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We study the electronic structure and dynamical correlations in antiferromagnetic BiFeO₃, a prototypical room-temperature multiferroic, using a variety of static and dynamical first-principles methods. Conventional static Hubbard corrections (DFT + U , DFT + U + V) incorrectly predict a deep-valence Fe 3d peak (around -7 eV) in antiferromagnetic BiFeO₃, in contradiction with hard x-ray photoemission. We resolve this failure by using a recent generalization of DFT + U to include a frequency-dependent screening—DFT + $U(\omega)$ —or using a dynamical Hubbard functional. The screened Coulomb interaction $U(\omega)$, computed with spin-polarized random-phase approximation and projected onto maximally localized Fe 3d Wannier orbitals, is expressed as a sum over poles, yielding a self-energy that augments the Kohn-Sham Hamiltonian. This DFT + $U(\omega)$ approach predicts a fundamental band gap of 1.53 eV, consistent with experiments, and completely eliminates the unphysical deep-valence peak. The resulting simulated hard x-ray photoelectron spectroscopy spectrum reproduces the experimental line shape with an accuracy comparable to state-of-the-art approaches. Our work highlights the critical nature of dynamical screening in complex oxides and of DFT + $U(\omega)$ as a predictive and computationally efficient approach to address the electronic structure of correlated materials.

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BiFeO₃ (bismuth ferrite) is the archetypal room-temperature multiferroic, distinguished by the coexistence of robust ferroelectricity ($T_C \approx 1103$ K) and antiferromagnetism ($T_N \approx 643$ K) [1–3]. Its distorted $R3c$ perovskite structure [4,5], driven by the stereochemically active Bi 6s² lone pair, hosts a large electric polarization coupled to a complex magnetic cycloid [3,6]. This rare simultaneous ordering of charge and spin degrees of freedom establishes BiFeO₃ as a unique platform for fundamental research and a leading candidate for magnetoelectric applications.

Despite extensive experimental characterization, achieving an accurate theoretical description of BiFeO₃'s electronic structure remains a formidable challenge, primarily due to intricate electronic correlations within the partially filled Fe 3d shell [7,8]. Density-functional theory (DFT) with local and semilocal exchange-correlation functionals [i.e., local-density approximation (LDA) and generalized-gradient approximation (GGA)] notoriously fails, predicting a near-metallic state by severely underestimating the band gap and often misrepresenting orbital occupancies [8]. Static mean-field corrections

(DFT + U , DFT + U + V) attempt to remedy this by adding a local constant Hubbard-like penalty for on-site and intersite Coulomb repulsion. A persistent and well-documented issue in all static Hubbard-based treatments (DFT + U , DFT + U + V) of BiFeO₃ is the appearance of an unphysical, sharp peak attributed primarily to Fe 3d states at binding energies around -7 to -8 eV below the Fermi level [7,9,10]. This feature starkly contradicts experimental photoemission spectra, which instead reveal a dip at the corresponding valence band energy [7,10]. The persistence of this artifact underscores the need to improve static mean-field corrections.

More advanced many-body techniques, such as dynamical mean-field theory (DMFT) combined with DFT (DFT + DMFT), offer a more rigorous treatment of local correlations, introducing a dynamical self-energy [11,12]. DMFT applications to BiFeO₃ and related multiferroics have indeed yielded improved density of states and theoretical spectra, showing better agreement with experiments [7,13,14]. However, fully self-consistent DMFT calculations are computationally very demanding, especially for systems with large unit cells or complex magnetic structures like the spin cycloid in BiFeO₃.

Recently, a new class of computationally efficient dynamical embedding methods has emerged, bridging the gap between static corrections and full DMFT. These approaches, which include the dynamical Hubbard functional (dynH) [15–17] and the related DFT + $U(\omega)$ method [18], incorporate dynamical screening by promoting the static Hubbard interaction to a local, frequency-dependent interaction $U(\omega)$, typically evaluated within the random-phase approximation

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(RPA). In dynH, the static density functional is augmented by a dynamical Hubbard correction formulated as a spectral (Klein) variational functional of the Green's function projected onto a localized correlated (Hubbard) manifold, with $U(\omega)$ defined as the manifold-averaged local screened Coulomb interaction; the corresponding local dynamical self-energy follows from the functional derivative and takes the form of a convolution between $U(\omega)$ and the projected Green's function, plus a static double-counting term. This construction fully generalizes the rotationally invariant DFT + U functional [19] to a dynamical and complex correction. DFT + $U(\omega)$ can be viewed as an approximate version of dynH acting only at the self-energy level, retaining the local, complex and frequency-dependent self-energy while avoiding the numerical convolution of the local Green's function and screened interaction and the full solution of the Dyson equation, thereby capturing the essential dynamical correlations at a computational cost only modestly higher than static DFT + U ; as a result, it is an ideal tool for exploring complex correlated materials, especially with low-symmetry structures where computational costs might rise rapidly.

In this article, we apply this dynamical DFT + $U(\omega)$ scheme to antiferromagnetic BiFeO₃ to resolve the failures of static corrections. We demonstrate its effectiveness through a direct comparison of simulated hard x-ray photoelectron spectroscopy (HAXPES) spectra against static DFT + U + V , and DMFT results, clarifying how different correlation treatments affect the band gap and key spectral signatures. The antiferromagnetic order provides the experimentally relevant spin-polarized reference state; we do not address here the magnetic phase diagram, but compare static and dynamical local-correlation treatments within this phase.

First, we perform DFT + U + V calculations using the PBEsol functional [20] to reproduce results consistent with prior static treatments [7,9,10]. Here, the Hubbard U and intersite V parameters are the ones determined self-consistently via density functional perturbation theory by Inizan [9]: $U_{\text{Fe}} = 5.5$ eV (on-site Fe 3d), $V_{\text{Fe-O}_1} = 0.9$ eV, and $V_{\text{Fe-O}_2} = 0.7$ eV for Fe-O interactions. The calculations yield an optimized G-type antiferromagnetic structure in good agreement with experimental data [5] and prior theoretical work [9]. However, analysis of the projected density of states (PDOS) confirms the presence of the spurious Fe 3d-derived peak around -7 eV (Figs. 4 and 7), the known artifact of static Hubbard corrections in this system [7,9,10].

Our dynamical treatment is built on a collinear G-type antiferromagnetic PBEsol Kohn-Sham reference without Hubbard corrections. Starting from these spin-polarized wavefunctions, we compute the frequency-dependent screened Coulomb interaction, $W(\omega; \mathbf{r}_1, \mathbf{r}_2)$, within the random-phase approximation. The local matrix elements are obtained by projecting $W(\omega)$ onto a basis of maximally localized Wannier functions (MLWFs) $|\phi_m^\sigma\rangle$ [21]. The Wannier construction targets the Fe 3d, O 2p, and Bi 6p states, yielding a 34-orbital model per spin channel. This enlarged dp -like Wannier space provides a faithful representation of the hybridized valence manifold, while the correlated Hubbard manifold $\mathcal{C}$ entering the self-energy is the Fe 3d subset, with size $N = 5$ on each Fe site. The on-site interaction in the local basis at a given Fe

site I and spin σ is then

$$U_{I,m'_1,m'_2,m_1,m_2}^\sigma(\omega) = \langle \phi_{Im'_1}^\sigma \phi_{Im'_2}^\sigma | W(\omega) | \phi_{Im_1}^\sigma \phi_{Im_2}^\sigma \rangle. \quad (1)$$

Following Refs. [16,18,22], we define the scalar interaction used in the DFT + $U(\omega)$ self-energy by averaging the direct density-density matrix elements within the Fe 3d manifold and over both spin channels,

$$U_I(\omega) \equiv \frac{1}{2N^2} \sum_{m_1,m_2 \in \mathcal{C}; \sigma} U_{I,m_1,m_2,m_1,m_2}^\sigma(\omega). \quad (2)$$

The spin average is justified by the spin-polarized RPA calculation itself: As shown in Appendix B 2, the spin-up and spin-down interactions on a given Fe site have essentially identical pole structures and differ by less than 0.2 eV in the low-energy real part. After this spin average, the two antiferromagnetic Fe sublattices are corrected with the same local interaction, and we drop the site index, $U_I(\omega) \equiv U(\omega)$.

