters	Functional form
Anismiov <i>et al.</i> (AMF) [89]	✓	✓	✓	
Anismiov <i>et al.</i> (FLL) [202]	✓	✓		
Czyżyk <i>et al.</i> (AMF) [203]	✓	✓	✓	
Pickett <i>et al.</i> (AMF) [148]	✓	✓	✓	
Seo [204]	✓	✓		
Czyżyk <i>et al.</i> (FLL) [203]	✓	✓		
Liechtenstein <i>et al.</i> [206]	✓			
Dudarev <i>et al.</i> [176]	✓			
Petukhov <i>et al.</i> [209]	✓		✓	
DFT+ $U+J$ [149]	✓			
DFT+ $U+J$ (with min. spin) [149]	✓			
DFT+ $U+U_{\uparrow\downarrow}$ [210]	✓			
DFT+ $U+V$ [212]	✓			
DFT+ $U+F$ [213]	✓	✓	✓	✓
jmDFT [218]	✓			✓
BLOR [220]	✓			✓
mBLOR [187]	✓			✓
DFT+UCI [221]	✓		✓	
Dudarev <i>et al.</i> (Non-collinear) [222]	✓			

X. CHECKLIST FOR EIGENVALUE-BASED BAND-GAP VALIDITY

The proof of the validity of the DFT+ U bulk band gap has been established above using the conventional DFT+ U functional of Dudarev *et al.* [176], however, the same proof holds for all known DFT+ U functionals, discussed in the preceding section, subject only to caveats that are either satisfied or accounted for in practice. In the case of all DFT+ U functionals it is, for example, necessary but also safely assumed that the bulk total energy calculations of the $N - 1$, N and $N + 1$ electron systems are evaluated using a fixed set of Hubbard corrective parameters. In the case of the DFT+ U functional of Liechtenstein *et al.* [206] we refer here to fixing the orbital averaged U and J parameters as opposed to fixing the full four orbital indexed corrective parameters $\{U_{mm'm''m'''}\}$, similarly only the single orbital and site indexed parameter U_m^I is fixed in the DFT+ U CI functional.

For some corrective functionals, additional auxiliary parameters must also be fixed across all three bulk total energy calculations. Again, in practice, for the bulk limit it is natural to treat such auxiliary parameters on the same footing as the Hubbard corrective parameters. In the case of DFT+ U functionals with around-mean-field double-counting schemes, the auxiliary parameters refers to the reference occupancies $\{n_0\}$ which, depending on the DFT+ U functional, may include spin and orbital indices. In the case of the DFT+ U functional of Petukhov *et al.* [209] and the DFT+ $U+F$ [213] functional, the auxiliary parameters refer to the α parameter and the four fitting parameters F_1 – F_4 , respectively, while in the case of the DFT+ U CI functional it refers to the full multiconfigurational correlation energy term, which is evaluated non-self-consistently.

The on-site atomic orbital basis set axes through which the subspace projection operator is defined must also be kept

fixed for all three bulk total energy calculations in the case of DFT+ U functionals that are not invariant with respect to an on-site unitary transformation of spatial projector orbitals. This corresponds to ordinary practice, and there is no physical cause to do otherwise in the bulk limit. It goes without saying that the spatial form of the orbitals must be kept fixed, as well as any unitary orbital mixing between different sites. Finally, several modern DFT+ U functionals are defined piecewise with respect to subspace occupancy, namely the jmDFT, BLOR, mBLOR and DFT+ $U+F$ functionals, due to their explicit dependence on $N_0 = \lfloor N \rfloor$. In such cases, the same functional form must be applied in the three bulk total energy calculations to ensure agreement with the GKS gap. However, in the unusual scenario that application of two or more distinct functional forms was deemed necessary when simulating the bulk limit, the deviation between the GKS gap and the fundamental gap amounts to an explicit derivative discontinuity. This may be easily evaluated using the derivative discontinuity “potentialization” scheme mentioned in the BLOR subsection. These various caveats, which are of theoretical interest more so than practical consequence, are summarized in Table I.

A. DFT+ U energetic correction for the idealized hydrogen lattice

The DFT+ U functionals examined in Secs. VI–IX will each offer a distinct energetic correction to the total electronic energy. In Fig. 3, these energetic corrections within the spin-unrestricted formalism are compared and contrasted. As arguably the chemical system that most closely resembles the Hubbard model, the hydrogen lattice at the infinite separation limit was selected for this comparative study. In the infinite separation limit, a single electron will localize on each of the hydrogen atomic sites. In the case of the non-spin-polarized

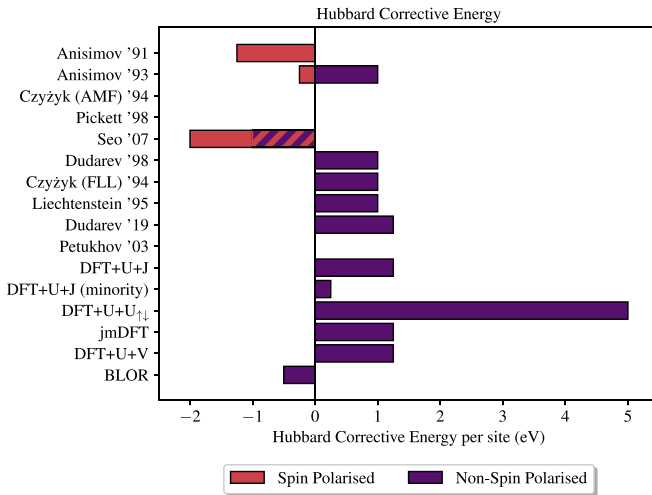


FIG. 3. DFT+*U* correction to the total energy of the spin-polarized and non-spin-polarized hydrogen lattice at the infinite separation limit upon non-self-consistent application of each DFT+*U*-type functional. The Hubbard *U*, Hund's *J*, and intersite *V* parameters were set at 5, 1, and 0 eV, respectively. Seo's DFT+*U* functional yields a negative energetic correction for both the spin-polarized and non-spin-polarized hydrogen lattices of -2 and -1 eV, respectively.

hydrogen lattice $n^\sigma = 0.5$, while in the fully spin-polarized case $n^\uparrow = 1.0$ and $n^\downarrow = 0.0$.

For this highly idealized system, almost all DFT+*U* functionals offer no energetic correction in the spin-polarized case. The notable exceptions to this are the original DFT+*U* functionals of Anisimov *et al.* The unusual performance of these two DFT+*U* functionals can be attributed to the spin-agnostic character of their double-counting correction schemes. Seo's DFT+*U* functional also offers an energetic correction in the spin-polarized case. Unlike the well-known functional of Dudarev *et al.*, Seo's functional lacks a linear term in n_{mm}^σ . Therefore, in the case of single orbital subspaces, its energetic correction will increase quadratically with respect to spin-resolved orbital occupancy.

By contrast, in the non-spin-polarized case, almost all DFT+*U* functionals offer a nonzero energetic correction. The spin-polarized and non-spin-polarized hydrogen lattices should be degenerate in the infinite separation limit. However, standard local and semilocal XC functionals are known to energetically favor the spin-polarized hydrogen lattice, an error which Fig. 3 shows will be exacerbated by application of a DFT+*U* functional, despite such corrective functionals being explicitly designed for Mott-Hubbard insulators. With the exception of BLOR and Seo '07, the spin-polarized energy correction $E_u \leq 0$ while the non-spin-polarized energy correction $E_u \geq 0$ and hence the energy difference will only increase upon application of a DFT+*U* functional. Seo '07 offers a negative energetic correction for both systems; however, the spin-polarized lattice will receive a larger energetic correction, and this functional too will exacerbate this error. By contrast, the BLOR DFT+*U* functional offers a negative energetic correction to the non-spin-polarized hydrogen lattice and no energetic correction for the spin-polarized system.

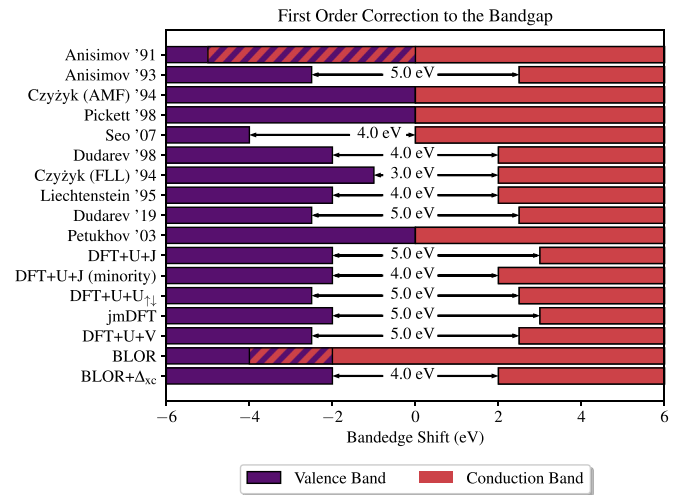


FIG. 4. Correction to the band gap of the spin-polarized hydrogen lattice at the infinite separation limit upon non-self-consistent application of each DFT+*U*-type functional. The Hubbard *U*, Hund's *J*, and intersite *V* parameters were set at 5, 1, and 0 eV, respectively. Two DFT+*U* functionals, namely Anisimov '91 and BLOR (if neglecting its unusual explicit derivative discontinuity contribution Δ_{xc}), reduce the generalized Kohn-Sham gap by 5 and 2 eV, respectively, while most other functionals increase the generalized Kohn-Sham gap of this system.

It is thus the sole DFT+*U* functional considered here that can, in principle, successfully correct this energy error given reasonable values of the parameters, i.e., whenever $U > 0$, $J > 0$ and $U > J$. Therefore, almost all DFT+*U* functionals will exacerbate the above mentioned hydrogen lattice energy error for any reasonable choice of values for the corrective parameters. The only exception to this result is the DFT+*U*+*J* functional with the minority spin term, which, like the BLOR functional, will offer a negative energetic correction to the non-spin-polarized hydrogen lattice whenever $U < 4J$.

B. DFT+*U* band-gap correction for the idealized hydrogen lattice

In practice, DFT+*U* functionals are often employed to ameliorate the band-gap problem [57,228], i.e., standard (semi)local XC functionals' tendency to vastly underestimate the fundamental band gap, frequently even predicting insulators as being metallic.

In order to elaborate further on the use of DFT+*U*-type functionals to alleviate the band-gap problem, in Figs. 4 and 5 the band-gap correction offered by a variety of DFT+*U*-type functionals within the spin-unrestricted formalism is presented. To ascertain the reported corrections to the band gap, the main result of this work is used, i.e., that the fundamental band gap of a pristine bulk system is given by the frontier GKS eigenvalue difference as specified by Eq. (32). Furthermore, it is assumed that in the infinite separation limit, the GKS orbitals at the bare DFT level can be approximated as a linear combination of the hydrogen atomic orbitals, the same atomic orbitals which are used in the definition of the projection operator $\hat{P}$ for non-self-consistent application of the DFT+*U*-type corrective functionals.

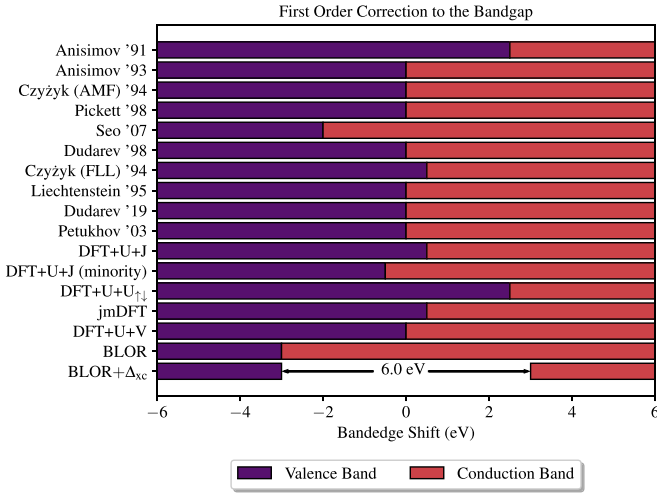


FIG. 5. Correction to the band gap of the non-spin-polarized hydrogen lattice at the infinite separation limit upon non-self-consistent application of each DFT+ U -type functional. The Hubbard U , Hund's J , and intersite V parameters were set at 5, 1, and 0 eV, respectively. Most DFT+ U functionals fail to modify the generalized Kohn-Sham gap of this system.

Specifically, in Fig. 4, the shift to the valence and conduction band edges of the spin-polarized hydrogen lattice upon non-self-consistent application of a variety of DFT+ U -type functionals is shown. The Hubbard U , Hund's J , and intersite V parameters were set at 5, 1, and 0 eV, respectively. We emphasize that setting $V = 0$ eV is, of course, a sensible choice in the infinite separation limit. It is worth noting for single orbital subspaces, multiple DFT+ U functionals take the same functional form, such as Dudarev '98 and Liechtenstein '95, which both simplify to

$$E_u = \frac{U - J}{2} \sum_{l\sigma} n^{l\sigma} - n^{l\sigma} n^{l\sigma}. \quad (102)$$

It is thus unsurprising that, for the spin-polarized hydrogen lattice, many DFT+ U functionals yield similar corrections to band gap, increasing its value by 4 or 5 eV. Interestingly, with the exception of Seo '07, the DFT+ U functionals with around-mean-field double-counting schemes fail to increase the band gap of the spin-polarized hydrogen lattice, with Czyżyk (AMF) '94 and Pickett '98 yielding no shift to the valence and conduction band edges, while Anisimov '91 reduces the magnitude of the generalized Kohn-Sham gap by 5 eV. The BLOR functional also reduces the generalized Kohn-Sham gap, in this case by 2 eV. However, the derivative discontinuity corrected version of the BLOR functional (BLOR + Δ_{xc}), which is the recommended version for achieving suitable band-gap predictions, opens the gap of the spin-polarized hydrogen lattice by 4 eV, in line with most other DFT+ U -type functionals.

In Fig. 5, the analogous results are presented for the non-spin-polarized hydrogen lattice. Interestingly, in this case most DFT+ U functionals fail to offer any correction to the valence and conduction band edges, while the functionals which do offer a correction all shift both band edges by the same

amount, resulting in no first-order correction to the band gap. The notable exception to this is the BLOR + Δ_{xc} functional, which opens the gap by 6 eV.

