Self-energy corrected tight binding parameters for few $p$-block semiconductors in the hybridized atomic orbital basis constructed from first principles

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We present self-energy corrected tight-binging(TB) parameters in the basis of the directed hybridised atomic orbitals constructed from first principles, for nano-diamonds as well as bulk diamond and zinc blende structures made of elements of group 13, 14 and 15 in the 2p, 3p and 4p blocks. With increasing principal quantum number of frontier orbitals, the lowering of self-energy corrections(SEC) to the band-gap and consequently to the dominant inter-atomic TB parameters, is much faster in bulk than in nano-diamonds and hence not transferable from bulks to nano-structures. However, TB parameters transferred from smaller nano-diamonds to much larger ones exclusively through mapping of neighbourhoods of atoms not limited to nearest neighbours, are found to render HOMO-LUMO gaps of the larger nano-diamonds with few hundreds of atoms in good agreement with their explicitly computed values at the DFT as well as DFT+$\text{G}_0\text{W}_0$ levels. TB parameters and their SEC are found to vary significantly from $2p$ to $3p$ block but negligibly from $3p$ to $4p$, while varying rather slowly within each block, implying the possibility of transfer of SEC across block with increasing principal quantum number. The demonstrated easy transferability of self-energy corrected TB parameters in the hybrid orbital basis thus promises computationally inexpensive estimation of quasi-particle electronic structure of large finite systems with thousands of atoms.

I. INTRODUCTION

Starting with the advent of the quantum theory of solids [1], tight-binding(TB) frameworks in the basis of spatially localized Wannier functions (WF) [2], have been envisioned as a generic approach to compute electronic structure of materials. Slater-Koster (SK) parametrization [3, 4] of elements of a TB Hamiltonian marked the beginning of reasonable band structure calculations of solids. With the advent of the Kohn-Sham(KS) density functional theory(DFT) [5, 6], the mean field approximation of KS-DFT [7, 8] and tight-binding parameters [9-11] determined by fitting the energy bands at the DFT level, have been the work horse for studies of ground states properties of materials with weak to modest localization of valence electrons for about three decades now.

With our increasing capability to fabricate devices with ever shrinking size - now well within double digits in nanometers, interest in accurate computation of physical and electronic structure of such systems, which typically consist of thousands of atoms, led to the evolution of tight-binding frameworks for finite systems with structural inhomogeneities. Efforts to derive TB parameters for large finite systems, particularly with $sp^3$ hybridization of orbitals, have been reported not only in the orthogonal $sp^3$ basis [12-17] but also more generalizable in the non-orthogonal basis as well [18-20] and used extensively in molecular dynamics simulation [15, 21] and calculation of optical properties [22-26]. Evolution of computational techniques to construct spatially localized Wannier functions [WF] [27, 28], opened up the scope for construction of realistic localized orbitals from KS single particle states, [29, 30], leading to explicit computation of realistic TB parameters from first principles.

With improved spectroscopic measurements enhanced correlation due to spatial confinement near surfaces and interfaces of nano-structures became apparent which made it imperative to take the frameworks of computation of electronic structure beyond the mean field regime leading to formidable increase in computational complexity and cost. While much effort in this direction has been underway in terms of improving the exchange-correlation functionals [31] to include effects of many-electron interactions within the KS energy eigen-spectrum, the GW approximation [32] of the many body perturbation theory (MBPT) [33, 34] is so far the most general abinitio framework to unmissably account for correlations starting from the KS single particle states. However, both the approaches are computationally expensive and almost prohibitive for systems with thousands of atoms. These limitations have led to attempts to incorporate effects of correlations within the tight-binding(TB) frameworks. Efforts reported in recent years mostly improve TB parameters [35-39] by matching QP structure in specific systems and orbital subspaces.

