

DFT + U + V is equivalent to DFT + U with density-dependent hybridized projectorsEdward Linscott^{1,*} and Alberto Carta²¹*PSI Center for Scientific Computing, Theory and Data, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), Paul Scherrer Institute, 5232 Villigen PSI, Switzerland*Nicola Marzari³²*PSI Center for Scientific Computing, Theory and Data, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland; National Centre for Computational Design and Discovery of Novel Materials (MARVEL), Paul Scherrer Institute, 5232 Villigen PSI, Switzerland;*
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Hubbard-corrected density-functional theory (DFT + U) is a popular tool for first-principles modeling of materials with localized d or f electrons, but its on-site corrections tend to over-localize charge and break covalent bonds. Intersite + V corrections were introduced to counter this and are now widely used, but a formal justification has been lacking. Here, we show that—to first order in V/U —intersite corrections are exactly equivalent to on-site DFT + U evaluated on a density-matrix-dependent redefinition of the Hubbard projectors, hybridized with those of neighboring sites, providing insight into the explicit mechanism by which V affects covalency. If the projectors are held frozen, as is common practice, the equivalence partially breaks down. Beyond reinterpreting the formalism, these results sharpen the questions of how V should be computed and what the Hubbard subspaces fundamentally are.

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Density-functional theory (DFT) is a cornerstone of first-principles modeling across physics, chemistry, and materials science [1–5], but it fails for so-called “strongly correlated” materials—loosely, those whose ground-state wavefunction has no single dominant electronic configuration—for instance, wrongly predicting many transition metal oxides to be metallic [6,7]. DFT + U was initially developed to address this failure, inspired by the success of the Hubbard model (a comparatively simple model Hamiltonian that captures the essential physics of the Mott transition [8]). The DFT + U energy functional—here, in its rotationally invariant simplified form, using fully-localized-limit double counting and with the Hund’s coupling J absorbed into an effective Hubbard parameter [9–11]—is given by

$$E_{\text{DFT}+U} = E_{\text{DFT}} + \sum_{I\sigma} \frac{U^I}{2} \text{Tr}[\mathbf{n}^{I\sigma} (1 - \mathbf{n}^{I\sigma})], \quad (1)$$

where the occupancy matrix

$$n_{mm'}^{I\sigma} = \langle \phi_m^{I\sigma} | \hat{\rho}^\sigma | \phi_{m'}^{I\sigma} \rangle = \sum_v f_v^\sigma \langle \phi_m^{I\sigma} | \psi_v^\sigma \rangle \langle \psi_v^\sigma | \phi_{m'}^{I\sigma} \rangle \quad (2)$$

is the projection of the spin-dependent Kohn-Sham density-matrix operator $\hat{\rho}^\sigma = \sum_v f_v^\sigma |\psi_v^\sigma\rangle \langle \psi_v^\sigma|$ (with v being a compound index for both crystal momentum and band index) onto a local subspace (indexed I) as defined by a set of orbitals $\{\phi_m^{I\sigma}\}$ [12–14]. Typically, these orbitals are atom centered, fixed, localized, orthonormal (as in the “orthoatomic” scheme employed in this work), and correspond to the $3d$ or $4f$ subshell of a transition metal/lanthanide [15]. Meanwhile, U^I is the Hubbard parameter for site I and defines the strength of the Hubbard correction that will be applied to this particular subspace. Because the correction depends on the Kohn-Sham orbitals via the projected density matrix, DFT + U is an orbital-dependent, generalized Kohn-Sham theory.

The derivation of DFT + U from the Hubbard model rests on several severe approximations—chief among them, that all electronic interactions are neglected except for local Hartree-Fock terms within each Hubbard site. Consequently, DFT + U does not model genuinely strongly correlated chemistry—indeed, in some cases it degrades predictions relative to uncorrected DFT [16–18]—but for the most part it has been applied with remarkable success to many different classes of materials (see Refs. [19–21], among many others).

DFT + U can be placed on more rigorous and transparent footing by framing it as a correction not of strong correlations, but of self-interaction [22–24]. This alternative interpretation rests on an exact condition: For the exact functional, the total energy is piecewise linear in the total number of electrons in the system, whereas approximate functionals exhibit

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erroneous curvature [25,26]. This is known as many-electron self-interaction error (SIE) or delocalization error [27,28]. The key observation of Refs. [22,23] is that the Hubbard correction of Eq. (1) directly reduces the curvature of the total energy with respect to the occupations of each Hubbard subspace (more specifically, the eigenvalues $\lambda_i^{I\sigma}$ of the on-site occupation matrices $\mathbf{n}^{I\sigma}$). With a judicious choice of U^I , the DFT + U energy term can therefore remove this local curvature entirely. This is an ansatz, not an exact condition: Correcting local curvature may, but need not, remedy the *global* curvature with respect to total particle number [29]. It can be partly justified by noting that if the rest of the system interacts with the Hubbard site only through an energy that is linear in the site occupation—as it does if the on-site electronic interactions are so strong that it is a good approximation to neglect all other electron-electron interactions, or if the rest of the system acts through a constant potential—the exact total energy is then piecewise linear in the subspace occupation itself, so any local curvature is genuinely spurious and the ansatz becomes exact [30].

