Mass enhancement in 3d and s-p perovskites from symmetry breaking

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In some d-electron oxides, the measured effective mass $m^*$ has long been known to be significantly larger than the model effective mass $m^{\text{model}}$ deduced from mean-field band theory, i.e., $m^* = \beta m^{\text{model}}$, where $\beta > 1$ is the “mass-enhancement” or “mass-renormalization” factor. Previous applications of density functional theory (DFT), based on a symmetry-restricted structure with the smallest number of possible magnetic, orbital, and structural degrees of freedom, missed such mass enhancement. This fact has been taken as evidence of strong electron correlation, often described via the symmetry-restricted dynamic mean-field approach of the many-body theory, being the exclusive enabling physics. This paper uses instead a static density functional approach that does not restrict positional or spin degrees of freedom (symmetry-broken structures). This approach analyzes the contributions of different symmetry-broken modalities to mass enhancement for a few nominally highly correlated d-electron perovskites as well as the nominally uncorrelated, closed-shell s-p bonding perovskites. It shows that the energy-lowering symmetry-broken spin effects (e.g., nonzero local moment in the paramagnetic phase) and structural effects (e.g., atomic displacement) as described in mean-field DFT already manifest mass enhancement for both electrons and holes in a range of d-electron perovskites SrVO$_3$, SrTiO$_3$, BaTiO$_3$, and LaMnO$_3$, as well as p-electron perovskites CsPbI$_3$ and SrBiO$_3$, including both metals (SrVO$_3$) and insulators (the rest). This is revealed only when enlarged unit cells of the same parent global symmetry, which are large enough to allow for symmetry-breaking distortions and concomitant variations in spin order, are explored for their ability to lower the total energy. Positional symmetry breaking that leads to mass enhancement includes octahedral rotation in halide perovskites such as CsPbI$_3$, Jahn-Teller-like $Q^2_2$ distortion in LaMnO$_3$, and bond disproportionation in SrBiO$_3$, while magnetic symmetry breaking resulting in mass enhancement includes the formation of a distribution of local moments in SrVO$_3$ that averages to zero in the paramagnetic phase. Not all symmetry breaking leads to significant mass enhancement, e.g., the rather small octahedral rotations in the nearly perfectly cubic SrTiO$_3$ cause negligible mass enhancement, as do the paraelectric displacements in BaTiO$_3$. In principle, by ergodicity, the two descriptions, i.e., the symmetry-restricted dynamic approach with a single time-fluctuating magnetic moment and the symmetry-broken mean-field approach with a static distribution of spatially fluctuated local moments, are not mutually exclusive but are a choice of representation and consequently, a choice of computational efficiency. In approximate implementations, the symmetry-broken mean-field approach appears to remove much of what was strong correlation in dynamically correlated symmetry-restricted solutions, leaving smaller (“weak”) residual correlation with respect to the exact solution.

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I. INTRODUCTION

The effective mass $m^*$ defined as the reciprocal of the wave vector curvature $\partial^2 E/\partial k_i \partial k_j$ of the band dispersion relation $E(k)$ (where $k_i$ and $k_j$ are wave vectors) is a central quantity in condensed matter physics, widely used to characterize the band structure, carrier transport, and wave function localization [1]. Recently, this quantity has attracted attention in the context of d-electron correlated oxide physics, where the measured effective mass $m^\text{exptl}$ has been noted in some cases to be significantly larger than the model effective mass $m^{\text{model}}$, deduced from simplified mean-field band theory $m^\text{exptl} = \beta m^{\text{model}}$, where $\beta$ is the “mass-enhancement” or “mass-renormalization” factor. Here, $m^\text{exptl}$ are generally deduced from experiment via model assumptions (such as band parabolicity or various averages over the mass tensor), leading to different effective mass definitions in different experiments, including the mass deduced from Fermi velocity ($v_F$) as $m^* \propto 1/v_F$, from density of states (DOS) $m^* \propto (D(E))^2/3$, from specific-heat coefficient $m^* \propto \gamma$, from magnetic susceptibility $\chi \propto m^*(1 - m^2/m_{\text{exptl}}^2)$, and from the band width $W \propto m^2/2$. Values of $\beta > 1$ were reported in the literature for Fe-based superconductors [2,3], halide perovskites [4], titanites [5–7], ruthenates [8–10], and vanadates [11–14]. These mass enhancement factors from experiment $\beta(\text{exptl/model}) = m^\text{exptl}/m^{\text{model}}$ were then compared with the theoretical values $\beta(\text{Theory/model}) = m^\text{theory}/m^{\text{model}}$ obtained from many-body approaches (such as dynamic mean-field theory (DMFT) [15–24]). Because $m^{\text{model}}$ comes from the mean-field band theory, the predicted theoretical enhancement $\beta(\text{Theory/model}) > 1$ has been interpreted to be due to strong correlation effects [15–24]. For example, in DMFT, wavefunction localizes and band-width narrows (thus leading to mass enhancement) due to pure electronic symmetry breaking induced by the dynamic

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self-energy from the impurity atom embedded in a mean-field bath [24,25]. Finding for a compound that $\beta$(DMFT/model) > 1 is consistent with $\beta$(exptl/model) > 1 helped classify the pertinent compounds as being highly correlated, given that mean-field theory has been argued as unable to describe the mass enhancement.

This line of thinking, however, does not consider the possibility that mass enhancement could be described by methods other than using symmetry-restricted structures. Indeed, the model calculations used to extract $m^{*}_{\text{model}}$ have invariably been rather naïve (N) level of density functional theory (N-DFT), based on symmetry-restricted structures with the least number of possible magnetic, orbital, and structural degrees of freedom [15–24]. Such calculations have assumed one or a few of the following approximations: A highly symmetric unit cell [e.g., $Pm\overline{3}m$ cubic containing only a single formula unit (f.u.)], no atomic displacements relative to the averaged high-symmetry structure, and/or a nonmagnetic (NM) spin configuration. The shortcomings of such simplistic N-DFT approaches are evident among others in (i) predicting metallic states for known insulators (as illustrated for binary 3 NiO, MnO, CoO, and FeO insulators [26], ternary 3 NiO$_2$-$\beta$Sn, CuBi$_2$O$_4$, Sr$_2$IrO$_4$, Li$_2$TiO$_2$, and Ba$_4$As$_2$ [28,29]), and by the fact that (ii) they predict a total energy far higher (by $\sim 1$ eV/f.u.) than what conventional DFT [27] provides, as well as by (iii) missing the orbital order [27].

The failures of these naïve applications of mean-field band theory to predict electronic properties often go hand in hand with the assumption of a symmetry-restricted structure. For example, the cubic crystal structure of halide perovskites $ABX_3$ ($A = \text{Cs, MA, FA}; B = \text{Sn, Pb}; X = \text{Cl, Br, I}$) has been described in x-ray diffraction (XRD) databases as $Pm\overline{3}m$ cubic, having a single $ABX_3$ f.u., with all octahedra being ideally shaped, untitled, and oriented parallel to each other, representing a single $B\bar{X}_6$ local motif (monomorphous structure). This $Pm\overline{3}m$ cubic structure has been extensively used [30–33] to calculate the standard electronic band structure as well as phonon lattice dynamics. However, in reality, the cubic phase of such $ABX_3$ perovskites often manifests static atomic distortions off Wyckoff positions as an intrinsic expression of their chemical bonding, as seen by local probes [34,35] and reproduced by static total energy optimization [36], even before the contribution of thermal motion sets in. Whereas this symmetry breaking is observable from x-ray local probe measurements, e.g., the extended x-ray-absorption fine-structure (EXAFS) and pair distribution function (PDF) [37–42], it is easy to miss in DFT if one uses the average XRD $Pm\overline{3}m$ cubic cell because such a single cell geometrically excludes the creation of a periodic lattice with tilted octahedra. Permitting a larger cell ("supercell") with constrained cubic lattice vectors provides the geometrical freedom to distort octahedra. Similarly, there are reasons to suspect that this simpler symmetry-breaking physics, positional as well as magnetic (both sanctioned by single-determinant mean-field band theory view), could also affect the effective mass. For example, oxide perovskites are known to manifest octahedral rotations and tilting [43], displacements [44], bond disproportionation [45], and Jahn-Teller distortions [46], while such local modes can couple to the electronic structure, leading to shifted band energies [30,47–52], thus, possibly leading to mass renormalization. Also, whereas the paramagnetic (PM) phases in 3d oxides were once treated as NM [12–18,53–55] (thus, interpreting the zero global magnetic moment as being zero on an atom-by-atom basis), more recent theories allowed for the existence of a distribution of different spin environments adding up to zero, constituting a polymorphous network that couples to electronic properties [36,56–58]. The existence of a distribution of positional as well as local magnetic environments needs to be investigated for its ability to affect the band structure and hence the effective masses.