The computed frequency-dependent interaction, plotted in Fig. 2, encapsulates the dynamical screening within the Fe 3d subspace. In the static limit ($\omega \rightarrow 0$), the interaction is strongly screened, yielding $U_0 = 2.56$ eV, compared to the bare unscreened value $U_\infty = 21.75$ eV. To remove the dependence on the discrete RPA frequency grid and to evaluate the interaction on the frequency grids required by the self-energy, the calculated $U(\omega)$ is fitted to a sum-over-poles (SOP) representation [23]. The SOP fit is not an additional adjustable Hubbard parameter: It is a compact representation of the *ab initio* RPA interaction that preserves the relevant structure of both $\text{Re } U(\omega)$ and $\text{Im } U(\omega)$ over the energy window used in the spectral calculation. It also provides the natural input for the comparison with the dynH framework, which is formulated in terms of SOP propagators. The imaginary part, $\text{Im } U(\omega)$, identifies the spectrum of screening processes. Besides a continuum of low-energy electron-hole excitations, the SOP fit identifies three dominant screening poles at 9.84, 20.44, and 30.11 eV within the 0–40 eV range. This structured frequency dependence, which cannot be represented by a single scalar U , is the central physical ingredient captured by the dynamical correction.

As said previously, to incorporate these dynamical effects into the electronic structure, we use an approximate on-site self-energy, $\Delta \Sigma_m^I(\omega)$ [18]. This correction assumes correlations are localized on the Fe 3d orbitals and retains the scalar, spin-averaged direct density-density channel of the screened interaction:

$$\Delta \Sigma_m^I(\omega) = \left(\frac{1}{2} - n_m^I \right) U_\infty + \left[\frac{1}{2} \left(1 + \frac{\omega - \varepsilon_m^I}{\omega_0} \right) - n_m^I \right] \times (U(\omega - \varepsilon_m^I) - U_\infty). \quad (3)$$

Accordingly, explicit Hund's exchange J , spin-flip terms, and pair-hopping terms are not included in the present scalar $U(\omega)$ implementation; their treatment would require a tensorial dynamical interaction beyond the scope of this work. Here, n_m^I is the initial occupation of the localized orbital m on the Fe site I , and the parameter ω_0 represents a characteristic energy for the screening, obtained by approximating the full spectrum of neutral excitations with a single effective frequency [18,24]. We set $\omega_0 = 20$ eV, a choice justified by the analysis of $\text{Im}[U(\omega)]$, where this value corresponds to the broadest

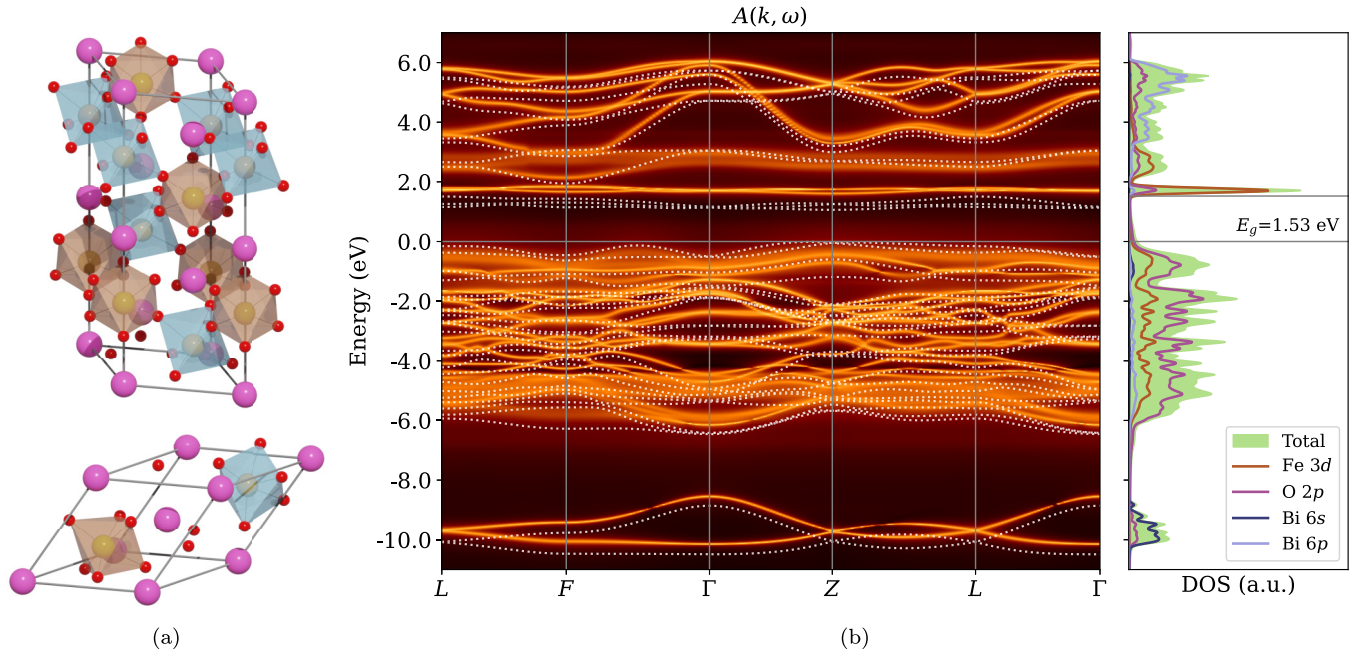


FIG. 1. (a) Conventional (top) and primitive (bottom) $R3c$ BiFeO₃ unit cells. Bi atoms are purple, and FeO₆ octahedra are colored by Fe spin orientation (spin-up: red; spin-down: blue). (b) Band structure from PBEsol (white dashed lines) compared with the DFT + $U(\omega)$ spectral function and projected density of states. Dynamical correlations increase the fundamental gap from 1.03 to 1.53 eV and introduce significant incoherent spectral weight.

plasmon pole (at 20.44 eV) and is also approximately the average of the three main poles. ε_m^I are the Kohn-Sham eigenvalues in the local basis m , analogous to the local occupations n_m^I , used in the DFT + U context, and they stem from the frequency-dependent extension of the formalism [18]. This self-energy can be decomposed of exchange and correlation parts, plus a double-counting correction term in the fully localized limit, with a static value of $U_\infty = 21.75$ eV. See Ref. [15] for details. The final electronic structure is obtained

by computing the spectral function as $A_{nk}(\omega) = -\frac{1}{\pi} \text{Im}[(\omega - \varepsilon_{nk} - \sum_{I,m} |\langle I, m | n\mathbf{k} \rangle|^2 \Delta \Sigma_m^I(\omega))^{-1}]$, i.e., by projecting back the local self-energy onto the Kohn-Sham space and correcting Kohn-Sham eigenvalues [18]. Since this correction is applied one shot to the spin-polarized reference, it modifies the spectral function but does not update the self-consistent spin density; we therefore do not extract a renormalized ordered moment.

Our DFT + $U(\omega)$ calculations yield two crucial improvements over static methods. First, the fundamental band gap is corrected to 1.53 eV—a value that rectifies both the underestimation by plain DFT (1.03 eV) and the overestimation by DFT + $U + V$ (2.61 eV). This result aligns well with experimental reports, which suggest an indirect gap of approximately 1.2–1.9 eV [25–29]. Second, and most critically, our dynamical approach resolves the primary failure of static mean-field corrections. The spectral function [Fig. 1(b)] shows that the spurious, localized Fe 3d peak near -7 eV is entirely eliminated. Instead, the Fe 3d spectral weight is now correctly distributed across the upper valence band, from the Fermi level down to around -6 eV, reflecting its strong hybridization with O 2p and Bi 6p states.