Framing DFT + U as a correction to SIE not only helps to explain its success, but also provides us with a class of recipes to calculate the Hubbard parameters $\{U^I\}$: compute the local curvature directly from linear response DFT, and then set $\{U^I\}$ to match the observed error (see Sec. S1 of the Supplemental Material [31]). Since DFT + U predictions depend strongly on the value of U , an unbiased first-principles procedure is a prerequisite for the theory to be predictive.

However, even with a recipe for computing Hubbard parameters, the DFT + U method is not without its shortcomings—not least that the choice of the Hubbard projectors themselves remains largely arbitrary [32], a point to which we will return. In addition, it has been observed that DFT + U can over-localize charge and artificially break covalent bonds [17,33]. This arises because the Hubbard corrections shift the energy levels of the projector orbitals, disrupting any hybridization (i.e., covalency) that might be occurring between these orbitals and those of neighboring atoms (because effective hybridization between orbitals requires them to have similar energies) [34,35]. This is not a corner case: Away from the most ionic compounds, metal-ligand hybridization is the rule rather than the exception, and a purely on-site correction cannot see it. In an effort to address this, DFT + U has been extended to DFT + U + V :

$$E_{\text{DFT}+U+V} = E_{\text{DFT}+U} - \sum_{IJ\sigma} \frac{V^{IJ}}{2} \text{Tr}[\mathbf{n}^{IJ\sigma} \mathbf{n}^{J\sigma}], \quad (3)$$

where the strength of these intersite corrections is defined by the V^{IJ} parameters [16,17]. Typically, V^{IJ} is chosen to be nonzero only between neighboring sites. Like the DFT + U functional, it follows from the Hubbard model under a single-Slater-determinant approximation [10], now also retaining Hartree-Fock interactions between adjacent sites.

V parameters are typically calculated from the off-diagonal components of the same response matrices constructed to determine U . However, the formal justification for doing so is unclear: While the diagonal response measures the local curvature of the total energy with respect to the occupation of the Hubbard subspace, $\frac{d^2E}{d\lambda_i^2}$, which the + U framework treats

as spurious and can therefore be framed as a correction to SIE, there is no equivalent reason why the off-diagonal $\frac{d^2E}{d\lambda_i d\lambda_j}$ should also be zero. Put another way, + U has a clear target—removing the spurious on-site curvature $\frac{d^2E}{d\lambda_i^2}$ —whereas it is far less clear what error of approximate DFT the + V correction is meant to remedy. There is also a mismatch of a more basic kind: The response matrices measure curvature with respect to the site-diagonal occupations n^{II} and n^{JJ} , whereas E_V introduces curvature with respect to the intersite blocks, $\partial^2 E_V / \partial n_{mm'}^{IJ\sigma} \partial n_{m'm}^{JJ\sigma} = -V^{IJ}$ —so the quantity computed and the quantity corrected are not the same object [36]. Nevertheless, DFT + U + V has proven remarkably successful in practice, improving the description of band gaps, oxidation states, cathode voltages, and defect chemistry [37–44]. Its advantage over DFT + U can occasionally be marginal [45–47], but its quantitative accuracy can be excellent: Computed intercalation voltages of olivine-type Li-ion cathodes fall within a few percent of experiment, outperforming DFT, DFT + U , and HSE06 alike [41]. This raises the question: What is the physical meaning of the V corrections, and why do they typically improve over DFT + U ?

This Letter demonstrates that to first order in V/U , DFT + U + V is exactly on-site DFT + U evaluated on a redefinition of the Hubbard projectors. To prove this, we first rewrite the DFT + U energy in the basis $\{|\varphi_i^{I\sigma}\rangle\}$ of eigenvectors of the on-site occupation matrix $\mathbf{n}^{II\sigma}$, with eigenvalues $\lambda_i^{I\sigma}$. These “block-diagonalizing projectors” are the natural orbitals of each site—oriented by the local chemical environment rather than by the arbitrary orientation of the original projectors—and their occupations $\lambda_i^{I\sigma}$ are precisely the quantities whose spurious curvature the + U correction removes. The block-diagonalizing projectors of antiferromagnetic NiO are shown in Figs. 1(d)–1(f) alongside the original projectors [panels (a)–(c)]. We then hybridize each site with its V -coupled neighbors by rotating $|\varphi_i^{I\sigma}\rangle \rightarrow e^{\hat{T}} |\varphi_i^{I\sigma}\rangle$, where $\hat{T}$ is an as-yet-unknown anti-Hermitian generator that induces a weak hybridization between neighboring sites, built from the Hubbard parameters and the intersite occupations $\Lambda_{ij}^{IJ\sigma} = \langle \varphi_i^{I\sigma} | \hat{\rho}^\sigma | \varphi_j^{J\sigma} \rangle$ (the off-diagonal density-matrix elements that quantify the covalency between sites I and J). In the Appendix, we prove that there is a specific choice $\hat{T} = \hat{S}$ for which the DFT + U energy of the hybridized projectors reproduces the DFT + U + V energy,