Therefore, instead of leapfrogging from N-DFT to dynamically correlated methods such as DMFT, it would seem informative to retain the $m^{*}_{\text{model}}$ mass but replace $m^{*}_{\text{Theory}}$ in $\beta$(Theory/model) = $m^{*}_{\text{Theory}}$/m$^{*}_{\text{model}}$ by mean-field theory, which allows for possible magnetic, orbital, and structural degrees of freedom, which could break symmetries while lowering the total energy. It can be done by using DFT that is free from oversimplified symmetry-restricted approximations which are not an essential part of DFT. This $\beta$(DFT/N-DFT) = $m^{*}_{\text{DFT}}$/m$^{*}_{\text{N-DFT}}$ might include many symmetry-broken effects routinely included in contemporary DFT calculations, such as (i) positional symmetry breaking, e.g., octahedral rotations, Jahn-Teller distortions, and bond disproportionation, all observed experimentally, and (ii) magnetic symmetry breaking, e.g., allowing spin configurations such as antiferromagnetic (AFM) and PM rather than the NM approximation. Effective allowance for (i) and (ii) also necessitates the use of exchange-correlation (XC) functionals that produce correctly compact orbitals (due to closer adherence to the generalized Koopmans condition [59]) but not an overestimated orbital localization (such as in the Hartree-Fock functional).

That symmetry breaking in approximate mean-field theory could capture events that in restricted symmetric structures would require a complex correlated treatment has been amply illustrated in molecular systems. For example, as pointed out by Bagus and Schaefer [60], describing a core hole state in diatomic O$_2$ while retaining the high $D_{\infty h}$ symmetry is made computationally difficult by the extreme complexity of packing the electron-electron pair correlation into a small, symmetric space, yet breaking molecular orbital symmetry by placing the hole initially on a single atom in Hartree-Fock calculation agrees well with the experiment. In principle, by ergodicity, the two descriptions, i.e., (a) the symmetry-restricted dynamic approach with a single time-fluctuating magnetic moment vs (b) the symmetry-broken mean-field approach with spatially fluctuated local moments, are not mutually exclusive but are a choice of representation and, consequently, a choice of computational efficiency, at least if both approaches are carried out exactly. In the exact implementations, (a) dynamic symmetry-restricted and (b) static symmetry-broken ground states should have the same ground state energies [59–63]. In approximate implementations, experience in a two-center molecular system (such as stretched H$_2$, Li$_2$, or O$_2$) indicated that symmetry-broken mean field removes much of what was strong correlation in symmetry-restricted dynamically correlated solutions.
leaving smaller ("weak") residual correlation with respect to the exact solution. Thus, a correlation that has been dynamic in the symmetry-restricted case can become static in the symmetry-broken cases, and the correlated methods in symmetry-restricted structures might not be the only way to describe mass enhancement [63]. Symmetry can be restored afterward [64] and often gives localized states but small additional energy lowering. A review of the traditional role of symmetry-broken mean field vis-à-vis symmetry-restricted correlation and that these are nonadditive effects has been recently presented by Perdew et al. [63]. Such a symmetry-broken mean-field approach can further provide clear intuition as to the mechanism whereby the electronic structure (here, mass enhancement) is established. The classic picture of the face-centered cubic "empty lattice" band structure having the symmetry of a primitive cell without interactions, as illustrated by Herman [65], shows broad bands and high degeneracies with low masses. Any successive introduction of interaction terms into this empty lattice Hamiltonian (starting with the point-ion pseudopotential) would progressively remove band degeneracies, split broad bands into sets of subbands, and lead to mass enhancement. Examples of known modalities of symmetry breaking that are now shown to lead specifically to mass enhancement are summarized in Fig. 1 and discussed in the following sections. We find that indeed these energy-lowering, mean-field, symmetry-broken modalities (lines 2–6) can enlarge the band gap and/or contribute to more localized wavefunctions, thus leading to mass enhancements, not only for electrons but also for holes, which were previously attributed exclusively to explicitly correlated methodologies.

The intuition behind this investigation originates from the fact that effective masses can be gleaned qualitatively from $k \cdot p$ perturbation theory [66],

$$
\frac{1}{m^*_nj} = \frac{1}{m_0} + \frac{2}{m_0^2 k^2} \left( \sum_{j,l[n]} |\langle n | 0 \rangle k \cdot p | l, 0 \rangle|^2 \right) \frac{E_{n0} - E_{l0}}{E_{n0} - E_{l0} + \epsilon_{nj,k}},
$$

where $m^*_nj$ is the effective mass of state $| nj, 0 \rangle$ at band edge, $0$ denotes the momentum where the band edge is located, subscript $j$ is the index of degenerated wave functions, $m_0$ is the free-electron mass, $E_{n0} - E_{l0}$ are interband energy gaps, and $\epsilon_{nj,k}$ are the energy shifts from band degeneracy (zero if no degeneracy). The sum is over all eigenstates $| n0 \rangle$. This classic expression shows that the effective mass in solids is generally enhanced by any effects that increase the interband energy gaps ($E_{n0} - E_{l0}$) and/or reduce the wavefunction momentum matrix element $\langle n0 | k \cdot p | 0 \rangle$, i.e., producing more compact wavefunctions.

In this paper, we use the textbook definition of the effective mass $m^*$ as the reciprocal of the wave vector curvature $\frac{\partial^2 E}{\hbar^2 \partial k_i \partial k_j}$, except that instead of insisting on an electronic structure based on a symmetry-restricted primitive unit cell, we allow energy-lowering symmetry breaking in a larger
cell. While there is no “theorem,” to our knowledge, showing if DFT can describe exactly band energies, thus effective masses, our justification and indeed method of analysis rely on the insight (but not literal details) from this $\mathbf{k} \cdot \mathbf{p}$ theorem [Eq. (1)], indicating how effective masses are related to band gap. The fact that effective masses are often evaluated from band widths in DFT and in many-body calculations (as implied in previous DMFT [15–24]), as well as in experimental literature [2,3,6,13,14] supports this tradition. Note that the DFT band gap is described as the total-energy difference gap, i.e., the difference between ionization potential $I = E(M-1) - E(M)$ and the electron affinity energy $A = E(M) - E(M+1)$ where $M$ is the number of electrons. Such a total energy difference gap is a proxy to the quasiparticle gap. Since, in this definition, only the ground-state energies are involved, this total energy difference gap can be calculated in principle exactly from DFT and can be directly compared with that measured from experiments [67–69]. Now the quantity that is practically calculated often is the single-particle band gap between conduction band minimum (CBM) and valence band maximum (VBM) $E_{\text{CBM}} - E_{\text{VBM}}$. Reference [69] has shown that such a single-particle gap is equal to the total energy difference band gap for the same XC functional, if the XC is a nonmultiplicative potential (operator is continuous) and the density change is delocalized when an electron or hole is added. This applies to local spin density approximation (LSDA), Perdew-Burke-Ernzerhof (PBE), strongly constrained and appropriately normed (SCAN), and hybrid functionals. The following Secs. III and IV will provide the different definitions of effective mass that have been examined. Our DFT results with symmetry breaking and no dynamic correlation show comparable masses with DMFT and experimental data.

Table I lists mass enhancements calculated by symmetry-broken mean-field DFT in this paper for six compounds compared with experimental observations previously reported for SrVO$_3$, CsPbI$_3$, LaMnO$_3$, and SrTiO$_3$. Previous DMFT calculations for SrVO$_3$, LaMnO$_3$, and SrTiO$_3$ are also given in Table I. Many of the mass enhancements found by symmetry-broken DFT here are comparable in magnitude with the values suggested by the correlated methods. We see that mass enhancement by symmetry-broken DFT is not unique to open-shell $d$-electron compounds, and similar magnitudes of mass enhancements also exist for $s$-$p$-bonding compounds. This further suggests that viewing the presence of mass enhancement in the considered compounds as evidence for the exclusive need for strong dynamically correlated methodologies [15–24] is not a safe practice before examining the effect of positional and magnetic symmetry breaking on the band structure.

