Maximally valent orbitals in systems with non-ideal bond-angles

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In pursuit of a minimal basis for systems with non-ideal bond angles, in this work we try to pinpoint the exact orientation of the major overlapping orbitals along the nearest neighbouring coordination segments in a given systems such that they maximally represent the covalent interactions through out the system. We compute Mayer’s bond order, akin to the Wiberg’s bond index, in the basis of atomic Wannier orbitals with customizable non-degenerate hybridization constructed from first principles, in a representative variety of molecules and layered systems. We put them in perspective with unbiased maximally localized descriptions of bonding and non-bonding orbitals, and energetics to tunneling of electrons through them between nearest neighbours, to describe the different physical aspects of covalent interactions, which are not necessarily represented by a single unique set of atomic or bonding orbitals.

I. INTRODUCTION

To represent the electronic structure of a given covalent system with minimal tight-binding parameters it is preferable to resort to a directed localized basis\(^{11,12}\) such that the basis orbitals maximally represent the dominant covalent interactions in the system. At a fundamental level the problem is essentially that of finding the orientation of the atomic orbitals such that a minimum number of them facilitate maximum sharing or tunneling of electrons between neighbouring atoms. An associated problem is to partition the electrons in a covalent system among atoms and bond\(^{13}\) such that the population of bonds are contributed by a minimum number of orbitals. Solutions are rather straightforward for systems with ideal bond-angles corresponding to degenerate hybridizations like \(sp^2\). Complication arises with non-ideal bond angles, since for such systems, as we show in this work, making a choice becomes difficult, as different facets of covalent interactions are represented by different sets of orbitals for the same coordination. In fact, “bent bonds”\(^{14}\) have been long suggested in such systems, indicating deviation of orientation of atomic orbitals from the direction of coordination, as they take part in such covalent bonds.

Hybrid orbitals have been central to description of covalent bonding since their introduction\(^{15}\) almost a century ago. Molecular orbitals theory based methodologies for construction of hybrid orbitals\(^ {16,17}\) predating the advent of the Kohn-Sham(KS) density functional theory(DFT)\(^ {18,19}\) based framework, have been grossly based on the maximum overlap condition, wherein either the overlap matrix\(^ {20}\) or the first-order density matrix\(^ {11,15}\), calculated typically in the basis of Slater\(^{16}\) or the Gaussian\(^ {17,18}\) type orbitals, are transformed into block diagonal forms, where each blocks are spanned by orbitals centered on a pair of nearest neighbouring atoms. The resultant variants of the hybrid orbitals like the natural hybrid orbital\(^ {21}\), the effective atomic orbital\(^ {22}\), the generalized hybrid orbital\(^ {23}\), the oriented quasi-atomic orbital\(^ {24}\), or the ones constructed using the maximal orbital analysis\(^ {25}\) approach, constituted the bedrock for understanding chemical bonding in molecules, although limited or biased by the selection of the semi-analytic basis states with adjustable parameters. With the advent of DFT\(^ {13}\) based computation of electronic structure from first principles, attempts to construct localized description of electronic structure in the basis of the KS single particle states, has been primarily undertaken in terms of the spatially localized Wannier functions(WF)\(^ {26}\) which rendered bonding and non-bonding orbitals if constructed from the occupied KS states. Since WFs cannot be uniquely localized in more that one direction simultaneously unless facilitated by symmetry, template based construction of WFs with numerically chosen gauge for the KS states to ensure maximal localization\(^ {22,25}\) has been the mainstay. However with only \(\Gamma\) point, as is the case for finite systems and acceptable for large super-cells, the maximally localized WFs can be constructed without using any template\(^ {23,25}\) as done in this work.

Methodologically, in this work we introduce the notion of maximally valent orbitals (MVO), which are essentially a selection of major overlapping orbitals along coordinations, oriented such that a minimal of them maximally account for sum of bond-orders along coordinations across the system, at the level of nearest neighbourhoods or beyond. Wannier function based on the template of MVOs thus constitute the maximally valent Wannier functions(MCWF). We demonstrate search of MVOs within the sets of orthonormal Wannierized counterparts of non-degenerate \(sp^2\) and \(sp^3\) orbitals, referred here onwards as the n-\(sp^2\) and n-\(sp^3\) orbitals, with customizable orientation, constructed from first principles. The n-\(sp^2\) and n-\(sp^3\) orbitals are the custom hybridized atomic orbitals(CHAO) with tunable hybridization as per the geometry of nearest neighbour coordination around atoms in systems with non-ideal bond angles. CHAOs are generalization of degenerate HAOs constructed from KS states of isolated atoms as demonstrated in Ref.\(^ {29}\). At the heart of the search of MVOs is the formulation and computation of bond-order in the basis of CHAWOs, as defined by Mayer\(^ {27}\) and found anal-
ogous to the Wiberg’s bond index\textsuperscript{23} priorly introduced. We further calculate energetics and tight-binding parameters in the basis of CHAWOs, and calculate their projection on maximally localized WFs constructed without any template of CHAOs, in order to compare MVOs and MCWFs with other possible descriptions of atomic and bonding orbitals representing different aspects of covalent interactions, demonstrated in a wide range of systems starting with cyclopropane which has the smallest C-C-C bond, to cyclobutadiene, diborane, ammonia and water, and finally fullerene and MoS\textsubscript{2}, all with bond angles different from that of degenerate \(sp^2\) or \(sp^3\) coordination.