In this work we calculate self-energy correction(SEC) to TB parameters from the SEC of the KS energy eigenstates at the DFT+$\text{G}_0\text{W}_0$ level. With tetrahedrally coordinated atoms exclusively considered in this work except the passivating H atoms at the surface of the nano-diamonds, TB parameters are calculated in the orthonormal basis of Wannier functions(WF) constructed following a realistic template of $sp^3$ hybridized atomic orbitals(HAO) obtained from KS single particle states of isolated atoms. The resultant WFs resemble hybrid atomic orbitals and orient towards directions of coordination by construction, and thereby locked to the immediate neighbourhood of atoms. The aim of this work is to present a comparative analysis of TB parameters and their SEC in such directed hybrid orbital basis beyond the nearest neighbourhood for bulk and finite structures made of a representative variety of $2p$, $3p$ and $4p$ bands.
block elements which exists in diamond or zinc-blend structures in three dimensions. We also demonstrate that such TB parameters can be transferred from smaller nano-diamonds to their much larger iso-structural counterparts exclusively through mapping of neighbourhoods typically up to 2nd or third nearest neighbours, to render HOMO-LUMO gaps of the larger systems in good agreement with their explicitly calculated values at the DFT and DFT+\textit{G}_{0}\textit{W}_{0} level.

II. METHODOLOGICAL DETAILS

A. Construction of hybrid atomic orbitals (HAO) and their transfer to system of atoms

Hybrid orbital basis (HAO) are constructed for isolated atoms as the approximate eigenstates of the non-commuting set of three first moment matrices (FMM) \(X, Y\) and \(Z\) projected in a finite subspace of orthonormal basis states. FMMs calculated as:

\[
(X, Y, Z)_{ij} = \langle \phi_i | (x, y, z) | \phi_j \rangle.
\]

are maximally joint diagonalized using an iterative scheme based on the Jacobi method of matrix diagonalization where off-diagonal elements are minimized through rotation of coordinates by a specific analytic choice of angles as detailed in ref.\cite{ref}. HAOs are naturally oriented towards direction of coordinations around atom as per the set of basis states considered for construction of the HAOs. The charge centres of HAOs thus render coordination polyhedra around an atom for a given sub-shell. For construction of the \(sp^3\) HAOs used in this work, the lowest four KS states of a single atom are used as basis. Although in principle, any localized atomic orbitals like the pseudo-atomic orbitals or the Slater or Gaussian type orbitals parametrized for the given atoms can also be used for the purpose, it is important to have appropriate length-scale of localization of the HAOs for their correct representation within the KS states of the given system of atoms where the HAOs are to be used as template to construct WFs. Same pseudo-potential thus preferably be used for generation of HAOs and also for calculation of electronic structure of the given system.

Separate sets of HAOs are constructed for each types of atoms, and transferred to the corresponding atoms in the given system through mapping of directions of coordination from the atoms to their nearest neighbours on to the directions of charge centres of HAOs from the isolated atom for which they are explicitly constructed. Through such mapping a distribution of projected charge centres of HAOs are generated for the entire system prior to the transfer of HAOs, as seen in Fig.1. For perfect tetrahedral coordination, as seen in the bulk diamond and zinc blende structures, the transferred HAOs would thus retain intra-atomic orthonormality, whereas for the nano-diamonds such intra-atomic orthogonality will be marginally compromised owing to deviations of perfect tetrahedral coordination more towards the surface. However this is not a problem as such not only because the deviations are minimal but because all transfered HAOs are symmetrically orthonormalized during the construction of the WFs.

B. Wannier functions based on HAOs

HAOs transferred from isolated atoms to the system of atoms constitute a non-orthogonal basis primarily due to their inter-atomic non-orthogonality. A set of quasi-Bloch states are subsequently constructed as:

\[
\hat{\psi}_{\vec{k}, j}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \phi_{\vec{R}, j}(\vec{r}),
\]

where \(\phi_{\vec{R}, j}(\vec{r})\) is the \(j\)-th HAO localized in the unit-cell denoted by the lattice vector \(\vec{R}\) which spans over \(N\) unit-cells as per the the Born-von Karman periodicity. The quasi-Bloch states are projected on the orthonormal Bloch states constructed from the KS single-particle states at all allowed \(\vec{k}\):

\[
O_{\vec{k}, m, j} = \langle \hat{\psi}_{\vec{k}, m} | \hat{\psi}_{\vec{k}, j} \rangle.
\]
which is twice the number of occupied states in our case. Overlaps between the non-orthogonal quasi-Bloch states are calculated within the manifold of the considered KS states as:

$$S_{k,m,n} = \sum_l O_{k,l,m}^* O_{k,l,n}.$$  

(4)