II. APPROACH

A. Supercell model

To allow for inclusion of the pertinent symmetry-lowering effects, the tradition of using the most economical minimal unit cell must be avoided because it might geometrically disallow symmetry breaking. Instead, one should use a $N_1 \times N_2 \times N_3$ replica of such a minimal cell (i.e., a supercell). Table I shows for each compound (i) the observed low-symmetric ground state at low temperature, (ii) the mass-enhanced phase studied in this paper, (iii) the symmetry-restricted minimal-cell model previously used in the literature. We see that the structure for which mass enhancement was reported in the experiment and studied in previous DMFT calculation is not always the ground-state structure, e.g., for halide perovskites such as CsPbI$_3$ and oxide perovskite SrTiO$_3$, the ground states are orthorhombic and tetragonal, respectively, while it is the cubic phase where mass enhancements were reported [4,73]. In such cases where the phase studied is not the ground-state phase, the supercell model is constrained throughout the calculation to have the global lattice symmetry of the phase studied (e.g., cubic), but all internal atomic positions can attain the values that minimize the (constrained) total energy. To assure that the relaxed atomic positions are reliable (e.g., not saddle points on the potential surface), all atoms have been initially “nudged” by applying random atomic displacements (random for both direction and amplitude) before starting the process of following total energy minimization. The size of the supercell is increased until convergence on total energy is found; the cell size is not directly important per se except that certain cells cannot, by symmetry, allow symmetry breaking even if it will lower the energy. This dependence of total energy per atom on the cell size is unique to certain (polymorphous network) compounds but not in conventional materials, such as silicon or ZnSe, where it does not show different total energies between supercell and minimal-cell model. Thus, larger than minimal (super) cells do not necessarily lead to disorder or mass enhancement unless energy lowering takes place.

In all magnetic calculations, the directions of spin moment on every site are collinear and fixed (i.e., spin flip is not allowed), while the amplitudes of magnetic moment are free to evolve during the total energy minimization. In principle, spins can relax during the electron self-consistency calculations to produce nonrandom configurations. We have confirmed that our DFT self-consistent calculations give negligible net magnetization for all AFM and PM structures (<0.001 Bohr magneton per atom).

B. Band unfolding

Whereas the supercell approach has the advantage of allowing the incorporation of local structural and spin motifs, it has the disadvantage of producing a nonintuitive and difficult-to-analyze dense band structure in the small reciprocal-space Brillouin zone (BZ) associated with the large real-space cell dimensions. This difficulty is overcome by applying rigorous band unfolding [74–76] to the supercell band structure, producing effective band structures (EBBs) that replace the sharp bands of ordinary band theory by spectral functions (including both coherent and incoherent components).

C. Calculation of effective mass

We apply four models to calculate the mass and mass enhancement: (1) deducing the mass from the mass tensor
of the reciprocal for the second derivative of $E$ vs $k$ at the band edges; if the mass tensor is anisotropic ($m_1^* \neq m_2^* \neq m_3^*$), the result mass will be calculated as $m^* = (\frac{1}{m_1^*} + \frac{1}{m_2^*} + \frac{1}{m_3^*})^{-1}$; (2) deducing the mass from the DOS at Fermi level, i.e., the Fermi velocity ($v_F$), as $m^* \propto \frac{1}{v_F}$; and (3) deducing the mass from the bandwidth $m^* \propto \frac{1}{W}$. Note that method (1) can give the absolute mass, while methods (2)–(4) are used only for the relative mass-enhancement factor $\beta = m_{\text{theory}}^*/m_{\text{model}}^*$ but not the absolute mass. We focus here on the mass-enhancement factors (relative masses) rather than on the absolute values of masses.

### III. MAGNETIC POLYMORPHOUS NETWORK IN PARAMAGNETS LEADS TO MASS ENHANCEMENT: SrVO₃

#### A. Representation of the PM phase as a distribution of local spin environment

All calculations reported here are spin-polarized, allowing up and down spins. In addition, we allow for spatial spin symmetry breaking: the PM phases of 3$d$ oxides are often described in the DFT literature as being NM, interpreting the PM condition of globally zero moment on an atom-by-atom basis, deducing that each atom must be NM [12–18, 53–55]. This strong restriction does not follow from the definition of

| Compound | Ground state | Phase studied in this paper | Symmetry-restricted model (ref. $\beta = 1$) | Symmetry-broken mode found by DFT | Mass enhancement |
|----------|--------------|-----------------------------|---------------------------------------------|-----------------------------------|-----------------|
| SrVO₃    | PM cubic     | PM cubic                    | Magnetic \(\beta_e\) symmetry breaking       | \(\beta_e\)                        | DFT: 1.5 ± 0.1  |
|          |              |                             |                                              |                                   | (exp.: 1.3², 2.2³, 2.9³, DMFT: 1.8 ± 0.2) |                 |
| CsPbI₃   | NM orthorhombic | NM cubic                  | Octahedral rotation \(\beta_e\)          | \(\beta_e\)                         | DFT: 1.8, (exp.: \(m^* = 0.12m_0\)) |
| LaMnO₃   | AFM orthorhombic | AFM orthorhombic          | Jahn-Teller distortion \(\beta_e\)         | \(\beta_e\)                         | DFT: 1.8 ± 0.5  |
|          |              |                             |                                              |                                   | (exp.: 2.6–2.8, DMFT: 1.3–1.7)     |
| SrBiO₃   | NM monoclinic | NM monoclinic             | Bond disproportionation \(\beta_e\)       | \(\beta_e\)                         | DFT: 1.3 ± 0.2  |
| SrTiO₃   | NM tetragonal | NM cubic                  | Octahedral rotation \(\beta_e\)           | \(\beta_e\)                         | DFT: 1.1, (exp.: 2–3, DMFT: 1³)    |
| BaTiO₃   | NM rhombohedral | NM cubic                 | Ferroelectric displacement \(\beta_e\)     | \(\beta_e\)                         | DFT: 1           |

*Reference [16].

Reference [17].

References [11,12,14].

²Estimated from Ref. [71].

²DFT calculated reduced mass $m^* = 0.14m_0$, and experimentally measured reduced mass (for cubic CsPbBrI₂) $m^* = 0.12m_0$ [70].

¹Reference [72].

²By comparing this paper with Ref. [53].

²Reference [73].
SrVO$_3$ (paramagnetic cubic phase, PBE+U)

N-DFT result

with high symmetry

(a) Minimal cell band structure

E$_{\text{Fermi}}$ (eV) vs k (meV/f.u.)

PM phase

Nature of symmetry breaking

(b) Vanadium magnetic moment ($\mu_B$)

Frequency count

PM phase

Consequence of symmetry breaking

(c) Supercell band structure

1.725 eV

$\beta_0(R) = 1$ $\beta_0(T) = 1.5$

$E_{\text{tot}} = -31$ meV/f.u.

Spectral function

FIG. 2. Mass enhancements in the paramagnetic (PM) cubic phase of SrVO$_3$. (a) The band structure obtained from the same naïve density functional theory (N-DFT) restriction as in previous literature [12–18], namely a single-cell, cubic, nonmagnetic (NM) SrVO$_3$ model using PBE + U ($U = 1.25$ eV on V $d$ orbitals). (b) The distribution of spin moments in the present PM phase: blue lines show that, in the minimal-cell NM phase, all vanadium sites have zero magnetic moment, while the red curve shows that, in the PM phase, different vanadium sites have a distribution of different, nonzero magnetization. (c) The unfolded band structure when removing the minimal-cell restrictions by using instead a cubic, 128 f.u. PM supercell SrVO$_3$ with the same PBE$^\ast$ method. The total internal energy $E_{\text{tot}}$ from DFT of (c) is 31 meV per formula unit (meV/f.u.) lower than that of (a). Masses in (c) are calculated via density of states (DOS) at Fermi level (which gives $\beta_e = 1.4$ and $\beta_h = 1$); the subscripts $e$ and $h$ denote the electron and hole mass enhancements; uncertainty is due to the variation of DOS nearby the Fermi level, second derivative of $E$ vs $k$ (which gives $\beta_e = 1.46$ and $\beta_h = 1$), and bandwidth (which gives $\beta_e = 1.43$ and $\beta_h = 1$). The vertical arrows in (a) and (c) show the bandwidths. The same PBE + $U$ method has been applied for all SrVO$_3$ calculations.