II. METHODOLOGICAL DETAILS

In this section first we briefly outline the construction of the template free maximally localized WFs used in this work, and the HAOs, following similar approach. Next we describe construction of CHAOs from HAOs and their Wannierization, followed by formulation of bond-order in terms of the Wannierized CHAO, that is, the CHAWOs. Finally we introduce MVOs as a particular choice of CHAWOs, and MCWFs.

The construction of the template free MLWF\textsuperscript{24,25} to describe bonding and non-bonding orbitals, is precursor to the construction of HAOs\textsuperscript{26} in terms of the technique for spatial localization. The only difference is that the MLWFs are constructed exclusively within the subspace of the occupied KS states of a given system, while the HAOs are constructed within an extended sub-space beyond the occupied sub-space of an isolated atom. The localization scheme in both cases is based on maximal joint diagonalization of the generally non-commuting set of the first moment matrices (FMM) which are the representation of the three position operators \(\hat{x}, \hat{y}, \hat{z}\) within a finite sub-space of basis states. The procedure follows from the fact that the total spread of a set of finite \(N\) number of orbitals along \(\hat{x}\), given by:

\[
\Omega_x = \sum_{i=1,N} \left[|\phi_i| x^2 |\phi_i\rangle - |\langle \phi_i | x | \phi_i \rangle|^2\right],
\]

(1)

can be expressed as:

\[
\Omega_x = \sum_{i=1,N} \left(\sum_{j \neq i}^{N} |X_{ij}|^2 + \sum_{j=N+1}^{\infty} |X_{ij}|^2\right),
\]

(2)

where \(X_{ij} = \langle \phi_i | x | \phi_j \rangle\). The off-diagonal elements of the FMM in the first term in the RHS of Eqn\textsuperscript{2} are simultaneously minimized through an iterative scheme based on the Jacobi method of matrix diagonalization, wherein the off-diagonal elements of a single or a commuting set of matrices are set to zero through successive application of two dimensional rotation. In case of a set of non-commuting matrices, a choice of rotation matrices which will maximally diagonalize the non-commuting matrices has been derived in Ref\textsuperscript{29}. The same has been used in this work, as well as for construction of HAOs described in Ref\textsuperscript{29}, which may be refer for relevant details of computation of the rotation matrices.

Construction of CHAOs from HAOs involve two steps - (1) Reconstruction of unhybridized atomic orbitals(UAO) from degenerate HAOs, and (2) Re-hybridization of UAOs to construct CHAOs. In step 1, for a given element, linear combination of HAOs renders UAO aligned perfectly as per a preferred Cartesian system of axes, with the variation of the radial part determined by the pseudo-potential used. In principle this process is straightforward since the analytic hybridization matrix for degenerate \(sp^{n}d^{m}\) hybridization is known. Surmountable technical complication arises with the arbitrary overall orientation of the set of degenerate HAOs. Notably, up to \(n = 2\), UAOs obtained this way are essentially the rotated KS states, since for elements with 2s and 2p valence electrons, the lowest three degenerate block of KS states are the three orthonormal 2p states in random orientation. However, for \(n > 2\) arbitrary mixing of degenerate KS states of the valence shells makes it impossible to directly use them individually as pure atomic orbitals after simple rotation. UAOs obtained from the HAOs, which are maximally localized by construction, are thus assured to render the most localized form of pure orbitals aligned along any preferred set of Cartesian axes as per the pseudo-potential used.

Re-hybridization of UAOs to \(n-sp^2\) or \(n-sp^3\) CHAOs are performed using hybridization matrices specific to symmetries as per that of the nearest neighbourhoods. For example, for CHAOs of the nitrogen atom in NH\textsubscript{3} we use a hybridization of form

\[
\begin{pmatrix}
 a & b & c \\
 a & c & b \\
 d & e & e
\end{pmatrix}
\begin{pmatrix}
 s \\
 p_x \\
 p_y \\
 p_z
\end{pmatrix}.
\]

(3)

The unitarity of the matrix allows one independent parameter and if we choose it to be \(c\) then the other parameters can be calculated as: \(a = \sqrt{1-3c^2+4c}, b = c-1, e = -\frac{b}{\sqrt{(3c-2)^2+4c^2}}, d = \sqrt{1-3c^2}\). More generally, an irregular tetrahedral orientation of orbitals can be assigned with hybridization matrix of form:

\[
\begin{pmatrix}
 a & \frac{1}{\sqrt{2}} & \sqrt{\frac{1}{2}-a^2} & 0 \\
 a & -\frac{1}{\sqrt{2}} & \sqrt{\frac{1}{2}-a^2} & 0 \\
 b\sqrt{\frac{1}{2}-a^2} & 0 & -ab & \sqrt{1-\frac{b^2}{2}} \\
\sqrt{2-b^2}\sqrt{\frac{1}{2}-a^2} & 0 & -a\sqrt{2-b^2} & \frac{b}{\sqrt{2}}
\end{pmatrix}
\]