XI. PROJECTION DEPENDENCE OF DFT+ U BAND-GAP CORRECTION FOR CRYSTALLINE MATERIALS

We have shown that the frontier GKS eigenvalue difference of a well-converged periodic system, evaluated using a conventional DFT+ U functional, is rigorously equal to the fundamental band gap at the same level of theory, and that this equality holds independently of the nature of the subspace projection. This does not necessarily imply, however, that application of a DFT+ U functional will open a band gap of magnitude U_{eff} . To elaborate further on this, we again consider the widely used Hubbard corrective functional of Dudarev *et al.* [176], whose corrective potential in the spin-unrestricted formalism may be expressed in terms of the effective Hubbard parameter U_{eff}^I by

$$\hat{v}^\sigma = \sum_I \frac{U_{\text{eff}}^I}{2} (\hat{P}_I - 2\hat{P}_I \hat{\rho}^\sigma \hat{P}_I), \quad (103)$$

where $\hat{P}_I$ is the subspace projection operator at site I and $\hat{\rho}^\sigma$ is the spin- σ generalized Kohn-Sham (GKS) density operator. This expression for the corrective potential can be readily recast in terms of the subspace occupancy eigenvalues $\{\lambda_j^{I\sigma}\}$ and corresponding eigenstates $\{\varphi_j^{I\sigma}\}$,

$$\hat{v}^\sigma = \sum_{I,j} \frac{U_{\text{eff}}^I}{2} (|\varphi_j^{I\sigma}\rangle \langle \varphi_j^{I\sigma}| - 2|\varphi_j^{I\sigma}\rangle \lambda_j^{I\sigma} \langle \varphi_j^{I\sigma}|). \quad (104)$$

To first-order in perturbation theory and assuming no GKS orbital reordering or geometry re-optimization on application of the Hubbard U correction, Dudarev's functional will offer a correction to every spin-resolved GKS state $\{\Psi_i^\sigma\}$, the strength of which may be expressed as

$$\langle \Psi_i^\sigma | \hat{v}^\sigma | \Psi_i^\sigma \rangle = \sum_{I,j} \frac{U_{\text{eff}}^I}{2} (1 - 2\lambda_j^{I\sigma}) (|\langle \Psi_i^\sigma | \varphi_j^{I\sigma} \rangle|^2). \quad (105)$$

To first order in perturbation theory, the spin-resolved correction to the GKS band gap is given by

$$\Delta_{\text{GKS}}^\sigma = \sum_{I,j} \frac{U_{\text{eff}}^I}{2} (1 - 2\lambda_j^{I\sigma}) (|\langle \Psi_L^\sigma | \varphi_j^{I\sigma} \rangle|^2 - |\langle \Psi_H^\sigma | \varphi_j^{I\sigma} \rangle|^2), \quad (106)$$

where Ψ_H^σ and Ψ_L^σ are the highest occupied and lowest unoccupied spin- σ GKS states. If we now assume that we are treating only one equivalent set of sites at the DFT+ U level, the site index dependence of both the Hubbard parameter and the subspace occupancy eigenvalue, $\lambda_j^{I\sigma}$, can be removed to yield the expression

$$\Delta_{\text{GKS}}^\sigma = \frac{U_{\text{eff}}}{2} \sum_j \left\{ (1 - 2\lambda_j^\sigma) \sum_I (|\langle \Psi_L^\sigma | \varphi_j^{I\sigma} \rangle|^2 - |\langle \Psi_H^\sigma | \varphi_j^{I\sigma} \rangle|^2) \right\}. \quad (107)$$

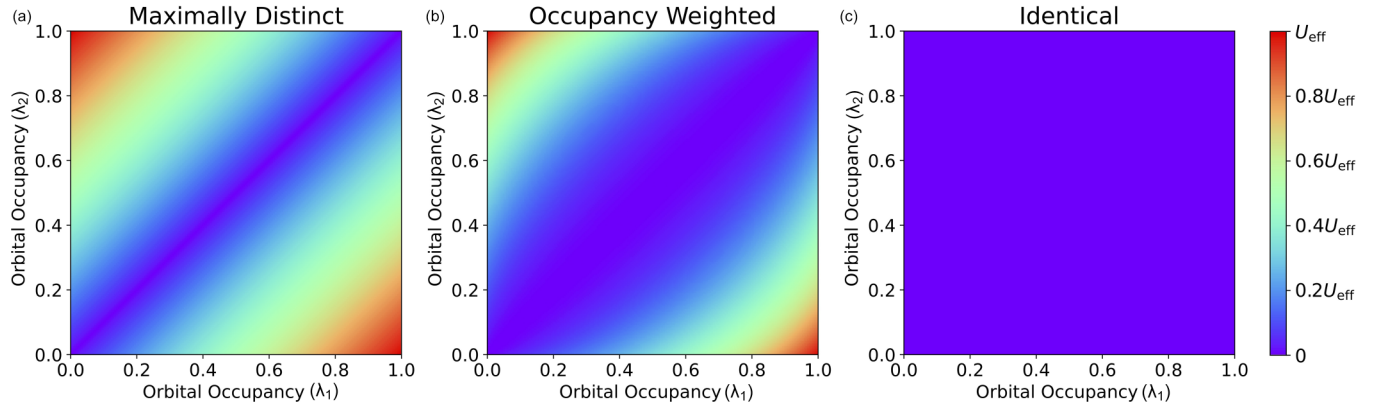


FIG. 6. Dudarev's DFT+ U correction to the band gap $\Delta_{\text{GKS}}^{\sigma}$ as a function of the spin-resolved subspace occupancy eigenvalues of a d -orbital subspace under octahedral or tetrahedral crystal field splitting. Under octahedral or tetrahedral crystal field splitting, in the absence of further symmetry breaking, there will be two eigenspaces (of dimensions 2 and 3) of the d -orbital spin-resolved subspace occupancy matrix, the eigenvalues of which we label $\lambda_1 = \lambda_{e_g}^{\sigma}$ and $\lambda_2 = \lambda_{t_{2g}}^{\sigma}$. The existence of only two distinct spin-resolved subspace occupancy eigenvalues enables the DFT+ U band-gap correction of Eq. (107) to be readily plotted as a function of $\lambda_{e_g}^{\sigma}$ and $\lambda_{t_{2g}}^{\sigma}$ once a suitable model for the orbital-resolved subspace projection, i.e., the inner summation of Eq. (107), has been selected. In panel (a), the highest occupied GKS orbital projects onto whichever eigenspace, be it the e_g or t_{2g} orbitals, that has a higher subspace occupancy eigenvalue, and vice versa for the lowest unoccupied GKS orbital. Hence, the total projection of the e_g orbitals onto the highest occupied and lowest unoccupied GKS orbitals is equal to 1 or 0, and the difference in the total projection onto the e_g orbitals, $\sum_{l, j \in e_g} (|\langle \Psi_L^{\sigma} | \varphi_j^{l\sigma} \rangle|^2 - |\langle \Psi_H^{\sigma} | \varphi_j^{l\sigma} \rangle|^2) = \pm 1$ and similarly the difference in the total projection onto the t_{2g} orbitals, $\sum_{l, j \in t_{2g}} (|\langle \Psi_L^{\sigma} | \varphi_j^{l\sigma} \rangle|^2 - |\langle \Psi_H^{\sigma} | \varphi_j^{l\sigma} \rangle|^2) = \mp 1$. In panel (b), the projection of the highest occupied and lowest unoccupied GKS orbitals onto the subspace orbitals is instead weighted by their respective subspace occupancy eigenvalues as detailed in Eq. (108). In panel (c), the highest occupied and lowest unoccupied GKS orbitals have the same orbital-resolved subspace occupancies so that $\sum_l (|\langle \Psi_L^{\sigma} | \varphi_j^{l\sigma} \rangle|^2 - |\langle \Psi_H^{\sigma} | \varphi_j^{l\sigma} \rangle|^2) = 0$, in which case there can be no first-order correction to the band gap.

The inner summation of Eq. (107) evaluates the difference in the Ψ_L^{σ} and Ψ_H^{σ} occupancy of orbital $\varphi_j^{l\sigma}$ over all sites with index label l . From Eq. (107), it is immediately apparent that Dudarev's functional will offer no first-order correction to the band gap if Ψ_H^{σ} and Ψ_L^{σ} have the same orbital-resolved subspace occupancies, i.e., identical projection. In contrast, Dudarev's functional will offer the maximum band-gap correction when Ψ_L^{σ} and Ψ_H^{σ} project onto different orbitals within the subspace, i.e., maximally distinct projection. This is a subtle but important point.

In at least some solid-state materials that are gapless at the (semi)local DFT level, one can expect both Ψ_H^{σ} and Ψ_L^{σ} to have the same orbital-resolved subspace occupancies as they come from the same partially filled band at the Fermi level. In such cases, Dudarev's functional cannot, to first order in perturbation theory, offer a correction to the band gap.

In contrast, in the case of materials which exhibit an erroneously small but finite gap at the (semi)local DFT level, Ψ_H^{σ} and Ψ_L^{σ} are in distinct valence and conduction bands and as such, in most cases one can expect Ψ_H^{σ} and Ψ_L^{σ} to have different orbital-resolved subspace occupancies. Such cases are thus amenable to band-gap correction. However, even in the case of such maximally distinct projection, Dudarev's functional offers no first-order correction to the band gap if all the spin-resolved subspace occupancy eigenvalues are equal; this is due to the $(1 - 2\lambda_j^{\sigma})$ factor in Eq. (107).

These findings are summarized in Figs. 6(a) and 6(c) in the case of a d -orbital subspace with octahedral or tetrahedral crystal field splitting and both Ψ_L^{σ} and Ψ_H^{σ} projecting perfectly onto the Hubbard subspace. In Fig. 6(b), assuming no

symmetry breaking, we interpolate between these two limits, allowing a subspace occupancy-weighted projection taking the form

$$\sum_l |\langle \Psi_H^{\sigma} | \varphi_j^{l\sigma} \rangle|^2 = \frac{\lambda_j^{\sigma}}{N^{\sigma}} \quad \text{and} \quad \sum_l |\langle \Psi_L^{\sigma} | \varphi_j^{l\sigma} \rangle|^2 = \frac{1 - \lambda_j^{\sigma}}{(2l + 1) - N^{\sigma}}, \quad (108)$$

where, like in Eq. (107), we assume only one equivalent set of sites and N^{σ} and l are the spin- σ subspace occupancy and subspace orbital angular momentum quantum number, respectively. This subspace occupancy-weighted projection ensures that Ψ_H^{σ} projects more strongly on the more occupied subspace orbitals and vice versa for Ψ_L^{σ} .

In Fig. 6 we label the two distinct spin-resolved subspace eigenvalues as $\lambda_{e_g}^{\sigma}$ and $\lambda_{t_{2g}}^{\sigma}$, although strictly speaking this labeling should be reserved for the atomic d orbitals through which the subspace projection operator is defined and not for labeling the subspace occupancy eigenstates. Nevertheless, under octahedral or tetrahedral crystal field splitting in the absence of further symmetry breaking, there will be two eigenspaces (of dimensions 2 and 3) of the d -orbital spin-resolved subspace occupancy matrix. The decision of what labels to ascribe to these two eigenspaces is arbitrary and does not affect the results. Here, we choose the e_g and t_{2g} labels as in many materials of interest with octahedral and tetrahedral crystal field splittings; the subspace occupancy eigenvectors will closely resemble the e_g and t_{2g} atomic orbitals, respectively. Furthermore, we also note that, strictly speaking, the

gerade (g) symmetry subscript should be omitted in the case of tetrahedral crystal field splitting.

In summary, for this section, the band edge states must project onto DFT+ U subspaces in such a way that their corresponding (GKS-) orbital-resolved subspace occupancies differ, if DFT+ U is to be able to change the band gap (to first order in perturbation theory). The efficacy of even the Dudarev DFT+ U functional, in this regard, has a subtle dependency on GKS-orbital-resolved DFT+ U projector orbital-resolved occupancies. This is a different matter entirely, however, from the question of band-gap validity from DFT+ U in principle, which holds for well-converged crystals even with very poor DFT+ U subspace choices.

XII. FUTURE OUTLOOK

Strongly correlated materials, for which the DFT+ U method was originally designed, critically underpin numerous current and nascent technologies, including high-performance ion-insertion battery cathodes [229], multiferroics [230], heterogeneous catalysts for renewable energy [231], and high-temperature superconductivity [232,233]. The challenge of modeling these materials is a compelling and rewarding one due to the very rich variety of emergent many-body effects that these materials exhibit, such as exotic magnetism [234,235], multiple exciton generation [236], quasiparticle satellites [237,238], and heavy-fermion behavior [239].

A particularly urgent emphasis is falling upon new materials that may facilitate a prompt transition to renewable energy technologies, such as catalysts and electrodes for batteries and photovoltaic cells. Moreover, the state-of-the-art in the applied simulation of energy differences of relevance to heterogeneous catalysis is also focused on correlated-electron metals and metal oxides [229,231], due to their multiple-valence character (i.e., changeable oxidation state) and adsorption energies ranging from low (for metals) to high and even tuneable (for oxides) [240]. In all of the areas mentioned, the energies central to phase stability and functionality are now almost ubiquitously calculated using DFT+ U [55,56,241–243] with empirically fitted parameters [94]. Although hybrid DFT [244–246] is very widely used in solid-state chemistry, it has become evident that DFT+ U currently provides the only empirically accurate methodological framework that remains practicable in high-throughput contexts [9,247,248] and suitable for the large simulation cell sizes needed for complex physics [10,249]. However, it has been shown that DFT+ U does not yield reliable total energies in practice [82,250–255]. It is so potent and highly efficient, however, being an excellently scalable and almost cost-free correction to approximate DFT, that it is very worthwhile to try to understand the reasons why this current failure comes about [220]. The DFT+ U family of functionals, over their three-decade history, have been applied in thousands of published research articles, as detailed in Fig. 1. It is an important challenge to see if it can be made reliable.

On one hand, there is no reliable numerical comparability of total energies across stoichiometries and structures when using a fixed Hubbard U parameter, since the latter is an inherently system-dependent quantity [72,142,256]. On the other hand, when one advances to using system-dependent

first-principles U parameters, within state-of-the-art linear-response theory [143,149], the direct comparability of total energies can sometimes break down [250]. Various pragmatic approaches have been devised to deal with the necessary stoichiometry dependence of the Hubbard U . One pioneering empirical technique, developed in the context of high-throughput battery-material simulation, defined a Hubbard U that interpolated between first-principles values based on the stoichiometric ratio of the compound of interest [257]. Another proposed solution is to mix the DFT and DFT+ U total energies [251], which has been found to be a successful workaround for calculating first-row transition-metal oxide formation energies and phase diagrams, resulting in good agreement with experiment. Indeed, the accurate calculation of phase diagrams is of central importance in this area [256,258,259]. Pragmatic measures such as the fitting of U values to experimental results such as binary formation energies [142], or the mixing of energies from different theories, albeit insightful and successful [259–262], highlight the need for a fundamental breakthrough in this area of condensed matter theory. Without it, progress in strongly correlated materials prediction is hampered.

Recent advances made by incorporating findings from quantum chemistry [219,263–265] in the development of DFT+ U -type functionals have shown much promise. In particular, developing corrective functionals to enforce the most relevant exact conditions [183,186,263,266,267], rather than following the traditional approach of requiring derivability from the Hubbard model [89,268]. Underpinning this approach is the working hypothesis that significant accuracy gains are inexpensively within reach, within generalized Kohn-Sham DFT [23], by efficiently imposing known exact conditions [45,183,266] on selected error-prone subspaces. Indeed, there exists a large body of evidence, found in the literature over the past decade and more [143,242,243], that has strongly indicated that DFT+ U may be interpreted as an efficient corrector for electronic self-interaction error (SIE) or, more generally, delocalization error [182,269–271], in approximate DFT [272], given a differential definition of that error based on spurious energy-occupancy curvature.

As well as affecting the total energy, SIE is associated with a characteristic underestimation of the insulating gap [273,274]. This definition is technically distinct but complementary to the SIE corrected by Perdew-Zunger type DFT-SIC [49,275,276]. Further progress in this area will require suitably constructed subspaces, together with the necessary form of corrective functional, which requires parameters appropriately calculated from first principles. Ideally, these features together might be packaged in a self-contained and automated way, from the user's perspective, so that reliable, minimal-empiricism total energy differences may be extracted from DFT+ U with the same convenience (we can now be assured, for crystals) that band gaps may be.

XIII. CONCLUSIONS

We have rigorously proven that the GKS eigenspectrum gap of a pristine periodic system as computed by a DFT+ U or hybrid functional is a valid measure of the fundamental gap of a material, in the sense that it matches its own fundamental

gap calculated using total-energy differences. Furthermore, under the same conditions, the negative of the highest occupied and lowest unoccupied GKS eigenvalues are rigorously equal to the ionization potential and electron affinity of the material, respectively. This proof was theoretically verified to hold for all known DFT+*U*-type functionals, subject only to caveats that are met or accounted for in practice. Our proof recovers the previously demonstrated same result for local and semilocal functionals, with a somewhat different argument.

The diverse set of DFT+*U*-type functionals will continue to grow in the coming decades. To date, the vast majority of DFT+*U* functionals have been constructed by starting with one of a range of interaction terms, typically inspired either by Hartree-Fock theory or the Hubbard model, and subtracting off a double-counting correction, the form of which often strongly depends on the choice of interaction term.