PM or from the DFT, and as was recently recognized, it leads to rather high total energy [27]. A correct description of PM entails allowing a larger (super) cell that can accommodate different local spin environments should they lower the total (DFT) energy. For example, in a PM crystal where each magnetic ion is locally coordinated by $N$ other magnetic ions, one can have in the collinear description a distribution of local spin environments, e.g., an up-spin ion can be coordinated by $(N-m)$ up-spin ions plus $m$ down-spin ions, where $0 \leq m \leq N$; if the up and down orientations are chosen randomly (which corresponds to the high-temperature limit of the PM phase), it follows the binomial statistics, i.e., finding an ion with $m$ down-spin neighbors follows the probability distribution function $P(m; N, 0.5) = \binom{N}{m}0.5^N$. This model of PM local order represents a generalization of the AFM spin configuration that includes a single local environment (e.g., up-spin site coordinated only by down-spin sites), whereas in the PM phase, the above-noted additional local environments could exist. This is accomplished in practice by borrowing an idea known from the theory of substitutional $A_xB_{1-x}$ alloys [77]: construct an $M$-atom supercell for composition $x$ with sites occupied by $A$- and $B$-type atoms (here, up-spin and down-spin atoms), so that the atom-atom correlation function will mimic for a finite supercell a given statistic for the infinite cell (here, random binomial statistics) the best possible way for an $M$-atom supercell. Such special quasirandom structures (SQSs) identify the most economical supercells for given size $M$. We currently use the random spin-spin correlation (corresponding to the high-temperature limit), although the use of nonrandom short-range order (SRO) in SQS is possible [78,79].

We consider next the PM phase of SrVO$_3$ modeled by a 128 f.u. supercell (i.e., 640 atoms per cell) with collinear up- and down-spin configuration. Figure 2(b) shows in red the distribution of DFT calculated up-spin and down-spin magnetic moments, whereas the single vertical blue line shows the all-site-having-zero-spin condition in the minimal-cell NM case. For all relaxed SrVO$_3$ supercells, we have found negligible atomic displacement, consistent with the fact that the size mismatch factor revealed by the Goldschmidt factor is negligible. Comparing different spin configurations including ferromagnetic (FM), AFM, and PM phases in SrVO$_3$ (Table II in Appendix B) shows nearly degenerate total energy, suggesting that the spin ground state could be a mixture of many possible magnetic orders, i.e., in agreement with experiment [80,81] that SrVO$_3$ is a PM metal down to low temperatures and does not form magnetic order. Note that all magnetic phases show significant energy lowering when compared with the conventional NM model.

B. Electron mass enhancement in SrVO$_3$

Figure 2(a) shows the N-DFT band structure (cubic unit cell containing a single f.u., no relaxation, with NM spin configuration having zero moments at all sites) giving a metallic phase, with a conduction bandwidth of 2.5 eV. This model was used for $m^*_\text{e,layer}$ in many previous studies [12–17] to calculate mass enhancement using, e.g., DMFT and GW theories. Figure 2(c) shows the spectral functions calculated in DFT from such a 640 atom supercell unfolded into the primitive BZ of SrVO$_3$. The unfolding procedure used in Fig. 2(c) allows one to reduce the band structure complexity of a supercell, converting the sharp bands from the monomorphous case to an EBS having a finite band spread that depends on the distribution function used to describe the spin in a PM supercell (in the current case, we neglect the spin-spin SRO, so the fuzziness may be overestimated). Figure 3 shows the
evolution of the unfolded band structure as the real-space supercell size increases, finding convergence.

The significant result is that the conduction band in the PM phase, allowed to have a distribution of local spin motifs, is narrowed relative to the minimal-cell NM case from 2.5 eV [Fig. 2(a)] to 1.75 eV [Fig. 2(c)]. This leads to an electron mass-enhancement factor ($\beta_e$) in the PM supercell $\beta_e(DFT/N-DFT) = 1.43$. Note that different definitions of effective mass give somewhat different results: the bandwidth mass enhancement of 1.43 can be compared with the DOS mass enhancement 1.4–1.6 at Fermi level, while the second derivative of $E$ vs $k$ at the conduction band edge gives 1.46. Note that we have not attempted to fit the result by adjusting $U$, although the choice of more localizing XC functional can increase the enhancement factor. We note that, whereas the values obtained depend somewhat on the definition of effective mass used, the lattice constant (here, we used $a = 3.83$ Å), and the $U$ value, allowing for polymorphous spin configuration, leads in all cases to an enhancement factor of $1.5 \pm 0.1$. These calculated mass enhancements are comparable with the experimentally measured factor $\beta_e(exptl/N-DFT) \approx 1.8 \pm 0.2$ [11,12,14], while smaller than the enhancement factors from DMFT, e.g., $\beta_e(DMFT/N-DFT) = 2.9$ [17] (using a much larger $U = 5.5$ eV that narrows bands further) and from GW + DMFT $\beta_e = 1.3$ [16], 2.2 [17] (where the two values correspond to different versions of accounting approximately for the double-counting error in GW + DMFT).

C. Hole mass enhancement in SrVO$_3$

The DFT calculations naturally provide all bands with equal approximations, both the electron conduction band (mainly V d orbitals) and the valence hole band (mainly O p orbitals). We find no mass enhancement for hole states in the principal valence band, consistent with the fact that the spin configuration in the O $p$-like principal valence band corresponds to a closed electronic shell and negligible magnetic moment that show no distribution of motifs. We will see later that, in $ABX_3$ perovskites, where the local environment is made of a distribution of positional motifs rather than from spin motifs, there will be both electron and hole mass enhancements.

D. Analysis of the contributing factors to spin-induced mass enhancement in SrVO$_3$

The real-space symmetry-broken supercell approach provides for an intuitive understanding of the results. The degree of freedom within our PM supercell is the local spin configuration (as we have found that the positional relaxation is negligible in this system). A local spin motif consists at the first order of a central 3$d$ atom and its first-shell 3$d$ (next nearest) neighbors. Whereas in the case of the minimal-cell NM model, each and every motif has zero spin, and in the case of AFM order, each motif has maximum dissimilarity between the spin of the central atom and the spins of its coordination shell (e.g., the AFM-G-like local motif when the central atom is up-spin, while all its neighbors are all down-spin), in our model of the PM phase, each spin can have a local distribution of spins, including the case of maximum similarity (e.g., the FM-like local spin motif when the central atom is up-spin, and so are all its neighbors), maximum dissimilarity, or any configurations in between. Figures 4(a)–4(c) show the random (high-temperature limit) statistical weight for each spin motif. Each local spin motif might have its unique, projected local DOS. The vertical arrows in Figs. 4(d)–4(i) indicate that each local spin motif contributes differently to the conduction bandwidth, whereas the reference minimal-cell result using the NM model [shown in Fig. 4(d)] has considerably wider DOS. Figures 4(e)–4(i) show that the locally AFM-G-like vanadium sites with maximum spin dissimilarity with their neighbors have the most compressed DOS [Fig. 4(i); smallest range in energy and the highest peak in DOS, indicating enhanced electron mass], while the locally FM-like sites with maximum spin similarity with the neighbors have the most expanded DOS [Fig. 4(e); similar to the bandwidth in the NM model in Fig. 4(d), hence not contributing to mass enhancement]. Figure 4 suggests that the mass enhancement depends on spin SRO, i.e., the spin configuration at the center site and the neighbors, through the statistical weight for each spin motif [Fig. 4(b)]; an AFM-like, anticlustering SRO can lead to a larger enhancement coefficient $\beta$, while a FM-like, clustering SRO can reduce $\beta$. This analysis shows that the existence of a polymorphous distribution of spin-polarization motifs with their attendant, different local DOS contributing differently.
FIG. 4. Total density of states (DOS) of cubic SrVO₃ (the same PBE + U method) as a weighted superposition of the partial DOS (PDOS) of the local spin motifs. Upper panel: the weight of local spin configuration in: (a) statistical weights of ferromagnetic (FM) primitive cell [all the first-neighbor vanadium have the same spin direction as the center vanadium, see insert in (a)]; (b) distribution of statistical weights of different spin configurations in the cubic paramagnetic (PM) supercell; (c) statistical weights of G-type antiferromagnetic (AFM-G) double perovskite cell [all the first neighbor vanadium have the opposite spin direction to the center vanadium, see insert in (c)]. Lower panel: the vanadium d-PDOS in different spin configurations: (d) nonmagnetic (NM) primitive cell in which each site has zero spin; (e) FM motif; (f)-(h) different local spin motifs in PM phase, and (i) AFM-G motif. The dash lines and vertical arrows in (d)–(i) show the bandwidths of the d orbital for guide of eyes. Note that, in (d)–(i), we only show the d-PDOS of the central vanadium atoms (neighbors are not included to avoid multiple counting).

to the total DOS creates the possibility of spin-induced mass enhancement.

