

Environment-dependent tight-binding models from *ab initio* pseudoatomic orbital Hamiltonians

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Ab initio pseudoatomic orbital (PAO) Hamiltonians express the electronic structure of a solid in a compact, localized basis that spans the same Hilbert space as a conventional Slater-Koster tight-binding model, thereby providing an exact *ab initio* representation without any loss of accuracy. Building on this correspondence, we develop an environment-dependent tight-binding framework in which Slater-Koster hopping integrals are augmented with bond-screening functions that capture the local coordination environment. All parameters are determined by fitting to the PAO eigenvalue spectrum across multiple atomic configurations simultaneously, which breaks the degeneracy between screening and hopping parameters and yields physically meaningful, transferable models capable of generating Hamiltonians for large systems with *ab initio* precision. We demonstrate the efficiency and accuracy of the approach on four prototypical systems: bulk platinum, silicon surfaces, Si/Ge [001] superlattices, and twisted bilayer graphene with up to 4324 atoms. The method is implemented in the PAOFLOW code and integrates seamlessly with its full postprocessing suite, enabling the evaluation of a broad range of electronic, optical, and transport properties.

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I. INTRODUCTION

The electronic structure of solids and nanostructures underpins a vast range of physical phenomena—from charge transport and optical response to topological order and correlated electron behavior. First-principles density-functional theory (DFT) provides a parameter-free description of these properties, but its computational cost scales with system size, limiting routine application to unit cells of at most a few hundred atoms. Tight-binding (TB) models offer a complementary approach: by representing the Hamiltonian in a compact basis of localized orbitals, they reduce the problem dimension by orders of magnitude while retaining the essential orbital physics of the band structure [1–3]. However, the method is intrinsically semiempirical, since the TB parameters need to be fitted with existing experimental or theoretical data.

In recent years, we have developed a robust framework for constructing accurate, compact Hamiltonians in a (pseudo) atomic orbital (PAO) basis (either from the pseudo-orbitals of the pseudopotential or from external atomic basis functions) directly from plane-wave DFT calculations: the PAOFLOW code [4,5]. The main advantage of this representation is that the (pseudo) atomic orbital basis provides a direct matching with a TB-like model without any loss of accuracy, since the Hilbert space of both Hamiltonians share the same dimensionality. It is thus natural to integrate the PAOFLOW representation

with the classic Slater-Koster TB framework and develop TB models with full *ab initio* accuracy.

In the Slater-Koster (SK) framework [1], hopping integrals between atomic orbitals are decomposed into a small set of on-site energies and two-centers bond integrals $V_{l'l'\mu}$ ($\mu = \sigma, \pi, \delta$) modulated by geometric direction-cosine factors. These two-center integrals are fitted to reproduce band structures from experiments or other theoretical methods and are bound to the equilibrium configuration used in the fitting. As such, their transferability to configurations with different local environments—surfaces, interfaces, defects, or strained geometries—is inherently limited.

Several strategies have been developed to extend the reach of TB models beyond equilibrium bulk geometries. Among these are the rescaling methods originally proposed by Harrison [2] and then extended by Goodwin, Skinner, and Pettiford [6], the Naval Research Laboratory (NRL) tight-binding method [3,7–9] where the SK parameters are expressed as smooth functions of distance fitted to DFT data across multiple crystal structures and volumes, thereby encoding environment dependence implicitly through the training set, and the environment-dependent tight-binding (EDTB) formalism introduced by Tang, Wang, Chan, and Ho [10], where each hopping integral is multiplied by a screening factor that depends on a bond screening sum—a measure of how crowded the local bonding environment is around a given bond.

In this work we present a method for constructing EDTB models capable of flexible screening granularity and distance-dependent hopping functions by fitting to the eigenvalue spectrum of PAO Hamiltonians from PAOFLOW. Fitting directly to PAO eigenvalues avoids the gauge ambiguity of Wannier-function approaches [11] and leverages the orbital properties of the PAO basis. The fitting is done using an

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efficient nonlinear least-square Levenberg-Marquardt optimization with exact derivatives of the eigenvalue residuals via analytic Hellmann-Feynman Jacobians. Combined with optimized software design such as fully vectorized and parallelized algorithms and a block-sparse design-tensor formulation, we have developed a comprehensive EDTB code now integrated in the PAOFLOW software ecosystem.