Representability of an HAO within the set of KS states considered, is ensured by setting a lower cutoff on individual $S_{k,m,n}$ values for all HAO index $n$, which we typically set at 0.85. In all the systems considered in this work, such a cutoff is found to be well satisfied for all HAOs within the set of KS states whose count is set to the total number of HAOs of all the atoms in the given system. Using the Löwdin symmetric orthogonalization scheme a new set of orthonormal Bloch states are constructed from the KS single particle states as:

$$\Psi_{k,n}(\vec{r}) = \sum_m S^{-\frac{1}{2}}_{k,m,n} \sum_l O_{k,l,m} \psi_{k,l}^{KS}(\vec{r}).$$  

(5)

FIG. 3: TB and self-energy correction to TB parameters in (a) carbon, (b) silicon and (c) germanium nano-diamonds from adamantane to pentamantane.

where $l$ spans over the KS states and the sum over $m$ ensures orthonormalization. Finally a orthonormal set of localized Wannier functions referred here onwards in this paper as the hybrid atomic Wannier orbitals (HAWO), are constructed as:

$$\Phi_{\vec{R},j}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_k e^{-i\vec{k} \cdot \vec{R}} \psi_{\vec{R},j}(\vec{r}).$$  

(6)

The resultant HAWO resemble the corresponding HAOs $\{\phi_{\vec{R},j}(\vec{r})\}$ as seen in Fig. 3. Notably, the number of KS states which can be considered for construction of HAWOs are not limited by the total number of HAOs transferred to the system. In fact the localization of the HAWOs increase with increasing size of the KS subspace used. However in such a case the matrix $(OS^{-\frac{1}{2}})$ would become semi-unitary. TB parameters are computed in the HAWO basis from energetics of KS single particle states as:

$$t_{\vec{R}',\vec{R},i,j} = \langle \Phi_{\vec{R}',i} | H^{KS} | \Phi_{\vec{R},j} \rangle = \sum_k e^{i\vec{k} \cdot (\vec{R}' - \vec{R})} \sum_l (OS^{-\frac{1}{2}})_{il} (OS^{-\frac{1}{2}})_{lj} E_{k,l}^{KS}.$$  

(7)

Notably, although TB parameters have been derived from first principles based on the maximally localized Wannier function [42-47] or atomic orbitals [48-51] constructed from KS states over the years, attempts to calculate TB parameters in the basis of directed hybrid orbital has been primarily limited so far to analytical models [52-53]. Self-energy corrected TB parameters (SEC-TB) $\{t_{\vec{R}',\vec{R},i,j}^{QP}\}$ in the HAWO basis are calculated by substituting $E_{k,n}^{KS}$ in Eqn. (7) by quasi-particle energies $E_{k,n}^{QP}$ obtained at the $G_0W_0$ level of the GW approximation of MBPT [52-53]. Efforts have been reported in recent years on incorporating SEC in TB parameters computed in terms of the MLWFs [37-39, 54].
FIG. 5: Variation of HOMO-LUMO gap computed with TB and SEC-TB parameters mapped to un-relaxed structures from relaxed pentamantane structure, and the same computed from first principles at the DFT and DFT+G0W0 level with relaxed structure, as a function of size of carbon nano-diamonds increasing in (a) pyramidal and (b) bi-pyramidal structures. Comparison of DOS of C₆₈H₅₆ calculated from (c) TB mapped to un-relaxed structures and DFT of relaxed structure, and (d) SEC-TB mapped to un-relaxed structure and DFT+G0W0 of relaxed structure.