As discussed above, static DFT calculations permitting symmetry breaking and ensuing creation of local spin motifs naturally show mass enhancement. The scope of the current calculation of $E$ vs $k$ dispersion does not extend, however, to fully model angle-resolved photoemission spectroscopy (ARPES) spectra, including ARPES matrix element effects [82,83], or lifetime effects [84,85] associated with the observed sharpening of the ARPES states as they approach the Fermi level [12–14]. Description of lifetime broadening generally requires a time-dependent dynamics analysis, e.g., spin dynamics combined with molecular dynamics, possible in the mean-field DFT framework [86].

IV. POSITIONAL SYMMETRY BREAKING CAUSES COUPLING OF THE ELECTRONIC BANDS LEADING TO MASS ENHANCEMENT

A. Octahedral rotation enhances masses in $s$-$p$ halide perovskite CsPbI$_3$

Octahedral tilting (rotations) [43] have been known to exist in perovskites; here, we point out that such observed local modes can cause mass enhancement. The perovskite structure consists of corner-sharing octahedra that allow octahedral rotation and tilting. The classic atomic size mismatch between the $A$ and $B$ sublattices in $ABX_3$ drives static octahedral tilting and rotations, as was recognized in Ref. [87] and verified by modern PDF measurements [88] as well as by DFT total energy minimization [52,89–92]. This kind of deformation...
derivatives from classical atomic size mismatch and therefore exists even in close-shell s-p electron compounds such as halide perovskites [52,90,91]. Octahedral tilting (rotation) effects have been investigated in lead and tin halide perovskites for the low-temperature tetragonal and orthorhombic phases. However, for the cubic phase, it has been generally assumed [30–33] that, because of its XRD designation as a Pm\overline{3}m structure with a single f.u. per cell, such tilting is disallowed by symmetry, hence absent. Here, we point out that (i) a minimal 2 × 2 × 2 cubic supercell is needed to reveal tilting, (ii) single tilting modes [43] already change the mass, and (iii) larger supercells such as 4 × 4 × 4 can reveal multimode tilting, showing further lowering of the total energy relative to the monomorphous Pm\overline{3}m cubic model. Such multimodes significantly affect mass enhancement. Although, technically, this can be posed as an electron-phonon effect, given that the pattern of tilting and atomic displacements are complex and imply the participation of a significant number of phonons, we do not use the phonon terminology; instead, we explicitly (and nonperturbatively) minimize the generally anharmonic DFT energy surface with respect to all atomic positions, dislodge atoms from metastable local positions to stable positions, then calculate the ensuing band structure and masses.

1. Qualitative analysis of how octahedral tilting affects band edge energies in CsPbI₃

The coupling between octahedral tilting and electronic structure in low-temperature phases has been discussed in oxide [5] and halide perovskites [30] as a band-gap-tuning mechanism. Here, as schematically shown in Fig. 5, we demonstrate how the octahedral rotation in the s-p bonded compound CsPbI₃ affects band edge states. In cubic CsPbI₃ without distortion, the valence band maximum (VBM) is an antibonding state formed from the Pb s and I p orbitals, while the conduction band minimum (CBM) is weakly antibonding state of Pb p and I p orbitals. Allowing rotations of the (PbI₄) octahedron weakens both the p-p and s-p bonding between Pb and I. Consequently, being antibonding states, both CBM and VBM move to lower energies. However, because the VBM is more sensitive to octahedral deformation (being composed of inner-shell 6s-3p antibonding) than the CBM (being composed of outer-shell 6p-3p antibonding) [93], the VBM moves further than CBM, leading to a larger band gap due to rotation (Fig. 5, right panel).

2. Model DFT calculations on the effect of frozen rotations on mass enhancement in CsPbI₃

The results of the simple model of Fig. 5 are then validated by DFT calculations of small (8 f.u.) model supercells, where we artificially impose given octahedral rotation angles, followed by band unfolding to the single-cell cubic primitive BZ. The unfolded band structure is shown in Fig. 6. The imposed octahedral rotation here is $a^+da^{-}$ mode (Glazer notation [43]) or $M_{x}^{+} \oplus R_{z}^{-}$ (irreducible representation from Miller and Love [94]). The imposed octahedral rotations can affect the curvature of both valence and conduction bands at the band edges. Choosing the band gap and effective masses of the zero-rotated structures as the reference, as shown in Fig. 6, one can see that, under a uniformed arbitrary rotation of (10⁰, 10⁰, 10⁰), the band gap of CsPbI₃ increases by 0.52 eV (∼40%), and the electron and hole masses are enhanced by 77% and 113%, respectively.

3. Full supercell calculation of rotation-induced mass enhancement in CsPbI₃

Having clarified the effect of classical rotation on the band structure by the model (Fig. 5) and validated it by DFT (Fig. 6), we next study a large supercell with optimized rotating geometries in the cubic phase of CsPbI₃. Recall that the rotations discussed here are not thermal, but in fact, they are energy-lowering distortions derived by the nature of the chemical bonds (here, steric effects) even at low temperatures. Thus, we obtain these deformations by minimization of the DFT internal energy. However, this requires that we allow a larger-than-the-minimal unit cell so that rotations can be accommodated geometrically. The electronic structure of a single-cell cubic (Pm\overline{3}m) model (monomorphous model) is shown in Fig. 7(a). Restricted by the small size and periodic boundary condition, such a structure cannot accommodate rotations [as shown by the blue lines in Fig. 7(b)]. We avoid such a restrictive assumption using a supercell representation (32 f.u. supercell) instead. We perform a constrained minimization of the internal energy ($T = 0$) of the cubic phase that retains the macroscopic cubic supercell shape (or else the minimization will converge to the ground-state orthorhombic or tetragonal structures that are not the subject of the current study). At the same time, we allow all cell-internal degrees of freedom to locally adjust to find the structure with the lowest total energy. This is done by using a set of random initial nudging to dislocate atoms from possible local minima.

It has been shown in our recent paper [36] that, for lead halide perovskites with organic molecules on the A site, such a supercell representation following the constrained DFT total energy minimization explains various anomalies in the cubic phase, where the minimal-cell model disagrees with experimental observation. This includes a close agreement with the measured PDF, significant increase in the band gap, and dielectric constant. For the cubic CsPbI₃ supercell, we have found that, when abandoning the restriction of the minimal-cell model, the atomic configuration of cubic phase that gives the lowest total energy of the cubic phase (the supercell outline has been constrained to be cubic) is not the single f.u. Pm\overline{3}m cubic model but a supercell representation for the cubic phase with many local octahedral tilting. The many

![FIG. 5. Energy level diagram for CsPbI₃, before and after octahedral rotation. The red solid lines show the trends of band gap change.](image-url)
FIG. 6. The unfolded spectral function [effective band structure (EBS)] in the cubic primitive Brillouin zone, (a) before and (b) after a uniformed (10°, 10°, 10°) rotation for cubic CsPbI₃. Both (a) and (b) are calculated using the 8 f.u. supercell. Note that EBS shown in (a) is identical to the band structure obtained from a minimal-cell cubic model because (a) has no atomic distortion. Band gap is 1.31 eV in (a) and 1.83 eV in (b). Taking effective masses of CBM and VBM in (a) as references, the mass-enhancement factors in (b) are \( \beta_e = 1.77 \) (for electron, counting all three states near CBM) and \( \beta_h = 2.13 \) (for hole), respectively. All masses come from band dispersion (second derivative of \( E \) vs \( k \)).

local tilts in the cubic supercell cannot be written using the simple Glazer notations but must involve complex notations [43] and cannot be reduced into smaller cell models. We find that (i) the rotation angles are distributed among 5–13° [red lines in Figs. 7(b) and 7(e)]; (ii) the supercells have lower total energy (−124.4 meV/f.u.) compared with the single-cell model. Recall that, during the DFT calculation, we used the equivalent k-point mesh for all cells (12 × 12 × 12 \( \Gamma \)-center k-point mesh in primitive cubic BZ) and a total energy tolerance of \( 10^{-8} \) eV/atom. We therefore suggest that the −124.4 meV/f.u. energy lowering is robust. Furthermore, (iii) we find, as expected from the simple model of Fig. 5, a significant band gap increase and thus mass-enhancement factors: the band gap increases from 1.31 eV in the monomor-