A key control calculation disentangles the effect of the static magnitude of the interaction from the effect of its frequency dependence. As shown in Appendix C, a static DFT + U scan reveals that increasing a scalar U progressively localizes the Fe 3d states: The isolated deep-valence Fe peak appears for U above approximately 2 eV and becomes more pronounced as U is increased. Since the fully averaged dynamical interaction has a comparatively small static limit, $U_0 = 2.56$ eV, one might therefore ask whether the improved DFT + $U(\omega)$ spectrum is simply a consequence

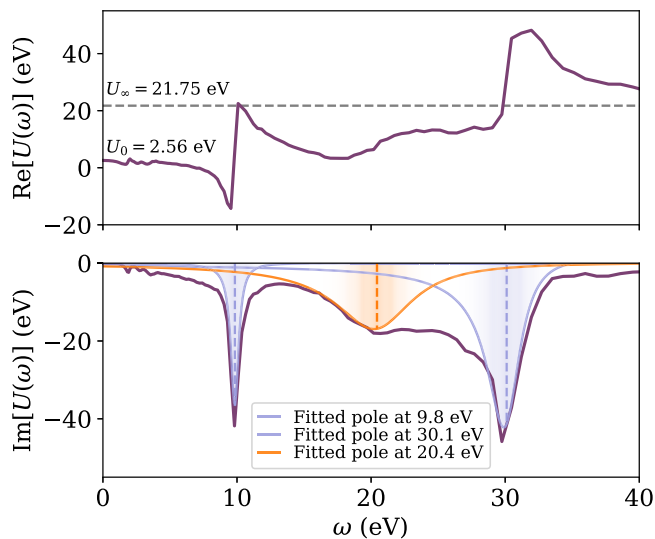


FIG. 2. Real and imaginary parts of the dynamically screened on-site Coulomb interaction $U(\omega)$ for Fe 3d orbitals. The static limit is $U_0 = 2.56$ eV, and the bare limit is $U_\infty = 21.75$ eV.

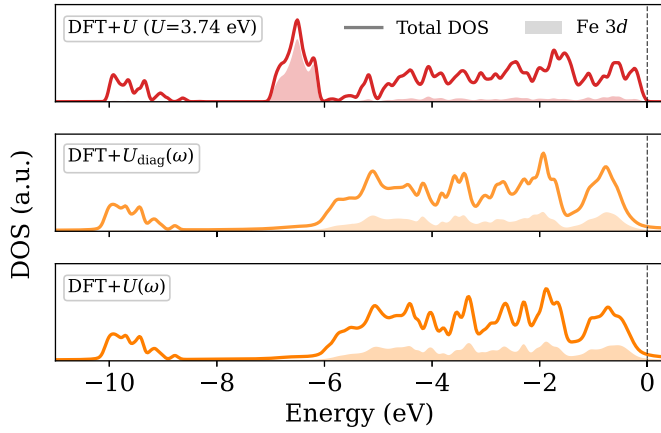


FIG. 3. Disentangling static and dynamical effects on the Fe 3d PDOS. A static DFT + U calculation using $U = 3.74$ eV, equal to the static limit of $U_{\text{diag}}(\omega)$, produces a spurious Fe peak. In contrast, the dynamical DFT + $U_{\text{diag}}(\omega)$ calculation, which has the same static limit but retains the frequency dependence, eliminates this artifact and closely matches the result from DFT + $U(\omega)$ with full averaging.

of using a static interaction close to the onset of this artifact, rather than a genuine effect of dynamical screening.

To test this possibility, we construct an alternative scalar interaction from the same local screened Coulomb matrix by averaging only the orbital-diagonal density-density elements, $U_{I,\text{diag}}(\omega) \equiv \frac{1}{2N} \sum_{m \in C, \sigma} U_{I,m,m,m}^{\sigma}(\omega)$. This diagonal average preserves a dynamical profile very similar to that of the fully averaged $U(\omega)$, but yields a substantially larger static limit, $U_{\text{diag}}(0) = 3.74$ eV, well within the range where a static DFT + U calculation produces the spurious Fe 3d peak. As shown in Fig. 3, static DFT + U , with $U = 3.74$ eV, indeed produces this artifact, whereas the dynamical DFT + $U_{\text{diag}}(\omega)$ calculation, with the same static limit but retaining the frequency dependence, removes it and closely follows the result obtained with the fully averaged $U(\omega)$. This control shows that the disappearance of the deep-valence Fe peak is not due merely to reducing the scalar Hubbard parameter, but to the dynamical screening encoded in $U(\omega)$.

Following other theoretical work [7], to provide a more direct comparison with experiment, we simulated HAXPES spectra from the calculated valence spectral function. The simulation accounts for atomic orbital photoionization cross sections at an incident energy of 2100 eV, weighting the orbital-projected DOS with tabulated values [10] and applying a Gaussian broadening to match instrumental resolution. Figure 4 compares our results from DFT + $U(\omega)$ and DFT + $U + V$ against experimental data [7,10] and DFT + DMFT [7].

The DFT + $U(\omega)$ spectrum demonstrates remarkable agreement with the experimental data. In contrast to the static DFT + $U + V$ result, which incorrectly places a pronounced peak at the position of feature IV, our dynamical calculation correctly shows a valley in this region and entirely eliminates the spurious Fe 3d artifact. The energy positions of all key spectral features—peaks I, II, III, and the deeper-lying peak V—are accurately reproduced, matching both experimental measurements and DFT + DMFT calculations. Peak positions and intensities were determined by fitting the spectra

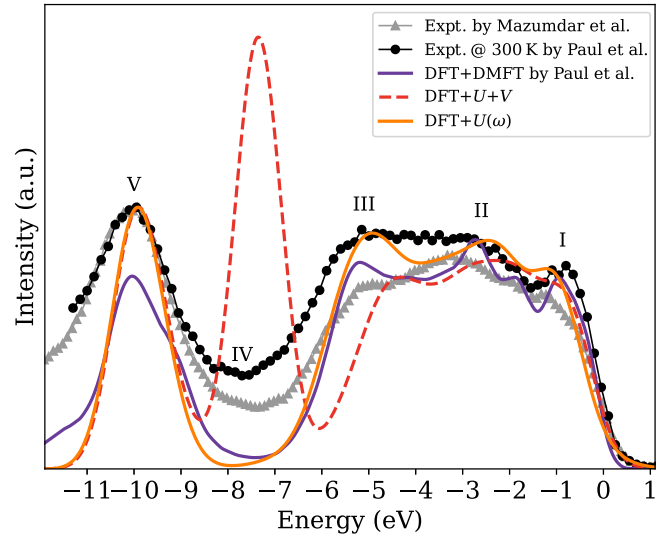


FIG. 4. Comparison of simulated HAXPES spectra with experimental data from Refs. [7,10] (points). The DFT + $U(\omega)$ spectrum (orange) provides the best overall agreement with experiment, eliminating the spurious peak of static DFT + $U + V$ (red, dashed) and matching or exceeding the accuracy of DFT + DMFT (purple).

with Voigt functions, as detailed in Appendix D. Notably, our method surpasses the DMFT result in one key aspect: It more faithfully captures the relative intensity of the Bi 6s-related peak V with respect to the main valence band features (I–III) (Fig. 5). This success in reproducing the experimental line shape highlights the predictive power of the DFT + $U(\omega)$ approach.

The robustness of these findings is supported by several additional checks reported in the Appendixes. First, the spin-resolved RPA interactions have nearly identical pole structures and only small low-energy differences in $\text{Re } U(\omega)$, validating the spin-averaged scalar interaction used in the main text. Second, the SOP representation closely reproduces the raw RPA $U(\omega)$ over the relevant frequency window. Third, static DFT + U scans show that the isolated Fe 3d peak emerges once the scalar U exceeds approximately 2 eV, and both DFT + $U + V$ and advanced static functionals such as

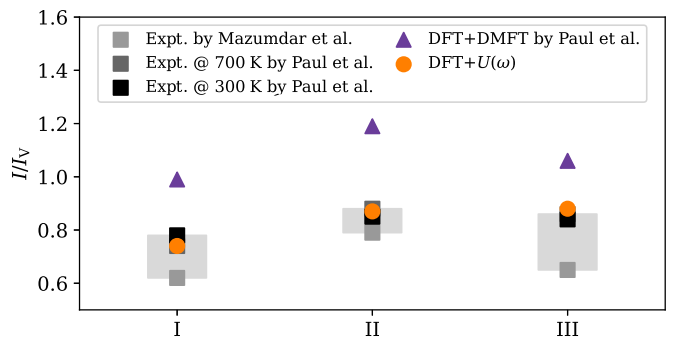


FIG. 5. Relative intensity of HAXPES features. The plot shows the intensity ratios of valence features I–III relative to peak V. The DFT + $U(\omega)$ results fall within the experimental range (gray bars), while the DFT + DMFT [7] method consistently overestimates these ratios.

r^2 SCAN, HSE, and PBE0 fail to reproduce the experimental HAXPES line shape. Finally, the same qualitative spectral correction is obtained with the more complete DFT + dynH treatment, which solves the Dyson equation explicitly. Taken together, these tests show that the removal of the spurious Fe 3d peak is robust with respect to spin averaging, the SOP representation, and the formulation of the dynamical self-energy, and that it cannot be reproduced by simply changing the static functional or static Hubbard parameters.