(4)

with two independent parameters \(a\) and \(b\) representing the two angles which complete the assignment of four orthonormal orbitals. As evident in the matrix, we consider two of the orbitals, the first two, oriented in xy
plane symmetrically about the $y$ axis, while the other two orbitals are in the $yz$ plane. The third and fourth orbitals can also be chosen to be symmetric about the $y$ axis, which reduces the number of independent parameters to one, and geometrically akin to the majority of tetrahedral coordination, like those of C in C$_n$H$_{2+2n}$.

Given a system of atoms, we construct separate sets of CHAOs for atoms of different elements and relative orientation of nearest neighbours (nn) around them. Through choice of parameters in the hybridization matrix we can orient the CHAOs exactly along the direction of coordinates, or in any systematic variation expressible in terms of those directions. Sets of CHAOs constructed for each such type of atoms are then transferred from their atomic nurseries to the given system and oriented according to nn coordinations around each atom, to constitute a set of localized non-orthogonal basis made of transferred CHAOs with intra-atomic orthogonality.

Wannierization of the transferred CHAOs, say $N$ in number, in the basis of $N_{KS}$ ($\geq N$) number of KS states, starts with construction of a set of quasi-Bloch states $\{\psi_{k,j}^{i}(\vec{r})\}$ from CHAOs, and subsequently projecting them on the orthonormal Bloch states constructed from the KS single-particle states:

$$O(\vec{k})_{m,n} = \langle \psi_{k,m}^{KS} | \psi_{k,n}^{i} \rangle.$$  \hfill (5)

Overlaps between the non-orthogonal quasi-Bloch states are calculated within the manifold of the considered KS states as:

$$S(\vec{k})_{m,n} = \sum_{l}^{N_{KS}} O(\vec{k})_{l,m}^{*} O(\vec{k})_{l,n}.$$  \hfill (6)

Values of $\sum_{k} |S(\vec{k})_{m,n}|^2/N_k$ implies representability of the $n$-th CHAO within the set of KS states considered, and should be typically above 0.85 for good agreement of KS band-gap and valence band width, with those calculated with the resultant tight-binding parameters, as mostly studies in this work.

Through Löwdin symmetric orthogonalization (LSO) a new set of orthonormal Bloch states can be constructed as:

$$\Psi_{k,n}^{i}(\vec{r}) = \sum_{m}^{N} S(\vec{k})_{m,n}^{m} \sum_{l}^{N_{KS}} O(\vec{k})_{l,m}^{*} \psi_{k,l}^{KS}(\vec{r}),$$  \hfill (7)

which can be used to construct an orthonormal set of localized Wannier functions referred in this paper as the custom hybrid atomic Wannier orbitals (CHAWO):

$$\Phi_{\vec{R},j}^{i}(\vec{r}) = \frac{1}{\sqrt{N_k}} \sum_{\vec{k}}^{N_{KS}} e^{-i\vec{K}_{\vec{R}} \cdot \vec{r}} \sum_{l}^{N_{KS}} U(\vec{k})_{ij} \psi_{k,l}^{KS}(\vec{r}),$$  \hfill (8)

where $U(\vec{k}) = O(\vec{k})S(\vec{k})^{-1}$.

A. Bond-order in CHAWO basis

To derive an expression of bond-order (BO) similar to that proposed by Mayer, we start with the traditional or classical definition of BO involving the $i$-th and $j$-th atomic orbitals for a given spin:

$$B_{\vec{R},\vec{R},ij}^{+} = \frac{n_{\vec{R},\vec{R},ij}^{+} - n_{\vec{R},\vec{R},ij}^{-}}{2},$$

where $n_{\vec{R},\vec{R},ij}^{+}$ being the occupation of the bonding (+) and antibonding (-) orbitals considered in the CHAWO basis as:

$$\phi_{\vec{R},\vec{R},ij}^{+} = \frac{1}{\sqrt{2}} \left( \Phi_{\vec{R},i}^{+} \pm \Phi_{\vec{R},j}^{-} \right).$$
Within the subspace of occupied KS states:

\[ B_{\vec{R} \vec{R}'} = \text{Re}[\langle \Phi_{\vec{R} l} | \hat{P} | \Phi_{\vec{R} j} \rangle] \]

\[ = \sum_{k} \sum_{l} f_{k,l} \frac{e^{i\vec{k} \cdot (\vec{R} - \vec{R}')}}{N_k} \text{Re}[U(\vec{k})_{il} U(\vec{k})_{lj}] \]

(10)

where \( \hat{P} \) is the projection operator for a given spin:

\[ \hat{P} = \sum_{k} \sum_{l} \langle \psi_{k,l}^{KS} | \hat{P} | \psi_{k,l}^{KS} \rangle \]