Future DFT+*U* functionals will almost certainly be constructed within the “extended DFT+*U*” category, via the retention of additional subspace-averaged parameters from the Hartree-Fock-inspired interaction term, and within the “flat-plane condition” category, via the imposition of additional exact conditions on the selected subspaces or the identification of more advanced interaction terms inspired by quantum chemistry techniques.

The proof of the DFT+*U* eigenspectrum gap being a valid measure of the fundamental gap of a material does not, however, ensure close agreement with experiment. In this sense, DFT+*U* is no different from conventional hybrid functionals. If progress is to be made, novel functional forms must retain the desirable features of conventional DFT+*U* functionals, such as improved band gaps and magnetic moments of transition-metal oxides, while also offering improved total energies and band gaps in more challenging electronic systems. Model yet chemical systems, exemplified by the non-spin-polarized hydrogen lattice, can helpfully simplify and reveal the differences in behavior between different functionals and methods, and guide progress.

ACKNOWLEDGMENTS

This research was supported by Taighde-Éireann—Research Ireland under Grant No. GOIPG/2020/1454 and under Prime Award No. 12/RC/2278_P2, the latter of which is cofunded by the European Regional Development Fund. The authors further acknowledge Enterprise Ireland, Project CS20212086. The authors wish to thank Tim Gould, Stefano de Gironcoli, Nathalie Vast, and Nicola Marzari for stimulating discussions.

DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

APPENDIX A: COMPUTATIONAL DETAILS

Electronic structure calculations to investigate the numerical difference between the DFT+*U* eigenspectrum gap and the fundamental gap (as calculated via total-energy differences) were executed using Quantum Espresso code version

7.4 [105]. The conventional DFT+*U* functional of Dudarev *et al.* [176] with an effective Hubbard *U* parameter of 5 eV was applied with the Perdew-Burke-Ernzerhof XC functional [41]. DFT+*U* projectors were of standard pseudo-atomic type, without orthonormalization. A 2-dimensional square hydrogen lattice with an inter-nuclear separation length of $7a_0$ was selected for this study. A rectangular primitive unit cell composed of two antiferromagnetically ordered hydrogen atoms was used, giving ordering in the *x*-direction. A large out-of-plane unit cell length of $50a_0$ was used, in conjunction with the Coulomb interaction truncation technique for 2-dimensional systems devised by Sohler *et al.* [277]. A SG15 v1.0 [278] scalar-relativistic optimized norm-conserving Vanderbilt pseudopotential [279] was applied, and the plane-wave cutoff energy was set at 400 Ry (2000 Ry for the density). The default mixing scheme proved adequate.

For the charged calculations, the total charge of the primitive unit cell was set as $\pm 1/N_k$, where N_k is the total number of *k*-points [170]. This is equivalent to a collection of N_k primitive unit cells in periodic boundary conditions with a single electron added or removed. In the bulk limit, i.e., where $N_k \rightarrow \infty$, the total energy per unit cell is equal to that of the ± 1 charged system, assuming the added electron or hole delocalizes over the lattice. The total magnetization of the primitive unit cell was set in accordance with the total charge. The cold-smearing method of Marzari *et al.* [280] was applied with a low smearing temperature of 1×10^{-9} Ry to ensure that integer GKS orbital occupancies were retained under such conditions.

APPENDIX B: EXPLICIT DERIVATIVE DISCONTINUITIES

The need for the exact functional to exhibit an explicit derivative discontinuity in the case of the hydrogen atom has already been discussed in detail by Mori-Sánchez *et al.* [186]. Here we review this hitherto underappreciated point in the case of exact GKS theory. By exact GKS theory here, we refer to all possible forms of exact GKS theory in which any functional of the occupied GKS orbitals can be made exact through the use of a complementary remainder functional [23,24]. The absence of a minority spin population in the hydrogen atom complicates matters, so we consider here the neutral lithium atom with two spin-up electrons and one spin-down electron and a ground state electron configuration $1s^2 2s^1$. By comparison, the lithium anion has a spin singlet ground state of the form $1s^2 2s^2$ composed of two spin-up and two spin-down electrons, while the lithium cation has a ground state electron configuration $1s^2$, with one spin-up and one spin-down electron. This simple atomic system has also been analyzed extensively within the context of exact KS theory [281] and ensemble DFT [282].

In the case of GKS theory, in order to reproduce the correct fundamental gap in the absence of an explicit derivative discontinuity, the difference between the highest occupied spin-up and lowest unoccupied spin-down GKS eigenvalues of the neutral lithium atom must be equal to 4.77 eV, which is the difference between lithium’s ionization potential (5.39 eV) and electron affinity (0.62 eV). However, in order to reproduce the correct spin-flip energy [169,214,217,281,283–288] in the absence of an explicit derivative discontinuity, defined in this

case as the energy difference between the neutral lithium atom with an unpaired spin-up electron versus an unpaired spin-down electron, the same frontier GKS eigenvalue difference must, due to spin degeneracy, be equal to 0 eV. Both of these conditions cannot be satisfied simultaneously, which thus warrants the introduction of an explicit derivative discontinuity [169].

APPENDIX C: BAND GAPS IN THE PRESENCE OF NORM-CONSERVING PSEUDOPOTENTIALS

In most practical calculations, the bare Coulomb potential of the static nuclei is replaced by a pseudopotential to avoid explicit and costly treatment of the core electrons. Norm-Conserving Pseudopotentials (NCPP), as originally devised by Hamann *et al.* [289], are local in the radial coordinate but nonlocal in angular coordinates Ω and may be expressed in terms of the set of spherical harmonics $\{|Y_{lm}\rangle\rangle$ and element-specific local and nonlocal contributions, v_I^L and Δv_{II}^{NL} , located at atom site I as given by $v_{\text{NCPP}}(\mathbf{r}, \mathbf{r}')$ in Eq. (C1). In practice, in order to improve computational efficiency, most modern NCPPs are converted into a fully nonlocal form via the Kleinman-Bylander scheme [290]. The resulting nonlocal potentials may be expressed as

$$\begin{aligned} v_{\text{NCPP}}(\mathbf{r}, \mathbf{r}') &= \sum_I v_I^L(|\mathbf{r} - \mathbf{R}_I|) \delta(\mathbf{r} - \mathbf{r}') \\ &+ \sum_I \sum_{lm} Y_{lm}(\Omega_{\mathbf{r}-\mathbf{R}_I}) \Delta v_{II}^{NL}(|\mathbf{r} - \mathbf{R}_I|) \\ &\times \delta(|\mathbf{r} - \mathbf{R}_I| - |\mathbf{r}' - \mathbf{R}_I|) Y_{lm}^*(\Omega_{\mathbf{r}'-\mathbf{R}_I}), \\ v_{\text{KB}}(\mathbf{r}, \mathbf{r}') &= \sum_I \langle \mathbf{r} - \mathbf{R}_I | v_I^L | \mathbf{r}' - \mathbf{R}_I \rangle \delta(\mathbf{r} - \mathbf{r}') + \sum_I \sum_{lm} \\ &\times \frac{\langle \mathbf{r} - \mathbf{R}_I | \Delta v_{II}^{NL} \phi_{Ilm} \rangle \langle \Delta v_{II}^{NL} \phi_{Ilm} | \mathbf{r}' - \mathbf{R}_I \rangle}{\langle \phi_{Ilm} | \Delta v_{II}^{NL} | \phi_{Ilm} \rangle}, \end{aligned} \quad (\text{C1})$$

where the radial coordinate dependence of v_I^L and Δv_{II}^{NL} has been suppressed in $v_{\text{KB}}(\mathbf{r}, \mathbf{r}')$ for clarity and $\{\phi_{Ilm}\}$ are the reference pseudo-atomic wavefunctions. Unlike the Hubbard, Hartree, and base Exchange-Correlation potentials, the NCPPs of Eq. (C1) are independent of the first-order reference-system reduced density matrix and, by extension, are independent of the frontier orbital occupancy. As such, the NCPPs do not offer an explicit contribution to the GKS eigenvalue derivative of Eq. (27) or any higher-order derivatives. Thus, the simple expressions for the ionization potential, electron affinity, and fundamental band gap of defect-free infinitely extended systems, given by Eqs. (30), (31), and (32), remain valid in the case of frontier GKS eigenvalues evaluated using NCPPs. To be clear, these values will match the ionization potential, electron affinity, and fundamental band gap, respectively, evaluated via explicit total-energy differences employing the same set of NCPPs.

APPENDIX D: BAND GAPS WITHIN THE ULTRASOFT AND PROJECTOR-AUGMENTED WAVE FORMULATIONS

In the case of ultrasoft pseudopotential (USPP) [291,292] and Projector-Augmented Wave (PAW) [293,294] formulations, the orthonormality condition of the pseudo-GKS states $\{\tilde{\psi}_i\}$ is relaxed to ensure a relatively “soft,” i.e., smooth profile in the atomic core region. The pseudo-GKS states instead satisfy a generalized orthonormality condition of the form

$$\langle \tilde{\psi}_i | \hat{S} | \tilde{\psi}_j \rangle = \delta_{ij}, \quad (\text{D1})$$

where $\hat{S}$ is an overlap (a.k.a., augmentation) operator. In both the USPP and PAW formalisms, the overlap operator may be defined using a set of smooth projector functions $\{\tilde{p}_\mu\}$ and takes the following form:

$$\begin{aligned} \hat{S}_{\text{USPP}} &= 1 + \sum_{\mu\nu} q_{\mu\nu} |\tilde{p}_\mu\rangle \langle \tilde{p}_\nu| \quad \text{and} \\ \hat{S}_{\text{PAW}} &= 1 + \sum_{\mu\nu} [\langle \phi_\mu | \phi_\nu \rangle - \langle \tilde{\phi}_\mu | \tilde{\phi}_\nu \rangle] |\tilde{p}_\mu\rangle \langle \tilde{p}_\nu|, \end{aligned} \quad (\text{D2})$$

where $\{\phi_\mu\}$ and $\{\tilde{\phi}_\mu\}$ are the all-electron atomic and pseudo-atomic states and $\{q_{\mu\nu}\}$ are the USPP augmentation charges. Here, μ and ν are combined atomic state and site indices, and the summations in both Eq. (D2) and below are restricted to on-site terms only. This necessitates a modification of the total energy expression of Eq. (2), which may be expressed as

$$\begin{aligned} E_v &= - \sum_i \tilde{f}_i \frac{\langle \tilde{\psi}_i | \nabla^2 | \tilde{\psi}_i \rangle}{2} + E_{\text{Hxc}+U+\Delta E_a}[\{\tilde{\psi}_i\}, \{\tilde{f}_i\}] \\ &+ \sum_{ij} \lambda_{ij} (\delta_{ji} - \langle \tilde{\psi}_j | \hat{S} | \tilde{\psi}_i \rangle) + \epsilon_F \left(N - \sum_i \tilde{f}_i \langle \tilde{\psi}_i | \hat{S} | \tilde{\psi}_i \rangle \right), \end{aligned} \quad (\text{D3})$$

where the external energy due to the bare Coulomb potential of the static nuclei has been replaced by a USPP or PAW specific atomic energy correction (including kinetic contributions) ΔE_a . This total energy expression is similarly minimized with respect to its degrees of freedom $\{\tilde{\psi}_i\}$, $\{\tilde{\psi}_i^*\}$, $\tilde{f}_i$, λ_{ij} , and ϵ_F , and so again the partial derivatives of E_v with respect to these vanish. The total derivative of E_v with respect to electron count is thus, again, given by

$$\frac{dE_v}{dN} = \frac{\partial E_v}{\partial N} = \epsilon_F, \quad (\text{D4})$$

in all but points of eigenvalue cross-over or degeneracy change of the frontier orbitals. Therefore, the general expressions for the electron affinity, ionization potential, and band gap as given by Eqs. (14), (16), and (17) are also valid within the USPP and PAW formalisms once the GKS eigenvalues and occupancies are replaced by their soft-pseudo analogs.

Unlike NCPPs, the USPP and PAW formulations offer non-negligible contributions to the frontier GKS eigenvalue derivatives. Therefore, we must again examine the bulk limit of the frontier GKS eigenvalue derivatives to assess if the electron affinity, ionization potential, and fundamental band gap expressions of Eqs. (30), (31), and (32) for a pristine periodic system remain valid. In the case of the USPP formalism, the first derivative of the frontier pseudo-GKS eigenvalue with respect to its occupancy consists of a Hxc, Hubbard, and

USPP contribution, and may be expressed as

$$\begin{aligned} \frac{d\tilde{\epsilon}_F}{d\tilde{f}_F} = & \langle \tilde{\Psi}_F | \left\{ \int d\mathbf{r} d\mathbf{r}' |\mathbf{r}\rangle f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \left(\tilde{F}_{\pm}(\mathbf{r}', \mathbf{r}') + \sum_{\mu\nu} \int d\mathbf{r}'' d\mathbf{r}''' \langle \mathbf{r}'' | \tilde{p}_{\mu} \rangle \langle \tilde{p}_{\nu} | \mathbf{r}''' \rangle \tilde{F}_{\pm}(\mathbf{r}''', \mathbf{r}'') Q_{\mu\nu}(\mathbf{r}') \right) \langle \mathbf{r} | \right. \\ & - \sum_I \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' |\mathbf{r}\rangle \langle U^I | \langle \mathbf{r} | \hat{S} \hat{P}^I \hat{S} | \mathbf{r}'' \rangle \langle \mathbf{r}''' | \hat{S} \hat{P}^I \hat{S} | \mathbf{r}' \rangle \rangle \tilde{F}_{\pm}(\mathbf{r}'', \mathbf{r}''') \langle \mathbf{r}' | + \sum_{\mu\nu} \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}'''' |\mathbf{r}\rangle \langle \mathbf{r}' | \tilde{p}_{\mu} \rangle \\ & \times \left(\tilde{F}_{\pm}(\mathbf{r}''', \mathbf{r}''') + \sum_{\mu'\nu'} \int d\mathbf{r}'' d\mathbf{r}''' \langle \mathbf{r}'' | \tilde{p}_{\mu'} \rangle \langle \tilde{p}_{\nu'} | \mathbf{r}''' \rangle \tilde{F}_{\pm}(\mathbf{r}''', \mathbf{r}'') Q_{\mu'\nu'}(\mathbf{r}''') \right) f_{\text{Hxc}}(\mathbf{r}''', \mathbf{r}''') Q_{\mu\nu}(\mathbf{r}''') \langle \tilde{p}_{\nu} | \mathbf{r}' \rangle \langle \mathbf{r}' | \left. \right\} | \tilde{\Psi}_F \rangle, \end{aligned} \quad (\text{D5})$$

where $\{Q_{\mu\nu}(\mathbf{r})\}$ are the augmentation charge densities, the integrals of which yield the augmentation charges $\{q_{\nu\mu}\}$ of Eq. (D2), $\tilde{F}_{\pm}(\mathbf{r}, \mathbf{r}')$ is the soft-pseudo Fukui matrix, and the Hxc kernel is evaluated on the total electron density, i.e., including both soft and hard contributions. Focusing on the Hxc contribution, the term in parentheses consists of a Fukui matrix and a second term with two spatial integrals and a summation over the combined atomic state and site indices μ and ν . For a given site I , the $\langle \mathbf{r}'' | \tilde{p}_{\mu} \rangle \langle \tilde{p}_{\nu} | \mathbf{r}''' \rangle Q_{\mu\nu}(\mathbf{r}')$ term will offer a negligible contribution for large values of $|\mathbf{R}_I - \mathbf{r}'|$, $|\mathbf{R}_I - \mathbf{r}''|$ and $|\mathbf{R}_I - \mathbf{r}'''|$. This counters the two spatial integrals and the summation over μ and ν , noting that the augmentation charge density $Q_{\mu\nu}(\mathbf{r}')$ is diagonal in site index. Finally, the two Fukui matrices are left to ensure that both terms in parentheses vanish in the bulk limit. Outside the parentheses, there are two more spatial integrals, but these are countered by the Hxc kernel and the frontier orbital density $\langle \tilde{\Psi}_F | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\Psi}_F \rangle$. Therefore, the Hxc contribution to the GKS eigenvalue derivative evaluated with USPPs vanishes in the bulk limit. Same too goes for the Hubbard contribution, whose only modification is the subspace projection operator $\hat{P}^I$, which has been replaced by $\hat{S} \hat{P}^I \hat{S}$ [295].