$$E_U[\hat{S}] = E_U + E_V + \mathcal{O}(V^2/U), \quad (4)$$

where $E_U[\hat{S}]$ denotes the DFT + U correction energy evaluated using the “hybridized” projectors $\{e^{\hat{S}} |\varphi_i^{I\sigma}\rangle\}$ and $E_U + E_V$ is the energy of the DFT + U + V correction applied to the original projectors. This generator $\hat{S}$ is given explicitly by

$$\langle \varphi_i^{I\sigma} | \hat{S} | \varphi_j^{J\sigma} \rangle = \frac{V^{IJ} \Lambda_{ij}^{IJ\sigma}}{U^I (1 - 2\lambda_i^{I\sigma}) - U^J (1 - 2\lambda_j^{J\sigma})}. \quad (5)$$

(For bulk systems, $\hat{S}$ takes the $\mathbf{k}$ -dependent form given in Sec. S2 of the Supplemental Material [31].) The expansion is controlled by the norm of the generator $\|\hat{S}\|$, which, for typical magnitudes V and U of the intersite couplings and on-site potentials, is of order V/U (see Sec. S4 of the Supplemental Material for details [31]). For reference, in bulk NiO, $\|\hat{S}\| \approx 0.08$.

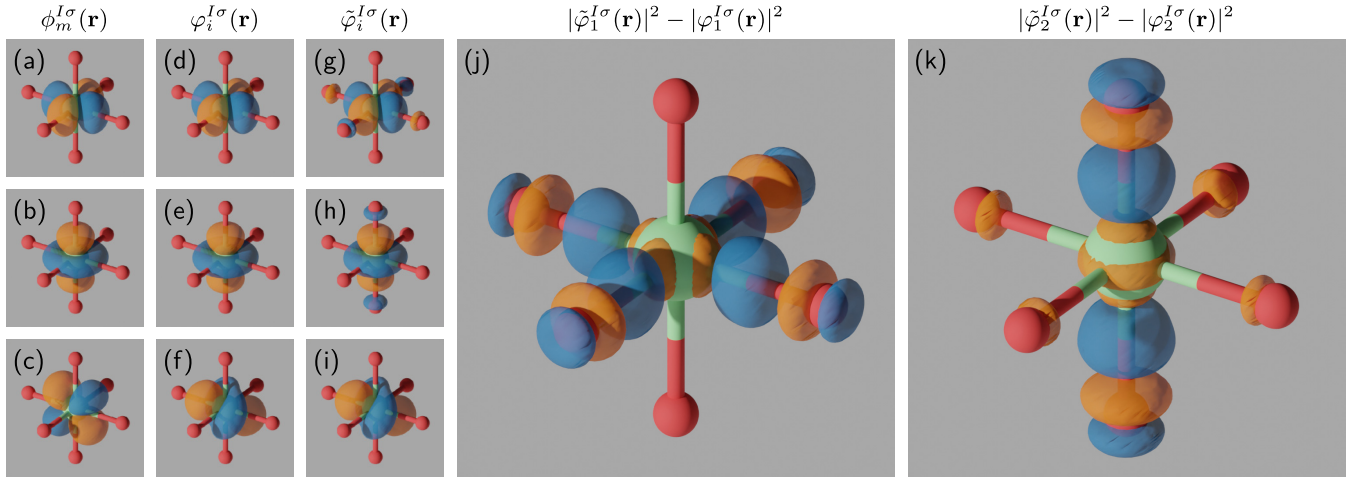


FIG. 1. The original $\phi_m^{I\sigma}(\mathbf{r})$, block-diagonalizing $\varphi_i^{I\sigma}(\mathbf{r})$, and doubly hybridized Hubbard projectors $\tilde{\varphi}_i^{I\sigma}(\mathbf{r}) = e^{2\hat{S}}\varphi_i^{I\sigma}(\mathbf{r})$ of nickel in antiferromagnetic NiO for the minority spin channel. For simplicity, only one nickel atom (green) and its nearest-neighbor oxygen atoms (red) are shown. The left column [panels (a)–(c)] shows three of the five original Hubbard projectors, defined as orthogonalized pseudoatomic orbitals oriented with the Cartesian axes. (The crystal structure happens to align with the Cartesian directions, but in general the orientation of these orbitals is arbitrary.) The second column [panels (d)–(f)] shows the block-diagonalizing projectors $|\varphi_i^{I\sigma}\rangle$, i.e., the eigenvectors of $\mathbf{n}^{II}$; unlike the original projectors, these are oriented with respect to the local chemical environment, with the octahedral crystal field and the exchange field of the antiferromagnetic ordering producing a $d_{x^2-y^2}$ orbital [panel (d)], a d_{z^2} orbital [panel (e)], and a combination of the degenerate t_{2g} orbitals [panel (f)]. The third column [panels (g)–(i)] shows the doubly hybridized projectors; the first two weakly hybridize with the oxygen $2p$ orbitals. Panels (j) and (k) show the density difference between the first two hybridized and block-diagonalizing orbitals (orange regions positive, blue negative), revealing the increased antibonding character with the chemically relevant oxygens.

Equation (4) can be differentiated, upon which we find that, to first order, the DFT + U potential applied to these hybridized projectors reproduces the DFT + U + V potential. This is the central result of this work: In the limit $V \ll U$, the intersite + V correction is exactly a redefinition of the Hubbard projectors. Since $\hat{S}$ is built from the occupations themselves, this redefinition is intrinsically *density matrix dependent*. This also identifies the error that + V remedies: To first order, it imposes the very same occupation-curvature penalty as + U —a correction to SIE—but measured on the hybridized projectors rather than the bare ones.