\( f_{k,l} \) being the occupancy of the \( l \)-th KS state with wave-vector \( \vec{k} \). \( B_{\vec{R} \vec{R}'} \) in (10) is essentially the Coulson’s bond order(CBO)\(^4\), used primarily in case of a single orbital per atom, where \( i \) and \( j \) effectively become the atom indexes. For a given covalent bond, CBO values, as evaluated in \([10] \), can be positive or negative depending on the relative phase of the two orbitals involved. This indicates that CBO values can not be associated with any form of electron population. In fact, the total number of electrons for a given spin:

\[ N_e = \frac{1}{N_k} \sum_{R} \sum_{j} \langle \Phi_{\vec{R} j} | \hat{P} | \Phi_{\vec{R} j} \rangle \]

\[ = \frac{1}{N_k} \sum_{R} \sum_{j} B_{\vec{R} \vec{R} j} \]

\[ = \sum_{A} \sum_{j \in A} B_{00,j} = \sum_{A} Q_A \]

(11)

\( Q_A \) being the number of electrons which can be associated with atom \( A \). Notably, \( Q_A \) is analogous to the Mulliken’s gross atomic population\(^{13} \), which is same as the net atomic population in case of orthonormal basis, like the CHAWOs, since the overlap population vanishes due to the orthonormality of the basis in the Mulliken’s population analysis scheme. Eqn. \([11] \) also reiterated that the CBO values can not be used in partitioning of electrons into atoms or bonds since they do not contribute to the total number of electrons, whereas, the general classical notion of bond-order is that it is half the total number of electrons shared in a covalent bond including both the spins.

However, using the indempotency of \( \hat{P} \) for integral occupancy of states for a given spin, we can write:

\[ N_e = \frac{1}{N_k} \sum_{R} \sum_{j} \langle \Phi_{\vec{R} j} | \hat{P} \hat{P} | \Phi_{\vec{R} j} \rangle \]

\[ = \frac{1}{N_k} \sum_{R} \sum_{j} \langle \Phi_{\vec{R} j} | \hat{P} \hat{P} | \Phi_{\vec{R} j} \rangle \]

(12)

Inserting \( \sum_{R} \sum_{j} \langle \Phi_{\vec{R} j} | \hat{P} | \Phi_{\vec{R} j} \rangle \) between the two \( \hat{P} \) in \([12] \) we obtain:

\[ N_e = \frac{1}{N_k} \sum_{R} \sum_{j} \sum_{l} \sum_{l} B_{0l,ij} B_{lR,ij} \]

\[ = \sum_{R} \sum_{j} \sum_{l} \sum_{l} B_{0l,ij} B_{lR,ij} \]

(13)

using \([10] \). In \([13] \), for an atom in the 0-th unit-cell, all other atoms in the 0-th or in any other unit-cell(\( \vec{R} \)) can be generalized as neighbours. Therefore we can generalize \([13] \) and partition \( N_e \) as:

\[ N_e = \sum_{R} \sum_{j} \sum_{l} B_{jl} B_{lj} \]

\[ = \sum_{A} \sum_{j \in A} \sum_{l} \sum_{l} B_{jl} B_{lj} \]

\[ = \sum_{A} \sum_{j \in A} \sum_{l} \sum_{l} B_{jl} B_{lj} \]

\[ = \sum_{A} \sum_{j \in A} \sum_{l} \sum_{l} B_{jl} B_{lj} \]

(14)

where \( Q_{AA} \) is the net atomic population of atom \( A \) and the \( Q_{AB} \) is the overlap population between atoms \( A \) and \( B \), as defined by Mayer\(^3\). Note that this version of overlap population is different from the Mulliken’s overlap population since the later is zero for orthonormal basis.

The quantity \( Q_{AB} \) was originally introduced as a bond-index\(^{23} \) and has been later interpreted as the bond order following Wiberg’s original introduction of covalent bonding capacity of a basis orbital, say \( \Phi_j \), as:

\[ b_j = 2P_{jj} - P_{jj}^2 \]

(15)

where \( P = \sum_{l} P^2 \). As easily seen, \( b_j \) will be 1 if \( \Phi_j \) takes part in a bonding orbital, and 0 if it is one in a lone-pair. Using the indempotency property of \( \hat{P} \) again,

\[ b_j = P_{jj}^2 \]

which implies

\[ b_j = \sum_{l \in A} P_{jl} P_{lj} + \sum_{l \in A} P_{jl} P_{lj} \]

with more than one orbitals per atom. Therefore if \( j \in A \)
then for the atom A we can write using (10):

\[ \sum_{j \in A} b_j = Q_{AA} + \sum_{B \neq A} Q_{AB}, \]

where

\[ Q_{AB} = \sum_{j \in A} \sum_{i \in B} q_{AB,ij}, \]

with

\[ q_{AB,ij} = P_{ji} P_{ij} |i \in A, j \in B|. \]

Thus with more than one basis orbitals centred on A, the net covalent bonding capacity or the valency \( V_A \) of atom A is assessed after subtracting the intra-atomic term \( Q_{AA} \) from the net \( \sum_{j \in A} b_j \):

\[ V_A = \sum_{j \in A} b_j - Q_{AA} = \sum_{B \neq A} Q_{AB} \quad (16) \]

Which notionally identifies \( Q_{AB} \) as the bond order in the classical sense of valency of an atom in a covalent system.