The present case also suggests a practical, material-specific way to decide when a dynamical interaction should be tested. A scalar static U is an effective representation of a much richer screened interaction, and its adequacy depends on the observables of interest. Static treatments may be insufficient when no single value of U can reproduce the relevant properties simultaneously, as in BiFeO₃, where increasing U may improve the gap but also creates an unphysical localized Fe 3d feature in the valence spectrum. This situation can arise when the same localized states that require a Hubbard correction also participate in screening processes on energy scales relevant to the measured excitations; in such cases, a static parameter cannot capture both localization and dynamical spectral-weight redistribution. The computed $U(\omega)$ then provides a useful guide: Pronounced structure in $\text{Im } U(\omega)$, or a strong variation of $\text{Re } U(\omega)$ over the energy window relevant to valence-band or charge-transfer excitations, indicates that a dynamical self-energy may be needed. Finally, controls such as the $U_{\text{diag}}(\omega)$ test used here, where static and dynamical calculations are compared at the same static limit, provide a direct material-specific check. These considerations are not intended as a universal criterion, but in BiFeO₃ they consistently identify dynamical screening, rather than the scalar value of $U(0)$ alone, as the key ingredient behind the HAXPES line shape.

In conclusion, we have shown that incorporating dynamical screening via a frequency-dependent Hubbard interaction resolves the long-standing failure of static mean-field methods to describe the electronic structure of BiFeO₃. Our DFT + $U(\omega)$ calculations eliminate the spurious deep-valence Fe 3d peak, correct the fundamental band gap, and reproduce experimental HAXPES spectra with a fidelity that matches or exceeds that of far more computationally demanding DMFT calculations. This work not only clarifies the crucial role of dynamical correlations in multiferroics but also establishes DFT + $U(\omega)$ as a predictive, first-principles tool with a compelling balance of accuracy and efficiency. Its success here paves the way for reliable, large-scale simulations of a wide range of complex correlated materials where such effects are paramount.

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DATA AVAILABILITY

The data that support the findings of this article are openly available in Ref. [30].

APPENDIX A: DFT + U + V

1. Computational details

Calculations are performed using Quantum ESPRESSO [31] with parameters from Ref. [9]: $U = 5.45$ eV, $V_1 = 0.94$ eV (Fe-O₁), and $V_2 = 0.72$ eV (Fe-O₂), determined via self-consistent density functional perturbation theory (DFPT) [9,32]. We employ the PBEsol functional [20] and standard solid-state pseudopotentials [33] with wavefunction and charge density cutoffs of 90 Ry and 1080 Ry, respectively. A cold smearing of 0.02 Ry [34] is used for self-consistent-field (SCF) calculations on a $9 \times 9 \times 9$ Monkhorst-Pack grid [35], while non-self-consistent-field (NSCF) calculations use the tetrahedron method on a $14 \times 14 \times 14$ grid [36].

2. Electronic structure

The static DFT + U + V calculation overestimates the band gap relative to most experimental measurements. Specifically, an indirect gap of 2.61 eV is obtained, as shown in Fig. 6. Although this value appears reasonable *a priori* for an oxide with correlation effects, it slightly exceeds the commonly cited experimental range of ~ 1.2 to 1.9 eV for BiFeO₃ [25–29]. A crucial point of concern can be seen in the partial Fe 3d density of states. As indicated in Fig. 7, a pronounced unphysical peak appears around -7 eV, mirroring the issue reported by Paul *et al.* using the simpler LSDA + U scheme [7]. Its persistence in our DFT + U + V calculations highlights that static Hubbard corrections, even with additional intersite terms, are not sufficient to fully capture the intricate many-body effects in BiFeO₃.

APPENDIX B: DFT + $U(\omega)$

1. Computational details

DFT + $U(\omega)$ calculations employ PBEsol [20] and ON-CVPSP pseudopotentials (PseudoDojo v0.4.1) [37]. We use energy cutoffs of 106 Ry (wavefunction) and 424 Ry (density), with 0.007 Ry cold smearing [34]. The SCF step uses a $10 \times 10 \times 10$ grid [35], while NSCF steps use a $6 \times 6 \times 6$ mesh.

We employ a *dp* model (Fe 3d, O 2p, Bi 6p) with 34 MLWFs [21]. $U(\omega)$ is computed with a 10 Ry dielectric cutoff, 100 bands, and 200 frequency points distributed logarithmically [38].

The workflow proceeds as follows: Quantum ESPRESSO [31] generates Bloch wavefunctions, which a customized version of RESPACK [38] uses to construct MLWFs (calc_wannier) and compute the frequency-dependent dielectric function via spin-polarized RPA (calc_chi_qw). The on-site $U(\omega)$ is obtained by projecting the screened interaction onto the Wannier basis (calc_w3d) and averaging the matrix elements. Finally, $U(\omega)$ is fitted to a sum-over-poles form [23] for the self-energy correction [18], and spectral functions are computed via upfolding.