In the case of the explicit USPP contribution to the GKS eigenvalue derivative, the term in parentheses is the same as that discussed for the Hxc term and thus vanishes in the bulk limit. Outside of the parentheses, the $\langle \mathbf{r} | \tilde{p}_{\mu} \rangle \langle \tilde{p}_{\nu} | \mathbf{r}' \rangle Q_{\mu\nu}(\mathbf{r}''')$ term offers a negligible contribution for large values of $|\mathbf{R}_I - \mathbf{r}|$, $|\mathbf{R}_I - \mathbf{r}''|$ and $|\mathbf{R}_I - \mathbf{r}'''|$. This term, along with the Hxc kernel and frontier orbital density matrix $\langle \tilde{\Psi}_F | \mathbf{r}' \rangle \langle \mathbf{r} | \tilde{\Psi}_F \rangle$, counteracts the summation and four spatial integrals. Therefore, the explicit USPP contribution to the GKS eigenvalue derivative also vanishes in the bulk limit.

For PAW, we follow the formalism proposed by Kresse and Joubert [294] to arrive at an expression for the derivative of the soft-pseudo GKS eigenvalue with respect to frontier pseudo-GKS orbital occupancy, namely,

$$\begin{aligned} \frac{d\tilde{\epsilon}_F}{d\tilde{f}_F} = & \langle \tilde{\Psi}_F | \left\{ - \sum_I \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' |\mathbf{r}\rangle \langle U^I | \langle \mathbf{r} | \hat{S} \hat{P}^I \hat{S} | \mathbf{r}'' \rangle \langle \mathbf{r}''' | \hat{S} \hat{P}^I \hat{S} | \mathbf{r}' \rangle \rangle \tilde{F}_{\pm}(\mathbf{r}'', \mathbf{r}''') \langle \mathbf{r}' | \right. \\ & + \int d\mathbf{r} d\mathbf{r}' |\mathbf{r}\rangle f_{\text{Hxc}}[\tilde{n} + \hat{n} + \tilde{n}_c](\mathbf{r}, \mathbf{r}') \left(\tilde{F}_{\pm}(\mathbf{r}', \mathbf{r}') + \sum_{\mu\nu lm} \int d\mathbf{r}'' d\mathbf{r}''' \langle \mathbf{r}'' | \tilde{p}_{\mu} \rangle \langle \tilde{p}_{\nu} | \mathbf{r}''' \rangle \tilde{F}_{\pm}(\mathbf{r}''', \mathbf{r}'') Q_{\mu\nu}^{lm}(\mathbf{r}') \right) \langle \mathbf{r} | \\ & \left. + \sum_{\mu\nu} \int d\mathbf{r} d\mathbf{r}' |\mathbf{r}\rangle \langle \mathbf{r} | \tilde{p}_{\mu} \rangle \frac{dD_{\mu\nu}}{d\tilde{f}_F} \langle \tilde{p}_{\nu} | \mathbf{r}' \rangle \langle \mathbf{r}' | \right\} | \tilde{\Psi}_F \rangle, \end{aligned} \quad (\text{D6})$$

where $D_{\mu\nu} = \hat{D}_{\mu\nu} + D_{\mu\nu}^I - \tilde{D}_{\mu\nu}$. The latter three quantities are defined in Eqs. (44), (45), and (46) of Kresse and Joubert [294] and their derivatives with respect to frontier pseudo-GKS occupancy $\tilde{f}_F$ may be expressed as

$$\begin{aligned} \frac{d\hat{D}_{\mu\nu}}{d\tilde{f}_F} = & \sum_{lm} \int d\mathbf{r} Q_{\mu\nu}^{lm}(\mathbf{r}) \int d\mathbf{r}' f_{\text{Hxc}}[\tilde{n} + \hat{n} + \tilde{n}_c](\mathbf{r}, \mathbf{r}') \left(\tilde{F}_{\pm}(\mathbf{r}', \mathbf{r}') + \sum_{\mu'\nu' l'm'} \int d\mathbf{r}'' d\mathbf{r}''' \langle \mathbf{r}'' | \tilde{p}_{\mu'} \rangle \langle \tilde{p}_{\nu'} | \mathbf{r}''' \rangle \tilde{F}_{\pm}(\mathbf{r}''', \mathbf{r}'') Q_{\mu'\nu'}^{l'm'}(\mathbf{r}') \right), \\ \frac{dD_{\mu\nu}^I}{d\tilde{f}_F} = & \langle \phi_{\mu} | \left\{ \int d\mathbf{r} |\mathbf{r}\rangle \left(\int d\mathbf{r}' f_{\text{Hxc}}[n^I + n_c](\mathbf{r}, \mathbf{r}') \sum_{\mu'\nu'} \int d\mathbf{r}'' d\mathbf{r}''' \langle \mathbf{r}'' | \tilde{p}_{\mu'} \rangle \langle \tilde{p}_{\nu'} | \mathbf{r}''' \rangle \tilde{F}_{\pm}(\mathbf{r}''', \mathbf{r}'') \langle \phi_{\mu'} | \mathbf{r}' \rangle \langle \mathbf{r}' | \phi_{\nu'} \rangle \right) \langle \mathbf{r} | \right\} | \phi_{\nu} \rangle, \text{ and} \end{aligned}$$

$$\begin{aligned}
\frac{d\tilde{D}_{\mu\nu}^1}{d\tilde{f}_F} = & \langle \tilde{\phi}_\mu | \left\{ \int d\mathbf{r} |\mathbf{r}\rangle \left[\int d\mathbf{r}' f_{\text{Hxc}} [\tilde{n}^1 + \hat{n} + \tilde{n}_c](\mathbf{r}, \mathbf{r}') \right. \right. \\
& \times \sum_{\mu'v'} \int d\mathbf{r}'' d\mathbf{r}''' \langle \mathbf{r}'' | \tilde{p}_{\mu'} \rangle \langle \tilde{p}_{v'} | \mathbf{r}''' \rangle \tilde{F}_{\pm}(\mathbf{r}'', \mathbf{r}''') \left(\langle \tilde{\phi}_{\mu'} | \mathbf{r}' \rangle \langle \mathbf{r}' | \tilde{\phi}_{v'} \rangle + \sum_{l'm'} Q_{\mu'v'}^{l'm'}(\mathbf{r}') \right) \left. \right] \langle \mathbf{r} | \rangle | \tilde{\phi}_\nu \rangle \\
& + \sum_{lm} \int_{\Omega_r} d\mathbf{r} Q_{\mu\nu}^{lm}(\mathbf{r}) \left[\int d\mathbf{r}' f_{\text{Hxc}} [\tilde{n}^1 + \hat{n} + \tilde{n}_c](\mathbf{r}, \mathbf{r}') \right. \\
& \times \sum_{\mu'v'} \int d\mathbf{r}'' d\mathbf{r}''' \langle \mathbf{r}'' | \tilde{p}_{\mu'} \rangle \langle \tilde{p}_{v'} | \mathbf{r}''' \rangle \tilde{F}_{\pm}(\mathbf{r}'', \mathbf{r}''') \left(\langle \tilde{\phi}_{\mu'} | \mathbf{r}' \rangle \langle \mathbf{r}' | \tilde{\phi}_{v'} \rangle + \sum_{l'm'} Q_{\mu'v'}^{l'm'}(\mathbf{r}') \right) \left. \right] \rangle. \quad (\text{D7})
\end{aligned}$$

The charge densities $\tilde{n}$, $\tilde{n}_c$, and $\hat{n}$ are the soft pseudo-charge density, the frozen-core all-electron charge density, and the total augmentation charge density, the latter of which can be written as a one-electron multipole expansion of the form

$$\hat{n}(\mathbf{r}) = \sum_{\mu\nu lm} Q_{\mu\nu}^{lm}(\mathbf{r}) \sum_i \tilde{f}_i \langle \tilde{\Psi}_i | \tilde{p}_\mu \rangle \langle \tilde{p}_\nu | \tilde{\Psi}_i \rangle. \quad (\text{D8})$$

The GKS eigenvalue derivative in the PAW formulation as exposed by Eq. (D6) takes an almost analogous form to that of the USPP formulation, with the Hxc and Hubbard terms vanishing in the bulk limit. As for the explicit PAW contribution to the GKS eigenvalue derivative, using the same arguments as before, it can be readily shown that the $dD_{\mu\nu}/d\tilde{f}_F$ term vanishes in the bulk limit. The two spatial integrals and summation are countered by the frontier orbital density matrix and the $\langle \mathbf{r} | \tilde{p}_\mu \rangle \langle \tilde{p}_\nu | \mathbf{r}' \rangle$ term, which offers a negligible contribution for large values of $|\mathbf{R}_I - \mathbf{r}|$ and $|\mathbf{R}_I - \mathbf{r}'|$. Thus, the PAW contribution to the GKS eigenvalue derivative also vanishes in the bulk limit, and the simple expressions for the ionization potential, electron affinity, and fundamental band gap of pristine periodic systems as given by Eqs. (30), (31), and (32) remain valid in the case of frontier GKS eigenvalues evaluated using the USPP or PAW formulation.

APPENDIX E: GENERALIZATION TO SPIN-UNRESTRICTED GKS THEORY

In the case of the spin-unrestricted GKS formalism, we must derive an explicit expression for the first-order derivative of the frontier spin- σ GKS eigenvalue with respect to its own occupancy, which for collinear spin-systems may be expressed as

$$\frac{d\epsilon_F^\sigma}{df_F^\sigma} = \langle \Psi_F^\sigma | \frac{d\hat{H}_\sigma^{\text{GKS}}}{df_F^\sigma} | \Psi_F^\sigma \rangle. \quad (\text{E1})$$

The derivative of the spin- σ GKS Hamiltonian will again consist of two terms, namely the derivative of the spin- σ Hxc potential $\hat{v}_{\text{Hxc}}^\sigma$ and the derivative of the Hubbard potential $\hat{v}_u^\sigma$. In the case of the spin- σ Hxc potential, its dependence on both the spin-up and spin-down ground-state densities must be accounted for and, as such, its derivative with respect to frontier spin- σ GKS orbital occupancy may be

expressed as

$$\frac{dv_{\text{Hxc}}^\sigma(\mathbf{r})}{df_F^\sigma} = \sum_{\sigma'} \int d\mathbf{r}' f_{\text{Hxc}}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') F_{\pm}^{\sigma\sigma'}(\mathbf{r}'), \quad (\text{E2})$$

where $F_{\pm}^{\sigma\sigma'}(\mathbf{r}')$ is the spin-resolved analog of the right- or left-hand Fukui function, or, to be explicit, the derivative of the ground-state spin- σ' density with respect to spin- σ electron count. In contrast, the spin- σ Hubbard potential of Dudarev *et al.* [176] depends only on the ground-state spin- σ GKS density matrix $\rho_0^\sigma(\mathbf{r}'', \mathbf{r}''')$. Its derivative with respect to frontier spin- σ GKS orbital occupancy may be expressed as

$$\begin{aligned}
\frac{dv_U^\sigma(\mathbf{r}, \mathbf{r}')}{df_F^\sigma} = & - \sum_I U^I \int d\mathbf{r}'' d\mathbf{r}''' (\langle \mathbf{r} | \hat{P}^I | \mathbf{r}'' \rangle \langle \mathbf{r}''' | \hat{P}^I | \mathbf{r}' \rangle) \\
& \times F_{\pm}^{\sigma\sigma}(\mathbf{r}'', \mathbf{r}'''), \quad (\text{E3})
\end{aligned}$$

where $F_{\pm}^{\sigma\sigma}(\mathbf{r}'', \mathbf{r}''')$ is the spin-resolved analog of the right- or left-hand Fukui matrix. More advanced spin-resolved Hubbard potentials such as that of the DFT+ U + J or BLOR functionals [149,220] will warrant a summation over spin-index σ' , akin to that of the Hxc term, due to their dependence on both the spin-up and spin-down subspace occupancies. From Eqs. (E1), (E2), and (E3), it follows that the derivative of the spin-resolved GKS eigenvalue may be expressed as

$$\begin{aligned}
\frac{d\epsilon_F^\sigma}{df_F^\sigma} = & \langle \Psi_F^\sigma | \int d\mathbf{r} d\mathbf{r}' |\mathbf{r}\rangle \left\{ \sum_{\sigma'} \int d\mathbf{r}'' f_{\text{Hxc}}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}'') \right. \\
& \times F_{\pm}^{\sigma'\sigma}(\mathbf{r}'', \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \\
& - \sum_I \int d\mathbf{r}'' d\mathbf{r}''' (U^I \langle \mathbf{r} | \hat{P}^I | \mathbf{r}'' \rangle \langle \mathbf{r}''' | \hat{P}^I | \mathbf{r}' \rangle) \\
& \times F_{\pm}^{\sigma\sigma}(\mathbf{r}'', \mathbf{r}''') \left. \right\} \langle \mathbf{r}' | \Psi_F^\sigma \rangle. \quad (\text{E4})
\end{aligned}$$

Applying the same scaling arguments as before, one can readily show that each term in the spin-resolved GKS eigenvalue derivative vanishes in the bulk limit. The spin-resolved analogues of Eqs. (30), (31), and (32) thus immediately follow in the pristine bulk limit. The same argument of course also holds for hybrid functionals, in which case the derivative of the frontier spin-resolved GKS eigenvalue may instead be

expressed as

$$\frac{d\epsilon_F^\sigma}{df_F^\sigma} = \langle \Psi_F^\sigma | \int d\mathbf{r} d\mathbf{r}' |\mathbf{r}\rangle \left\{ -a_{\text{HF}} \frac{F_{\pm}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \sum_{\sigma'} \int d\mathbf{r}'' (f_{\text{Hc}}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}'') + (1 - a_{\text{HF}}) f_{\text{x}}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}'')) F_{\pm}^{\sigma'\sigma}(\mathbf{r}'', \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \right\} |\mathbf{r}'\rangle \Psi_F^\sigma \rangle. \quad (\text{E5})$$