To understand how this rotation affects the Hubbard projectors, consider one common DFT + U + V setup, in which intersite corrections couple a $3d$ or $4f$ site to the $2p$ orbitals of ligands that are not themselves Hubbard corrected. For this case, the rotation acts on the projectors as

$$|\varphi_i^{I\sigma}\rangle \longrightarrow |\varphi_i^{I\sigma}\rangle - \sum_j \sum_{\sigma'} \frac{\Lambda_{ji}^{J\sigma}}{1 - 2\lambda_i^{I\sigma}} \frac{V^{IJ}}{U^I} |\varphi_j^{J\sigma'}\rangle. \quad (6)$$

Equation (6) shows that the new hybridized projectors remain centered on site I but acquire weight from the orbitals of its V -coupled neighbors (e.g., the $2p$ orbitals of oxygen in a transition metal oxide). The admixture of $|\varphi_j^{J\sigma}\rangle$ grows with V^{IJ}/U^I and with the off-diagonal occupancy $\Lambda_{ji}^{J\sigma}$, and is smallest when orbital i is near integer occupation. As $\lambda_i^{I\sigma} \rightarrow \frac{1}{2}$, its on-site + U potential $\frac{U^I}{2}(1 - 2\lambda_i^{I\sigma})$ vanishes, so a finite intersite term is no longer small by comparison and the expansion fails even for $V \ll U$. (The more general form, Eq. (5), has a vanishing denominator if V couples degenerate levels. The $\lambda_i^{I\sigma} \rightarrow \frac{1}{2}$ divergence discussed above falls into this category; so too would, e.g., NiO with an

unconventional V applied between like-spin nickel sites, in which case the two sites mix evenly rather than weakly and the hybridized-projector picture breaks down—see Sec. S3 of the Supplemental Material [31].)

Example hybridized orbitals for bulk NiO are shown in Figs. 1(g)–1(i). In particular, the spin-minority e_g hybridized projectors gain antibonding character [Figs. 1(j) and 1(k)]. Because they are less than half-filled, the + U penalty drives their occupation even further down, depleting antibonding density and strengthening the Ni–O bond—so applying + U to the hybridized projectors enhances covalency, the opposite of the over-localization caused by + U on the bare projectors. This makes precise the common intuition that + V “restores covalency”: To first order, + V adds no physics beyond the occupation-curvature penalty of + U . What changes is where that penalty is measured: Now, it is applied to hybridized projectors that already contain the bond’s covalent character, rather than to bare projectors, where the same correction would disrupt that covalency. DFT + U + V thus improves on DFT + U wherever the bare projectors misrepresent the covalent character of the subspace—though whether a deeper principle selects these hybridized projectors is a question to which we will return.

