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Orbital mixing in solids as a descriptor for materials mapping

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ABSTRACT

The creation of "maps" for solid-state materials has a long-standing history in condensed matter theory. Here, based on periodic density-functional theory (DFT) output, a heuristic numerical indicator is constructed to assess s–p orbital mixing in materials (or, depending on one's viewpoint, the tendency toward "sp^3 hybridization"). Other than before, this now intrinsically includes structural information and the microscopic effects associated with it. The new method provides useful insights to understand physical relationships in composition space and promises to help to identify hitherto unknown material candidates.

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The rational design of new and improved functional materials is a key challenge for the solid-state sciences. An abundance of candidates and possible compositions exists, however, and the sheer amount of them is too large to oversee, let alone to handle. It has long been advocated to partition the compositional and structural space according to suitably chosen criteria, or, in a more plastic language, to "map out" promising compounds according to their physical or chemical relationship. Indeed, the creation of structure maps to classify materials has a long-standing tradition in condensed-matter theory. Examples are the scheme by Phillips and Van Vechten to predict the crystal structures of the octet A^NB^{8-N} compounds [1], the subsequent extension to suboctet compounds by St. John and Bloch [2], and the classification of IV–VI compounds by Littlewood [3].

Building upon this groundwork, one of us (M.W.) has recently proposed a first "treasure map" for phase-change materials (PCMs) [4], which are leading contenders for new information storage and processing technologies [5–8]. Later, it has been suggested that this map can be extended to other classes of functional materials, such as topological insulators and thermoelectrics [7], which would further increase its scope. Similar conclusions were reached very recently when a link between the bonding nature of PCMs and the application in thermoelectrics has been suggested [9]. Finally, PCMs on this map have other emerging applications such as in optical displays [10] or brain-like computing [11]. Hence, further exploration of this map would seem worthwhile, without any doubt.

Despite its appeal, the above-mentioned map has an important limitation which now needs to be remedied: it uses orbital radii to estimate s–p mixing and ionicity in a heuristic manner, essentially following the scheme of St. John and Bloch [2] and, as a consequence, the structural nature of the compounds under study is missing. This is best seen when looking at an exemplary map of some textbook compounds. Fig. 1 shows a St. John–Bloch plot for two carbon and boron nitride (BN) polymorphs, as well as two rocksalt-type compounds. Diamond, with its dense rigid network, will surely be of different bonding nature than graphite, but they form a single data point in the above-mentioned map because they are all allotropes of elemental carbon and thus possess identical orbital radii. The same is true for the BN polymorphs.

In this contribution, we demonstrate that one can include the important structural information intrinsically in such map by replacing the coordinate for the *y*-axis (s–p orbital difference) by a better suited quantity based on first-principles calculations. To exemplify this concept, we introduce an indicator to quantify orbital mixing in solid materials. The new technique is based on unambiguous density-functional theory (DFT) output and hence applicable for all kinds of valence configurations. This allows one to project out the electron density situated in "sp^3" mixed levels in the style of a fat-band plot and thus to assess the degree of orbital mixing as a revised coordinate, as will be demonstrated shortly.

In what follows, we rely on periodic DFT simulations in the local density approximation (LDA) [12], using the projector augmented-wave (PAW) method [13] as implemented in VASP [14]. It is known that chemical information can be extracted from plane-wave based functions by fitting a set of atomic orbitals to replace these very plane-wave functions [15] and thus combine the advantages of both widely used computational techniques for

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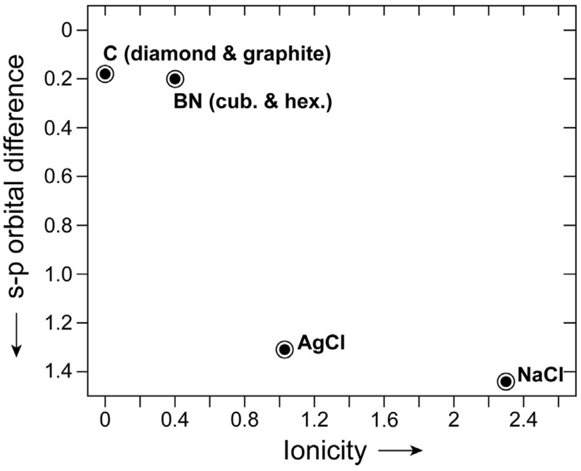

Fig. 1. Orbital-radii based St. John–Bloch plot [2] for textbook solid-state compounds. Different allotropes possess the same orbital radii, and so attain the same data point for s–p mixing and ionicity.

electronic-structure calculation. In this paper, the reconstruction of the *l*-resolved density channels (or orbital nature) is achieved by an *analytical* projection onto a minimal local basis of Slater-type orbitals [16]. The viability of this plane-wave/PAW based approach has been demonstrated before, especially when it comes to reconstructing bonding information from structurally complex systems such as crystal surfaces [17] or amorphous matter [18].

We briefly recall the utility of this technique by considering fat-band plots resolved according to the out-of-plane p_z-orbital (Fig. 2b) of graphite, and also to the p_z-orbital in diamond. Crosses indicate the course of energy eigenvalues through momentum space; the size of the superimposed circles indicates the p_z-projection in arbitrary scaling. On the right, the densities of states (DOS) are displayed as they emerge from the bands. While the p_z-contributions in diamond are well distributed over the entire energy range (as apparent from the DOS, which covers the entire Brillouin zone and not just one specific path through $\vec{k}$-space), in graphite they form the characteristic π-system located around the Fermi edge.