- [1] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, B864 (1964).
- [2] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**, A1133 (1965).
- [3] A. M. Teale, T. Helgaker, A. Savin, C. Adamo, B. Aradi, A. V. Arbuznikov, P. W. Ayers, E. J. Baerends, V. Barone, P. Calaminici, E. Cancès, E. A. Carter, P. K. Chattaraj, H. Chermette, I. Ciofini, T. Daniel Crawford, F. De Proft, J. F. Dobson, C. Draxl, T. Frauenheim, *et al.*, DFT exchange: Sharing perspectives on the workhorse of quantum chemistry and materials science, *Phys. Chem. Chem. Phys.* **24**, 28700 (2022).
- [4] J. P. Perdew and A. Ruzsinszky, Fourteen easy lessons in density functional theory, *Int. J. Quantum Chem.* **110**, 2801 (2010).
- [5] R. Van Noorden, B. Maher, and R. Nuzzo, The top 100 papers, *Nat. News* **514**, 550 (2014).
- [6] R. Haunschild, A. Barth, and B. French, A comprehensive analysis of the history of DFT based on the bibliometric method RPYS, *J. Cheminform.* **11**, 72 (2019).
- [7] K. Lejaeghere, G. Bihlmayer, T. Björkman, P. Blaha, S. Blügel, V. Blum, D. Caliste, I. E. Castelli, S. J. Clark, A. Dal Corso, S. de Gironcoli, T. Deutsch, J. K. Dewhurst, I. Di Marco, C. Draxl, M. Dulak, O. Eriksson, J. A. Flores-Livas, K. F. Garrity, L. Genovese, *et al.*, Reproducibility in density functional theory calculations of solids, *Science* **351**, aad3000 (2016).
- [8] E. Dagotto, Complexity in strongly correlated electronic systems, *Science* **309**, 257 (2005).
- [9] S. Curtarolo, G. L. W. Hart, M. B. Nardelli, N. Mingo, S. Sanvito, and O. Levy, The high-throughput highway to computational materials design, *Nat. Mater.* **12**, 191 (2013).
- [10] J. K. Nørskov, T. Bligaard, J. Rossmeisl, and C. H. Christensen, Towards the computational design of solid catalysts, *Nat. Chem.* **1**, 37 (2009).
- [11] G. Goldbeck, The economic impact of molecular modelling, Tech. Rep. (Goldbeck Consulting Limited, 2012).
- [12] G. Goldbeck, Industry interactions of the electronic structure research community in europe, Tech. Rep. (Goldbeck Consulting Limited, 2015).
- [13] R. O. Jones, Density functional theory: Its origins, rise to prominence, and future, *Rev. Mod. Phys.* **87**, 897 (2015).
- [14] M. J. G. Peach, P. Benfield, T. Helgaker, and D. J. Tozer, Excitation energies in density functional theory: An evaluation and a diagnostic test, *J. Chem. Phys.* **128**, 044118 (2008).
- [15] S. Sharma, J. K. Dewhurst, N. N. Lathiotakis, and E. K. U. Gross, Reduced density matrix functional for many-electron systems, *Phys. Rev. B* **78**, 201103(R) (2008).
- [16] P. Ziesche, Pair density functional theory—A generalized density functional theory, *Phys. Lett. A* **195**, 213 (1994).
- [17] P. Geerlings, S. Fias, Z. Boisdenghien, and F. De Proft, Conceptual DFT: Chemistry from the linear response function, *Chem. Soc. Rev.* **43**, 4989 (2014).
- [18] L. Hedin, New method for calculating the one-particle Green's function with application to the electron-gas problem, *Phys. Rev.* **139**, A796 (1965).
- [19] G. Onida, L. Reining, and A. Rubio, Electronic excitations: density-functional versus many-body Green's-function approaches, *Rev. Mod. Phys.* **74**, 601 (2002).
- [20] C. A. Taft and J. G. S. Canchaya, Review on simulation models for materials and biomolecular study and design, in *Recent Advances in Complex Functional Materials: From Design to Application* (Springer International Publishing, Cham, 2017), pp. 373–408.
- [21] G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, and C. A. Marianetti, Electronic structure calculations with dynamical mean-field theory, *Rev. Mod. Phys.* **78**, 865 (2006).
- [22] The term “implicit” here is used to mean that while the potential operator is orbital index independent (there is only a single potential), its action upon each orbital may be, and typically will be, different. Functionals in this restricted class are functionals of the GKS density-matrix sufficiently, i.e., they don't use the full variational freedom made available by the orbitals.
- [23] A. Seidl, A. Görling, P. Vogl, J. A. Majewski, and M. Levy, Generalized Kohn-Sham schemes and the band-gap problem, *Phys. Rev. B* **53**, 3764 (1996).
- [24] R. Garrick, A. Natan, T. Gould, and L. Kronik, Exact generalized Kohn-Sham theory for hybrid functionals, *Phys. Rev. X* **10**, 021040 (2020).
- [25] K. Nakamura, Y. Nohara, Y. Yosimoto, and Y. Nomura, *Ab initio* GW plus cumulant calculation for isolated band systems: Application to organic conductor (TMTSF)₂PF₆ and transition-metal oxide SrVO₃, *Phys. Rev. B* **93**, 085124 (2016).
- [26] F. Aryasetiawan and O. Gunnarsson, The GW method, *Rep. Prog. Phys.* **61**, 237 (1998).
- [27] T. Kotani, M. van Schilfgaarde, and S. V. Faleev, Quasiparticle self-consistent GW method: A basis for the independent-particle approximation, *Phys. Rev. B* **76**, 165106 (2007).
- [28] S. Biermann and A. van Rooyeghem, Electronic polarons, cumulants and doubly dynamical mean field theory: Theoretical spectroscopy for correlated and less correlated materials, *J. Electron. Spectrosc. Relat. Phenom.* **208**, 17 (2016).
- [29] M. van Schilfgaarde, T. Kotani, and S. Faleev, Quasiparticle self-consistent GW theory, *Phys. Rev. Lett.* **96**, 226402 (2006).
- [30] D. Vollhardt and A. I. Lichtenstein, Dynamical mean-field approach with predictive power for strongly correlated materials, *Eur. Phys. J. Spec. Top.* **226**, 2439 (2017).

- [31] K. Held, I. A. Nekrasov, G. Keller, V. Eyert, N. Blümer, A. K. McMahan, R. T. Scalettar, T. Pruschke, V. I. Anisimov, and D. Vollhardt, Realistic investigations of correlated electron systems with LDA+DMFT, *Physica Status Solidi (b)* **243**, 2599 (2006).
- [32] X. Deng, J. Mravlje, R. Žitko, M. Ferrero, G. Kotliar, and A. Georges, How bad metals turn good: Spectroscopic signatures of resilient quasiparticles, *Phys. Rev. Lett.* **110**, 086401 (2013).
- [33] A. Georges, L. de' Medici, and J. Mravlje, Strong correlations from Hund's coupling, *Annu. Rev. Condens. Matter Phys.* **4**, 137 (2013).
- [34] S. Biermann, F. Aryasetiawan, and A. Georges, First-principles approach to the electronic structure of strongly correlated systems: Combining the *GW* approximation and dynamical mean-field theory, *Phys. Rev. Lett.* **90**, 086402 (2003).
- [35] J. M. Tomczak, M. Casula, T. Miyake, F. Aryasetiawan, and S. Biermann, Combined *GW* and dynamical mean-field theory: Dynamical screening effects in transition metal oxides, *Europhys. Lett.* **100**, 67001 (2012).
- [36] C. Taranto, M. Kaltak, N. Parragh, G. Sangiovanni, G. Kresse, A. Toschi, and K. Held, Comparing quasiparticle *GW*+DMFT and LDA+DMFT for the test bed material SrVO_3 , *Phys. Rev. B* **88**, 165119 (2013).
- [37] G. Knizia and G. K.-L. Chan, Density matrix embedding: A simple alternative to dynamical mean-field theory, *Phys. Rev. Lett.* **109**, 186404 (2012).
- [38] S. H. Vosko, L. Wilk, and M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis, *Can. J. Phys.* **58**, 1200 (1980).
- [39] U. von Barth and L. Hedin, A local exchange-correlation potential for the spin polarized case. I, *J. Phys. C: Solid State Phys.* **5**, 1629 (1972).
- [40] J. P. Perdew and Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy, *Phys. Rev. B* **45**, 13244 (1992).
- [41] Perdew J. P., K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [42] C. Lee, W. Yang, and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* **37**, 785 (1988).
- [43] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Restoring the density-gradient expansion for exchange in solids and surfaces, *Phys. Rev. Lett.* **100**, 136406 (2008).
- [44] A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A* **38**, 3098 (1988).
- [45] I. Dabo, A. Ferretti, N. Poilvert, Y. Li, N. Marzari, and M. Cococcioni, Koopmans' condition for density-functional theory, *Phys. Rev. B* **82**, 115121 (2010).
- [46] G. Borghi, A. Ferretti, N. L. Nguyen, I. Dabo, and N. Marzari, Koopmans-compliant functionals and their performance against reference molecular data, *Phys. Rev. B* **90**, 075135 (2014).
- [47] N. Colonna, R. De Gennaro, E. Linscott, and N. Marzari, Koopmans spectral functionals in periodic boundary conditions, *J. Chem. Theory Comput.* **18**, 5435 (2022).
- [48] E. B. Linscott, N. Colonna, R. De Gennaro, N. L. Nguyen, G. Borghi, A. Ferretti, I. Dabo, and N. Marzari, Koopmans: An open-source package for accurately and efficiently predicting spectral properties with koopmans functionals, *J. Chem. Theory Comput.* **19**, 7097 (2023).
- [49] J. P. Perdew and A. Zunger, Self-interaction correction to density-functional approximations for many-electron systems, *Phys. Rev. B* **23**, 5048 (1981).
- [50] M. R. Pederson, A. Ruzsinszky, and J. P. Perdew, Communication: Self-interaction correction with unitary invariance in density functional theory, *J. Chem. Phys.* **140**, 121103 (2014).
- [51] S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction, *J. Comput. Chem.* **27**, 1787 (2006).
- [52] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.* **132**, 154104 (2010).
- [53] A. Tkatchenko and M. Scheffler, Accurate molecular van der Waals interactions from ground-state electron density and free-atom reference data, *Phys. Rev. Lett.* **102**, 073005 (2009).
- [54] M. Kim, W. J. Kim, T. Gould, E. K. Lee, S. Lebègue, and H. Kim, uMBD: A materials-ready dispersion correction that uniformly treats metallic, ionic, and van der Waals bonding, *J. Am. Chem. Soc.* **142**, 2346 (2020).
- [55] B. Himmetoglu, A. Floris, S. de Gironcoli, and M. Cococcioni, Hubbard-corrected DFT energy functionals: The LDA+*U* description of correlated systems, *Int. J. Quantum Chem.* **114**, 14 (2014).
- [56] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, First-principles calculations of the electronic structure and spectra of strongly correlated systems: The LDA+*U* method, *J. Phys.: Condens. Matter* **9**, 767 (1997).
- [57] N. E. Kirchner-Hall, W. Zhao, Y. Xiong, I. Timrov, and I. Dabo, Extensive benchmarking of DFT+*U* calculations for predicting band gaps, *Appl. Sci.* **11**, 2395 (2021).
- [58] G. Sai Gautam and E. A. Carter, Evaluating transition metal oxides within DFT-SCAN and SCAN + *U* frameworks for solar thermochemical applications, *Phys. Rev. Mater.* **2**, 095401 (2018).
- [59] N. Artrith, J. A. Garrido Torres, A. Urban, and M. S. Hybertsen, Data-driven approach to parameterize SCAN+*U* for an accurate description of 3d transition metal oxide thermochemistry, *Phys. Rev. Mater.* **6**, 035003 (2022).
- [60] Y. Crespo and N. Seriani, Electronic and magnetic properties of $\alpha\text{-MnO}_2$ from *ab initio* calculations, *Phys. Rev. B* **88**, 144428 (2013).
- [61] A. Floris, S. de Gironcoli, E. K. U. Gross, and M. Cococcioni, Vibrational properties of MnO and NiO from DFT+*U*-based density functional perturbation theory, *Phys. Rev. B* **84**, 161102(R) (2011).
- [62] C. Franchini, R. Podloucky, J. Paier, M. Marsman, and G. Kresse, Ground-state properties of multivalent manganese oxides: Density functional and hybrid density functional calculations, *Phys. Rev. B* **75**, 195128 (2007).
- [63] Z. Hu and H. Metiu, Choice of *U* for DFT+*U* calculations for titanium oxides, *J. Phys. Chem. C* **115**, 5841 (2011).
- [64] A. Kiejna, T. Ossowski, and T. Pabisiak, Surface properties of the clean and Au/Pd covered $\text{Fe}_3\text{O}_4(111)$: DFT and DFT+*U* study, *Phys. Rev. B* **85**, 125414 (2012).

