Spin-orbital coupling predicts whether a material class will exhibit unconventional superconductivity with low error rate

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A data-based predictor for unconventional superconductivity is constructed, which has three ingredients: a layered crystal structure, stable local magnetic moments and an intermediate spin-orbital (not spin-orbit) coupling. This classifier is sufficiently specific to clearly distinguish cuprate and iron-based superconductors from most other materials. Multiple DFT calculations allow for higher computational accuracy. Our results suggest that Sr$_2$FeO$_4$, Sr$_2$CoO$_4$, Sr$_2$VO$_4$, BaCo$_2$As$_2$ and K$_2$CoF$_4$ may have the necessary physics to exhibit unconventional superconductivity or other spin-orbital effects.

I. INTRODUCTION

Understanding high temperature unconventional superconductivity and finding new superconductors have been major goals in condensed matter physics over the past few decades. Much progress has been made on this front, including among others identification of the d-wave pairing symmetry in the cuprates and studies of the non-Fermi liquid behavior in both the cuprates and iron-based superconductors [1–5]. A major barrier, however, is that there are only a few material classes that exhibit unconventional superconductivity. To date only two classes of materials are known to show this effect at high temperatures: the cuprates and the iron-based superconductors. These materials differ in many microscopic and electronic structure details, yet have similar phase diagrams and both exhibit high temperature superconductivity. Meanwhile, there are materials that are similar to the copper and iron based superconductors, but do not exhibit superconductivity.

The study of high-temperature unconventional superconductivity is in a data poor situation. While there are large quantities of data about the few known examples, the fact that there are only two distinct material classes severely limits the interpretability of that data. One can contrast this situation with the conventional superconductors, for which there are many disparate examples and one can more easily extract common threads. The fact that the parent compounds of cuprates and iron-based superconductors (i.e. the pure materials) typically do not superconduct, requiring doping or pressure, further complicates the discovery of new material classes, since often doping materials is extremely challenging. Thus the discovery of new material classes is of utmost importance to further the study of unconventional superconductivity.

There has been a large amount of work put into searching for new unconventional superconductors. Unlike the field of conventional superconductivity (e.g. H$_3$S [6]), these searches have been largely unsuccessful in finding new material classes, although they have been often very successful in finding new examples under the two known families. The only discovery of a new high-temperature class of materials, the iron-based superconductors [7, 8], was achieved through serendipity. There have also been several computational searches [9–11] based on similarity to the cuprates, but to our knowledge they have not resulted in the discovery of new classes. For instance, the iridates have been proposed as cuprate analogues [12, 13], and indeed they do show some similarity to the cuprates, but to date no superconductivity has been observed in these materials.

In this manuscript, we present an easily computable quantity which probes spin-orbital coupling, long thought to be relevant to the mechanism of unconventional superconductivity [14]. Leo Tolstoy observed that “each unhappy family is unhappy in its own way;” similarly, the lack of superconductivity in a given class of materials might be due to many distinct mitigating factors. Still, we hypothesize that there is underlying physics which must be present in a material class for it to have high temperature unconventional superconductivity at all. Spin-orbital coupling appears to be an important component in this way, since it distinguishes material classes that support unconventional superconductivity from most other material classes. For example, La$_2$CuO$_4$ has an intermediate spin-orbital coupling, but La$_2$NiO$_4$ does not, which may explain why the nickelate does not superconduct. On our test set, it appears that intermediate spin-orbital coupling is necessary but not sufficient for a material class to exhibit unconventional superconductivity. We suggest that Sr$_2$CoO$_4$, Sr$_2$FeO$_4$, Sr$_2$VO$_4$, BaCo$_2$As$_2$ and K$_2$CoF$_4$ may have the necessary physics to exhibit unconventional superconductivity based on this analysis.

II. METHODS

A. Test set

In this work we concentrate on a test set comprised of 35 layered materials containing transition metal atoms arranged in 2D planes. It is well known that some of the materials in this test set support unconventional super-
As can be seen in Fig. 1, a predictor that singles out materials with both a layered structure and magnetic moments alone does a poor job at distinguishing the copper oxides and the iron-based superconductors from other classes of materials that do not support unconventional superconductivity. This classifier’s large rate of false predictions of superconductors stems from the fact that if it is true that on one hand all the known high-temperature superconductors are layered and have stable local magnetic moments in their ground state, on the other hand, most of the layered magnetic materials do not support unconventional superconductivity. To improve this we need to incorporate in our predictor other physical at-

### B. Descriptors

Both the iron-based and the cuprate superconductors possess a layered crystal structure, with unpaired $d$-electrons originating from transition metal atoms, generally arranged in a 2D square lattice. In these materials, superconductivity exists close to a magnetic phase. The superconducting phase typically arises from manipulation of a control parameter (eg., charge doping or pressure) which, when made sufficiently large, ends up suppressing superconductivity [14]. Two clear descriptors emerge from this phenomenology: the layered crystal structure and unpaired electrons, which we will refer to as local magnetic moments.