FIG. 7. Mass enhancements in cubic CsPbI₃. (a) The band structure from the same naïve density functional theory (N-DFT) restriction as in previous literature [30–33], namely a single-cell cubic model, using PBE functional. (b) The distribution of octahedral rotation angles. The blue arrow in (b) shows that, in the minimal-cell model, all octahedra have zero rotation, while the red curve shows that, in the supercell, different octahedra have a distribution of different, nonzero rotations. (c) The unfolded band structure when removing the minimal-cell restrictions by using instead a cubic, 32 f.u. supercell CsPbI₃ with the same PBE method. Masses in (c) are calculated via the second derivative of \( E \) vs \( k \), which gives \( \beta_e = 1.8 \) and \( \beta_h = 2.2 \). To the best of our knowledge, the experimental measurement for separate electron and hole masses for cubic CsPbI₃ has not been reported yet; while for cubic CsPbBrI₂, the reduced mass \( m^* = -m_e^*m_h^*/(m_e^* + m_h^*) \) has been reported as 0.12\( m_0 \), very similar to the reduced mass calculated from (c), which is 0.14\( m_0 \), but 1.8 times heavier than the reduced mass from (a), which is 0.07\( m_0 \).
phous single-cell model to 1.85 eV in the polymorphous supercell model (the measured band gap is $E_g = 1.73$ eV [30]) leading to mass enhancements $\beta_e = 1.8$ and $\beta_h = 2.2$ for electrons and holes, respectively [Figs. 7(a) and 7(c)]. Although, as far as we know, the effective mass has not been reported from experiments for cubic CsPbI$_3$, the reduced mass $m^* = -m_e^*m_h^*/(m_e^* + m_h^*)$ for cubic CsPbBrI$_3$ has been measured [70] as $m^* = 0.12 \pm 0.01m_n$, which is close to our prediction (masses are calculated via the second derivative of $E$ vs $k$), here, $m^* = 0.14m_n$ using symmetry-broken DFT. Recall that neglecting the distortions gives a mass 1.8 times smaller. We conclude that semiclassical octahedral rotations in ABX$_3$ can derive quantum mechanical band gap increases and significant mass enhancements. The same physics is expected to contribute to oxides; the magnitude of the effect would naturally depend on the extent of rotations and the response of the host crystal to deformations.

B. Jahn-Teller-like $Q_{12}^+$ distortion enhances masses in LaMnO$_3$

To draw the analogy between mass enhancement in $s$-$p$ bonding perovskites (previous section) and the better-known effect in $d$-electron perovskites, we treat next the compound LaMnO$_3$. The observed positional symmetry breaking in orthorhombic LaMnO$_3$ is a pseudo-Jahn-Teller distortion, leading to inequivalent Mn-O bond lengths in the MnO$_6$ octahedron. It has been previously argued that such a Jahn-Teller distortion is specifically attributed to dynamic correlations [53] and that mean-field DFT fails to predict the ensuing structural or electronic properties [95]. Previous DFT + $U$ calculations reproducing the Jahn-Teller distortion in the orthorhombic LaMnO$_3$ [96–98] gave perhaps the impression that the presence of $+U$ in DFT implies the same correlation role as $+U$ in the Hubbard Hamiltonian. More recently, Varignon et al. [99] showed that DFT without $U$ is already enough to capture such distortions, provided that a more accurate XC functional was used. It was also clarified [100] that proper Jahn-Teller distortion is associated with degeneracy removal (i.e., electronic instability such as the $Q_{12}^+$ mode [101]), whereas the $Q_{12}^+$ mode [101] originates from classic steric effects (the Goldschmidt tolerance) that can be classified as pseudo-Jahn-Teller distortions. Here, we show that such modes cause mass enhancement.

Figures 8(c) and 8(d) show the atomic structure and band structure of an orthorhombic AFM cell with $Q_{12}^+$ deformation taken from previous DFT calculation [100]; while Figs. 8(a) and 8(b) show the atomic structure and band structure of the same AFM cell (the same AFM order, the same octahedral rotation and octahedral volume) as (c) and (d) but only removing the $Q_{12}^+$ deformation. Such a $Q_{12}^+$-free model [Figs. 8(a) and 8(b)] has been used as the DFT model in previous studies, giving metallic behavior [53,102,103]. In this work, for all LaMnO$_3$ calculations we used the SCAN functional. The band structure lacking the $Q_{12}^+$ mode (b) is metallic, while the band structure with $Q_{12}^+$ mode (d) is gapped. (Using $b$ as the reference and considering the bandwidths of Mn $d$ $e_g$ bands in (d), the bandwidth enhancement factors is $\beta_e = 1.8 \pm 0.5$ and $\beta_h = 1.6 \pm 0.4$ for electrons and holes, respectively; the uncertainty is because bandwidths along different $k$ paths give different enhancement factors. The enhancement factor obtained by DMFT with $Q_{12}^+$ deformation is $\beta_h = 1.3−1.7$ (values are extracted by comparing this work with results reported in DMFT Ref. [53]) and comparable with experimental observation of $\beta_h = 2.6−2.8$ in La$_{1-y}$Sr$_y$MnO$_3$ [72]. We conclude that the pseudo-Jahn-Teller distortion $Q_{12}^+$ captured by mean-field DFT is capable of producing significant mass renormalizations, even though in this case both DFT and DMFT give smaller renormalization than what was measured, which may be due to the A-site alloy effect in the measured sample La$_{0.6}$Sr$_{0.4}$MnO$_3$ [72].

C. Bond disproportionation enhances masses in SrBiO$_3$

Bond disproportionation in perovskites corresponds to the spontaneous transformation of two equal octahedra into two inequivalent octahedra, also known as octahedral breathing distortion, belonging to $M_{1g}^*$ or $R_{1g}^*$ mode [104]. A cell model of ABX$_3$ containing a single f.u. allows obviously a single volume for all (B$_n$) octahedra, while some compounds, e.g., SrBiO$_3$ and BaBiO$_3$ [29] prefer bond disproportionation on $B$ ions, appearing as some octahedra dilate while others contract, eventually leading to multiple local environments instead of a single local environment. Total energy calculations [105] show that this disproportionation is energy lowering.
We choose SrBiO₃ as an example to investigate such a bond disproportionation effect on effective masses. SrBiO₃ is known to be insulating in its low-temperature monoclinic phase with a disproportionate $R_1^+$ distortion \cite{106}. The monoclinic phase shows a tilting $M_2^+ \oplus R_1^+$ mode (Glazer notation $a^* b^* c^*$), which could also contribute to the mass enhancement. To isolate the contribution of $R_1^+$ disproportionation from tilting, we apply here a three-level model: (1) we start from a level 1 model, which is minimal-cell cubic $Pm\overline{3}m$ structure; (2) then we apply a tilting $M_2^+ \oplus R_1^+$ mode to construct a level 2 monoclinic ($P2_1/n$) structure without disproportionation; and (3) finally, a level 3 model uses the experimentally observed SrBiO₃ monoclinic phase (also $P2_1/n$) with both tilting (the same amplitude as in level 2) and disproportionation. The atomic structures, together with the band structures using the PBE functional + spin-orbit coupling (SOC) effect for these three levels, are shown in Fig. 9.

(1) Level 1 [$Pm\overline{3}m$ cubic; Figs. 9(a) and 9(b)] is a p-type degenerate metal, as its Fermi level crosses its wide [as denoted by the blue arrow on the right side of Fig. 9(b)] principal valence band made of O $p$ orbitals. The total DFT energy of level 1 is extremely high (+980 meV/f.u. above the convex hull), clarifying that it is not a low-temperature ground state.