As noted above, because the generator $\hat{S}$ is a functional of the density matrix, the hybridized projectors $\{e^{\hat{S}}|\varphi_i^{I\sigma}\rangle\}$ are density matrix dependent. This is a major departure from standard DFT + U practice, in which the Hubbard projectors are externally specified functions, chosen once and held frozen throughout the calculation—with only rare exceptions, such as the projector-self-consistent scheme of Ref. [48]. Given that using frozen projectors is standard practice, let us briefly consider this regime. Using frozen projectors does not affect

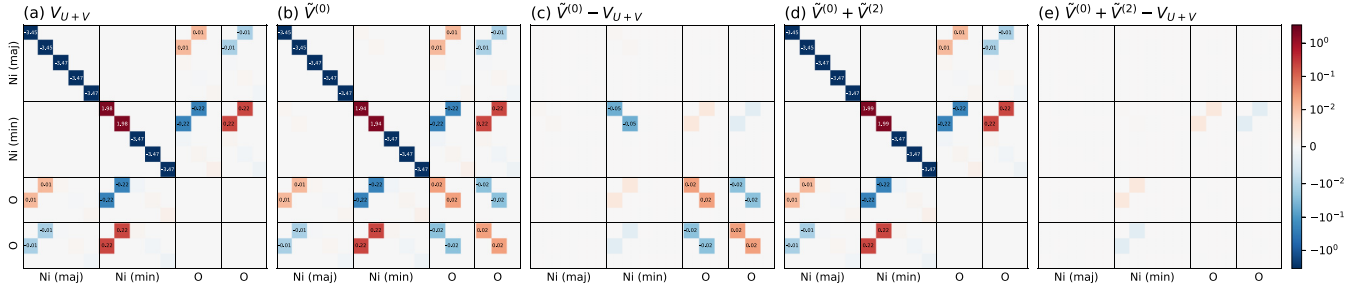


FIG. 2. The frozen-projector approximation reproduces the exact DFT + U + V potential in bulk antiferromagnetic nickel oxide to within a small residual [panels (a)–(c)], which can be almost entirely accounted for by a single analytic second-order term [panels (d) and (e)]. Each panel shows the matrix elements of various potentials in the basis of block-diagonalizing orbitals $\{\varphi_i^{I\sigma}\}$ evaluated at the Γ point. The matrices are subdivided by Hubbard site; one can clearly see the five d orbitals of each Ni and the three p orbitals of each O. (The unit cell contains four atoms: two Ni and two O.) Panel (a) shows the matrix elements of the full (i.e., exact) DFT + U + V potential $\langle \varphi_i^{I\sigma} | \hat{V}_U + \hat{V}_V | \varphi_j^{J\sigma} \rangle$. The on-site blocks of the potential are clearly diagonal in this basis (by design). Panel (b) shows the matrix elements of the approximate potential $\langle \varphi_i^{I\sigma} | \hat{V}^{(0)\sigma} | \varphi_j^{J\sigma} \rangle$ [Eq. (9)], which, as desired, closely replicate the full DFT + U + V potential: The differences between the two are shown in panel (c). Panel (d) shows the matrix elements of the potential $\langle \varphi_i^{I\sigma} | \hat{V}^{(0)\sigma} + \hat{V}^{(2)\sigma} | \varphi_j^{J\sigma} \rangle$, where $\hat{V}^{(2)\sigma}$ is the higher-order correction (Eq. (S48) of the Supplemental Material [31]). This potential even more closely matches the full DFT + U + V potential, as shown by their difference in panel (e). Computational details can be found in Sec. S5 of the Supplemental Material [31].

the energy equivalence, because the proof in the Appendix is an identity for any fixed density matrix: At the density matrix for which $\hat{S}$ is constructed, the frozen hybridized projectors still reproduce the DFT + U + V energy. However, the same is not true of the potential. The full potential with density-matrix-dependent projectors corresponds to the functional derivative of the energy with respect to the density matrix:

$$\frac{\delta E_U[\hat{S}[\hat{\rho}]]}{\delta \hat{\rho}^\sigma} = \frac{\delta E_U}{\delta \hat{\rho}^\sigma} \Big|_{\hat{S}} + \left\langle \frac{\partial E_U}{\partial \hat{S}}, \frac{\partial \hat{S}}{\partial \hat{\rho}^\sigma} \right\rangle. \quad (7)$$

Evaluating this derivative (see Sec. S6 of the Supplemental Material [31]) gives

$$\frac{\delta E_U[\hat{S}[\hat{\rho}]]}{\delta \hat{\rho}^\sigma} = \hat{V}_U^\sigma + \hat{V}_V^\sigma + \mathcal{O}(V^2/U); \quad (8)$$

that is, the DFT + U potential applied to hybridized projectors reproduces the DFT + U + V potential to first order, as expected. Freezing the projectors amounts to dropping the second term in Eq. (7). Doing so, one finds that if $\hat{T} = 2\hat{S}$ (i.e., twice the rotation that reproduces the energy), then