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table 1. Relevant experimental information on our test set materials: chemical formula, existence of magnetic moments, gap and whether it can be made a superconductor.

| Material | MagMs? | Gap? | uSC? | \(P(\text{SC})\) |
|----------|--------|------|------|------------------|
| BaCr\(_2\)As\(_2\) | [15] Yes | [16] No | [16] No | 0.110 |
| BaMn\(_2\)As\(_2\) | [17] Yes | [18] Yes | [18] Yes | 0.071 |
| t-BaFe\(_2\)As\(_2\) | [19] Yes | [20] No | [20] Yes | 0.891 |
| o-BaFe\(_2\)As\(_2\) | [21] Yes | [20] No | [20] Yes | 0.784 |
| BaCo\(_2\)As\(_2\) | [15] Yes | [22] No | [22] No | 0.447 |
| BaNi\(_2\)As\(_2\) | [23] No | [23] No | [23] No | 0.000 |
| BaCu\(_2\)As\(_2\) | [24] No | [24] No | [24] No | 0.000 |
| CaCu\(_2\)O\(_4\) | [25] Yes | [26] Yes | [26] Yes | 0.634 |
| SrCu\(_2\)O\(_2\) | [28] Yes | [29] Yes | [29] Yes | 0.546 |
| T-La\(_2\)CuO\(_4\) | [31] Yes | [32] Yes | [32] Yes | 0.466 |
| T’-La\(_2\)CuO\(_4\) | [33] Yes | [33] Yes | [33] Yes | 0.581 |
| t-FeSe | [35] No | [36] No | [37] No | 0.907 |
| o-FeSe | [35] Yes | [36] No | [37] Yes | 0.890 |
| Fe\(_3\)Se | [38] Yes | [39] No | [38] Yes | 0.970 |
| FeTe | [40] No | [41] No | [42] Yes | 0.970 |
| La\(_2\)Co\(_2\)O\(_4\) | [43] Yes | [44] Yes | [44] Yes | 0.064 |
| La\(_2\)Ni\(_4\)O\(_4\) | [45] Yes | [45] Yes | [45] Yes | 0.088 |
| Sr\(_3\)VO\(_4\) | [46] Yes | [46] Yes | [46] No | 0.532 |
| Sr\(_2\)CrO\(_4\) | [47] Yes | [48] Yes | [47] No | 0.140 |
| Sr\(_2\)MnO\(_4\) | [49] Yes | [50] Yes | [50] No | 0.059 |
| Sr\(_2\)FeO\(_4\) | [51] Yes | [51] Yes | [52] No | 0.812 |
| Sr\(_2\)CoO\(_4\) | [53] Yes | [53] No | [53] No | 0.629 |
| K\(_2\)CoF\(_4\) | [54] Yes | [55] Yes | [56] No | 0.357 |
| K\(_2\)NiF\(_4\) | [57] Yes | [58] Yes | [58] No | 0.058 |
| K\(_2\)CuF\(_4\) | [59] Yes | [60] Yes | [61] No | 0.058 |
| TiSe\(_2\) | [62] No | [63] Yes | [63] No | 0.000 |
| NbSe\(_2\) | [64] No | [65] No | [65] No | 0.000 |
| TaSe\(_2\) | [66] No | [67] Yes | [67] No | 0.000 |
| WSe\(_2\) | [68] No | [69] Yes | [69] No | 0.000 |
| MoS\(_2\) | [70] No | [71] Yes | [72] No | 0.000 |
| TaS\(_2\) | [73] Yes | [74] Yes | [75] No | 0.277 |
| VPS\(_3\) | [76] - | - | - | 0.000 |
| NiPSe\(_3\) | [77] Yes | [78] Yes | [78] No | 0.071 |
| CdPSe\(_3\) | [77] No | [79] Yes | [80] No | 0.000 |
| CrGeTe\(_3\) | [81] Yes | [81] Yes | [81] No | 0.054 |
tributes that are shared by the cuprates and iron-based superconductors, but are absent in most other materials.

1. Charge-spin susceptibility as an estimate of spin-orbital coupling

Since magnetic correlations play a crucial role in the electronic pairing on the copper oxides and iron-based superconductors [14], one relevant feature to add to our descriptors is the coupling between orbital and spin degrees of freedom. While our methodology does not depend on any particular effective Hamiltonian being applicable, we will motivate our descriptor using a simple one. Consider an effective spin-orbital Hamiltonian

$$H = H_o + H_S + \lambda H_{oS},$$

where $H_o$ describes the orbital degrees of freedom, while $H_S$ describes deep spin levels. The term $H_{oS}$ accounts for interactions between the latter two sets of degrees of freedom, which are controlled by the coupling $\lambda$.

Eq. (1) is appropriate for systems where the orbital and spin degrees of freedom are well separated in energy. For instance, in hole-doped cuprates, the conduction states are mostly oxygen $p$ in character, while the half-filled copper $d$ orbitals in the lower Hubbard band are much deeper in energy. The lower Hubbard band can thus be viewed as giving rise to the local moments governed by $H_S$ in the above model, while $H_o$ shall describe states in the conduction band. Similarly, in the iron-pnictides, the majority and minority spin levels are well separated in energy due to Hund’s coupling. In this case, the lower-energy majority spins can be viewed as acting as local moments, while the minority spins can be identified with the orbital degrees of freedom governed by $H_o$.