In this work we calculated bond orders as defined by \( Q_{AB} \) and their decomposition in orbital pairs, as a function of orientation of the CHAWOs, in order to pinpoint the orientation which maximises the BO contribution from the dominant orbital pairs for a given pair of nearest neighbouring atoms. Since the net BO remains largely constant over different orientations [Fig 1] the dominant contribution can be numerically traced as the maxima of the variance of contributions from different pairs for a given coordination. In fact, the set of CHAWOs which maximizes the sum of standard deviation of BO contributions of all the coordinations in a given system should in principle pinpoint to the orientation of CHAOs which would render CHAWOs such that a minimum of them in principle pinpoint to the orientation of CHAOs which would render CHAWOs such that a minimum of them would maximally incorporate covalent interaction along all coordinations, led by the nn coordinations. We therefore propose to seek the maxima of:

\[ \Omega = \sum_{A} \sum_{B \neq A} \sum_{i \in A} \sum_{j \in B} (\bar{q}_{AB} - q_{AB,ij})^2 \frac{1}{n_An_B}, \quad (17) \]

where

\[ \bar{q}_{AB} = \sum_{i \in A} \sum_{j \in B \neq A} q_{AB,ij} \frac{1}{n_An_B}, \]

\( n_A \) and \( n_B \) being number of orbitals centered on atoms A and B respectively. CHAOs corresponding to the maxima of \( \Omega \) can thus be referred as maximally valent hybrid atomic orbitals (MVHAO). Correspondingly, WFs constructed using the template of MVHAOs can thus be referred as the maximally covalent Wannier functions (MCWF). Notably, for systems with inequivalent atoms, finding \( \Omega \) is in principle a multi-variable maximization problem. In this work however we have restricted to systems where single variable maximization of \( \Omega \) is sufficient or effectively so.

III. COMPUTATIONAL DETAILS

All the ground state geometries as well as ground state electronic structures are calculated using the Quantum Espresso (QE) code\(^{34}\) which is a plane wave based implementation of density functional theory (DFT).\(^{35}\) The BFGS scheme has been used to obtain the relaxed structures within the pseudo-potential used. For periodic systems variable cell relaxation has been performed to optimize lattice parameters and ionic positions. The KS ground states are calculated within the Perdew-Burke-Ernzerhof (PBE) approximation of the exchange-correlation functional. Plane wave basis with kinetic energy cutoff of of 60 Rydberg has been used for all systems considered in this work. We used a 21x21x1 Monkhorst-Pack grid of k-points for the layered systems.

For construction of WFs, CHAWOs and calculation of TB parameters and BO, we use our in-house implementation which used the KS states computed by the QE code. Towards construction of n-\( sp^2 \) and n-\( sp^3 \) CHAOs, the \( sp^2 \) HAOs for \( n = 2 \) are constructed in this work for B, C, N, O, S, Si, Ge and Sn using the lowest four KS states which include a triply degenerate block. For \( n > 2 \), \( sp^3 d^5 \) HAOs are constructed for Mo atoms in the basis of the lowest four KS states and further five states starting from the 6th to the 10th, which divide in two degenerate groups made of two and three KS sates with small difference in eigenvalues, the 5th non-degenerate KS state being the 5s state transferred as is.

IV. RESULTS AND DISCUSSION

To choose the criteria of seeking optimal orientation of CHAOs as they take part in covalent bonding, we can in principle take recourse to the different descriptions of covalent bond based on different physical aspects of covalent interaction, for the same coordination. Different choices of bonding orbital along a nn coordination, can differ on the degree of sharing of electrons between atoms, or the degree of spatial localization of electrons participating in the bond, besides the energetics of the orbitals. Similarly, different choices of orientations of CHAOs would differ not only on the degree of sharing of electrons they facilitate between atoms, but also on energetics of hopping of electrons through them, which has bearing on the strength of the covalent interaction they would support. Since systems with non-ideal bond angles have been reported to have bent bands,\(^ {13} \) making a choice of an optimal orientation would also thus amount to substantiating the bent nature from the different perspectives of covalent interaction. For a given nn coordination, we therefore first look for the peak for \( \Omega \) [Eqn. (17)] to find the orientation of the CHAOs which max-
localized description of the covalent interaction pointing arguably to the shortest path of tunnelling of electrons. And thirdly the maxima of the magnitude of the hopping parameter($t$) between the two major overlapping CHAWOs to find the energetically most favourable route of tunnelling of electron for the given coordination.
Water:

![Diagram of water molecule]

Ammonia:

![Diagram of ammonia molecule]

FIG. 2: Similar to Fig[1]. Plotted as function of $\alpha$[\(\alpha\)] variations of: (d) net BO and BO contributions from CHAWO pairs marked in (b), (e) $\Omega$, (f) hopping parameter between the major overlapping CHAWOs, (g) projection of template free WFs marked as in (c), on CHAWOs marked in (b), (h) energetics of WFs made with template of CHAOs.