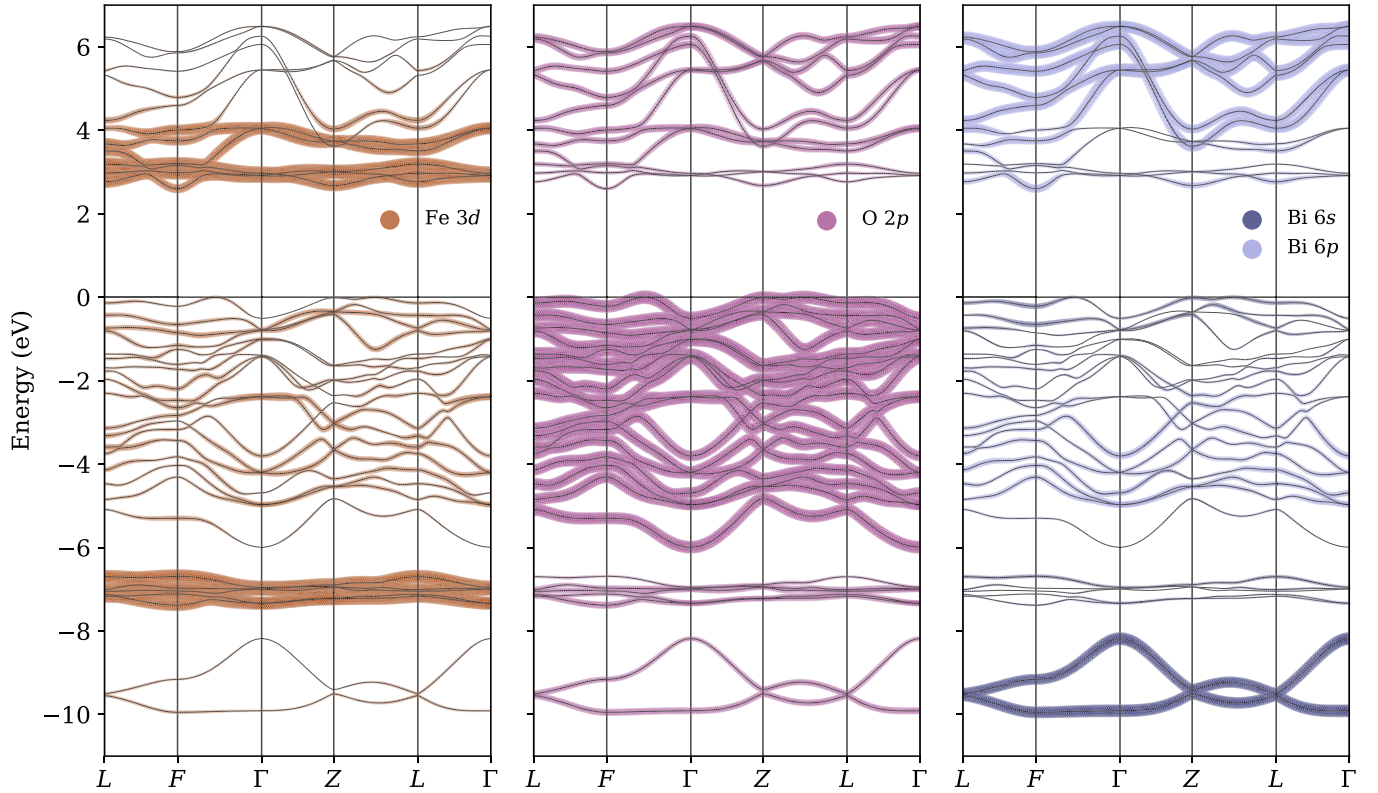


FIG. 6. Projected band structure calculated using the DFT + U + V method with $U = 5.45$ eV, $V_1 = 0.94$ eV, and $V_2 = 0.72$ eV. The left, middle, and right panels show the orbital projections onto Fe, O, and Bi atoms, respectively. The valence band maximum is set to zero energy, and the resulting indirect band gap is 2.61 eV.

2. Averaged $U(\omega)$

The DFT + $U(\omega)$ self-energy is obtained by approximating the convolution between the local Green's function and

the local screened Coulomb interaction of the system. For the complete derivation, we refer to see Ref. [18]. As the screened Coulomb interaction is averaged over a maximally localized

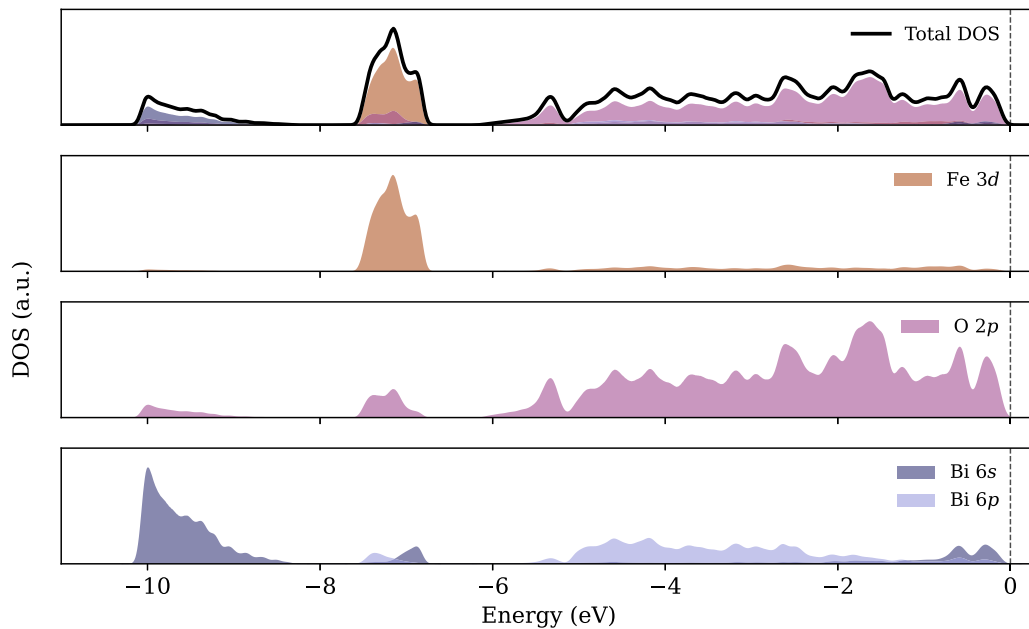


FIG. 7. Total and PDOS of BiFeO₃ from DFT + U + V . The PDOS highlights the orbital character of the valence band, showing the spurious, isolated Fe 3d peak near -7.6 eV.

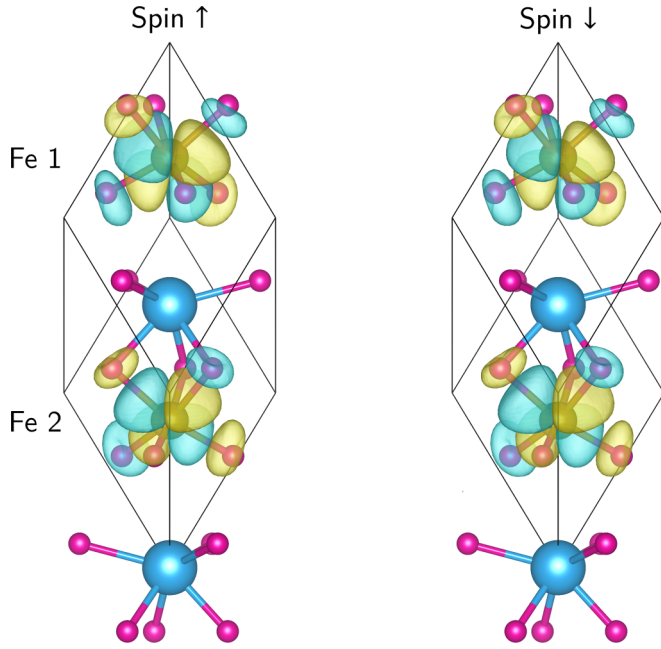


FIG. 8. Real-space $d_{x^2-y^2}$ -like Wannier functions centered at atomic sites Fe1 and Fe2 for spin-up and spin-down channels. The spin-up WF on Fe1 is identical in shape to the spin-down WF on Fe2, ensured by spatial and time-reversal symmetry. The gauge-invariant spread of the spin-up WF differs from the corresponding spin-down WF by only about 12%, confirming that the local orbital shapes remain nearly identical across different spin sectors at the same site. This can be understood as the spin-dependent part of the exchange correlation is small and perturbative.

Wannier function basis, the spin dependency of the matrix elements

$$U_{I,m'_1,m'_2,m_1,m_2}^\sigma(\omega) = \langle \phi_{I,m'_1}^\sigma \phi_{I,m'_2}^\sigma | W(\omega) | \phi_{I,m_1}^\sigma \phi_{I,m_2}^\sigma \rangle \quad (\text{B1})$$

stem from the spin dependency of the MLWFs $\phi_{I,m}^\sigma$, which in turn stems from the spin dependency of the Kohn-Sham states $\psi_{n\mathbf{k}}^\sigma$. Thus, the spin dependency of the interaction might be nontrivial if the spin-down and spin-up Kohn-Sham states comprising the local manifold significantly differ from each other in charge distribution around the iron ion. In Fig. 9, we show the spin-up and spin-down components of the screened interaction projected onto one of the two Fe atoms of the lattice (by antiferromagnetic symmetry, the other Fe atom has identical but swapped up and down MLWFs). As it can be seen, the up and down interactions have identical pole structures (imaginary part) and differ very little (less than 0.2 eV) in the real part across the low-energy range. This justifies the spin average of the local matrix elements [Eq. (B1)], leading thus to the total average for each iron site used in this work. Figure 8 shows $d_{x^2-y^2}$ -like Wannier functions in real space, centered at atomic sites Fe1 and Fe2, for spin-up and spin-down channels, where the similarity of the up and down orbitals per site can be appreciated

$$U_I(\omega) \equiv \frac{1}{2N^2} \sum_{m_1,m_2 \in \mathcal{C};\sigma} U_{I,m_1,m_2,m_1,m_2}^\sigma(\omega). \quad (\text{B2})$$