In a system governed by Eq. (1), consider a small deformation of the electronic wave function away from the ground state. Assume that this deformation amounts to a slight change in the ground state’s magnetic order, which results in a small change of the system’s spin density, $\Delta s_i = s_i(\mathbf{r}) - s_0(\mathbf{r})$, where $s_0(\mathbf{r})$ stands for the ground state spin density, while $s_i(\mathbf{r})$ stands for the new/formed state’s spin density. In such a case, one can show (see Appendix A) that, to first order in the deformation, the resulting change in the charge density, $\Delta \rho_i(\mathbf{r}) \equiv \rho_i(\mathbf{r}) - \rho_0(\mathbf{r})$ (with $\rho_0$ and $\rho_i$ standing for the ground state and deformed state charge density), is proportional to the change in the spin density,

$$\Delta \rho_i(\mathbf{r}) \approx \frac{\lambda}{w} \chi(\mathbf{r}) \Delta s_i(\mathbf{r}).$$

In the above expression $\lambda$ stands for the coupling constant connecting the orbital and the spin levels, while $w$ is the energy scale of the orbital degrees of freedom, and $\chi(\mathbf{r})$ is a numerical factor associated with the type of spin deformation. Thus the ratio $\Delta \rho_i(\mathbf{r})/\Delta s_i(\mathbf{r})$ gives direct access to the magnitude of $\lambda/w$.

A simple way of estimating the magnitude of the coupling $\lambda/w$ is to compute the average charge-spin susceptibility, $\chi_{cs}$, defined as [82]

$$\chi_{cs} \equiv \frac{1}{N} \sum_{i=1}^{N} \chi_i = \frac{1}{N} \sum_{i=1}^{N} \frac{\Delta \rho_i}{\Delta s_i},$$

where $N$ stands for the number of different magnetic orders considered, while $\Delta \rho_i (\Delta s_i)$ stands for the spatial fluctuations in charge (spin) density relative to that of the lowest-energy magnetic state. The former are given by

$$\Delta \rho_i = \int d\mathbf{r} |\rho_i(\mathbf{r}) - \rho_0(\mathbf{r})|,$$

$$\Delta s_i = \int d\mathbf{r} |s_i(\mathbf{r}) - s_0(\mathbf{r})|,$$

where $\rho_0(\mathbf{r})$ and $s_0(\mathbf{r})$ are the charge and spin distributions of the lowest-energy magnetic state.

In order to calculate $\chi_{cs}$, as defined in Eqs. (3)-(4), we generate several low energy magnetic textures for each material. We then compute $\chi_{cs}$ using Eqs. (3) and (4). In some materials, the charge response is strongly dependent on the type of change in the magnetic texture, which is shown in the Supplementary Information. The variance in this change does not affect our conclusions.

C. Classifying a material class’ potential for unconventional superconductivity

We will classify a material as superconducting or not, based on its charge-spin susceptibility $\chi_{cs}$, as well as on whether it has stable local magnetic moments and is layered (with 2D arrays of transition metal atoms). We encode such classification in the conditional probability, $P(SC|\chi_{cs}, M, 2D)$, that the material is superconducting provided it has a given value of charge-spin susceptibility, it has local moments and it is layered. Since $\chi_{cs}$ must be computed and therefore might have errors, we will consider a few different ways of computing it, mainly by varying $U$ in a DFT+U calculation.

1. Calculating descriptors

Since our long-term goal is to screen a large set of materials against the above classifier, we must base our search protocol on a low-cost but sufficiently accurate computational method. With that in mind we chose Kohn-Sham density functional theory (KS-DFT) [83]. However, it is well known that KS-DFT often fails at making accurate predictions for strongly correlated materials. In order to circumvent this issue, we combine multiple DFT+U calculations in an attempt to control computational errors that might otherwise contaminate our predictions. As
discussed in Appendix B, the lower computational uncertainty resulting from combining multiple DFT calculations, translates into a strongly suppressed rate of false positive and false negative predictions.

All the calculations presented in this work were performed using the KS-DFT approach \cite{83}, as implemented in the QUANTUM ESPRESSO code \cite{84}. The exchange-correlation energy was approximated by the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional \cite{85}. Coulomb interactions within the \( d \) shells of the transition metal atoms were accounted for by the DFT+U scheme of Cococcioni and de Gironcoli \cite{86}. Interactions between valence and core electrons were described by pseudopotentials in the accurate set of the Standard Solid-State Pseudopotentials library \cite{87, 88}. The Kohn-Sham orbitals were expanded in a plane-wave basis with different cutoff energies, \( E_c \) (Ry), for each material (see online data for \( E_c \) of each material), while a cutoff of 4\( E_c \) was used for the charge density. The Brillouin zone (BZ) was sampled using a Gamma-centered 6x6x6 grid following the scheme proposed by Monkhorst-Pack \cite{89}. The crystal structure for each material was set up with the information available on the ICSD database \cite{90} – see online data for the CIF(s) used in the calculations of each material. A supercell was used whenever the material unit cell had less than 4 transition metal atoms per unit cell.