Symmetry of cyclopropane allows a single variable maximization of $\Omega$ with one independent parameter in the hybridization matrix. As evident in Fig[1]d, the relative angle $\alpha_{BO}$, which is the $\alpha$ where the dominant BO contribution maximize for a given coordination, are close for C-C and C-H coordinations, and thus coincide with $\alpha$ which is where the $\Omega$ \((1e)\) maximizes. The value of $\alpha_{WF}$, which is the $\alpha$ where the dominant projection of the template free MLWF on CHAWOs maximize[Fig[1]f], for both the coordinations, is also close to $\alpha_{1}$ - at around 105°. Thus the CHAWOs of C at $\alpha_{1}$, namely, the MVHAOs of C as defined above, as well as the CHAWOs of C which have maximum overlap with the MLWFs representing the bonds, both have similar orientation and deviate from the directions of C-C and C-H by about 22.5° and 0.4° respectively. Therefore for cyclopropane both the kinds of bonding orbitals - MLWFs as well as MCWFs, are essentially same. Interestingly, while the values of $\alpha_{BO}$ and $\alpha_{WF}$ coincides with $\alpha_{1}$, the values of $\alpha_{t}$, which is the $\alpha$ where $[t]$ maximizes[Fig[1]f] for the major overlapping CHAWOs, occur respectively at lower and higher angles than $\alpha_{1}$ for the C-H and C-C coordinations. Such a trends of $\alpha_{t}$ values is consistent with the fact that the energies of the C-H$\sigma$ and C-C$\sigma$ WFs constructed based on template made of CHAOs, show a crossing[Fig[1]h] around $\alpha_{1}$, with the C-C(C-H)$\sigma$ being lower in energy below(above) $\alpha_{1}$. These trends clearly suggest a competing preference of the two bonds, to deviation or “bending” from their respective directions of coordinations, above and below $\alpha_{1}$.

In case of cyclobutadiene, the optimization of CHA-

WOs of C atoms is essentially a problem of two variable maximization of $\Omega$ owing to the lack of symmetry about C due to the inequivalent C-C bonds. However, motivated by the small deviation of MVHAOs from the C-H coordination in cyclopropane, we limit optimization of CHAOs for cyclobutadiene to their symmetric orienta-
tions about the C-H coordination, as evident in Fig[2]a. Within such a constraint, the dominant BO contributors for the C-H and the longer C-C coordination occurs between 110° and 115° [Fig[2]d], while it is about 120° for the shorter C-C coordination, leading to an $\alpha_{1}$ aro
implying a total of about $2 \times (0.425 + 2 \times 0.225) = 1.325$ electrons per spin for each of the B-B-H bond. Symmetry of diborane allows single parameter maximization of $\Omega$. Values of $\alpha_{BO}$ [Fig.1(3d)] are generally close to $\alpha_0$, are larger for the B-H1 and B-H2 coordinations than that for the B-B coordination, leading to an intermediate value of $\alpha_{\Omega}$ [(3e)] close to $\alpha_0$, implying a deviation of MVHAOs by about $4^\circ$ from both the B-H1 and B-H2 coordinations. Deviation of the $\alpha_{WF}$ values[Fig.3g)] from $\alpha_0$ for the B-H2-B and B-H1 WFs are similar to those of the respective $\alpha_{BO}$ values. Thus in this case also the MLWFs and the MCWFs suggest similar deviations of the B-H2-B and B-H1 bonds from the directions of B-H2 and B-H1 coordinations. Among the hopping parameters, like we saw in case of cyclopropane and cyclobutadiene, the deviation of $\alpha_t$ [Fig.1(3f)] of the B-H1, which is B-H $\sigma$ in this case, is the least, which is also corroborated by the energetics[Fig.3h)] of the template based WFs, as it shows that the B-H1 bonds do not prefer deviation, while the B-H2-B three centre bonds do. Thus the competing energetics of B-B covalent interaction mediated by the H, and that of the C-H $\sigma$ bonding, with the latter dominating over the former due to multiplicity, determines the structure of diborane.

For molecules of water and ammonia[Fig.2], each with only one kind of coordination, $\alpha_{BO}$ [Fig.24d,5d)] and $\alpha_{\Omega}$ [(4e,5e)] are same, and are clearly higher than their corresponding $\alpha_{WF}$ values [(4g,5g)], which interestingly almost coincides with the actual bond angles $\alpha_0$ for both the molecules. Therefore, while the template free ML-WFs suggest no deviation in effect, the MCWFs would suggest deviations of about $10^\circ$ and $5^\circ$ respectively from directions of O-H and N-H coordinations. Values of $\alpha_t$ [Fig.24d,5f)] for both the O-H and N-H $\sigma$ bonds clearly suggest even larger deviations, which is consistent with the energetics[Fig.4d,5h)] of the template based WFs for both the molecules, since in both cases the bonding WFs energetically prefers deviation which is opposed by the lone pairs.