Now, instead of looking at *single-orbital* contributions, it is desirable to evaluate the *orbital mixing*. For this, we take inspiration by the findings of Pauling [19], who concluded that the valence s- and p-orbitals can undergo a unitary basis-set transformation by linear combination of the atomic orbitals ϕ (LCAO) to yield a new directional one-electron function $\Psi_{sp^3} = a\phi_s + b\phi_{p_x} + c\phi_{p_y} + d\phi_{p_z}$. This new function is commonly referred to as "sp^3 hybrid orbital". The coefficients *a*–*d* are bound by the constraint of orthogonality, and their squares have to be normalized to unity, *i.e.*, $a^2+b^2+c^2+d^2=1$.

Pauling found that the best bonding function results when the squares of all four orbital coefficients assume a value of $\frac{1}{4}$. We now suggest to compare *ab initio* computed coefficients to these ideal value. To this end, we introduce a heuristic parameter μ_j. The quantity μ_j is specific for each atom, band (index *j*) and $\vec{k}$-point, and it is derived from the s- and p- orbital projections at this point in reciprocal space. The coefficients are squared and normalized to unity before entering the indicator, satisfying Pauling's constraint. The formula for μ_j reads

$$\mu_j(\vec{k}) = \left[\frac{2p_{\min}(\vec{k})}{p_{\max}(\vec{k})+s(\vec{k})}\right]\left[1-\left|\frac{p_{\max}(\vec{k})-s(\vec{k})}{p_{\max}(\vec{k})+s(\vec{k})}\right|\right]. \qquad (1)$$

Here, *s* is the squared and normalized coefficient of the s-orbital, $p_{\max}$ is the largest squared and normalized p-coefficient and $p_{\min}$ is the smallest one. The quantity μ_j is defined such that it equals unity if orbital mixing is complete, and zero if no "sp^3" character can be discerned.

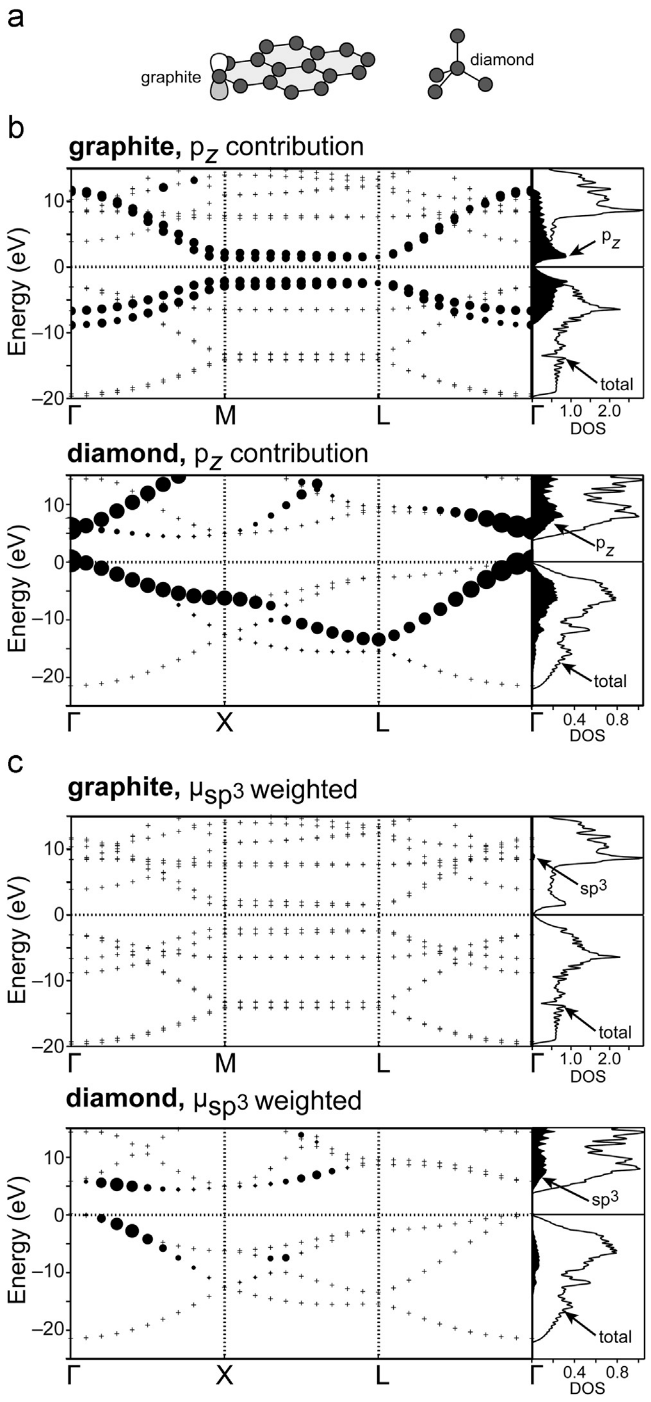

Fig. 2. (a) Structural sketch of textbook carbon allotropes, highlighting the out-of-plane p_z-orbital in graphite. (b) Computed electronic band structures as indicated by crosses; the size of the superimposed circles shows the p_z-contribution (fat-band plots). (c) As before, but weighted with the "sp^3" mixing indicator (Eq. (1)). The scaling of the weighting is arbitrary and differs between plots, for illustrative purposes.

While we employ Pauling's conclusions about ideal coefficients (see above), we—in sharp contrast—do *not* adopt the chemical thinking of an unitary basis-set transformation but use the physicists' notion of orbital mixing by bonding between atoms. Hence, the above definition is deliberately based on canonical orbitals (see below).

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