- [65] J. S. Lim, D. Saldana-Greco, and A. M. Rappe, Improved pseudopotential transferability for magnetic and electronic properties of binary manganese oxides from DFT+*U*+*J* calculations, *Phys. Rev. B* **94**, 165151 (2016).
- [66] O. Y. Long, G. Sai Gautam, and E. A. Carter, Evaluating optimal *U* for 3*d* transition-metal oxides within the SCAN+*U* framework, *Phys. Rev. Mater.* **4**, 045401 (2020).
- [67] A. C. M. Padilha, A. R. Rocha, and G. M. Dalpian, DFT+*U* Simulation of the Ti₄O₇-TiO₂ Interface, *Phys. Rev. Appl.* **3**, 024009 (2015).
- [68] C. Rödl, F. Fuchs, J. Furthmüller, and F. Bechstedt, Quasiparticle band structures of the antiferromagnetic transition-metal oxides MnO, FeO, CoO, and NiO, *Phys. Rev. B* **79**, 235114 (2009).
- [69] G. Rollmann, A. Rohrbach, P. Entel, and J. Hafner, First-principles calculation of the structure and magnetic phases of hematite, *Phys. Rev. B* **69**, 165107 (2004).
- [70] N. Tancogne-Dejean, M. A. Sentef, and A. Rubio, Ultrafast modification of Hubbard *U* in a strongly correlated material: *Ab initio* high-harmonic generation in NiO, *Phys. Rev. Lett.* **121**, 097402 (2018).
- [71] D. A. Tompsett, D. S. Middlemiss, and M. S. Islam, Importance of anisotropic Coulomb interactions and exchange to the band gap and antiferromagnetism of β -MnO₂ from DFT+*U*, *Phys. Rev. B* **86**, 205126 (2012).
- [72] F. Zhou, M. Cococcioni, C. A. Marianetti, D. Morgan, and G. Ceder, First-principles prediction of redox potentials in transition-metal compounds with LDA+*U*, *Phys. Rev. B* **70**, 235121 (2004).
- [73] J.-J. Zhou, J. Park, I. Timrov, A. Floris, M. Cococcioni, N. Marzari, and M. Bernardi, *Ab Initio* electron-phonon interactions in correlated electron systems, *Phys. Rev. Lett.* **127**, 126404 (2021).
- [74] G. Carchini, M. García-Melchor, Z. Łodziana, and N. López, Understanding and tuning the intrinsic hydrophobicity of rare-earth oxides: A DFT+*U* study, *ACS Appl. Mater. Interfaces* **8**, 152 (2016).
- [75] C. W. M. Castleton, J. Kullgren, and K. Hermansson, Tuning LDA+*U* for electron localization and structure at oxygen vacancies in ceria, *J. Chem. Phys.* **127**, 244704 (2007).
- [76] J. A. Colón Santana, J. M. An, N. Wu, K. D. Belashchenko, X. Wang, P. Liu, J. Tang, Y. Losovyj, I. N. Yakovkin, and P. A. Dowben, Effect of gadolinium doping on the electronic band structure of europium oxide, *Phys. Rev. B* **85**, 014406 (2012).
- [77] T. Hamada and T. Ohno, A new constraint DFT technique for self-consistent determination of *U* values, *J. Phys.: Condens. Matter* **31**, 065501 (2019).
- [78] M. Huang and S. Fabris, CO Adsorption and Oxidation on Ceria Surfaces from DFT+*U* calculations, *J. Phys. Chem. C* **112**, 8643 (2008).
- [79] S. Li, Y. Li, M. Bäumer, and L. V. Moskaleva, Assessment of PBE+*U* and HSE06 methods and determination of optimal parameter *U* for the structural and energetic properties of rare earth oxides, *J. Chem. Phys.* **153**, 164710 (2020).
- [80] A. H. Reshak, M. Piasecki, S. Auluck, I. V. Kityk, R. Khenata, B. Andriyevsky, C. Cobet, N. Esser, A. Majchrowski, M. Świrkwicz, R. Diduszko, and W. Szyrski, Effect of *U* on the electronic properties of neodymium gallate (NdGaO₃): Theoretical and experimental studies, *J. Phys. Chem. B* **113**, 15237 (2009).
- [81] Z. Yang, Q. Wang, S. Wei, D. Ma, and Q. Sun, The effect of environment on the reaction of water on the Ceria(111) surface: A DFT+*U* study, *J. Phys. Chem. C* **114**, 14891 (2010).
- [82] D. A. Scherlis, M. Cococcioni, P. Sit, and N. Marzari, Simulation of heme using DFT+*U*: A step toward accurate spin-state energetics, *J. Phys. Chem. B* **111**, 7384 (2007).
- [83] P. M. Panchmatia, M. E. Ali, B. Sanyal, and P. M. Oppeneer, Halide ligated iron porphines: A DFT+*U* and UB3LYP study, *J. Phys. Chem. A* **114**, 13381 (2010).
- [84] P. M. Panchmatia, B. Sanyal, and P. M. Oppeneer, GGA+*U* modeling of structural, electronic, and magnetic properties of iron porphyrin-type molecules, *Chem. Phys.* **343**, 47 (2008).
- [85] H. J. Kulik, L. C. Blasiak, N. Marzari, and C. L. Drennan, First-principles study of non-heme Fe(II) halogenase SyrB2 reactivity, *J. Am. Chem. Soc.* **131**, 14426 (2009).
- [86] H. J. Kulik, M. Cococcioni, D. A. Scherlis, and N. Marzari, Density functional theory in transition-metal chemistry: A self-consistent Hubbard *U* Approach, *Phys. Rev. Lett.* **97**, 103001 (2006).
- [87] I. E. Brumboiu, S. Haldar, J. Lüder, O. Eriksson, H. C. Herper, B. Brena, and B. Sanyal, Influence of electron correlation on the electronic structure and magnetism of transition-metal phthalocyanines, *J. Chem. Theory Comput.* **12**, 1772 (2016).
- [88] C. Cao, S. Hill, and H.-P. Cheng, Strongly correlated electrons in the [Ni(hmp)(ROH)X]₄ single molecule magnet: A DFT+*U* study, *Phys. Rev. Lett.* **100**, 167206 (2008).
- [89] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Band theory and Mott insulators: Hubbard *U* instead of Stoner *I*, *Phys. Rev. B* **44**, 943 (1991).
- [90] K. A. Hunnestad, H. Das, C. Hatzoglou, M. Holtz, C. M. Brooks, A. T. J. van Helvoort, D. A. Muller, D. G. Schlom, J. A. Mundy, and D. Meier, 3D oxygen vacancy distribution and defect-property relations in an oxide heterostructure, *Nat. Commun.* **15**, 5400 (2024).
- [91] O. Köksal and R. Pentcheva, Chern and Z₂ topological insulating phases in perovskite-derived 4*d* and 5*d* oxide buckled honeycomb lattices, *Sci. Rep.* **9**, 17306 (2019).
- [92] Y. Wang, Z. Li, X. Luo, J. Gao, Y. Han, J. Jiang, J. Tang, H. Ju, T. Li, R. Lv, S. Cui, Y. Yang, Y. Sun, J. Zhu, X. Gao, W. Lu, Z. Sun, H. Xu, Y. Xiong, and L. Cao, Dualistic insulator states in 1T-TaS₂ crystals, *Nat. Commun.* **15**, 3425 (2024).
- [93] E. M. Flores, M. L. Moreira, and M. J. Piotrowski, Structural and electronic properties of bulk ZnX (X = O, S, Se, Te), ZnF₂, and ZnO/ZnF₂: A DFT investigation within PBE, PBE + *U*, and hybrid HSE functionals, *J. Phys. Chem. A* **124**, 3778 (2020).
- [94] C. Loschen, J. Carrasco, K. M. Neyman, and F. Illas, First-principles LDA+*U* and GGA+*U* study of cerium oxides: Dependence on the effective *U* parameter, *Phys. Rev. B* **75**, 035115 (2007).
- [95] X. Ma, Y. Wu, Y. Lv, and Y. Zhu, Correlation effects on lattice relaxation and electronic structure of ZnO within the GGA+*U* formalism, *J. Phys. Chem. C* **117**, 26029 (2013).
- [96] B. J. Morgan and P. A. Madden, Lithium intercalation into TiO₂(B): A comparison of LDA, GGA, and GGA + *U* density functional calculations, *Phys. Rev. B* **86**, 035147 (2012).
- [97] M.-T. Nguyen, N. Seriani, and R. Gebauer, Water adsorption and dissociation on α -Fe₂O₃(0001): PBE+*U* calculations, *J. Chem. Phys.* **138**, 194709 (2013).

- [98] D. Stoeffler and C. Etz, *Ab initio* electronic structure and magnetism in Sr_2XMoO_6 ($\text{X} = \text{Fe}$ or Co) double perovskite systems: A GGA and GGA+ U comparative study, *J. Phys.: Condens. Matter* **18**, 11291 (2006).
- [99] W. Yang and Y.-W. Son, Effects of self-consistent extended Hubbard interactions and spin-orbit couplings on energy bands of semiconductors and topological insulators, *Phys. Rev. B* **110**, 155133 (2024).
- [100] Y. Zeng, Q. Hu, M. Pan, K. Zhang, S. Grasso, C. Hu, and Q. Feng, Investigation of double perovskites $\text{Sr}_2\text{SmNbO}_6$ and X_2CoNbO_6 ($\text{X} = \text{Sr}, \text{Ba}$) with SCAN functional and plus U correction, *Adv. Powder Mater.* **1**, 100019 (2022).
- [101] S. Kim, Lattice and electronic properties of VO_2 with the SCAN(+ U) approach, *J. Korean Phys. Soc.* **78**, 613 (2021).
- [102] Google Scholar, <https://scholar.google.com>.
- [103] G. Kresse and J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B* **54**, 11169 (1996).
- [104] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, and M. C. Payne, First principles methods using CASTEP, *Z. Krist.* **220**, 567 (2005).
- [105] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. Buongiorno Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. Dal Corso, S. de Gironcoli, P. Delugas, R. A. DiStasio Jr, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, *et al.*, Advanced capabilities for materials modelling with Quantum ESPRESSO, *J. Phys.: Condens. Matter* **29**, 465901 (2017).
- [106] T. D. Kühne, M. Iannuzzi, M. Del Ben, V. V. Rybkin, P. Seewald, F. Stein, T. Laino, R. Z. Khaliullin, O. Schütt, F. Schiffmann, D. Golze, J. Wilhelm, S. Chulkov, M. H. Bani-Hashemian, V. Weber, U. Borštnik, M. Taillefumier, A. S. Jakobovits, A. Lazzaro, H. Pabst, *et al.*, CP2K: An electronic structure and molecular dynamics software package - Quickstep: Efficient and accurate electronic structure calculations, *J. Chem. Phys.* **152**, 194103 (2020).
- [107] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, and T. Ziegler, Chemistry with ADF, *J. Comput. Chem.* **22**, 931 (2001).
- [108] P. Blaha, K. Schwarz, G. K. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k: An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties* (Vienna University of Technology, Austria, 2001).
- [109] E. Artacho, E. Anglada, O. Diéguez, J. D. Gale, A. García, J. Junquera, R. M. Martin, P. Ordejón, J. M. Pruneda, D. Sánchez-Portal, and J. M. Soler, The SIESTA method; developments and applicability, *J. Phys.: Condens. Matter* **20**, 064208 (2008).
- [110] X. Gonze, B. Amadon, P. M. Anglade, J. M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Côté, T. Deutsch, L. Genovese, Ph. Ghosez, M. Giantomassi, S. Goedecker, D. R. Hamann, P. Hermet, F. Jollet, G. Jomard, S. Leroux, *et al.*, ABINIT: First-principles approach to material and nanosystem properties, *Comput. Phys. Commun.* **180**, 2582 (2009).
- [111] The Elk Code: See <http://elk.sourceforge.net/> for The Elk Code (2026).
- [112] J. J. R. Mortensen, A. H. Larsen, M. Kuisma, A. V. Ivanov, A. Taghizadeh, A. Peterson, A. Haldar, A. O. Dohn, C. Schäfer, E. Jónsson, E. D. Hermes, F. A. Nilsson, G. Kastlunger, G. Levi, H. Jónsson, H. Häkkinen, J. Fojt, J. Kangsabanik, J. Söderquist, J. Lehtomäki, *et al.*, GPAW: An open Python package for electronic structure calculations, *J. Chem. Phys.* **160**, 092503 (2024).
- [113] A. Nakata, J. S. Baker, S. Y. Mujahed, J. T. L. Poulton, S. Arapan, J. Lin, Z. Raza, S. Yadav, L. Truflandier, T. Miyazaki, and D. R. Bowler, Large scale and linear scaling DFT with the CONQUEST code, *J. Chem. Phys.* **152**, 164112 (2020).
- [114] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, *Ab Initio* molecular simulations with numeric atom-centered orbitals, *Comput. Phys. Commun.* **180**, 2175 (2009).
- [115] N. Tancogne-Dejean, M. J. T. Oliveira, X. Andrade, H. Appel, C. H. Borca, G. Le Breton, F. Buchholz, A. Castro, S. Corni, A. A. Correa, U. De Giovannini, A. Delgado, F. G. Eich, J. Flick, G. Gil, A. Gomez, N. Helbig, H. Hübener, R. Jestädt, J. Jornet-Somoza, *et al.*, Octopus, a computational framework for exploring light-driven phenomena and quantum dynamics in extended and finite systems, *J. Chem. Phys.* **152**, 124119 (2020).
- [116] The FLEUR project, <https://www.flapw.de/> (2026).
- [117] K. Koepnick and H. Eschrig, Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme, *Phys. Rev. B* **59**, 1743 (1999).
- [118] J. C. A. Prentice, J. Aarons, J. C. Womack, A. E. A. Allen, L. Andrinopoulos, L. Anton, R. A. Bell, A. Bhandari, G. A. Bramley, R. J. Charlton, R. J. Clements, D. J. Cole, G. Constantinescu, F. Corsetti, S. M.-M. Dubois, K. K. B. Duff, J. M. Escartín, A. Greco, Q. Hill, L. P. Lee, *et al.*, The ONETEP linear-scaling density functional theory program, *J. Chem. Phys.* **152**, 174111 (2020).
- [119] G. Geudtner, P. Calaminici, J. Carmona-Espíndola, J. M. del Campo, V. D. Domínguez-Soria, R. F. Moreno, G. U. Gamboa, A. Goursot, A. M. Köster, J. U. Reveles, T. Mineva, J. M. Vázquez-Pérez, A. Vela, B. Zúñiga-Gutierrez, and D. R. Salahub, deMon2k, *WIREs Comput. Mol. Sci.* **2**, 548 (2012).
- [120] J. M. Wills, M. Alouani, P. Andersson, A. Delin, O. Eriksson, and O. Grechnev, *Full-Potential Electronic Structure Method: Energy and Force Calculations with Density Functional and Dynamical Mean Field Theory* (Springer Science and Business Media, New York, 2010).
- [121] L. E. Ratcliff, W. Dawson, G. Fisicaro, D. Caliste, S. Mohr, A. Degomme, B. Videau, V. Cristiglio, M. Stella, M. D'Alessandro, S. Goedecker, T. Nakajima, T. Deutsch, and L. Genovese, Flexibilities of wavelets as a computational basis set for large-scale electronic structure calculations, *J. Chem. Phys.* **152**, 194110 (2020).
- [122] R. Sundararaman, K. Letchworth-Weaver, K. A. Schwarz, D. Gunceler, Y. Ozhobes, and T.A. Arias, JDFTx: Software for joint density-functional theory, *SoftwareX* **6**, 278 (2017).
- [123] P. R. Briddon and M. J. Rayson, Accurate Kohn-Sham DFT with the speed of tight binding: Current techniques and future directions in materials modelling, *Physica Status Solidi (b)* **248**, 1309 (2011).
- [124] P. Motamarri, S. Das, S. Rudraraju, K. Ghosh, D. Davydov, and V. Gavini, DFT-FE-A massively parallel adaptive finite-element code for large-scale density functional theory calculations, *Comput. Phys. Commun.* **246**, 106853 (2020).

- [125] M. F. Herbst, A. Levitt, and E. Cancès, Dftk: A julian approach for simulating electrons in solids, *Proc. JuliaCon Conf.* **3**, 69 (2021).
- [126] S. Ono, Y. Noguchi, R. Sahara, Y. Kawazoe, and K. Ohno, TOMBO: All-electron mixed-basis approach to condensed matter physics, *Comput. Phys. Commun.* **189**, 20 (2015).
- [127] P. Schulz and R. Muller, QUantum Electronic STRucture (SeqQuest Electronic Structure Code), Sandia National Laboratories, Albuquerque (NM) (2004).
- [128] O. Jepsen, The stuttgart tb-Imto-asa program version 47, <http://www.mpi-stuttgart.mpg.de/andersen/> (2000).
- [129] T. Ozaki, Variationally optimized atomic orbitals for large-scale electronic structures, *Phys. Rev. B* **67**, 155108 (2003).
- [130] N. Colonna, N. L. Nguyen, A. Ferretti, and N. Marzari, Koopmans-compliant functionals and potentials and their application to the GW100 test set, *J. Chem. Theory Comput.* **15**, 1905 (2019).
- [131] J. M. de Almeida, N. L. Nguyen, N. Colonna, W. Chen, M. C. Rodrigues, A. Pasquarello, and N. Marzari, Electronic structure of water from Koopmans-compliant functionals, *J. Chem. Theory Comput.* **17**, 3923 (2021).
- [132] N. L. Nguyen, N. Colonna, A. Ferretti, and N. Marzari, Koopmans-compliant spectral functionals for extended systems, *Phys. Rev. X* **8**, 021051 (2018).
- [133] D. S. Lambert and D. D. O'Regan, Use of DFT+*U*+*J* with linear response parameters to predict non-magnetic oxide band gaps with hybrid-functional accuracy, *Phys. Rev. Res.* **5**, 013160 (2023).
- [134] I. Timrov, F. Aquilante, L. Binci, M. Cococcioni, and N. Marzari, Pulay forces in density-functional theory with extended Hubbard functionals: From nonorthogonalized to orthogonalized manifolds, *Phys. Rev. B* **102**, 235159 (2020).
- [135] C. Ricca, I. Timrov, M. Cococcioni, N. Marzari, and U. Aschauer, Self-consistent DFT+*U*+*V* study of oxygen vacancies in SrTiO₃, *Phys. Rev. Res.* **2**, 023313 (2020).
- [136] I. Timrov, P. Agrawal, X. Zhang, S. Erat, R. Liu, A. Braun, M. Cococcioni, M. Calandra, N. Marzari, and D. Passerone, Electronic structure of pristine and Ni-substituted LaFeO₃ from near edge x-ray absorption fine structure experiments and first-principles simulations, *Phys. Rev. Res.* **2**, 033265 (2020).
- [137] B.-C. Shih, T. A. Abtew, X. Yuan, W. Zhang, and P. Zhang, Screened Coulomb interactions of localized electrons in transition metals and transition-metal oxides, *Phys. Rev. B* **86**, 165124 (2012).
- [138] S. Fabris, S. de Gironcoli, S. Baroni, G. Vicario, and G. Balducci, Taming multiple valency with density functionals: A case study of defective ceria, *Phys. Rev. B* **71**, 041102(R) (2005).
- [139] A. Bajaj and H. J. Kulik, Molecular DFT+*U*: A transferable, low-cost approach to eliminate delocalization error, *J. Phys. Chem. Lett.* **12**, 3633 (2021).
- [140] A. Bajaj, C. Duan, A. Nandy, M. G. Taylor, and H. J. Kulik, Molecular orbital projectors in non-empirical jmdFT recover exact conditions in transition-metal chemistry, *J. Chem. Phys.* **156**, 184112 (2022).
- [141] S. M. Griffin, Origin of correlated isolated flat bands in copper-substituted lead phosphate apatite, [arXiv:2307.16892](https://arxiv.org/abs/2307.16892).
- [142] L. Wang, T. Maxisch, and G. Ceder, Oxidation energies of transition metal oxides within the GGA+*U* framework, *Phys. Rev. B* **73**, 195107 (2006).
- [143] M. Cococcioni and S. de Gironcoli, Linear response approach to the calculation of the effective interaction parameters in the LDA+*U* method, *Phys. Rev. B* **71**, 035105 (2005).
- [144] E. B. Linscott, D. J. Cole, M. C. Payne, and D. D. O'Regan, Role of spin in the calculation of Hubbard *U* and Hund's *J* parameters from first principles, *Phys. Rev. B* **98**, 235157 (2018).
- [145] O. K. Andersen and T. Saha-Dasgupta, Muffin-tin orbitals of arbitrary order, *Phys. Rev. B* **62**, R16219 (2000).
- [146] V. I. Anisimov and O. Gunnarsson, Density-functional calculation of effective coulomb interactions in metals, *Phys. Rev. B* **43**, 7570 (1991).
- [147] M. Springer and F. Aryasetiawan, Frequency-dependent screened interaction in Ni within the random-phase approximation, *Phys. Rev. B* **57**, 4364 (1998).
- [148] W. E. Pickett, S. C. Erwin, and E. C. Ethridge, Reformulation of the LDA + *U* method for a local-orbital basis, *Phys. Rev. B* **58**, 1201 (1998).
- [149] B. Himmetoglu, R. M. Wentzcovitch, and M. Cococcioni, First-principles study of electronic and structural properties of CuO, *Phys. Rev. B* **84**, 115108 (2011).
- [150] F. Aryasetiawan, K. Karlsson, O. Jepsen, and U. Schönberger, Calculations of Hubbard *U* from first-principles, *Phys. Rev. B* **74**, 125106 (2006).
- [151] T. Miyake and F. Aryasetiawan, Screened Coulomb interaction in the maximally localized Wannier basis, *Phys. Rev. B* **77**, 085122 (2008).
- [152] T. Miyake, F. Aryasetiawan, and M. Imada, *Ab initio* procedure for constructing effective models of correlated materials with entangled band structure, *Phys. Rev. B* **80**, 155134 (2009).
- [153] E. Şaşıoğlu, C. Friedrich, and S. Blügel, Effective Coulomb interaction in transition metals from constrained random-phase approximation, *Phys. Rev. B* **83**, 121101(R) (2011).
- [154] T. Kotani, *Ab initio* random-phase-approximation calculation of the frequency-dependent effective interaction between 3d electrons: Ni, Fe, and MnO, *J. Phys.: Condens. Matter* **12**, 2413 (2000).
- [155] F. Aryasetiawan, M. Imada, A. Georges, G. Kotliar, S. Biermann, and A. I. Lichtenstein, Frequency-dependent local interactions and low-energy effective models from electronic structure calculations, *Phys. Rev. B* **70**, 195104 (2004).
- [156] L. Vaugier, H. Jiang, and S. Biermann, Hubbard *U* and Hund exchange *J* in transition metal oxides: Screening versus localization trends from constrained random phase approximation, *Phys. Rev. B* **86**, 165105 (2012).
- [157] B. Amadon, T. Applencourt, and F. Bruneval, Screened Coulomb interaction calculations: cRPA implementation and applications to dynamical screening and self-consistency in uranium dioxide and cerium, *Phys. Rev. B* **89**, 125110 (2014).
- [158] M. Casula, A. Rubtsov, and S. Biermann, Dynamical screening effects in correlated materials: Plasmon satellites and spectral weight transfers from a Green's function ansatz to extended dynamical mean field theory, *Phys. Rev. B* **85**, 035115 (2012).
- [159] L. Huang and Y. Wang, Dynamical screening in strongly correlated metal SrVO₃, *Europhys. Lett.* **99**, 67003 (2012).
- [160] L. Boehnke, F. Nilsson, F. Aryasetiawan, and P. Werner, When strong correlations become weak: Consistent merging of GW and DMFT, *Phys. Rev. B* **94**, 201106(R) (2016).

