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Ab initio triangle maps for new insights into the crystal wave functions of carbon allotropes

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ABSTRACT

Recent years have brought forth an ever-increasing number of predicted carbon allotropes. In the spirit of Heimann's original categorization scheme for carbon-only materials, we here report an *ab initio* method to create triangular (ternary) maps based on their valence-orbital mixing. These maps group together allotropes of similar electronic structure——and, hence, physical properties——and can thus aid in finding allotropes with specific features. Moreover, these maps can be used to classify all carbon allotropes according to their bonding nature. We suggest to extract insights about the composition of the crystal wave function as emerging from individual atomic orbitals. To do so, we develop a way to visualize the entire linear-coefficient space of an extended LCAO wave function, also based on ternary diagrams. This scheme yields that lower-level mixed states always get realized and filled first before higher-level mixed states can be created, a consequence of symmetry breaking of canonical orbitals within the solid state. For the specific case of graphite, there is more sp mixing than in sp^2 mixing present, while diamond exhibits more sp and sp^2 mixing than sp^3 mixing. Once higher-level mixing is realized, however, these levels are more significant for the allotropes' properties than the lower-level ones.

1. Introduction

Carbon is sometimes called the structurally most versatile element of the periodic table, simply due to its ability to form C–C bonds of different character, often dubbed as "sp^3", "sp^2" and "sp" bonds using Pauling's original terminology. By altering the periodic binding motif of such bonding types, virtually endless structural diversities are achieved, thereby allowing for unique chemical and physical properties and generating some of the most exciting functional materials, e.g., fullerenes (1985, best electron acceptor in solar cells) [1, 2], carbon nanotubes (1991, mechanically strongest material) [3, 4] and, most recently, graphene (2004, discussed as a basis for field-effect transistors) [5]. Naturally, the interest in creating new functional materials solely containing carbon is very high: in 2015 alone, according to the Samara Carbon Allotrope Database (SACADA) [6] over 120 articles reported novel carbon allotropes, at least in terms of theoretical suggestion.

The sheer abundance of material candidates easily escapes the overview of any scientist. Clearly, a scheme helping to characterize and classify large amounts of allotropes is called for. The concept of such a scheme, based on the orbital hybridization and in particular for the carbon atom, was tentatively proposed in 1997 already by Heimann et al. [7] in this very journal but was not brought to practice in the existing literature so far. Heimann's idea is to draw a triangular diagram, similar to what is usually done for characterizing different compositions of ternary compounds with three elements constituting the three corners of a phase diagram. Accordingly, the axes then show the percental amount of the three elements in any given compound as charted in the diagram. In contrast to such a phase diagram, however, the corners of Heimann's triangle signify a "pure" kind of orbital mixing (or hybridization), namely "sp", "sp^2" and "sp^3", with the associated axes measuring the percental amount of each particular orbital mixing as being present in the charted compounds. For illustration, see the sketch in Fig. 1.

Corresponding to typical textbook knowledge, the corners are then taken by those three allotropes which are considered as the archetypes of the three aforementioned hybridization types, namely polyyne (a one-dimensional carbon chain made from alternating single and triple bonds: $\cdots\mathrm{C{-}C{\equiv}C{-}C{\equiv}C{-}C}\cdots$) [8],

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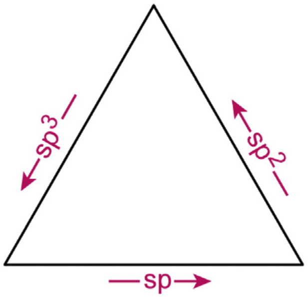

Fig. 1. Concept of material maps crafted from the orbital mixing space according to Heimann. (A colour version of this figure can be viewed online.)

graphite, and diamond. With the axes configured as shown in Fig. 1, polyyne would be located at the right corner, graphite at the top corner and diamond at the left corner of such diagram. Any other carbon allotrope will then be situated somewhere in-between these extreme forms and show some kind of hybridization mixture as achievable with the s- and p-valence states available in carbon.

There exist several theoretical methods to gauge the degree of hybridization within a given compound, two of which are the method of natural bond orbitals (NBOs) [9,10] and maximally localized Wannier functions [11]. NBO analysis is an option to translate a wavefunction into the language of chemical bonding in terms of Lewis formulas, in line with chemical intuition [12]. Such orbitals contain a maximum of electron density—ideally close to two electrons per orbital—to result in an easily interpretable Lewis formula. This approach has been successfully applied to gain knowledge about a vast variety of molecular carbon-based problems [12–15], and computer codes such as the NBO6 suite [16] and its predecessors are readily available. Also, the NBO scheme has been generalized to periodic systems [17], a prerequisite for the majority of solid-state structures. Nonetheless, we are not aware of NBO analysis in the field of novel theoretical carbon allotropes.