C. Bottom-up mapping of TB parameters

The orientation of HAWOs being locked to the local atomic neighbourhood of each atom, the multi-orbital TB parameters derive in HAWO basis are easily mappable from one system to another with matching atomic neighbourhoods. Transferability of the TB parameters in terms of reproducibility of band-gaps and band-width within acceptable ranges of deviation from their direct estimates from first principles, is demonstrate by transferring TB parameters from smaller reference systems to structurally similar larger target systems. Transfer of TB parameters is done in two steps. First all individual pairs of atoms of the target system beyond the nearest neighbourhood, are mapped on to matching pairs of atoms in the reference system through comparison of a collection of structural parameters like spatial separation, angles and dihedral angles subtended by the nearest neighbours and a measure (ζ) of proximity of atoms with respect to surfaces, interfaces and inhomogeneities defined as:

\[ ζ_i = \sum_j Z_j w(r_{i,j}) \]  

where \( N_i \) is the number of neighbours of the \( i \)-th atom within a chosen cutoff radius, and \( w \) being a weight factor which is a function of the distance \( r_{i,j} \) of the \( j \)-th neighbour of the \( i \)-th atom, and \( Z_i \) being a characteristic number to be associated with each type of atom, for example, the atomic weight.

For mapping of orbital pairs from reference to target, a projected map [Fig 1(b-c)] of locations of charge centres of HAOs for the target system is generated first and then among the mapped pair of atoms, pair of HAOs of system are mapped to pair of HAOs of the reference through mapping of their respective charge centres much like the mapping of atom pairs. The weight factor \( w \) is typically chosen to be 1.0 within half of the cutoff radius and smoothly reduced to zero at the cutoff radius using a cosine function. Cutoff radius is chosen based on the size of the reference system, since it should neither be too large for variations in \( Z_i \) to average out, nor should it be too small such that \( ζ \) varies abruptly only at the structural inhomogeneities. Cutoff radius and \( Z_i \) values should thus be so chosen that \( ζ \) values can effectively differentiate between atoms at the interior of a finite system from those at the surfaces in both reference and target systems such that relaxed structures of target systems are not required to adequately transfer effects of variation in bond lengths near the surfaces from reference to target systems.
III. COMPUTATIONAL DETAILS

All the ground state geometries as well as ground state electronic structures are calculated using the QUANTUM ESPRESSO (QE) code [55] which is a plane wave based implementation of density functional theory (DFT). BFGS scheme has been used to obtain the relaxed structures. For bulk systems variable cell relaxation has been performed to optimize lattice parameters and ionic positions. A separation of at least 10 Å between periodic images has been ensured for all the finite systems. The KS ground state properties are calculated within the Perdew-Zunger approximation of the exchange-correlation functional implemented in a norm-conserving pseudo-potential. Plane wave basis with kinetic energy cutoff in excess of 60 Rydberg along with a 15x15x15 Monkhorst-Pack grid of k-points have been used for all the bulk systems. The self-energy correction to KS energy eigenvalues are calculated at the G0W0 level of GW approximation of the many-body perturbation theory (MBPT) implemented in the BerkeleyGW (BGW) code[56]. To calculate the static dielectric matrix and extend to the finite frequencies the generalized plasmon-pole model [32] is used. For convergence of dielectric function as well as the self-energy term we used in excess of 250(5000) bands for bulks(nano-diamonds). To get a well converged band-gap for bulk structures we used a finer k-mesh of 30x30x30 grid. Finally, in-house implementation interfaced with the QE code is used for generation of HAOs, HAWOs from KS states, calculation of TB parameters in the HAWO basis, and mapping of TB parameters from smaller reference systems to larger target systems.