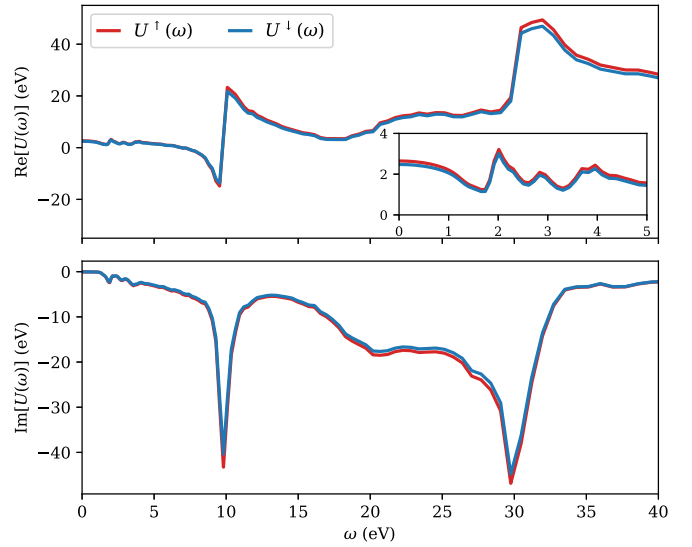


FIG. 9. Comparison of the frequency-dependent local Coulomb interaction in spin-up (red) and spin-down (blue) channels. They are almost identical, justifying to have an averaged spin-independent $U(\omega)$.

3. Dynamical correlations $U(\omega)$ in BiFeO_3

Since $U(\omega)$ will be used in later DFT + $U(\omega)$ or DFT + dynH calculations, it is beneficial to make $U(\omega)$ independent of the RPA energy grid by fitting it on an SOP representation [23]. Figure 10 compares the $U(\omega)$ from RPA (black dashed lines) to its SOP fit (orange lines). The SOP procedure attempts to capture the most relevant peaks in both $\text{Re } U(\omega)$

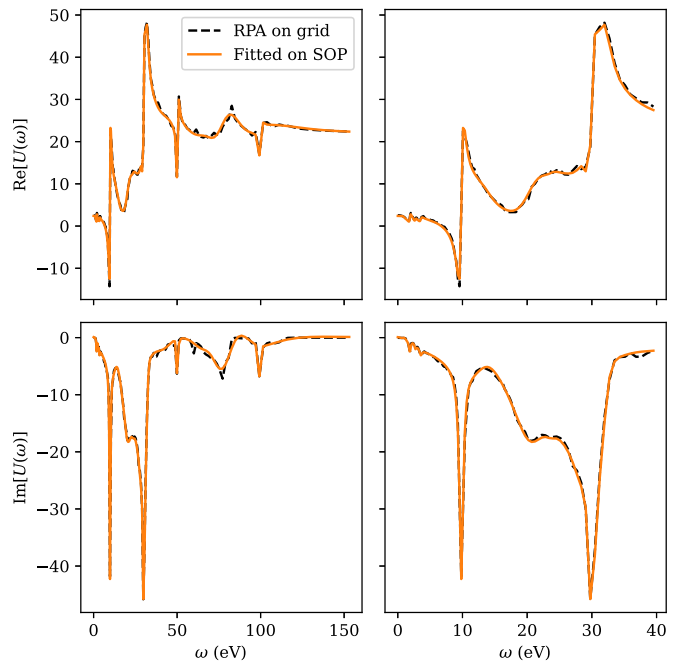


FIG. 10. Real and imaginary parts of the on-site screened interaction $U(\omega)$. The raw RPA calculation (black dashed line) is fitted to an SOP representation (orange line), which is used in later DFT + $U(\omega)$ and DFT + dynH calculations.

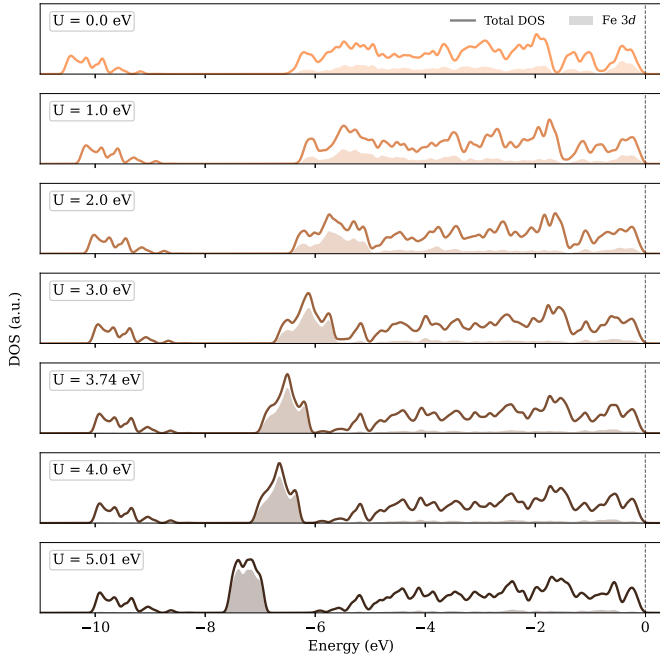


FIG. 11. Total DOS and PDOS projected onto the Fe 3d orbitals from static DFT + U calculations with increasing U . The spurious Fe peak emerges for U greater than 2 eV. 3.74 eV is the static limit for $U_{\text{diag}}(0)$ and 5.01 eV is the Hubbard parameter determined from self-consistent DFPT calculations.

and $\text{Im} U(\omega)$ with a small set of damped oscillators. The agreement is close across the entire 0–40 eV range, which are necessary to describe the low-energy frequency dependence of the on-site interaction in BiFeO_3 .

APPENDIX C: DISTINGUISHING DYNAMICAL FROM STATIC CORRELATION EFFECTS

A central failure of static Hubbard corrections in BiFeO_3 is the appearance of a spurious, localized Fe 3d peak in the

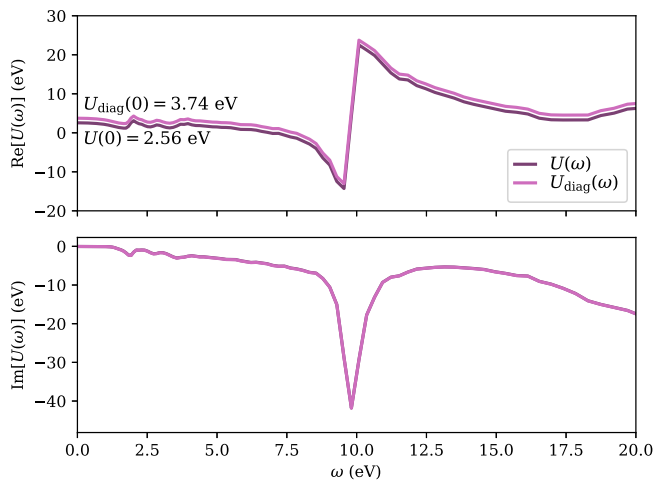


FIG. 12. Comparison of the frequency-dependent local Coulomb interaction from elementwise averaging [$U(\omega)$, dark plum] and diagonal averaging [$U_{\text{diag}}(\omega)$, magenta]. While the dynamical profiles are similar, the static limits are $U(0) = 2.56$ eV and $U_{\text{diag}}(0) = 3.74$ eV.