- [161] G. Moynihan, G. Teobaldi, and D. D. O'Regan, Inapplicability of exact constraints and a minimal two-parameter generalization to the DFT+ U based correction of self-interaction error, *Phys. Rev. B* **94**, 220104(R) (2016).
- [162] G. Moynihan, A self-contained ground-state approach for the correction of self-interaction error in approximate density-functional theory, Ph.D. thesis, School of Physics, Trinity College Dublin, 2018.
- [163] P. Verma and D. G. Truhlar, Does DFT+ U mimic hybrid density functionals? *Theor. Chem. Acc.* **135**, 182 (2016).
- [164] H. Eschrig, K. Koepnick, and I. Chaplygin, Density functional application to strongly correlated electron systems, *J. Solid State Chem.* **176**, 482 (2003).
- [165] D. D. O'Regan, N. D. M. Hine, M. C. Payne, and A. A. Mostofi, Projector self-consistent DFT+ U using nonorthogonal generalized wannier functions, *Phys. Rev. B* **82**, 081102(R) (2010).
- [166] D. Novoselov, D. M. Korotin, and V. I. Anisimov, Hellmann–feynman forces within the DFT+ U in wannier functions basis, *J. Phys.: Condens. Matter* **27**, 325602 (2015).
- [167] A. Carta, I. Timrov, S. Beck, and C. Ederer, Bridging constrained random-phase approximation and linear response theory for computing Hubbard parameters, *Phys. Rev. Lett.* **137**, 046503 (2026).
- [168] V. Ivády, R. Armiento, K. Szász, E. Janzén, A. Gali, and I. A. Abrikosov, Theoretical unification of hybrid-DFT and DFT+ U methods for the treatment of localized orbitals, *Phys. Rev. B* **90**, 035146 (2014).
- [169] W. Yang, A. J. Cohen, and P. Mori-Sánchez, Derivative discontinuity, bandgap and lowest unoccupied molecular orbital in density functional theory, *J. Chem. Phys.* **136**, 204111 (2012).
- [170] J. P. Perdew, W. Yang, K. Burke, Z. Yang, E. K. U. Gross, M. Scheffler, G. E. Scuseria, T. M. Henderson, I. Y. Zhang, A. Ruzsinszky, H. Peng, J. Sun, E. Trushin, and A. Görling, Understanding band gaps of solids in generalized Kohn–Sham theory, *Proc. Natl. Acad. Sci. USA* **114**, 2801 (2017).
- [171] S. Kurth and S. Pittalis, The optimized effective potential method and LDA+ U , in *Computational Nanoscience: Do It Yourself!*, edited by J. Grotendorst, S. Blügel, and D. Marx, NIC Series Vol. 31 (John von Neumann Institute for Computing, Jülich, 2006), pp. 299–334.
- [172] V. Ravindran, N. I. Gidopoulos, and S. J. Clark, Local exchange-correlation potentials by density inversion in solids, *Phys. Rev. B* **112**, 085208 (2025).
- [173] C.-O. Almbladh and U. von Barth, Exact results for the charge and spin densities, exchange-correlation potentials, and density-functional eigenvalues, *Phys. Rev. B* **31**, 3231 (1985).
- [174] T. Gould and J. Toulouse, Kohn-Sham potentials in exact density-functional theory at noninteger electron numbers, *Phys. Rev. A* **90**, 050502(R) (2014).
- [175] V. Vlček, H. R. Eisenberg, G. Steinle-Neumann, D. Neuhauser, E. Rabani, and R. Baer, Spontaneous charge carrier localization in extended one-dimensional systems, *Phys. Rev. Lett.* **116**, 186401 (2016).
- [176] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+ U study, *Phys. Rev. B* **57**, 1505 (1998).
- [177] N. D. Drummond, R. J. Needs, A. Sorouri, and W. M. C. Foulkes, Finite-size errors in continuum quantum Monte Carlo calculations, *Phys. Rev. B* **78**, 125106 (2008).
- [178] D. Ceperley, Ground state of the fermion one-component plasma: A Monte Carlo study in two and three dimensions, *Phys. Rev. B* **18**, 3126 (1978).
- [179] Orbital-dependent functionals can be applied within strict Kohn-Sham DFT by means of the optimized effective potential (OEP) procedure. Studies involving OEP are very rare by comparison to those within the overwhelmingly popular, even ubiquitous GKS framework.
- [180] N. Poilvert, Extending the Predictive Power and Scope of Electronic Structure Theory and Quantum Transport, Ph.D. Thesis, Department of Materials Science and Engineering, Massachusetts Institute of Technology, 2011, <http://hdl.handle.net/1721.1/69668>.
- [181] M. R. Pederson, R. A. Heaton, and C. C. Lin, Local-density Hartree-Fock theory of electronic states of molecules with self-interaction correction, *J. Chem. Phys.* **80**, 1972 (1984).
- [182] D. Hait and M. Head-Gordon, Delocalization errors in density functional theory are essentially quadratic in fractional occupation number, *J. Phys. Chem. Lett.* **9**, 6280 (2018).
- [183] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Density-functional theory for fractional particle number: Derivative discontinuities of the energy, *Phys. Rev. Lett.* **49**, 1691 (1982).
- [184] W. Yang, Y. Zhang, and P. W. Ayers, Degenerate ground states and a fractional number of electrons in density and reduced density matrix functional theory, *Phys. Rev. Lett.* **84**, 5172 (2000).
- [185] P. W. Ayers, The dependence on and continuity of the energy and other molecular properties with respect to the number of electrons, *J. Math. Chem.* **43**, 285 (2008).
- [186] P. Mori-Sánchez, A. J. Cohen, and W. Yang, Discontinuous nature of the exchange-correlation functional in strongly correlated systems, *Phys. Rev. Lett.* **102**, 066403 (2009).
- [187] A. C. Burgess and D. D. O'Regan, Flat plane based double-counting free and parameter free many-body DFT+ U , *Phys. Rev. B* **110**, 205150 (2024).
- [188] R. G. Parr and W. Yang, Density functional approach to the frontier-electron theory of chemical reactivity, *J. Am. Chem. Soc.* **106**, 4049 (1984).
- [189] P. W. Ayers and M. Levy, Perspective on “Density functional approach to the frontier-electron theory of chemical reactivity”, *Theor. Chem. Acc.* **103**, 353 (2000).
- [190] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1995).
- [191] W. Yang, A. J. Cohen, F. De Proft, and P. Geerlings, Analytical evaluation of Fukui functions and real-space linear response function, *J. Chem. Phys.* **136**, 144110 (2012).
- [192] P. W. Ayers, F. De Proft, A. Borgoo, and P. Geerlings, Computing Fukui functions without differentiating with respect to electron number. I. Fundamentals, *J. Chem. Phys.* **126**, 224107 (2007).
- [193] B. Wang, P. Geerlings, S. Liu, and F. De Proft, Extending the scope of conceptual density functional theory with second order analytical methodologies, *J. Chem. Theory Comput.* **20**, 1169 (2024).
- [194] D. Zhang, X. Zheng, C. Li, and W. Yang, Orbital relaxation effects on Kohn–Sham frontier orbital energies in density functional theory, *J. Chem. Phys.* **142**, 154113 (2015).

- [195] P. Bultinck, D. Clarisse, P. W. Ayers, and R. Carbo-Dorca, The Fukui matrix: A simple approach to the analysis of the Fukui function and its positive character, *Phys. Chem. Chem. Phys.* **13**, 6110 (2011).
- [196] D. Peng and W. Yang, Fukui function and response function for nonlocal and fractional systems, *J. Chem. Phys.* **138**, 184108 (2013).
- [197] B. Wang, P. Geerlings, F. Heidar-Zadeh, P. W. Ayers, and F. De Proft, Slope of the delocalization function is proportional to analytical hardness, *J. Phys. Chem. Lett.* **15**, 11259 (2024).
- [198] P. Bultinck, D. Van Neck, G. Acke, and P. W. Ayers, Influence of electron correlation and degeneracy on the Fukui matrix and extension of frontier molecular orbital theory to correlated quantum chemical methods, *Phys. Chem. Chem. Phys.* **14**, 2408 (2012).
- [199] G. Acke, D. Van Hende, X. De Vriendt, and P. Bultinck, Extending conceptual density functional theory toward first-order reduced density matrices: An open subsystems viewpoint on the Fukui matrix, *J. Chem. Theory Comput.* **19**, 5418 (2023).
- [200] The ground-state electron density is equal to the diagonal elements of the ground-state first-order reference system reduced density matrix and, as such, their left- and right-hand derivatives with respect to electron count are equal so that $F_{\pm}(\mathbf{r}, \mathbf{r}) = F_{\pm}(\mathbf{r})$.
- [201] K. Terakura, T. Oguchi, A. R. Williams, and J. Kübler, Band theory of insulating transition-metal monoxides: Band-structure calculations, *Phys. Rev. B* **30**, 4734 (1984).
- [202] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyżyk, and G. A. Sawatzky, Density-functional theory and NiO photoemission spectra, *Phys. Rev. B* **48**, 16929 (1993).
- [203] M. T. Czyżyk and G. A. Sawatzky, Local-density functional and on-site correlations: The electronic structure of La_2CuO_4 and LaCuO_3 , *Phys. Rev. B* **49**, 14211 (1994).
- [204] D.-K. Seo, Self-interaction correction in the LDA+*U* method, *Phys. Rev. B* **76**, 033102 (2007).
- [205] I. V. Solovyev, P. H. Dederichs, and V. I. Anisimov, Corrected atomic limit in the local-density approximation and the electronic structure of d impurities in Rb, *Phys. Rev. B* **50**, 16861 (1994).
- [206] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators, *Phys. Rev. B* **52**, R5467 (1995).
- [207] I. Dabo, Towards first-principles electrochemistry, Ph.D. thesis, Department of Materials Science and Engineering, Massachusetts Institute of Technology, 2008, <http://hdl.handle.net/1721.1/44320>.
- [208] E. Macke, I. Timrov, N. Marzari, and L. C. Ciacchi, Orbital-resolved DFT+*U* for molecules and solids, *J. Chem. Theory Comput.* **20**, 4824 (2024).
- [209] A. G. Petukhov, I. I. Mazin, L. Chioncel, and A. I. Liechtenstein, Correlated metals and the LDA + *U* method, *Phys. Rev. B* **67**, 153106 (2003).
- [210] M. Shishkin and H. Sato, DFT+*U* in Dudarev's formulation with corrected interactions between the electrons with opposite spins: The form of Hamiltonian, calculation of forces, and bandgap adjustments, *J. Chem. Phys.* **151**, 024102 (2019).
- [211] M. Shishkin and H. Sato, Evaluation of redox potentials of cathode materials of alkali-ion batteries using extended DFT+*U* + $U_{\uparrow\downarrow}$ method: The role of interactions between the electrons with opposite spins, *J. Chem. Phys.* **154**, 114709 (2021).
- [212] V. Leiria Campo Jr and M. Cococcioni, Extended DFT+*U* + *V* method with on-site and inter-site electronic interactions, *J. Phys.: Condens. Matter* **22**, 055602 (2010).
- [213] D. Soler-Polo, J. Ortega, and F. Flores, A local-orbital density functional formalism for a many-body atomic Hamiltonian: Hubbard–Hund's coupling and DFT+*U* functional, *J. Phys.: Condens. Matter* **33**, 425604 (2021).
- [214] G. K.-L. Chan, A fresh look at ensembles: Derivative discontinuities in density functional theory, *J. Chem. Phys.* **110**, 4710 (1999).
- [215] J. P. Perdew and E. Sagvolden, Exact exchange-correlation potentials in spin-density functional theory and their discontinuities at unit electron number, *Can. J. Chem.* **87**, 1268 (2009).
- [216] Y. Goshen and E. Kraisler, Ensemble ground state of a many-electron system with fractional electron number and spin: Piecewise-linearity and flat-plane condition generalized, *J. Phys. Chem. Lett.* **15**, 2337 (2024).
- [217] A. C. Burgess, E. Linscott, and D. D. O'Regan, Tilted-plane structure of the energy of finite quantum systems, *Phys. Rev. Lett.* **133**, 026404 (2024).
- [218] A. Bajaj, J. P. Janet, and H. J. Kulik, Communication: Recovering the flat-plane condition in electronic structure theory at semi-local DFT cost, *J. Chem. Phys.* **147**, 191101 (2017).
- [219] A. Bajaj, F. Liu, and H. J. Kulik, Non-empirical, low-cost recovery of exact conditions with model-Hamiltonian inspired expressions in jmDFT, *J. Chem. Phys.* **150**, 154115 (2019).
- [220] A. C. Burgess, E. Linscott, and D. D. O'Regan, DFT+*U*-type functional derived to explicitly address the flat plane condition, *Phys. Rev. B* **107**, L121115 (2023).
- [221] B. G. Janesko, Multiconfigurational correlation at DFT+*U* cost: On-site electron–electron interactions yield a block-localized configuration interaction Hamiltonian, *J. Phys. Chem. A* **128**, 5077 (2024).
- [222] S. L. Dudarev, P. Liu, D. A. Andersson, C. R. Stanek, T. Ozaki, and C. Franchini, Parametrization of LSDA+*U* for noncollinear magnetic configurations: Multipolar magnetism in UO_2 , *Phys. Rev. Mater.* **3**, 083802 (2019).
- [223] F. Bultmark, F. Cricchio, O. Grånäs, and L. Nordström, Multipole decomposition of LDA + *U* energy and its application to actinide compounds, *Phys. Rev. B* **80**, 035121 (2009).
- [224] E. Bousquet and N. Spaldin, *J* dependence in the LSDA+*U* treatment of noncollinear magnets, *Phys. Rev. B* **82**, 220402(R) (2010).
- [225] S. Ryee and M. J. Han, Comparative study of DFT+*U* functionals for non-collinear magnetism, *J. Phys.: Condens. Matter* **30**, 275802 (2018).
- [226] F. Gómez-Ortiz, N. Carral-Sainz, J. Sifuna, V. Monteseguro, R. Cuadrado, P. García-Fernández, and J. Junquera, Compatibility of DFT+*U* with non-collinear magnetism and spin-orbit coupling within a framework of numerical atomic orbitals, *Comput. Phys. Commun.* **286**, 108684 (2023).
- [227] L. Binci and N. Marzari, Noncollinear DFT+*U* and Hubbard parameters with fully relativistic ultrasoft pseudopotentials, *Phys. Rev. B* **108**, 115157 (2023).
- [228] J. P. Perdew, Density functional theory and the band gap problem, *Int. J. Quantum Chem.* **28**, 497 (1985).