$$\hat{V}_U^\sigma + \hat{V}_V^\sigma = \underbrace{\sum_{Ii} \frac{U^I}{2} (1 - 2\lambda_i^{I\sigma}) |\tilde{\varphi}_i^{I\sigma}\rangle \langle \tilde{\varphi}_i^{I\sigma}|}_{\equiv: \hat{V}^{(0)\sigma}} + \mathcal{O}(V^2/U), \quad (9)$$

which defines the frozen-projector potential $\hat{V}^{(0)\sigma}$: an on-site Hubbard correction, with no intersite term, evaluated on the doubly hybridized projectors $|\tilde{\varphi}_i^{I\sigma}\rangle = e^{2\hat{S}} |\varphi_i^{I\sigma}\rangle$ (see Secs. S6 and S7 of the Supplemental Material for the full proof). In other words, we can map DFT + U + V to DFT + U with frozen hybridized projectors, but no single choice reproduces both the spectrum (which calls for $e^{\hat{S}}$) and the energy ($e^{\hat{S}}$). This mismatch also manifests itself via the prefactor in Eq. (9), which is inconsistently built from the bare occupations $\lambda_i^{I\sigma}$ of the original projectors, not from the occupation matrix $n_{ij}^{II\sigma}[2\hat{S}] = \langle \tilde{\varphi}_i^{I\sigma} | \hat{\rho}^\sigma | \tilde{\varphi}_j^{I\sigma} \rangle$ of the hybridized

projectors on which it acts (see Sec. S8 of the Supplemental Material [31]).

With or without freezing the projectors, it is important to remember that the proof applies in the perturbative limit $V \ll U$. In practice, this limit is only approximately satisfied—in bulk NiO, typical values are $U \approx 7$ eV and $V \approx 1$ eV [16]—but the expansion remains well under control. Figure 2 compares the exact DFT + U + V potential [panel (a)] with the first-order approximation $\hat{V}^{(0)\sigma}$ [panel (b)]: the two agree to within a small residual [panel (c)], and even this residual is predicted analytically by the higher-order term $\hat{V}^{(2)\sigma}$ [panels (d) and (e)]—albeit at a cost: $\hat{V}^{(2)\sigma}$ no longer has the on-site + U form (see Sec. S9 of the Supplemental Material [31]. Note that the numerical superscript in $\hat{V}^{(n)\sigma}$ counts powers of $\hat{S}$, and the first-order correction $\hat{V}^{(1)\sigma}$ is precisely the term that the defining relation of $\hat{S}$ eliminates. This is why the leading correction to $\hat{V}^{(0)\sigma}$ is the second-order term $\hat{V}^{(2)\sigma}$.)

Our reinterpretation of DFT + U + V as DFT + U applied to hybridized density-matrix-dependent projectors has consequences for how V ought to be computed. If + V is really + U on the hybridized projectors, the self-consistent way to parametrize it would be to enforce linearity of the total energy in the occupations of these hybridized projectors, $n^{II}[\hat{S}]$. But that occupation responds through intersite channels—both the response of the intersite blocks $\mathbf{n}^{IJ\sigma}$ and the response to intersite perturbations—that the conventional response matrices do not contain (see Sec. S10 of the Supplemental Material for details [31]). In other words, the equivalence we have uncovered does not retroactively justify computing V as the off-diagonal elements of the response matrices used to compute U as is common practice [16]; instead, it compounds the preexisting discrepancy between the site-diagonal occupations the response matrices measure and the intersite blocks that E_V penalizes.

This line of thought raises deeper questions: Why might we want to linearize the total energy with respect to the occupation of the hybridized projectors, rather than the original

projectors—or any other choice? Is there an “optimal” set of projectors for DFT + U ? A broad family of DFT + U -inspired functionals—e.g., Koopmans functionals [49–51], the localized orbital scaling correction [52,53], Wannier-localized optimally tuned range-separated hybrid functionals [54], and Koopmans-Wannier functionals [55]—corrects quasiparticle energies by imposing piecewise linearity of the total energy with respect to localized orbitals (typically Wannier functions or variants thereof [56,57]), and the localized nature of these orbitals is crucial to their success [50]. Why correcting the curvature with respect to localized orbitals should so effectively correct the energies of delocalized quasiparticles deserves further investigation (see, e.g., Ref. [58]).

To conclude, the intersite + V corrections of DFT + U + V are equivalent—to first order in V/U —to an on-site DFT + U correction evaluated on a density-matrix-dependent set of Hubbard projectors hybridized with those of neighboring sites. The role of a + V correction is thus to make the on-site correction aware of covalency. This equivalence is rigorous: When the projectors are allowed to adapt to the density matrix, the single choice of rotation $e^{\hat{S}}$ reproduces both the DFT + U + V energy and, through the projectors’ own dependence on the density matrix, its potential [Eq. (A14)].