For each material, we performed DFT+U calculations with \( U = 0, 5, 10 \) eV. With the aim of converging different magnetic orders, we performed calculations in which the self-consistent cycle started from different magnetic states, i.e. different orderings and magnitudes for the magnetic moments on the transition metal atoms. In the online supporting information, the reader can find the core information characterizing all the DFT+U calculations that were performed: material, corresponding crystallographic identifier (CIF), starting magnetic state, final magnetic state, band gap estimate and total energy among others.

III. RESULTS AND DISCUSSION

A. Charge-spin susceptibility

Fig. 2 shows the calculated charge-spin susceptibility for the materials in our test set (Table I). Each panel corresponds to the results obtained with different DFT+U (\( U = 0, 5, 10 \) eV). Each material contributes one observation to the histogram. Regardless of the value of \( U \), superconducting materials show intermediate values of charge-spin susceptibility. They are clearly separated from the other materials, which either show small or large values of \( \chi_{cs} \).

The separation between superconducting and non-superconducting systems in Fig 2 suggests that if spin-orbital coupling (of which \( \chi_{cs} \) is an estimate) is either too weak or too strong, electronic pairing will not occur. Only moderate coupling strengths have the capacity to give rise to superconductivity. This is in qualitative agreement with a recent set of studies \cite{91, 92} in the context of conventional superconductivity, where a quantum Monte Carlo solution of the Holstein model showed that \( T_c \) is largest for an optimal value of the coupling between electrons and bosons; too much or too little coupling is detrimental for the superconducting state.

B. Classifier for unconventional superconductivity

We estimate the probability that a material can be made into an unconventional superconductor given its value of \( \chi_{cs} \), whether it has local magnetic moments, and whether it is layered. Formally, we write this as \( P(\text{SC}|\chi_{cs}, M, 2D) \). Despite the fact that metallic behavior is a prerequisite for superconductivity, we do not consider it since chemical doping can in principle make a material metallic. As all the materials in our test set are layered, for this paper we will drop the 2D part of
the descriptor; see Refs. 93 and 94 for methods to determine 2D motifs. We further approximate the above probability as $P(SC|\chi_{cs}, M) \approx P(SC|\chi_{cs})P(M)$, since if there are no local moments, then a material cannot exhibit superconductivity due to spin-orbital coupling.

We construct $P(SC|\chi_{cs})$ from the results in Fig. 2. For each set of DFT+U calculations we define

$$P(SC|\chi_{cs}) = \frac{\rho_{sc}^{U}}{\rho_{sc}^{U} + \rho_{ncsc}^{U}},$$

where $\rho_{sc}^{U}$ ($\rho_{ncsc}^{U}$) stands for the kernel density estimation of the $\chi_{cs}$ histogram for the superconductors (non-superconductors), as shown by the colored curves in Fig. 2. We construct $P(M)$ either from experiment (in which case it is 1 or 0), or from the ground state of DFT+U calculations. In the latter, we partially account for the inaccuracy of the DFT calculations by combining the results from the three sets of DFT+U calculations to construct an improved predictor for the existence of stable local magnetic moments – see Appendix C. We refer to these two different ways of estimating $P(M)$ as $P(M_{\text{exp}})$ and $P(M_{\text{calc}})$, respectively. The probability model is turned into a classifier by using a cutoff $\xi$ to separate superconducting from non-superconducting materials: whenever a material has $P(SC|\chi_{cs}, M) \geq \xi$ it is classified as superconducting, otherwise being classified as non-superconducting.

In Fig 3, we assess the quality of seven different classification schemes using their F1 score. This is defined as

$$F1 = \frac{2TP}{2TP + FP + FN},$$

where TP, FP and FN are the number of true positive, false positive and false negative classifications, respectively. The F1 score is a way of measuring the accuracy of a classification scheme without invoking the number of true negative classifications. This adjusts well to our problem, because we do not know the number of true negative classifications, i.e. we cannot know for sure whether a material family that was never shown to support unconventional superconductivity, can never be made superconducting. In Fig. 3 we plot the F1 score of each classifier as a function of the cutoff $\xi$ separating superconducting and non-superconducting materials.

The classifiers identified by Exp,U and Calc,U in Fig. 3, are generally much better (i.e., have larger F1 score) than the naive classifier labeled as Layered+LMs in Fig. 3. The maximal F1 score of the best classifiers is more than double that of such a naive classifier. The highest performing classifier is the Exp,U=5 one: this is constructed from the $U = 5\text{eV}$ calculations of the charge-spin susceptibility and from the experimental observations on the existence of stable magnetic moments.

Fig. 3 also shows that the Exp,U classifiers are generally more accurate than the Calc,U ones. This stems from the fact that the DFT calculations with $U = 0\text{ eV}$ wrongly predict that the cuprates are non-magnetic materials. This results in a $P(M_{\text{calc}}) \approx 0.6$ for the cuprates, making it different from the $P(M_{\text{exp}}) = 1$ value – see Fig. 4. As a matter of fact, estimating whether a material has stable magnetic moments from multiple DFT+U calculations, is the biggest source of uncertainty in our predictive model.