- [229] V. Etacheri, R. Marom, R. Elazari, G. Salitra, and D. Aurbach, Challenges in the development of advanced Li-ion batteries: a review, *Energy Environ. Sci.* **4**, 3243 (2011).
- [230] M. Fiebig, T. Lottermoser, D. Meier, and M. Trassin, The evolution of multiferroics, *Nat. Rev. Mater.* **1**, 16046 (2016).
- [231] A. Kudo and Y. Miseki, Heterogeneous photocatalyst materials for water splitting, *Chem. Soc. Rev.* **38**, 253 (2009).
- [232] Y. Shiohara, M. Yoshizumi, Y. Takagi, and T. Izumi, Future prospects of high T_c superconductors-coated conductors and their applications, *Physica C* **484**, 1 (2013).
- [233] Q. Si, R. Yu, and E. Abrahams, High-temperature superconductivity in iron pnictides and chalcogenides, *Nat. Rev. Mater.* **1**, 16017 (2016).
- [234] W. Eerenstein, N. D. Mathur, and J. F. Scott, Multiferroic and magnetoelectric materials, *Nature (London)* **442**, 759 (2006).
- [235] E. Morosan, D. Natelson, A. H. Nevidomskyy, and Q. Si, Strongly correlated materials, *Adv. Mater.* **24**, 4896 (2012).
- [236] J. B. Sambur, T. Novet, and B. A. Parkinson, Multiple exciton collection in a sensitized photovoltaic system, *Science* **330**, 63 (2010).
- [237] M. Gatti and M. Guzzo, Dynamical screening in correlated metals: Spectral properties of SrVO₃ in the *GW* approximation and beyond, *Phys. Rev. B* **87**, 155147 (2013).
- [238] M. Gatti, F. Bruneval, V. Olevano, and L. Reining, Understanding correlations in vanadium dioxide from first principles, *Phys. Rev. Lett.* **99**, 266402 (2007).
- [239] J. Chang, I. Eremin, P. Thalmeier, and P. Fulde, Theory of magnetic excitons in the heavy-fermion superconductor UPd₂Al₃, *Phys. Rev. B* **75**, 024503 (2007).
- [240] E. Fernández, P. Moses, A. Toftelund, H. Hansen, J. Martínez, F. Abild-Pedersen, J. Kleis, B. Hinnemann, J. Rossmeisl, T. Bligaard, and J. Nørskov, Scaling relationships for adsorption energies on transition metal oxide, sulfide, and nitride surfaces, *Angew. Chem. Int. Ed.* **47**, 4683 (2008).
- [241] S. L. Dudarev, A. I. Liechtenstein, M. R. Castell, G. A. D. Briggs, and A. P. Sutton, Surface states on NiO (100) and the origin of the contrast reversal in atomically resolved scanning tunneling microscope images, *Phys. Rev. B* **56**, 4900 (1997).
- [242] H. J. Kulik, Perspective: Treating electron over-delocalization with the DFT+*U* method, *J. Chem. Phys.* **142**, 240901 (2015).
- [243] M. Cococcioni, Accurate and efficient calculations on strongly correlated minerals with the LDA+*U* method: Review and perspectives, *Rev. Mineral. Geochem.* **71**, 147 (2010).
- [244] A. Iwaszuk and M. Nolan, Electronic structure and reactivity of Ce- and Zr-doped TiO₂: Assessing the reliability of density functional theory approaches, *J. Phys. Chem. C* **115**, 12995 (2011).
- [245] M. D. Krcha and M. J. Janik, Challenges in the use of density functional theory to examine catalysis by M-doped ceria surfaces, *Int. J. Quantum Chem.* **114**, 8 (2014).
- [246] A. Janotti and W. G. Van de Walle, LDA+*U* and hybrid functional calculations for defects in ZnO, SnO₂, and TiO₂, *Phys. Status Solidi B* **248**, 799 (2011).
- [247] A. Jain, G. Hautier, C. J. Moore, S. Ping Ong, C. C. Fischer, T. Mueller, K. A. Persson, and G. Ceder, A high-throughput infrastructure for density functional theory calculations, *Comput. Mater. Sci.* **50**, 2295 (2011).
- [248] W. Setyawan and S. Curtarolo, High-throughput electronic band structure calculations: Challenges and tools, *Comput. Mater. Sci.* **49**, 299 (2010).
- [249] D. R. Bowler, T. Miyazaki, and M. J. Gillan, Recent progress in linear scaling *ab initio* electronic structure techniques, *J. Phys.: Condens. Matter* **14**, 2781 (2002).
- [250] H. J. Kulik and N. Marzari, Accurate potential energy surfaces with a DFT+*U*(*R*) approach, *J. Chem. Phys.* **135**, 194105 (2011).
- [251] A. Jain, G. Hautier, S. P. Ong, C. J. Moore, C. C. Fischer, K. A. Persson, and G. Ceder, Formation enthalpies by mixing GGA and GGA+*U* calculations, *Phys. Rev. B* **84**, 045115 (2011).
- [252] S. Lutfalla, V. Shapovalov, and A. T. Bell, Calibration of the DFT/GGA+*U* method for determination of reduction energies for transition and rare earth metal oxides of Ti, V, Mo, and Ce, *J. Chem. Theory Comput.* **7**, 2218 (2011).
- [253] M. Shishkin and H. Sato, Challenges in computational evaluation of redox and magnetic properties of Fe-based sulfate cathode materials of Li- and Na-ion batteries, *J. Phys.: Condens. Matter* **29**, 215701 (2017).
- [254] E. B. Isaacs and C. A. Marianetti, Compositional phase stability of strongly correlated electron materials within DFT+*U*, *Phys. Rev. B* **95**, 045141 (2017).
- [255] M. Shishkin and H. Sato, Self-consistent parametrization of DFT+*U* framework using linear response approach: Application to evaluation of redox potentials of battery cathodes, *Phys. Rev. B* **93**, 085135 (2016).
- [256] G. Hautier, S. P. Ong, A. Jain, C. J. Moore, and G. Ceder, Accuracy of density-functional theory in predicting formation energies of ternary oxides from binary oxides and its implication on phase stability, *Phys. Rev. B* **85**, 155208 (2012).
- [257] S. P. Ong, L. Wang, B. Kang, and G. Ceder, Li-Fe-P-O₂ phase diagram from first principles calculations, *Chem. Mater.* **20**, 1798 (2008).
- [258] L. Wang, T. Maxisch, and G. Ceder, A first-principles approach to studying the thermal stability of oxide cathode materials, *Chem. Mater.* **19**, 543 (2007).
- [259] S. P. Ong, V. L. Chevrier, G. Hautier, A. Jain, C. Moore, S. Kim, X. Ma, and G. Ceder, Voltage, stability and diffusion barrier differences between sodium-ion and lithium-ion intercalation materials, *Energy Environ. Sci.* **4**, 3680 (2011).
- [260] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, and K. A. Persson, Commentary: The materials project: A materials genome approach to accelerating materials innovation, *APL Mater.* **1**, 011002 (2013).
- [261] G. Hautier, A. Jain, and S. P. Ong, From the computer to the laboratory: materials discovery and design using first-principles calculations, *J. Mater. Sci.* **47**, 7317 (2012).
- [262] D. S. Lambert and D. D. O'Regan, Evaluation of first-principles Hubbard and Hund corrected DFT for defect formation energies in non-magnetic transition metal oxides, *RSC Adv.* **14**, 38645 (2024).
- [263] P. Mori-Sánchez and A. J. Cohen, The derivative discontinuity of the exchange-correlation functional, *Phys. Chem. Chem. Phys.* **16**, 14378 (2014).
- [264] X. De Vriendt, L. Lemmens, S. De Baerdemacker, P. Bultinck, and G. Acke, Quantifying delocalization and static correlation errors by imposing (spin) population redistributions through constraints on atomic domains, *J. Chem. Theory Comput.* **17**, 6808 (2021).
- [265] N. Q. Su, C. Li, and W. Yang, Describing strong correlation with fractional-spin correction in density func-

- tional theory, *Proc. Natl. Acad. Sci. USA* **115**, 9678 (2018).
- [266] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Fractional spins and static correlation error in density functional theory, *J. Chem. Phys.* **129**, 121104 (2008).
- [267] J. C. Phillips, Generalized Koopmans' theorem, *Phys. Rev.* **123**, 420 (1961).
- [268] J. Hubbard, Electron correlations in narrow energy bands, *Proc. Roy. Soc. Math. Phys. Eng.* **276**, 238 (1963).
- [269] P. Mori-Sánchez, A. J. Cohen, and W. Yang, Many-electron self-interaction error in approximate density functionals, *J. Chem. Phys.* **125**, 201102 (2006).
- [270] A. Ruzsinszky, J. P. Perdew, G. I. Csonka, O. A. Vydrov, and G. E. Scuseria, Spurious fractional charge on dissociated atoms: Pervasive and resilient self-interaction error of common density functionals, *J. Chem. Phys.* **125**, 194112 (2006).
- [271] O. A. Vydrov, G. E. Scuseria, and J. P. Perdew, Tests of functionals for systems with fractional electron number, *J. Chem. Phys.* **126**, 154109 (2007).
- [272] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Insights into current limitations of density functional theory, *Science* **321**, 792 (2008).
- [273] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Fractional charge perspective on the band gap in density-functional theory, *Phys. Rev. B* **77**, 115123 (2008).
- [274] P. Borlido, T. Aull, A. W. Huran, F. Tran, M. A. Marques, and S. Botti, Large-scale benchmark of exchange-correlation functionals for the determination of electronic band gaps of solids, *J. Chem. Theory Comput.* **15**, 5069 (2019).
- [275] A. Svane and O. Gunnarsson, Localization in the self-interaction-corrected density-functional formalism, *Phys. Rev. B* **37**, 9919 (1988).
- [276] Z. Szotek, W. M. Temmerman, and H. Winter, Application of the self-interaction correction to transition-metal oxides, *Phys. Rev. B* **47**, 4029 (1993).
- [277] T. Sohier, M. Calandra, and F. Mauri, Density functional perturbation theory for gated two-dimensional heterostructures: Theoretical developments and application to flexural phonons in graphene, *Phys. Rev. B* **96**, 075448 (2017).
- [278] M. Schlupf and F. Gygi, Optimization algorithm for the generation of ONCV pseudopotentials, *Comput. Phys. Commun.* **196**, 36 (2015).
- [279] D. R. Hamann, Optimized norm-conserving Vanderbilt pseudopotentials, *Phys. Rev. B* **88**, 085117 (2013).
- [280] N. Marzari, D. Vanderbilt, A. De Vita, and M. C. Payne, Thermal contraction and disordering of the Al (110) surface, *Phys. Rev. Lett.* **82**, 3296 (1999).
- [281] O. V. Gritsenko and E. J. Baerends, The spin-unrestricted molecular Kohn-Sham solution and the analogue of Koopmans's theorem for open-shell molecules, *J. Chem. Phys.* **120**, 8364 (2004).
- [282] T. Gould, L. Kronik, and S. Pittalis, "Ensemblization" of density functional theory, *J. Chem. Phys.* **164**, 040901 (2026).
- [283] K. Capelle, G. Vignale, and C. A. Ullrich, Spin gaps and spin-flip energies in density-functional theory, *Phys. Rev. B* **81**, 125114 (2010).
- [284] T. Gál and P. Geerlings, Energy surface, chemical potentials, Kohn-Sham energies in spin-polarized density functional theory, *J. Chem. Phys.* **133**, 144105 (2010).
- [285] A. Hayman, N. Levy, Y. Goshen, M. Fraenkel, E. Kraisler, and T. Stein, Spin migration in density functional theory: Energy, potential, and density perspectives, *J. Chem. Phys.* **162**, 114301 (2025).
- [286] O. V. Gritsenko and E. J. Baerends, The analog of Koopmans' theorem in spin-density functional theory, *J. Chem. Phys.* **117**, 9154 (2002).
- [287] T. Gál, P. W. Ayers, F. De Proft, and P. Geerlings, Nonuniqueness of magnetic fields and energy derivatives in spin-polarized density functional theory, *J. Chem. Phys.* **131**, 154114 (2009).
- [288] M. Galvan and R. Vargas, Spin-potential in Kohn-Sham theory, *J. Phys. Chem.* **96**, 1625 (1992).
- [289] D. R. Hamann, M. Schlüter, and C. Chiang, Norm-conserving pseudopotentials, *Phys. Rev. Lett.* **43**, 1494 (1979).
- [290] L. Kleinman and D. M. Bylander, Efficacious form for model pseudopotentials, *Phys. Rev. Lett.* **48**, 1425 (1982).
- [291] D. Vanderbilt, Soft self-consistent pseudopotentials in a generalized eigenvalue formalism, *Phys. Rev. B* **41**, 7892 (1990).
- [292] K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, Car-Parrinello molecular dynamics with Vanderbilt ultrasoft pseudopotentials, *Phys. Rev. B* **47**, 10142 (1993).
- [293] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* **50**, 17953 (1994).
- [294] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* **59**, 1758 (1999).
- [295] I. Timrov, N. Marzari, and M. Cococcioni, Self-consistent Hubbard parameters from density-functional perturbation theory in the ultrasoft and projector-augmented wave formulations, *Phys. Rev. B* **103**, 045141 (2021).