Setting up extended wave functions directly leads to a ground-state representation in terms of Bloch orbitals, accordingly labeled in *reciprocal* space. An alternative representation may be achieved via a unitary basis-set transformation into socalled real-space Wannier functions to reach maximum localization [11]. Codes such as Wannier90 offer a projection function to map these maximally localized functions onto s, p, d, f atomic as well as hybrids orbitals, i.e., sp, sp^2, sp^3 and the like [18]. Since Wannier-based methods lend themselves to be used in conjunction with computationally efficient DFT methods for solids, they have been successfully applied for all-carbon materials [19–22].

While the NBO and Wannier methods are both valid starting points for constructing a material map as shown in Fig. 1, on purpose we chose a different theoretical ansatz developed recently to create first-principles material maps [23, 24]. To do so, we have introduced a quantity dubbed MDOS (= mixing density-of-states) serving as a visual indicator for valence orbital mixing. The latter is calculated from canonical Slater-type atomic orbitals by *direct* analytical projection from plane-waves in reciprocal space without going the detour over Wannier functions, specifically for the "sp^3" type at this point in time. More details about the projection scheme are given in the "Computational Methodology" section. Because we have now extended the method to "sp^2" and "sp" mixing, too, a full bonding analysis of carbon allotropes constituted by more than one type of mixed ("hybridized") levels is made possible. In other words, Heimann's suggested triangle maps for carbon allotropes may be quantitatively generated in this manner for the first time. Upon doing so, novel insights into the orbital interplay creating the carbon allotropes' crystal wave functions are to be expected.

2. Computational Methodology

To realize material maps capturing the orbital-mixing space of the carbon allotropes, DFT calculations were performed. To do so, we utilized the software package VASP [25–27], revision 5.3.5, and the generalized-gradient approximation (GGA) with the exchange-correlation functional as formulated by Perdew, Burke, and Enzerhof [28]. At this point, a word of caution is required. The outcome of any DFT calculation depends to some extent on the used exchange-correlation functional. While the GGA approach has been successfully applied to a plethora of materials, its limitations and possible pitfalls (e.g., the delocalization error) are known. For example, the energetic course of polymorphs may be incorrect, as given by the infamous HgNCN problem where the cyanamide is experimentally more stable than the carbodiimide but DFT predicts otherwise [29]. In extreme cases, which feature a significant contribution from halogen bonds, this can even lead to a structurally incorrect ground state, as reported for bromine and iodine [30]. And yet, in the case of carbon allotropes, the GGA functional is found to give sensible results and has been widely applied, successfully so, in the search for novel carbon-only materials. As such, it has also been used in the original papers for a multitude of theoretical carbon allotropes which we map in this contribution [31–36].

The carbon 2s and 2p valence levels were expanded into projector-augmented waves (PAW) [37] with a plane-wave cutoff of 500 eV. The Brillouin zone was sampled with a uniform density of about 50 k-points/Å in every reciprocal dimension for all bulk materials, utilizing $\boldsymbol{\Gamma}$-centered k-point meshes according to the Monkhorst–Pack scheme [38]. The Brillouin zone was sampled at the $\boldsymbol{\Gamma}$-point, exclusively, for the molecular buckminsterfullerene. The crystal structures were fully optimized until self-consistency with respect to all forces was reached within 10^{-3} eV/Å.

To yield DOS and orbital-coefficient information from PAW function, we used the computer program LOBSTER (local-orbital basis suite towards electronic-structure reconstruction) [39–41] featuring an analytical projection scheme to model the entire electronic structure using a minimal contracted Slater-type basis set; in other words, the entire PAW is reconstructed by an LCAO (linear combination of atomic orbitals) approach. The feasibility of this projection scheme has been demonstrated before using several textbook examples, including carbon allotropes [39, 40]. Also, other bonding analyses previously inaccessible to quantum-chemical investigation have been made possible, some of which revolve around carbon, e.g., the impact of boron substitution on local bonding in clathrates [42] or the interfacial chemical bonding between carbon nanotubes and aluminum substrates [43].

We modified a version of the LOBSTER revision 2.0.0 code to obtain the quantity dubbed MDOS, the latter serving as a visual indicator for orbital mixing for "sp^3" [23] and also "sp^2" and "sp" mixing, as said before. A generalization of this technique has recently been presented, intended to fit the orientation of the local basis to the local structural motifs in any given solid [24]. In what follows, we analyze the interplay of the canonic orbitals forming all three variants of s-p mixing in various carbon allotropes for the first time ever.

3. Novel insights about the crystal wave function

Every story has its beginning, so let's cover the background of electronic levels that are commonly labeled as "sp^3", "sp^2" or "sp". Any "sp^3" crystal wave function as given by a linear combination of atomic orbitals (LCAO) is created by a mixture of an s-function with three p-functions. According to Pauling [44], the ideal linear