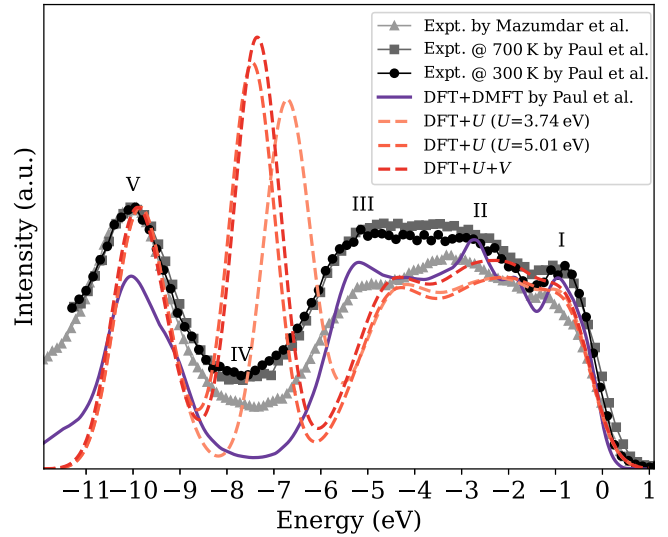


FIG. 13. Simulated HAXPES spectra from static calculations. All static treatments fail to reproduce experimental features, showing a pronounced Fe peak where a valley (feature IV) should be.

valence band around -7 eV, an artifact that is, however, absent in the plain DFT calculation (Fig. 1). To understand the origin of this feature, we perform a series of static DFT + U calculations, varying the Hubbard U from 0 to the self-consistent DFPT value of 5.01 eV. As shown in Fig. 11, the unphysical peak emerges for $U > 2$ eV and becomes progressively more pronounced, separating from the main valence band as U increases. This behavior is expected from the Hubbard model, which enforces localization with increasing U , but it contradicts experimental HAXPES data that suggest dynamical hybridization between Fe 3d and O 2p orbitals.

This raises a critical question: Does the DFT + $U(\omega)$ correction arise from true dynamical screening or merely its small

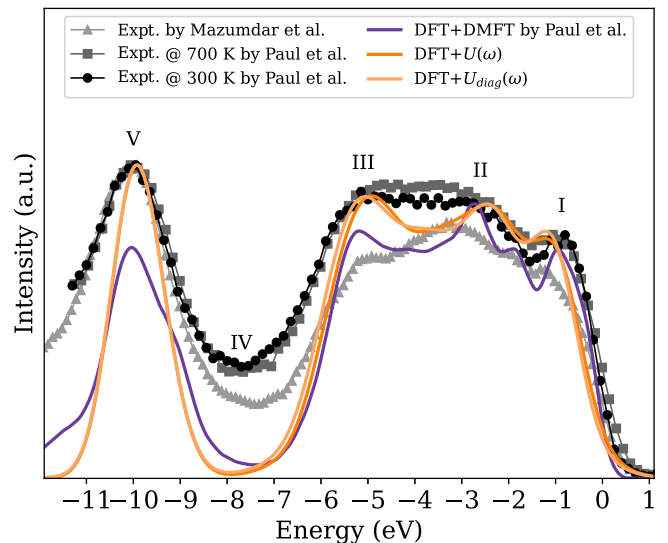


FIG. 14. Simulated HAXPES from dynamical DFT + $U(\omega)$ and DFT + $U_{\text{diag}}(\omega)$ calculations. Both methods eliminate the spurious static peak and show excellent agreement with experiments.

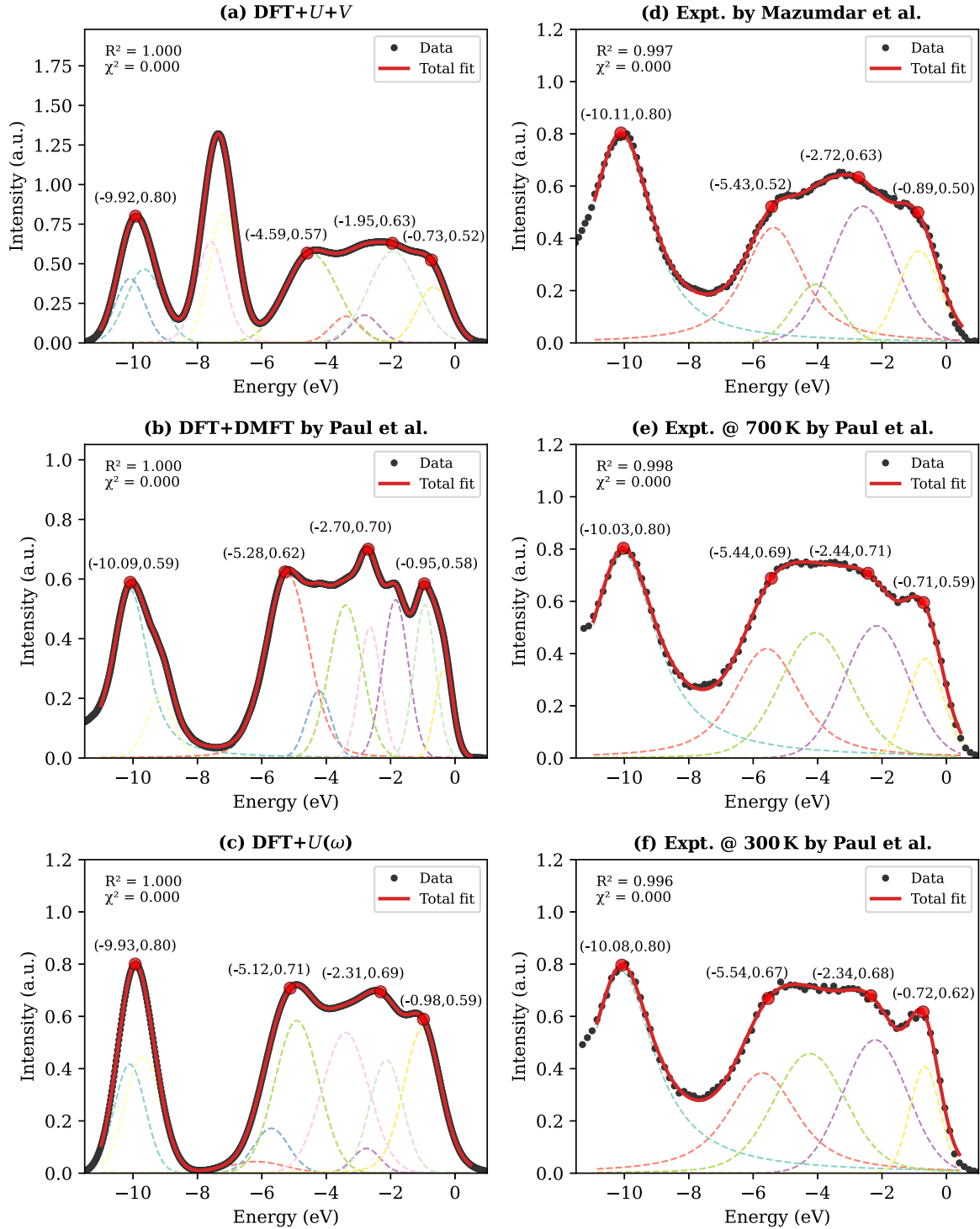


FIG. 15. Voigt function fits to HAXPES spectra. Raw data (points) are overlaid with the smooth Voigt function fit (red line) for experimental and theoretical spectra. The features identified via curvature analysis are highlighted with red points (I–V).

static limit ($U_0 = 2.56$ eV)? To test this, we constructed a hypothetical $U_{\text{diag}}(\omega)$ by averaging only the diagonal elements of the local interaction matrix:

$$U_{I;\text{diag}}(\omega) \equiv \frac{1}{2N} \sum_{m \in C; \sigma} U_{I;m,m,m}^{\sigma}(\omega). \quad (\text{C1})$$

As in the main text, we omit the atomic index here and demote $U_{\text{diag}}(\omega) \equiv U_{I;\text{diag}}(\omega)$. This yields a nearly identical

dynamical profile but a significantly larger static limit, $U_{\text{diag}}(0) = 3.74$ eV (see Fig. 12), well within the range where static DFT + U produces the spurious peak.