(2) Level 2 monoclinic phase without disproportionating $R_1^+$ distortion [Figs. 9(c) and 9(d)] shows a more compact O $p$ valence band; however, it is still a p-type gapped metal, i.e., the octahedral tilting cannot open the gap. The total DFT energy of level 2 is 71 meV/f.u. above the convex hull. (3) Finally, level 3, the monoclinic phase with disproportionate $R_1^+$ distortion [experimental structure; Figs. 9(e) and 9(f)], shows semiconducting behavior with a 0.26 eV gap between the two split O $p$ bands, a splitting induced by the bond disproportionation. Level 3 is at on the convex hull (i.e., the ground state). Nevertheless, as seen in Fig. 9, the disproportionate $R_1^+$ distortion is the key to band gap opening; therefore, the most interesting mass enhancement is the one from level 2 to level 3 $\beta(L_3 : L_2)$. Considering the bandwidths of O $p$ bands in Figs. 9(d) and 9(f), if using Fig. 9(d) as the reference, the bandwidth-related masses in Fig. 9(f) have the enhancement factors of $\beta_1(L_3 : L_2) = 1.3 \pm 0.2$ and $\beta_2(L_3 : L_2) = 1.5 \pm 0.2$; the uncertainty is because bandwidths along different $k$ paths give different enhancement factors. We conclude that disproportionation symmetry breaking, an effect that exists both in $s$-$p$ perovskites as well as in $d$-electron perovskites, is capable of significant mass enhancement.

V. NOT ALL POSITIONAL SYMMETRY BREAKINGS LEADS TO SIGNIFICANT MASS ENHANCEMENT

The examples shown in Secs. IV A, B, and C indicate cases where symmetry breakings result in large energy-lowering, and they couple significantly to the electronic manifold, altering its band structure, including effective mass enhancement. There are, however, cases where such deformations are small, or even if not small, they might couple only weakly to the electronic states that form the band edges, i.e., small deformation potentials, leading to small or negligible mass enhancement. We next illustrate two such examples.

A. Weak octahedral rotations in intrinsic SrTiO₃ cause negligible mass enhancement

Undoped SrTiO₃ is a NM insulator. Positional distortions, such as the octahedral tilting in SrTiO₃ [also known as the antiferrodistortive displacement (AFD)], have been noted in the low-symmetry tetragonal phase \cite{107–109} but are absent in the cubic phase \cite{109–112}. Some observations of distortion in the cubic phase were then attributed to extrinsic factors...
SrTiO₃ (nonmagnetic cubic phase, undoped, SCAN)

| N-DFT result with high symmetry | Nature of symmetry breaking | Consequence of symmetry breaking |
|--------------------------------|-----------------------------|--------------------------------|
| Minimal cell band structure   | (TiO₃) rotation (°)          | Supercell band structure       |
| ![Band Structure](image)      | ![Rotation Counts](image)   | ![Energy vs k](image)         |

FIG. 10. Mass enhancement in the nonmagnetic cubic phase of SrTiO₃. (a) The band structure from the same naïve density functional theory (N-DFT) restriction as in previous literature [110–112], namely a single-cell, cubic, nonmagnetic (NM) SrTiO₃ model, using the SCAN functional. (b) The distribution of octahedral rotation angles. The blue arrow in (b) shows that, in the minimal-cell model, all octahedra have zero rotation, while the red curve shows that, in the supercell, different octahedra have a distribution of tiny rotations around 3–4°. (c) The unfolded band structure when removing the minimal-cell restrictions by using instead a cubic, 64 f.u. NM supercell SrTiO₃ with the same SCAN method. Masses in (c) are calculated via the second derivative of $E$ vs $k$, which gives $\beta_\parallel \approx 1.1$ and $\beta_\perp \approx 1.1$.

such as strain [113–116], defects [117], impurities [118], interface [119], or thermal effect [120]. Indeed, AFD is not expected theoretically in the cubic phase unless one abandons the conventional single f.u. monomorphous description of the $Pm\overline{3}m$ XRD model and allows tilting degree of freedom in a supercell description of the cubic phase. As Table I indicates, here, we focus on the properties of the cubic phase, not the low-temperature ground state, performing a minimization of the cubically constrained total energy as a function of the cell internal atomic positions.

When doped n-type, e.g., SrTiO₃:Nb or SrTiO₃:La at doping concentration of 0.01–0.05 electron/f.u., one observes (i) the formation of a low dispersion (heavy mass) occupied in gap states [121–123], as well as (ii) a Fermi level inside the broad (light mass) principal conduction band. Using plasma frequency as a measure for electron mass such as strain [113–116], defects [117], impurities [118], in-gap polaron states [119] or PE phase [132]. Here, we aim to study if the AFE and PE nature in cubic BaTiO₃ can have effects on its electronic properties, such as band gap and effective mass.

Another well-known case where local atomic displacement occur involves ferroelectric (FE) compounds, often having paraelectric (PE) and antiferroelectric (AFE) phases. BaTiO₃ is one of the FE perovskite compounds [125–127] where the ferroelectricity is induced by the off-center displacement of the Ti atom in (TiO₆) octahedron. BaTiO₃ experiences a complex phase transition, from rhombohedral (<180 K) to orthorhombic (<280 K) to tetragonal (<400 K) to cubic [128]. While its rhombohedral, orthorhombic, and tetragonal phases all show ferroelectricity, the high-temperature cubic phase shows no net ferroelectricity. Therefore, it has been argued that such a cubic phase has no Ti atom off-center displacement in any octahedra [i.e., a nonelectric (NE) phase] and can be represented by a minimal cubic cell model [129–131]. However, recent investigations show that such a minimal-cell, NE cubic model cannot explain the Raman and x-ray fine structure observations, and the cubic phase could be instead an AFE [4] or PE phase [132]. Here, we aim to study if the AFE and PE nature in cubic BaTiO₃ can have effects on its electronic properties, such as band gap and effective mass.

The AFE phase is mimicked by an 8 f.u. supercell, constraining its lattice vectors to the macroscopically observed cubic structure while relaxing all cell-internal atoms. Figure 11(a) shows the band structure of the NE model (single f.u., NE cubic model) using the SCAN functional. The difference between the atomic positions in the NE monomorphous model and the AFE polymorphous supercell is plotted in Fig. 11(b): the monomorphous cell has no Ti-atom displacement ($\Delta R_i = 0$ for every Ti), while the AFE supercell...
BaTiO₃ (anti-ferroelectric cubic phase, SCAN)

**N-DFT result with high symmetry**

**Nature of symmetry breaking**

**Consequence of symmetry breaking**

shows a unique displacement pattern, where the eight Ti atoms move along eight (111) directions (i.e., [111], [11-1], [1-1-1], …); although the AFE supercell has a zero net polarization (⟨ΔR⟩ = 0), and the local polarization on each Ti site is nonzero and as large as 0.13 Å (⟨|ΔR|⟩ = 0.13 Å). Other distortions (rotations, Jahn-Teller distortion, etc.) have all been found to be negligible in the AFE supercell. This AFE displacement pattern agrees well with the previous theory [44]. Figure 11(c) shows the unfolded band structure of the AFE supercell. We found that, although the AFE displacement is large, the mass enhancement is still negligible (βₑ ≈ 1.1 and β₈ ≈ 1); in other words, the electronic response to such displacements (deformation potential) must be small.

The weak response of band-edge states to Ti off-center displacement can be understood by considering the symmetry mismatch between the orbitals making up the VBM and CBM and the symmetry of the Ti displacement mode: in the cubic primitive cell of BaTiO₃ (NE single f.u. model without displacements or tilting), the system has the space group of Pm̅3m, where according to the molecular orbital theory for octahedral O₆ symmetry [133], the CBM is pure Ti d orbital (irreducible representation T₂g), and the VBM is made up by O 2p + Ti 4p orbitals (irreducible representation T₄u). Considering that the Ti 4p orbital is very high in energy, the VBM is almost pure O p (T₁u). On the other hand, our supercell model of the AFE state has a large M̅₁z distortion mode due to Ti displacements (amplitude ≈ 0.13 Å, irreducible representation B₁u for D₄h symmetry), whereas tilting and rotation amplitudes are all smaller than 6 × 10⁻⁴ Å. Since the VBM and CBM are not B₁u, symmetric, they do not respond to the Ti displacements; thus, the AFE supercell only shows negligible mass enhancement for these states.

The PE phase has been modeled by a 32 f.u. supercell. After the atomic relaxation, all Ti atoms have developed nonzero, nonuniformed local polarizations, as shown by the red curve in Fig. 12(b). The Ti displacement forms a distribution not only on amplitude but also on directions. We note that the net displacement (vector summation of all Ti displacements) is not zero (0.1 Å per f.u.) because we do not force any net-polarization condition during the supercell relaxation, and the supercell is in fact weak FE. Nevertheless, the nature of a distribution of static (nonthermal), different displacement in the supercell is by itself different than the low-temperature FE phase. Solving the band structure and doing band unfolding [Fig. 12(c)] shows small mass enhancement of βₑ ≈ 1.1 and β₈ ≈ 1. The results of both AFE and PE seem consistent in that the coupling of polarization to VBM and CBM states is weak, illustrating cases that the FE displacement has a negligible effect on mass enhancement.