In Fig. 5 we use our best performing classifier, i.e. Exp,U=5, to rank the materials in our test set according to their potential for unconventional superconductivity. In this figure materials are ordered by increasing $P(SC|\chi_{cs}=5, M_{\text{exp}})$. Two groups of materials can be clearly distinguished: one with high potential for unconventional superconductivity, mostly composed of known superconductors; the other with low potential, being entirely composed by materials that do not superconduct. This is a sharp improvement on the simplistic classification of Fig. 1.

In Fig. 5 there are a few non-superconducting materials with large probability, $P(SC|\chi_{cs}, M)$, which are therefore ranked among the materials known to be unconventional superconductors. Them being so highly ranked means one of two things: either these are false positive classifications; or these materials can actually be made superconducting with the correct combination of pressure...
and/or chemical doping. In the following paragraphs we discuss some of the possibilities that might be behind the high ranking of these non-superconducting materials.

It might happen that, for some of these materials, the DFT+U calculations are too inaccurate. In those cases, our classifiers will yield poor predictions and wrongly rank those materials among the unconventional superconductors. Such mis-classifications might in principle be suppressed by using more accurate many-body methods.

Intermediate spin-orbital coupling in a layered material with local magnetic moments, solely qualify as necessary but not as sufficient ingredients for unconventional superconductivity. This is another possible explanation for why some of the non-superconducting materials in our test set are highly ranked by our model. If additional ingredients are necessary for unconventional superconductivity, then some non-superconducting materials that present the three ingredients considered by our model but lack the former, might end up wrongly ranked among superconducting materials. It can also happen that a material has all the necessary ingredients for unconventional superconductivity, but an instability other than superconductivity dominates.

Most copper oxides and iron-pnictides that can be driven into a superconducting phase only do so upon chemical doping. It might thus occur that a pure material to which our classifier attributes a good potential for unconventional superconductivity, might either be hard to dope in practice, or doping might end up spoiling its spin-orbital coupling. Finally, the most exciting possibility: some of the highly ranked non-superconducting materials in Fig. 5 might indeed be made unconventional superconductors, provided the correct combination of charge doping and pressure is attempted.

In the following paragraphs we will briefly discuss each of the non-superconducting materials highly ranked by our classifier. Despite never observed to be superconducting, these materials have interesting behavior which could be attributed to spin-orbital coupling.

Among the high ranking materials in Fig. 5, Sr$_2$FeO$_4$ is arguably the most explored. It was long ago shown that pressure induces a semiconductor-to-metal transition at $P \approx 18$ GPa that is accompanied by a change in magnetic order [52], but no superconductivity was ob-
served down to 5 K for pressures up to 30 GPa. Chemical doping weakens both its antiferromagnetic ordering and semiconducting character without completely suppressing the electronic gap [95–97]. Still, it may be worth exploring different ways of chemically doping this material and eventually combining it with pressure. 

Sr$_2$CoO$_4$ is ferromagnetic and metallic at low temperatures [53]. Upon chemical doping with Y [53], La [98] and Nd [99] it becomes an antiferromagnetic semiconductor. These observations show a clear connection between charge fluctuations and magnetism in this system, which is probably why our spin-orbital descriptor identified it. To our knowledge, there are no studies in which Sr$_2$CoO$_4$ resistance or Meissner effect were measured at low-temperatures under high pressures.

The multi-orbital Mott insulator with no long-range magnetic order [100] Sr$_2$VO$_4$, can be driven into a metallic state by hydrostatic pressure (≈ 20 – 24 GPa) [101]. An unconventional metal emerges at low temperatures in the vicinity of the pressure-driven transition [101]. Differently from what happens with Sr$_2$VO$_4$ thin films [102], the few attempts at chemically doping the bulk crystal did not succeed in making it metallic [103]. A more comprehensive exploration of different ways of chemically doping this material may reveal novel correlated phases.

BaCo$_2$As$_2$ is a disordered magnetic metal [22] that seems to remain so upon both chemical doping with K [22] and hydrostatic pressure (up to 8 GPa) [104]. It is possible that the lack of long-range magnetic ordering in this material and in Sr$_2$VO$_4$ is due to the spin-orbital coupling.

K$_2$CoF$_4$ has been classified as a 2D Ising magnet [55] owing to its strongly anisotropic magnetic interactions. To our knowledge, this material’s behavior under pressure or chemical doping has been very scarcely studied [105]. Further exploring its deformation space may thus prove fruitful.

**IV. CONCLUSION**

We have set up a search protocol aimed at a large-scale search for new unconventional superconductors. This protocol is based on a classifier that takes three ingredients: layered crystal structure with 2D arrays of transition metal atoms, existence of stable local magnetic moments and intermediate values of charge-spin susceptibility. The latter is the central component of our classifier. It measures the coupling between orbital degrees of freedom and deep spin levels in a given material.