In $C_{60}$, the two different C-C bonds - the shorter ones shared by two adjacent hexagons, and the longer ones shared by hexagons with adjacent pentagons, demand a two parameter maximization of $\Omega$ in terms of $\alpha$ and $\beta$ [Fig.36a)]. In this work however we restrict effectively to one parameter optimization by seeking maxima of $\Omega$ along the $(\alpha, \beta)$ trajectory plotted in Fig.36a), which nevertheless brings out the key aspect about the true nature of the MVHAOs. For both the C-C bonds the $\alpha_{BO}$ [Fig.36d)] and $\alpha_{\Omega}$ [(6e)] occur at around $111^\circ$ where the three $n-sp^3$ orbitals in effect become co-planar $n-sp^2$, and the fourth one becomes pure $p_z$, implying a $+\delta$ deviation of MVHAOs by about $13^\circ$ and $11^\circ$ from the direction of longer and shorter C-C coordination respectively. Although the MLWFs [Fig.36c)] in this case renders the $\pi$ bond exclusively along the shorter C-C coordination since the longer C-C bonds make pentagons, comparable BO contribution exists between $p_z$ orbitals along the longer C-C [(6d)] coordination as well. In fact the BO values

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**FIG. 3:** $C_{60}$: Plotted as function of $\alpha$ as shown in (6a) - (6d) net BO and BO contributions from the Wannierized pair of CHAOs marked in (6b), (6e) $\Omega$, (6f) hopping parameter between the major overlapping CHAWOs. Charge centres of template free MLWFs are shown in (6c). Note that same values of $\alpha$ recurs about the dotted line which corresponds to co-planarity of $\alpha$ and $\beta$ : $\alpha + 2\beta = 360^\circ$. The $(\alpha, \beta)$ trajectory considered is plotted in 6a.

115°, implying a deviation of MVHAOs from both the shorter and longer C-C coordinations by about $12^\circ$. Similar to cyclopropane, firstly, the values of $\alpha_{WF}$ [Fig.22g)] in this case are also close to the respective values of $\alpha_{BO}$, and secondly, the values of $\alpha_t$ [Fig.22f)] for C-H $\sigma$ and both the C-C$\sigma$ bonds, are respectively lower and higher than the $\alpha_0$ value. Competing preference to deviation from direction of coordination, as seen in cyclopropane, is also evident in cyclobutadiene from the variation of energetics of the C-H $\sigma$ and the C-C$\sigma$ bonds [Fig.22h)] with $\alpha$.

Next we calculate CHAWOs for diborane molecule well known for the B-H-B three centre two electron bond, which in this work is marked by the BO values of B-B and B-H2 [Fig.12f)] of about 0.425 and 0.225 per spin,
Silicene Germanene Stanene

CHAO centres

FIG. 4: Plotted as a function of $\alpha$ as shown in Fig. 3(a) - (b-d) total BO and contributions from orbital pairs marked in (a), (e-g) $\Omega$, (h-j) $t$ between nn $\sigma$, (k-m) Energy expectation values of WFs constructed using the template of CHAOs marked in (a).

along the two C-C coordinations are much comparable, in exception to that implied by MLWFs. Notably, for both the C-C, $\alpha_t$ for $t(2,7)$ and $t(5,3)$ suggests strongest $\sigma$-bond with similar or marginally less $+\delta$ deviation of participating CHAOs from the C-C coordinations, compared to that implied by $\alpha_O$. However, for the shorter C-C, the value of $\alpha_t$ [Fig. 3(f)] for $t(4,6)$ suggests stronger $\pi$-bond due to much larger $+\delta$ deviation from C-C coordination than that implied by $\alpha_O$, which would push the major lobe of the unpaired $n$-$sp^3$ orbital inside the fullerene cage. Thus the $\alpha_O$ allows strong enough $\sigma$-bonds but a weaker $\pi$-bond, reiterating that it is primarily the C-C $\sigma$-bonds constituting the pentagons which are responsible for the curved nature surfaces made of three coordinated carbon atoms with pentagon surrounded by hexagons.