IV. RESULTS AND DISCUSSION

Nano-diamonds starting with adamantane followed by diamantane, triamantane, tetramantane with increasing number of atoms up to pentamantane have been considered for explicit calculation of TB parameters at the DFT level and their further refinement due to SEC of KS energy eigenvalues at the G0W0 level. As evident in Fig.3 the dominant nearest neighbour(nn) TB parameters as well as those beyond the nearest neighbourhood, remains effectively invariant with respect to system size, implying transferability of TB parameters across length-scales of nano-diamonds at the DFT level as we demonstrate in this paper. Magnitudes of TB parameters in Si and Ge are similar but vary significantly from that of C, which is consistent with variation in their inter-atomic separations. Notably however, the SEC to the dominant TB parameters reduces slowly with increasing system size in a similar rate for C, Si and Ge based nano-diamonds, although the magnitude of correction itself reduces significantly with increasing principal quantum number owing to increased de-localization. The slow variation of SEC across system size also suggests possibility of SEC corrected TB parameters to be transferable as well to a workable degree.

Fig.4 clearly suggests that TB parameters of either Si or Ge can be used for SiGe nano-diamond as well, whereas for the SiC nano-diamonds the dominant inter-atomic TB parameters are effectively the average of that of the C and Si based nano-diamonds. These observations hint at increased transferability of SEC across elements in a block with increasing quantum number of frontier orbitals. The reorganization of the on-site terms of SiC nano-diamond compared to those made of Si or C can be attributed to the hetero-polarity of the Si-C nn.
bond due to difference of electro-negativities of Si and C, whereas electro-negativities of Si and Ge are similar and less than that of C.

To study transferability of TB parameters from smaller nano-diamonds to their larger counterparts we have mapped TB parameters from pentamentane to larger pyramidal and bi-pyramidal carbon based nano-diamonds with close to 1000 atoms. We have considered un-relaxed coordinates of the larger nano-diamonds and mapped the TB parameters calculated for relaxed structure of pentamentane, using ζ values calculated with a cutoff radius considered up to the next nearest neighbour. As evident in Fig.5(a,b), the match of the DFT HOMO-LUMO gap with that calculated from the transferred TB parameters from pentamentane is found to be quite exact for both pyramidal as well as bi-pyramidal nano-diamonds up to about 500 atoms, which is almost about ten times escalation of size of the target system compared to that of the reference system. Notably, for all the larger nano-diamonds the DFT HOMO-LUMO gaps were calculated explicitly with well relaxed structures, whereas the structures used to transfer TB parameters from pentamentane were completely un-relaxed. Therefore the match of the exact DFT HOMO-LUMO gaps with that evaluated with TB parameters transferred to an un-relaxed structure point to the efficacy of ζ in differentiating atoms as per their proximity to the surface in both reference and target systems so that the transferred TB parameters have the correct variation from surface to interior. The match of the quasi-particle (QP) HOMO-LUMO gap is also found quite satisfactory up to more than two time escalation of system size beyond pentamentane, till which GoW₀ calculations could be reliably performed with computational facilities at our end. QP HOMO-LUMO gap data available in the literature [57–60] allows us to compare for a bit further. These results thus confirms transferability of TB parameters with and without SEC over substantial escalation of system size.

Interatomic TB parameters for bulk Si and Ge in diamond structures are consistent with those in nano-diamonds notwithstanding the substantial drop of band-gap in bulk to about 0.5 eV(1 eV) from HOMO-LUMO gap around 4 eV(7 eV) in nano-diamonds at the DFT(DFT+G₀W₀) level as shown in Fig.6(b,c). However for bulk C in diamond structure the dominant nn hopping term strengthens substantially to -10 eV (Fig.7(a)) from -6.5 eV (Fig.8(a) red plots) in nano-diamonds, although the band-gap in bulk is comparable to that of HOMO-LUMO gap of nano-diamonds, which are about 4.2 eV and 5 eV respectively at the DFT level. The reason of this contrasting trend for C compared to those for Si and Ge can be traced to one obvious fact that sp³ HAWOs of C is stretched towards the nearest C compared to the HAWOs of Si and Ge. Overlap of such sp³ HAWOs of C would thus increase appreciably with reduction in C-C nn separation from nano-diamonds to bulk, leading to the increase in magnitude of nn hopping term. Thus the TB parameters are not transferable from bulk to nano-diamond for C even at the DFT level. However it may still be feasible for Si and Ge.