In contrast, if this redefinition is attempted with *frozen* projectors, as in most current implementations, the equivalence becomes partial: The total energy and the spectrum then call for differently hybridized projectors ($e^{\hat{S}}$ and $e^{2\hat{S}}$, respectively), and no frozen-projector functional reproduces the DFT + U + V potential exactly (see Sec. S8 of the Supplemental Material [31]). Even so, an ordinary DFT + U calculation with hybridized frozen projectors may stand in—approximately—for DFT + U + V , bringing the far broader ecosystem of DFT + U implementations and property extensions to bear.

The message to practitioners of DFT + U and DFT + U + V is that the choice of projectors, the choice of Hubbard parameters, and the choice of whether to apply intersite corrections are deeply intertwined and should never be treated as independent degrees of freedom. More deeply—with DFT + U + V now embedded in community codes and automated high-throughput workflows [36,59–62], increasingly the default extension of DFT + U —this work sharpens the question of what the Hubbard projectors fundamentally are, by revealing that even the established intersite correction is, at heart, a choice of projectors. Determining how projectors might be chosen optimally is now all the more pressing.

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Data availability. The data supporting the findings of this article are openly available on the Materials Cloud Archive [63].

Appendix. Here, we establish the central result of the main text—that, to first order in V/U , DFT + U + V is the DFT + U energy functional evaluated on a density-matrix-dependent redefinition of the Hubbard projectors.

The DFT + U and DFT + U + V corrections are most transparent in the basis $\{|\varphi_i^{I\sigma}\rangle\}$ that diagonalizes the on-site occupation matrices $\mathbf{n}^{II\sigma}$, with eigenvalues $\lambda_i^{I\sigma}$. The Hubbard projectors are taken orthonormal across sites as well as within them, $\langle\varphi_m^{I\sigma}|\varphi_{m'}^{I\sigma}\rangle = \delta^{IJ}\delta_{mm'}$ (the “orthoatomic” scheme), so that $\{|\varphi_i^{I\sigma}\rangle\}$ is orthonormal, the site projectors below are orthogonal, and the rotations $e^{\hat{T}}$ preserve this structure; nonorthogonal projectors would thread intersite overlap matrices through the operator algebra that follows. Writing $\Lambda_{ij}^{IJ\sigma} = \langle\varphi_i^{I\sigma}|\hat{\rho}^\sigma|\varphi_j^{I\sigma}\rangle$ for the density matrix in this basis (so that $\Lambda_{ij}^{II\sigma} = \lambda_i^{I\sigma}\delta_{ij}$), the on-site potential is diagonal,

$$\hat{V}_U^\sigma = \sum_i \frac{U^I}{2} (1 - 2\lambda_i^{I\sigma}) |\varphi_i^{I\sigma}\rangle\langle\varphi_i^{I\sigma}|, \quad (\text{A1})$$

while the intersite potential is purely off site (recall $V^{II} = 0$),

$$\hat{V}_V^\sigma = - \sum_{I \neq J} V^{IJ} \Lambda_{ij}^{IJ\sigma} |\varphi_i^{I\sigma}\rangle\langle\varphi_j^{J\sigma}|. \quad (\text{A2})$$

We start from the DFT + U energy evaluated on an arbitrary unitarily rotated set of projectors $e^{\hat{T}}|\varphi_i^{I\sigma}\rangle$, with $\hat{T}$ any anti-Hermitian generator:

$$E_U[\hat{T}] = \sum_{I\sigma} \frac{U^I}{2} \text{Tr}[\mathbf{n}^{II\sigma}[\hat{T}](1 - \mathbf{n}^{II\sigma}[\hat{T}])], \quad (\text{A3})$$

where

$$n_{ij}^{II\sigma}[\hat{T}] = \langle\varphi_i^{I\sigma}|e^{-\hat{T}}\hat{\rho}^\sigma e^{\hat{T}}|\varphi_j^{I\sigma}\rangle = \lambda_i^{I\sigma}\delta_{ij} + \delta n_{ij}^{II\sigma}[\hat{T}] + \mathcal{O}(\hat{T}^2) \quad (\text{A4})$$

and $\delta n_{ij}^{II\sigma}[\hat{T}] \equiv \langle\varphi_i^{I\sigma}|[\hat{\rho}^\sigma, \hat{T}]|\varphi_j^{I\sigma}\rangle$. It follows that

$$\begin{aligned} \text{Tr}[\mathbf{n}^{II\sigma}[\hat{T}](1 - \mathbf{n}^{II\sigma}[\hat{T}])] &= \sum_i \lambda_i^{I\sigma} (1 - \lambda_i^{I\sigma}) + \sum_i (1 - 2\lambda_i^{I\sigma}) \delta n_{ii}^{II\sigma}[\hat{T}] + \mathcal{O}(\hat{T}^2). \end{aligned} \quad (\text{A5})$$