In case of the layered systems formed from group 14 elements, moving down the group, the planar nature seen in graphene evolves into buckled structures of silicene, germanene and stanene with increasing non-co-planarity marked by decreasing bond-angles - around 116.2°, 112.3° and 111.2° respectively, as per the pseudopotentials used. In search of MVHAO, we consider n-$sp^3$ CHAOs, as considered for NH$_3$. With a consistent drop of the net nn BO[Fig. 4(c-e)] from silicene to stanene, the dominant contributions to nn BO, appear to have a broadening peak marginally above $\alpha_0$ leading to $\alpha_O$ [Fig. 4(e-g)] close to $\alpha_0$ as well. The deviation of MVHAOs are around 3°, 5° and 0.6° for silicene, germanene and stanene, in keeping with their increasing non-planarity. However the broadening peak of $\Omega$ from silicene to stanene also suggest increasing lack of directional preference for the CHAOs, consistent with decreasing BO, corroborated by decreasing strength of covalent interaction reflected by the values of hopping parameter[Fig. 4(h-j)]. Interestingly, the energetics[Fig. 4(k-m)] of WFs constructed using the template of CHAOs suggests a strong preference for the bonding WFs to be participated by almost co-planar $sp^2$ orbitals at $\alpha=120^\circ$, which however, according to the energetics, is least preferred by the non-bonding WFs. These trends appear to suggest that lowering of kinetic energy due to delocalization of the unpaired $n$-$sp^3$orbital, is dominated by the energetics of the steric repulsion of the other three $n$-$sp^3$ orbitals which are effectively co-planar as they take part in $\sigma$-bonds described by the WF, resulting into the increased degree of bucking with increasing Z.

In case of molybdenum disulfide (MoS$_2$)[Fig. 3] monolayer, where the Mo-S-Mo angle is around 81°, we considered 5$s$ and 4$sp^3d^5$ HAWOS [Fig. 5(a)] for Mo, as per the grouping of energetics of the K3 states of an isolated Mo atom. The 4$sp^3d^5$ hybridization results into three planar orbitals with C3 symmetry and six orbitals.

FIG. 5: Plotted as a function of $\alpha$ as shown in Fig. 3(a) - (b) total BO and contributions from orbital pairs marked in unitcell of MoS$_2$ (a), (c) $\Omega$, (d) $t$ between orbital pairs marked in (a). The dashed line corresponds to the actual bond angle ($\alpha_o$).
in trigonal prismatic orientation with symmetry as per the nearest neighbourhood of S atoms. For S, we consider n-sp$^3$ CHAOs, as we considered for NH$_3$ and the group 14 layered systems. Since the orientations of the six trigonal prismatic orbitals of Mo can not change unless the planarity of the other three trigonal orbitals is disturbed, we keep the orbitals of Mo unchanged and symmetrically vary the orientation of the n-sp$^3$ CHAOs of S in search of $\alpha_{\Omega}$, which we find to be around 100° [Fig.5(c)] which is close to $\alpha_t$ [Fig.5(d)] as well. Thus the n-sp$^3$ CHAOs of S participating in coordination with Mo make 100° among each other and deviate by 13.7° from the direction of Mo-S coordination. For a given Mo-S coordination, BO for both spins together is about 0.32 [Fig.5(b)], while for an Mo-Mo coordination it is about 0.12. The net atomic population ($Q_{AA}$) of Mo and S are about 11 and 4.7, implying a total of about 20.5 electrons localized on atoms, out of the total of 26 electrons per unit-cell, due to 14(6) valence electrons of Mo(S) as per the pseudo-potential considered. Of the rest of about 5.5 electrons, the majority ($0.32 \times 2 \times 6$) is contribute by the six Mo-S bonds, followed by the three Mo-Mo next nearest coordinations per unit-cell.

The deviation of MVHAOs from the direction of coordinations found in all the systems studied in this work is summerized in Fig.6, where the deviations of MVHAOs centred on four(three)-coordinated sites, are shown by up-triangles(circles). Deviations of such MVHAOs increases in effect linearly with the degree of lowering of bond angle from the ideal tetrahedral bond-angle, with clear pinch-off at the ideal bond-angle. Deviations of MVHAOs centred on three coordinated sites also appears to approache pinch-off at the ideal tetrahedral bond-angle with increasing tetrahedrality of the three nn coordinations and the lone-pair. Substantial deviations in case of cyclobutadiene and C$_6$O are rooted at substantial differences among their bond-angles. As obvious, the effectiveness of MVHAOs as minimal basis increases with their increasing deviation from nn coordinations.

V. CONCLUSION

In search of an optimally directed basis, we begin this work with construction of non-degenerate custom hybridized atomic orbitals(CHAO) with variable orientation, from the degenerate set of hybridized atomic orbitals, in the basis of KS states of isolated atoms. We next formulate Mayer’s bond order in the basis of the Wannierized counterparts of the CHAO, constructed from the KS states of a given system, and introduce the maximally valent hybrid atomic orbitals (MVHAO) and the corresponding template based WFs as the maximally covalent Wannier functions (MCWF), and use them to substantiate the deviation of hybrid atomic orbitals from directions of coordinations as they participate in covalent bonding, as summerized in Fig.6 leading to the bent nature of such bonds, in a host of molecules and layered systems with non-ideal bond angles. Through comparison of bond-order(BO) contributions and hopping parameters from the Wannierized pairs of CHAOs, and their overlap with template free maximally localized Wannier functions(MLWF), we point out how maximally covalent representation of a given coordination can differ from its maximally localized, and energetically favourable representations of covalent interactions in these systems, shedding light on different perspectives of inter-atomic sharing of electrons in general.

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