The calculations required for such classification were performed using DFT+U, a low-cost yet relatively accurate method. In order to control computational inaccuracies inherent to DFT, we combined multiple DFT+U calculations, which sharply decreases the rate of false negative and false positive classifications. These methods are inexpensive enough that they could be used in a large-scale search for new high-temperature unconventional superconductors.

Despite the fact that its ingredients solely qualify as necessary conditions for unconventional superconductivity, we demonstrated that this classifier is sufficiently specific to clearly distinguish cuprate and iron-based superconductors from other materials. Given this fact it may be worth further exploring the behavior of Sr$_2$CoO$_4$, Sr$_2$FeO$_4$, Sr$_2$VO$_4$, BaCo$_2$As$_2$ and K$_2$CoF$_4$ under different kinds of chemical doping, as well as under pressure. According to our model these materials have common underlying physics with the high temperature unconventional superconductors. While these materials may or may not ever be made superconducting, it is clear that they exhibit interesting physics.

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**Appendix A: Charge density response and spin-orbital coupling**

In the context of a system governed by the Hamiltonian in Eq. (1), assume that we fix the deep spin levels’ wave function to a particular magnetic order, described by $\phi_i(r)$. Then, the orbital degrees of freedom will be described by $\varphi(r; \phi_i)$. The charge and the spin density of such configuration will be given by

$$\rho_i(r) = \sum_\sigma \left( |\varphi_{i\sigma}(r)|^2 + |\phi_{i\sigma}(r)|^2 \right), \quad (A1a)$$

$$s_i(r) = \sum_\sigma \sigma \left( |\varphi_{i\sigma}(r)|^2 + |\phi_{i\sigma}(r)|^2 \right), \quad (A1b)$$

where $\sigma = \uparrow \downarrow$ identifies the spin projection, while $\varphi_{i\sigma}$ is a short-hand for $\varphi(r; \phi_i)$.

Assuming that this electronic configuration is a small deformation away from the system’s ground state, we can write the two components of the charge and spin
densities, $|\phi_{\sigma}|^2$ and $|\varphi_{\sigma}|^2$, as follows:

$$|\varphi_{\sigma}|^2 = |\phi_{\sigma}|^2 + 2 \Re \left[ \varphi_{\sigma}^* \delta \phi_{\sigma} \right] + O(\delta \phi_{\sigma}^2), \quad (A2a)$$

$$|\varphi_{\sigma}|^2 = |\phi_{\sigma}|^2 + 2 \Re \left[ \varphi_{\sigma}^* \frac{\delta \varphi_{\sigma}}{\delta \phi_{\sigma}} \right] \delta \phi_{\sigma} + O(\delta \phi_{\sigma}^2), \quad (A2b)$$

where $\Re[\ldots]$ gives the real part, while $\phi_{\sigma}$ and $\varphi_{\sigma}$ stand for the ground state wave function’s components associated with, respectively, the deep spin levels and the orbital degrees of freedom. Above we express the small deformation on the orbital degrees of freedom wave function component, $\delta \varphi_{\sigma} = \varphi_{\sigma} - \phi_{\sigma}$, in terms of the deformation of the deep spin levels component, $\delta \phi_{\sigma} = \phi_{\sigma} - \phi_{\sigma}$. In order not to clutter the expressions in Eqs. (A2), we omitted the spatial dependence of the wave functions.

Consider now that the small deformation is such that it only changes the deep levels’ magnetic order, preserving their charge density, i.e., $\sum_{\sigma} |\phi_{\sigma}|^2 \approx \sum_{\sigma} |\phi_{\sigma}|^2$. This then implies that $\sum_{\sigma} \Re \left[ \phi_{\sigma}^{*} \delta \phi_{\sigma} \right] \approx 0$, which for small deformations, can be written as

$$\sum_{\sigma} |\phi_{\sigma}| \left( \delta |\phi_{\sigma}| \cos \delta \theta_{\sigma} - \delta \theta_{\sigma} \sin \delta \theta_{\sigma} \right) \approx 0, \quad (A3)$$

where $\delta \theta_{\sigma} = \theta_{\sigma} - \theta_{\sigma}$, with $\theta_{\sigma}$ and $\theta_{\sigma}$ standing for the complex phase of $\phi_{\sigma}$ and $\phi_{\sigma}$. As for small deformations $\delta \theta_{\sigma} \ll 1$, the above assumption translates into $\delta |\phi_{\sigma}| \approx -\frac{\partial \phi_{\sigma}}{\partial \theta_{\sigma}} \delta \theta_{\sigma}$. Finally, we will also assume that the wave function’s orbital degrees of freedom component is only going to depend on the absolute value of the deep spin levels component, $\varphi_{\sigma}(\mathbf{r}; \phi_{\sigma}) \approx \varphi_{\sigma}(\mathbf{r}; |\phi_{\sigma}|)$. Under this approximation, we can write $|\varphi_{\sigma}|^2$ as

$$|\varphi_{\sigma}|^2 = |\phi_{\sigma}|^2 + 2 \sum_{\sigma} \Re \left[ \varphi_{\sigma}^{*} \frac{\delta \varphi_{\sigma}}{\delta \phi_{\sigma}} \right] |\phi_{\sigma}| + O(\delta |\phi_{\sigma}|^2), \quad (A4)$$