The test is decisive. Static DFT + U ($U = 3.74$ eV) produces the spurious Fe peak (Fig. 11) and a mismatched HAXPES spectrum (Fig. 13). In contrast, dynamical DFT + $U_{\text{diag}}(\omega)$ —despite the same large static limit—yields results (Fig. 14) in excellent agreement with the full DFT + $U(\omega)$

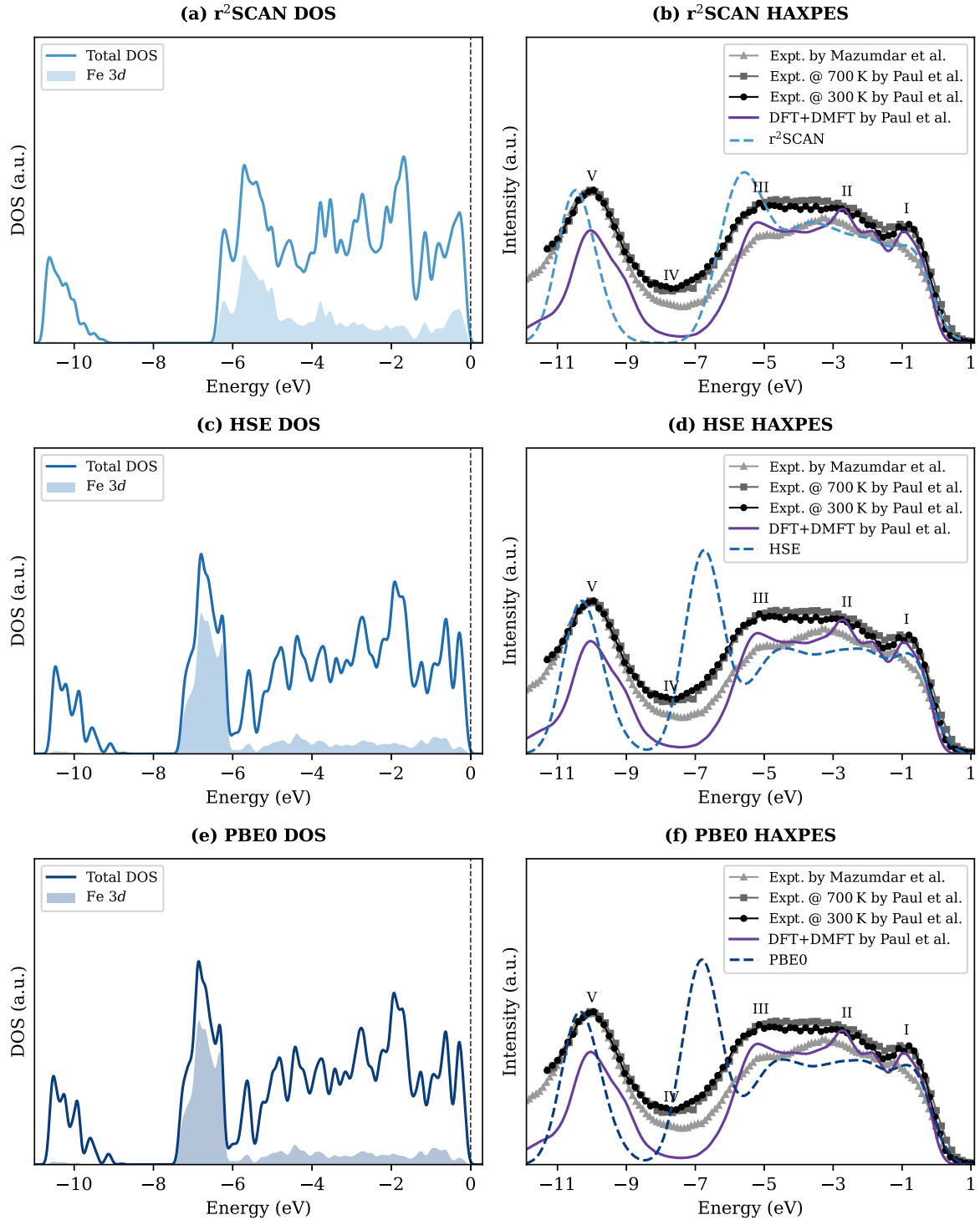


FIG. 16. Failure of advanced static exchange-correlation functionals (r^2 SCAN, HSE, and PBE0). All three functionals fail to reproduce the experimental spectrum, producing artifacts similar to those seen in static DFT + U .

calculation and experiments. This confirms that the correction is driven by dynamical screening, not a reduced static U_0 .

APPENDIX D: VOIGT-CURVATURE ANALYSIS OF SPECTRAL FEATURES

Quantitative comparison of HAXPES spectra is challenging because features I–III appear as broad shoulderlike

structures rather than sharp peaks. To address this, we employ a two-step analysis (Fig. 15). First, we fit each spectrum with a sum of Voigt functions to obtain a smooth, twice-differentiable analytic representation $f(E)$ that filters high-frequency noise. Second, we identify spectral features by locating points of maximum curvature, $\kappa(E) = |f''(E)|/[1 + (f'(E))^2]^{3/2}$. Geometrically, these correspond to points where the osculating circle has the smallest radius. This method

provides a robust, consistent metric to determine the position and intensity of broad spectral features across both experimental and theoretical datasets.

APPENDIX E: FAILURE OF HIGHER STATIC FUNCTIONALS

We also investigate whether advanced static functionals can resolve the electronic structure deficiencies. We test the meta-GGA r^2 SCAN and hybrid functionals HSE and PBE0 [39–41]. As shown in Fig. 16, all fail to correct the discrepancies with experiment.

r^2 SCAN mimics a DFT + U calculation with a small effective $U \approx 2$ eV, incorrectly predicting feature III to be more intense than feature V. The hybrid functionals (HSE, PBE0) strongly overlocalize the Fe 3d states, creating a sharp spurious peak deep in the valence band, analogous to DFT + U with $U \approx 4$ eV. These results confirm that static treatments—regardless of the functional’s complexity—cannot capture the necessary dynamical screening effects in BiFeO₃.

APPENDIX F: COMPARISON WITH DYNAMICAL HUBBARD FUNCTIONAL APPROACH

To validate our findings, we perform calculations using the dynH approach [16,17]. Unlike the one-shot self-energy correction used in our main work, DFT + dynH solves the Dyson equation via an algorithmic-inversion method (AIM-SOP) [42], offering a rigorous, nonperturbative treatment of the self-energy:

$$\begin{aligned} \Sigma_{\text{dynH}}^{\sigma,I}(\omega) &= 2\pi i \frac{\partial \Phi_{\text{dynH}}[G_I^{\sigma}]}{\partial G_I^{\sigma}} \\ &= - \int d\omega' U_I(\omega') G_I^{\sigma}(\omega + \omega') + \frac{U_I^{\infty}}{2}. \quad (\text{F1}) \end{aligned}$$

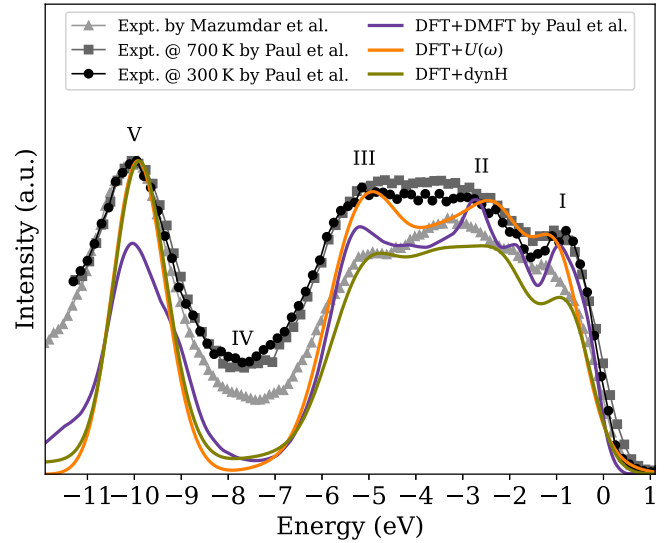


FIG. 17. Comparison of the simulated HAXPES spectrum from the DFT + dynH method (green) with the simpler DFT + $U(\omega)$ result (orange) and experimental data (black and gray scatters). The DFT + dynH approach validates the peak positions but yields lower spectral intensity for features I–III.

The results (Fig. 17) confirm our central conclusion: DFT + dynH eliminates the spurious Fe peak and accurately reproduces the spectral feature positions. The lower spectral intensity of features I–III in DFT + dynH compared to experiment likely reflects the absence of error cancellation present in the simpler one-shot approach (where approximate self-energy errors may offset PBEsol deficiencies). However, DFT + dynH more accurately captures the lineshape of features I–III, underscoring the physical robustness of the dynamical treatment.

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