Inserting this into Eq. (A3) and using Eq. (A1) gives the first-order energy of any such rotation,

$$\begin{aligned} E_U[\hat{T}] &= E_U + \sum_{I\sigma} \frac{U^I}{2} (1 - 2\lambda_i^{I\sigma}) \langle\varphi_i^{I\sigma}|[\hat{\rho}^\sigma, \hat{T}]|\varphi_i^{I\sigma}\rangle + \mathcal{O}(\hat{T}^2) \\ &= E_U + \sum_{\sigma} \text{Tr}[\hat{V}_U^\sigma[\hat{\rho}^\sigma, \hat{T}]] + \mathcal{O}(\hat{T}^2), \end{aligned} \quad (\text{A6})$$

where E_U is the DFT + U energy of the original projectors.

We now ask which specific rotation $\hat{S}$ makes the DFT + U energy of the rotated projectors equal the DFT + U + V energy $E_U + E_V$. By Eq. (A6), this means that

$$\sum_{\sigma} \text{Tr}[\hat{\rho}^{\sigma} [\hat{S}, \hat{V}_U^{\sigma}]] = E_V. \quad (\text{A7})$$

To simplify this condition, we can rewrite the intersite energy and its potential compactly using the site projector $\hat{P}^{I\sigma} = \sum_m |\phi_m^{I\sigma}\rangle \langle \phi_m^{I\sigma}| = \sum_i |\phi_i^{I\sigma}\rangle \langle \phi_i^{I\sigma}|$,

$$E_V = - \sum_{IJ\sigma} \frac{V^{IJ}}{2} \text{Tr}[\hat{P}^{I\sigma} \hat{\rho}^{\sigma} \hat{P}^{J\sigma} \hat{\rho}^{\sigma}], \quad (\text{A8})$$

$$\hat{V}_V^{\sigma} = \frac{\delta E_V}{\delta \hat{\rho}^{\sigma}} = - \sum_{IJ} V^{IJ} \hat{P}^{I\sigma} \hat{\rho}^{\sigma} \hat{P}^{J\sigma}. \quad (\text{A9})$$

It follows that these two quantities can be related via the identity

$$\sum_{\sigma} \text{Tr}[\hat{\rho}^{\sigma} \hat{V}_V^{\sigma}] = - \sum_{IJ\sigma} V^{IJ} \text{Tr}[\hat{\rho}^{\sigma} \hat{P}^{I\sigma} \hat{\rho}^{\sigma} \hat{P}^{J\sigma}] = 2E_V. \quad (\text{A10})$$

(This identity is analogous to the same result for the Hartree energy $2E_H = \int \rho v_H \text{d}\mathbf{r}$. We obtain the same relation because both energies are quadratic in ρ .)

Given this identity, the condition of Eq. (A7) becomes $\sum_{\sigma} \text{Tr}[\hat{\rho}^{\sigma} ([\hat{S}, \hat{V}_U^{\sigma}] - \frac{1}{2} \hat{V}_V^{\sigma})] = 0$, which is satisfied at every

density matrix if

$$[\hat{S}, \hat{V}_U^{\sigma}] = \frac{1}{2} \hat{V}_V^{\sigma}. \quad (\text{A11})$$

From this, we can obtain the explicit form

$$S_{ij}^{IJ\sigma} = \langle \phi_i^{I\sigma} | \hat{S} | \phi_j^{J\sigma} \rangle = \frac{V^{IJ} \Lambda_{ij}^{IJ\sigma}}{U^I (1 - 2\lambda_i^{I\sigma}) - U^J (1 - 2\lambda_j^{J\sigma})}, \quad (\text{A12})$$

which is Eq. (5). Note that (1) $S^{II\sigma} = 0$ since $V^{II} = 0$, and (2) because $(\Lambda_{ij}^{IJ\sigma})^* = \Lambda_{ji}^{JI\sigma}$, the generator remains anti-Hermitian—and the rotation unitary—even for complex occupations.

Given this choice of rotation, it follows that

$$E_U[\hat{S}] = E_U + E_V + \mathcal{O}(V^2/U), \quad (\text{A13})$$

precisely as desired. In other words, a DFT + U functional that uses the hybridized projectors $\{e^{\hat{S}} |\phi_i^{I\sigma}\rangle\}$ yields the same energy as the original DFT + U + V functional. Furthermore, because Eq. (A13) holds for every $\hat{\rho}^{\sigma}$, it may be differentiated:

$$\frac{\delta E_U[\hat{S}]}{\delta \hat{\rho}^{\sigma}} = \hat{V}_U^{\sigma} + \hat{V}_V^{\sigma} + \mathcal{O}(V^2/U), \quad (\text{A14})$$

which means the potentials are also equivalent.

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