while the change in the spin density $\Delta s_{\sigma}(\mathbf{r}) = s_{\sigma}(\mathbf{r}) - s_{\sigma}(\mathbf{r})$ can be written as

$$\Delta s_{\sigma}(\mathbf{r}) \approx \sum_{\sigma, \alpha} \left( \frac{2 \lambda}{w} \Re \left[ \varphi_{\sigma}^{*} f_{\sigma}^{\alpha} \right] + 2 \cos \theta_{\sigma} \right) \delta |\phi_{\sigma}|$$

$$+ O(\delta |\phi_{\sigma}|^2), \quad (A5)$$

where we used the definition $\frac{\delta \varphi_{\sigma}}{\delta \phi_{\sigma}} \equiv \frac{\lambda}{w} f_{\sigma}^{\alpha}$. Following the main text’s notation, $\lambda$ stands for the coupling between the deep spin levels and the orbital degrees of freedom, while $w$ corresponds to a material-specific energy scale.

Using the above expression relating $\delta |\phi_{\pm}|$, we can write to first order in the deformation, $\Delta s_{\sigma}(\mathbf{r}) \propto \delta |\phi_{\pm}|$, which results in a relation with the form of Eq. (2):

$$\Delta p_{\alpha}(\mathbf{r}) \approx \frac{2 \lambda}{w} \frac{\Upsilon_{+} - \varphi_{\sigma}|_{\phi_{\sigma}}}{\Xi_{+} + \varphi_{\sigma}|_{\phi_{\sigma}}} \Delta s_{\alpha}(\mathbf{r}), \quad (A6)$$

where $\Upsilon_{\alpha} = \sum_{\sigma} \Re \left[ \varphi_{\sigma}^{*} f_{\sigma}^{\alpha} \right]$ and $\Xi_{\alpha} = \frac{2 \lambda}{w} \Upsilon_{\alpha} + 2 \sum_{\sigma} \cos \theta_{\sigma}$. Appendix B: Controlling computational uncertainty by using multi-DFT calculations

The $d$- and $f$-electrons in transition metal atoms are typically ill-described in KS-DFT when LDA and GGA functionals are used. The DFT+U [86] modification of these functionals is arguably the simplest and lowest-cost improvement we can employ to smoothen this issue. However, when using DFT+U functionals we need to specify the value of the Hubbard parameter $U$. This turns out to be often a problem since there is no universal optimal value of $U$. Different materials (and even different properties of the same material) turn out to be optimally described by different values of $U$.

To combine multiple DFT+U calculations is then an attempt to bound our predictions. By doing DFT+U calculations with values of $U$ that are either smaller or larger than the optimal (unknown) value of $U$ for a given property, we expect to have a better control over the inaccuracies associated with our predictions.

To demonstrate in practice how we can take advantage of multiple DFT+U calculations, in Fig. 6 we compare the experimental observations and the results obtained from different DFT+U calculations, regarding the existence/absence of stable local magnetic moments. To keep things simple, we only show data for 5 of the 35 materials in our test set: BaCu$_2$As$_2$, SrCuO$_2$, TiSe$_2$, NbSe$_2$ and La$_2$NiO$_4$. In panels (a), (b) and (c) of Fig. 6 we compare the DFT+U results (x-axis) for, respectively, $U = 0.5$ and $10$ eV with the experimental observations (y-axis).

Any points on the top-left and bottom-right corners of these panels, correspond to, respectively, false negative and false positive predictions. By inspecting Fig. 6’s panels, we can readily confirm that, for a given material, DFT+U calculations with different values of $U$ can result in different predictions. For this set of materials, none of the $U$ values used in the DFT+U calculations yielded a zero rate of false negative and false positive predictions. This is in general true for a sufficiently diverse set of materials.

A way of minimizing the rate of false positive and false negative predictions, is to classify as Uncertain any material for which different values of $U$ give different predictions regarding the existence of magnetic moments. Panel (d) of Fig. 6 presents this information. However, while in this panel there is zero rate of false positive (bottom right corner) and false negative (top left corner) classifications, there is a rather high rate of Uncertain classifications.

In Appendix C we show that we can extract further information from a set of results like the ones above. That will allow us to avoid classifying materials as Uncertain, while keeping the false positive and false negative classifications at low rates.
FIG. 6. Error control through multiple DFT+U calculations: an example using results for the existence/absence of stable local magnetic moments in a material. In panels (a), (b), (c) we compare the experimental observations (y-axis) with the DFT+U results (x-axis) for, respectively, $U = 0, 5, 10$ eV. The label Moments (No Moments) indicates that experiment/calculation sees (does not see) stable local magnetic moments. Panel (d) combines the results in panels (a), (b) and (c), adding a new Uncertain category to the x-axis whenever different DFT+U calculations give distinct results for the existence of local magnetic moments. In panel (d), the rate of false positive (bottom-right) and false negative (top-left) are decreased (to zero) in comparison with panels (a)-(c).