**VI. CONCLUSIONS**

Symmetry-breaking DFT captures many of the mass enhancement effects previously attributed exclusively to strong electronic correlations under restricted symmetry. Whereas the theoretical methodology of supercell DFT has surely been used in previous studies on many different effects [26], the insights that mass enhancement can be described by mean-field DFT with broken symmetries rather than exclusively by symmetry-restricted many-body approach is noteworthy. The current study further provides a general and intuitive explanation for the physical origins of mass enhancement, as summarized in Fig. 1, including spin-symmetry-broken and positional symmetry-broken effects. There are cases where the coupling of distortions to the electronic states at band edges are weak, causing negligible mass renormalization (e.g., SrTiO₃ where the distortion is small, or BaTiO₃ where only Ti displacement, not tilting, lowers the total energy), yet other cases where the distortions and their coupling are strong, leading to large enhancement factors (e.g., SrVO₃, CsPbI₃, LaMnO₃, SrBiO₃), even by the single-determinant mean-field DFT method, which sometimes are even comparable with the...
FIG. 12. Mass enhancements in the paraelectric (PE) cubic phase of BaTiO$_3$. (a) The band structure from the same naïve density functional theory (N-DFT) restriction as in previous literature [129–131], identical to Fig. 11(a). (b) The distribution of Ti-atom displacements in the 32 f.u. PE supercell after atomic relaxation along $x$, $y$, and $z$ directions ([100], [010], and [001] directions). (c) The unfolded band structure of the 32 f.u. PE supercell BaTiO$_3$ with the same SCAN method. Masses in (c) are calculated via the second derivative of $E$ vs $k$, which gives $\beta_\text{e} \approx 1.1$ and $\beta_\text{h} \approx 1$.

mass enhancement suggested by the high-order dynamical electron-electron correlation theory. The presence of mass enhancement in the considered systems is not necessarily evidence for the exclusive need for strong dynamically correlated methodologies [15–24].

In principle, the spin fluctuations in a nonvibrating lattice can be either (i) longitudinal (single-site spin flip or intersite spin hopping) or (ii) transversal (single-site spin rotation or spin-wave excitation). The longitudinal fluctuations can be rather fast, e.g., a few femtoseconds, in a metallic system, but slow and very rare in insulators due to the large energy cost of overcoming the band gap. The transversal fluctuations, on the other hand, are typically much slower but not significantly dependent on the metallicity, e.g., in the ordered magnetic ground state of Fe, Ni, and Co, the spin-wave excitations evolve within 1 ps [134], while in the PM state of the small-gap semiconductor CrN, individual moments rotate with respect to its neighbors in the time scale of 50–100 fs [135]. Since ARPES measurement can be done in a time scale of femtoseconds [136], spin fluctuation effects longer than this time scale (longitudinal ones in insulators and transversal ones in both insulators and metals) will be measured as the time average over many properties of individual spin configurations (average of the properties), while spin fluctuation effects shorter than a few femtoseconds (longitudinal ones in some metals) will be observed as the properties of a time-averaged spin configuration (property of the average).

For the PM phase, in a symmetry-restricted many-body approach (a) containing a single magnetic moment (monomorphic limit) interacting with an average bath, the magnetic moment must fluctuate in time to conserve the zero total moment expected of a paramagnet. In a symmetry-broken representation (b) containing a polymorphic distribution of many local moments, as used in this paper, the orientation of the moment is static, but there are many orientations resolved spatially. In both cases (a) and (b), the average moment is zero (time average in symmetry-restricted approach and spatial average in symmetry-broken approach) as required of the PM state, while by ergodicity, the symmetry-broken approach with static, spatial distribution of individual moments can reproduce the ARPES observation if the spin fluctuations are longer than a few femtoseconds (e.g., longitudinal ones in insulators and transversal ones in both insulators and metals).

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APPENDIX A: DFT DETAILS

To calculate the total energy, band structure, and effective mass, the plane-wave pseudopotential DFT method, as implemented in the \textit{VASP} software package [137,138] has been used. (i) For transition metal oxides with localized orbitals SrTiO$_3$, BaTiO$_3$, and LaMnO$_3$, the SCAN functional [139], used previously [99,140] has been applied. (ii) For metallic SrVO$_3$, the SCAN functional could not reach a self-converged charge density in our large PM cubic supercell (640 atom/f.u.); therefore, for all SrVO$_3$ cells, the PBE functional $+ U$ (with $U = 1.25$ eV on V $d$ orbitals) used previously [27] has been applied instead. Figure 13 shows the difference of DOS between the SCAN and PBE $+ U$ DFT results for a smaller 32 atom supercell of PM cubic phase SrVO$_3$. It can be seen from Fig. 13 that the PBE $+ U$ and SCAN functionals give (1) very similar DOS at Fermi level and (2) very similar bandwidths; they, therefore, should predict very similar mass enhancement factors. (iii) The $s$-$p$-bonded halide CsPbI$_3$ has been calculated using the...
Ernzerhof, which is however beyond the scope of this paper. By using SOC with a hybrid functional such as Heyd-Scuseria-Ernzerhof, agreement with experimentally observed gap can be achieved with PBE functional theory (DFT) calculations using PBE magnetic (PM) cubic supercell of SrVO$_3$. The two functionals show remarkably similar DOS at Fermi level and very similar bandwidths (denoted by the red and blue arrows).

PBE functional. Note that no SOC has been considered for CsPbI$_3$ in this paper because the PBE functional will give too small a gap (~0.1 eV) if applied together with SOC; a better agreement with experimentally observed gap can be achieved by using SOC with a hybrid functional such as Heyd-Scuseria-Ernzerhof, which is however beyond the scope of this paper.

For each compound, we have applied the DFT lattice constants obtained from the minimal cell model to all supercell calculations: $a = 3.83$ Å (cubic SrVO$_3$); $a = 6.27$ Å (cubic CsPbI$_3$); $a = 5.51$ Å, $b = 5.81$ Å, and $c = 7.64$ Å (LaMnO$_3$ with Jahn-Teller-like distortion); $a = 5.57$ Å and $c = 8.78$ Å (LaMnO$_3$ without Jahn-Teller distortion); $a = 6.01$ Å, $b = 6.20$ Å, and $c = 10.49$ Å (monoclinic SrBiO$_3$); $a = 4.52$ Å (cubic SrBiO$_3$); $a = 3.91$ Å (cubic SrTiO$_3$); and $a = 4.03$ Å (cubic BaTiO$_3$). To minimize the numerical error, for all cells the same magnetic orders of cubic SrVO$_3$: NM = nonmagnetic, FM = ferromagnetic, AFM-G = G-type antiferromagnetic, AFM-A = A-type antiferromagnetic, and PM = collinear paramagnetic phase from SQS method, respectively. The DFT total energy of the NM phase has been chosen as the reference (0 eV).

### APPENDIX B: MAGNETIC STRUCTURE OF SrVO$_3$

Table II summarizes the DFT total energies of different magnetic orders of cubic SrVO$_3$. Their total energies are calculated using an uniformed energy cutoff for the plane-wave basis set, a uniformed tolerance for total energy convergence ($10^{-8}$ eV/atom), and an equivalent set of k-point sampling in BZ for every cell (equivalent to a $12 \times 12 \times 12 \Gamma$-centered k-mesh in the primitive BZ).

| Magnetic Phase | Total Energy (meV/f.u.) |
|---------------|-------------------------|
| NM (1 f.u.)   | 0 (reference)           |
| FM (1 f.u.)   | -15                    |
| AFM-G (8 f.u.)| -31                    |
| AFM-A (2 f.u.)| -26                    |
| PM (64 f.u.)  | -30                    |
| PM (128 f.u.) | -31                    |

their total energies are calculated using an uniformed energy cutoff for the plane-wave basis set, a uniformed tolerance for total energy convergence ($10^{-8}$ eV/atom), and an equivalent set of k-point sampling in BZ for every cell (equivalent to a $12 \times 12 \times 12 \Gamma$-centered k-mesh in the primitive BZ).

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