Consistent with the localized nature of HAWOs, SEC is higher for C based bulk and nano-diamonds compared to their Si and Ge based counterparts. However the relative variation of localization of HAWOs of C, Si and Ge are much dominated over by the localization imposed by the finiteness of nano-diamonds, leading to comparable values of SEC of band-gap of C, Si and Ge based nano-diamonds ranging from about 4 eV to 3 eV leading to comparable SEC correction to nn hopping term ranging from -1.75 eV to -1.3 eV. From nano-diamonds to bulk the SEC to band gap and thereby to the nn hopping term reduces consistently on account of de-localization. Thus the self-energy corrected TB parameters are not transferable from bulk to nano-diamonds even for Si and Ge.

As evident in Fig.7(a,c,e,g,i,k), the nn hopping parameter is almost exactly same for diamond structures of group 14 (C,Si,Ge) and zinc blende structures made of groups 13 and 15 (BN,AlP, GaAs) within each block, whereas the SEC to the nn (Fig.7(b,d,f,h,j,l)) hopping are consistently more for zinc blende structures than the diamond structures in each block owing likely to the enhanced localization of the bonding orbitals in the heteropolar B-N, Al-P and Ga-As nn bonds than in the C-C, Si-Si, and Ge-Ge bonds. Fig.7(q) summarizes the variation of the onsite terms and the major inter-atomic

![FIG. 8: Comparison of band-structures computed from first principles with that obtained with TB parameters derived from first principles at the DFT (upper panel) and DFT+G₀W₀(lower panel) levels for 2p, 3p and 4p block elements.](image-url)
hopping parameters at the DFT and DFT+G₀W₀ level. As evident in Fig. m.o,n.p,q, for zinc blend structure of SiC(SiGe) the nn hopping and it’s SEC both are average of their counterparts in diamond structures of Si and C(Ge). Fig. q clearly suggests the stepped evolution of TB parameters and SEC from 2p to 3p and 4p blocks and the similarity in the later two. Band structures obtained with TB parameters shown in Fig.8 are plotted along with DFT band structure. Notably, for the exact reproduction of band structure the TB parameters have to be obtained not only in a dense enough grid of \( \vec{k} \) but also using a KS band subspace of size exactly same as OS. The reproduction of band structure will become increasingly inexact if we use a larger KS subspace then the reproduction energy bands will become increasingly inexact with increasing energy.

V. CONCLUSIONS

For a representative variety of \( p \) block elements, we have presented TB parameters calculated at the level of DFT and DFT+G₀W₀ in the orthonormal hybridized atomic Wannier orbitals(HAWO) basis constituted of the KS single particles and are directed towards coordination by construction. We present TB parameters for nano-diamonds made of C, Si, Ge, SiC and SiGe and their bulks in diamond or zinc blende structures, and also of bulk BN, AIP and GaAs in the three consecutive \( p \) blocks. Transferability of inter-atomic TB parameters between bulk structures to nano-diamonds is generally poor and worsens with self-energy correction(SEC). However among nano-diamonds, the inter-atomic TB parameters at the DFT level are found to remains effectively unaltered with increasing size, implying robust transferability of the TB parameters from smaller to larger nano-diamonds. Slow reduction of SEC to TB parameters with increasing system size also implies good transferability of self-energy corrected TB parameters across nano-diamonds. Transfer of TB parameters are performed exclusively by mapping up to second or third nearest neighbourhoods between the reference and the target systems, and thus does not necessitates relaxed geometries of the target systems as long as all neighbourhoods could be mapped. Similarity of TB parameters and their self-energy corrections across 3p and 4p blocks compared to that in the 2p block hints at the possible transferability of SEC across blocks with increasing principal quantum number.

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