Appendix C: Existence of stable local magnetic moments

In this appendix we show how can we construct an improved predictor for the existence of local magnetic moments, by analyzing the predictions based on multiple DFT+U calculations done for the materials in our test set. For reference, let us first draw the reader’s attention to Fig. 7. Just as in panel (d) of Fig. 6, in this figure we plot an histogram that compares the multiple DFT+U predictions (x-axis) with the experimental observations (y-axis) for all the materials in our test set.

As explained in Appendix B, in order to plot Fig. 7, we use multiple DFT+U calculations (with $U = 0, 5, 10$) to classify each material in our test set according to one of the three categories: Moments (No Moments) whenever all the DFT+U calculations give that one of the magnetic states (the non-magnetic state) is the most stable; Uncertain for those cases where different DFT+U calculations give contradicting results.

Notice that we added an Uncertain category to the experiment axis, to account for materials for which we were not able to find published results regarding the existence or absence of stable local magnetic moments (case of VPS$_3$).

As argued in Appendix B, the multiple DFT+U scheme strongly suppresses the rates of false negative and false positive predictions, respectively, the top-left and bottom-right boxes in Fig. 7. However, under this classification scheme the rate of prediction (i.e., the rate of materials not classified as Uncertain) approaches $\approx 3/4$.

A rate of $\approx 1/4$ of Uncertain classifications is likely too high when we intend to look at a large set of materials. In order to circumvent this issue, we must re-analyze the relation between the experimental observations and the DFT+U classifications for the set of calculated values of $U$. In Fig. 8 we plot such information: the y-axis identifies the experimental observation, while the x-axis corresponds to the sequence of DFT+U predictions for each material.

In Fig. 8 we group the materials in our test set into 6 distinct families: the Ba-122 family, with formula BaM$_2$As$_2$ where M=Cr,Mn,Fe,Co,Ni,Cu; the cuprates, including XCuO$_2$ with X=Ca,Sr and the T- and T’-phases of La$_2$CuO$_4$; the iron-chalcogenide family, namely FeSe (both tetragonal and orthorhombic phases), PoS...
In parallel with what was done in Appendix C, we can also use multiple DFT+U calculations to predict whether a given material is gapped or gapless. As before, the simplest thing we can do is to: classify as Gapped (Gapless) a material for which all the DFT+U calculations (\(U = 0, 5, 10\)) show a band gap (no band gap) in the lowest energy magnetic state; classifying as Uncertain any material for which different DFT+U calculations give opposite results for the existence of a band gap.

In Fig. 9 we compare the experimental observations regarding the existence of a band gap in the materials in our test set and the above classification based on DFT+U. Notice that we again added an Uncertain category to the experiment axis to account for materials for which we could not find published results on the existence of a band gap (case of VPS3).

As before, Fig. 9 clearly shows that the multiple DFT+U calculations yield a very low rate of false negative and false positive predictions for the existence of band gap. However, the rate of prediction (i.e., the rate of materials that are not classified as Uncertain) is \(\approx 1/2\). The reason for such a low rate of prediction originates from a conjugation of factors: the existence/absence of a gap in the band structure of a particular material, is in general dependent, not only on the magnitude of the \(U\) used in the DFT+U calculation, but also on what magnetic state are we looking at. Calculations with different values of \(U\) might not only wrongly open/close a gap in a given magnetic state’s band structure, but they can also result in an unphysical prediction for that material’s lowest energy magnetic order.

We can circumvent the low rate of prediction, by look-

**Appendix D: Existence of band gap**

In parallel with what was done in Appendix C, we can also use multiple DFT+U calculations to predict whether a material is gapped or not. We do that in Appendix D.
Experiment
Gapless Uncertain Gapped
Calculation

FIG. 10. Dependence on \( U \) of the prediction for the existence of band gap. Each dot corresponds to one material in our test set and is colored according to the family it belongs to. Similarly to Fig. 9, the y-axis position stands for whether a material has a band gap according to the experimental observations. The x-axis position is set according to a given material’s sequence of DFT+U results regarding the existence of a band gap. For instance, \( YYN \) and \( YNN \), stands for a set of DFT+U results which predicted that there is a band gap for \( U = 0, 5 \) (but not for \( U = 10 \)) in the first case, and \( U = 0 \) (but not for \( U = 5, 10 \)) in the second case. Dependent band gap prediction for all the materials in our test set – see Fig. 10. As before, this data can help us devise a set of conditional probabilities for a material to be gapless, given a particular sequence of DFT+U results for the absence of a band gap. From the results in Fig. 10 we can write the following probabilities:

\[
P(\neg G|N N N) \approx 0.9, \quad (D1a)
\]

\[
P(\neg G|Y Y Y) \approx 0.0, \quad (D1b)
\]

\[
P(\neg G|\text{otherwise}) \approx 0.25, \quad (D1c)
\]

where \( P(\neg G|X_1X_2X_3) \) stands for the probability that a material is gapless, provided that the DFT calculations with \( U = 0.5 \) and \( 10 \) eV, respectively, gave \( X_1, X_2 \) and \( X_3 \), where \( X_i = Y \) or \( N \), with \( Y \) (\( N \)) indicating that the \( i \)th calculation showed a band gap (no band gap).