The paper is organized as follows. Section II summarizes the PAOFLOW framework and the PAO Hamiltonian construction. Section III presents the Slater-Koster formalism with environment-dependent screening and distance-dependent hopping functions. Section IV describes the fitting procedure, including the objective function, analytic Jacobian, regularization, and multigeometry training protocol. Section V presents applications to FCC platinum, silicon surfaces, Si/Ge superlattices, and twisted bilayer graphene. We summarize our conclusions in Sec. VI.

II. PAOFLOW FRAMEWORK

The reference electronic structure used throughout this work is provided by the PAOFLOW code [4,5], which constructs a tight-binding-like Hamiltonian in a compact pseudoatomic orbital basis from a standard plane-wave DFT calculation [12–14].

A. Projection onto the PAO basis

Starting from the self-consistent Kohn–Sham eigenstates $|\psi_n\rangle$ obtained with a plane-wave code (e.g., QUANTUM ESPRESSO [15,16]), one selects a set of M orthonormal atomiclike orbitals $|\phi_\alpha\rangle$ ($\langle\phi_\alpha|\phi_\beta\rangle = \delta_{\alpha\beta}$), typically the Löwdin-orthogonalized pseudoatomic orbitals provided with the pseudopotential. Here α is a composite orbital index labeling a specific PAO (atom plus n, l, m angular-momentum character); the index runs over all PAOs on all atoms in the cell. These orbitals span a subspace $\mathcal{A}$ of dimension M . The projector onto $\mathcal{A}$ is $\hat{P} = \sum_\alpha |\phi_\alpha\rangle\langle\phi_\alpha|$ and the projection of each Bloch state yields $|B_n\rangle = \hat{P}|\psi_n\rangle$ with coefficients $B_{\alpha n} = \langle\phi_\alpha|\psi_n\rangle$.

The *projectability* of each state,

$$p_n = \langle\psi_n|\hat{P}|\psi_n\rangle = \sum_\alpha |B_{\alpha n}|^2, \quad (1)$$

measures how completely $|\psi_n\rangle$ is described in $\mathcal{A}$. States with p_n below a threshold (typically $p_n < 0.95$) are excluded from the Hamiltonian reconstruction [12].

B. Hamiltonian construction

From the N retained states, one forms normalized projection vectors $|A_n\rangle = |B_n\rangle/\sqrt{p_n}$ and constructs the PAO Hamiltonian as [12]

$$\bar{H} = A E A^\dagger, \quad (2)$$

where $E = \text{diag}(\varepsilon_1, \dots, \varepsilon_N)$ contains the selected Kohn–Sham eigenvalues. Here M is the number of PAO basis orbitals spanning $\mathcal{A}$, so that $\bar{H}$ is an $M \times M$ matrix, whereas N is the number of *retained Kohn–Sham states*—those passing the projectability criterion $p_n \geq 0.95$. In general $N < M$, i.e., there are fewer high-projectability bands than basis orbitals.

Since $\bar{H}$ is an $M \times M$ matrix built from $N < M$ states, it possesses an unphysical null space of dimension $M - N$. This is removed by adding a shift projector [12]:

$$\tilde{H}_\kappa = \bar{H} + \kappa Q_N, \quad Q_N = I_M - A(A^\dagger A)^{-1}A^\dagger, \quad (3)$$

which pushes the null-space eigenvalues to an energy κ above the physical bands, leaving the projected eigenstates unaffected.

The PAO Hamiltonian provides an exact description of the electronic properties of the crystal without any iterative optimization of the basis functions and maps directly onto a corresponding SK Hamiltonian with the same orbital basis (angular momentum labels) [4,5]. The real-space representation $H_{\alpha\beta}(\mathbf{R})$, obtained by inverse Fourier transform on the DFT k mesh, decays rapidly with $|\mathbf{R}|$. The Bloch Hamiltonian at arbitrary wave vector $\mathbf{k}$ is reconstructed by

$$H_{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} H_{\alpha\beta}(\mathbf{R}) \quad (4)$$

and diagonalization yields the band structure $\varepsilon_{n\mathbf{k}}^{\text{PAO}}$.

III. SLATER-KOSTER TIGHT BINDING WITH ENVIRONMENT DEPENDENCE

A. Two-center hopping integrals

In the SK scheme [1], the hopping matrix element between orbital α on atom i and orbital β on atom j , connected by a bond vector $\mathbf{d}_{ij} = \mathbf{R} + \boldsymbol{\tau}_j - \boldsymbol{\tau}_i$ with $|\mathbf{d}_{ij}| = d_{ij}$, is

$$H_{\alpha\beta}^{\text{SK}}(\mathbf{d}_{ij}) = \sum_{\mu} c_{\alpha\beta\mu}(\hat{\mathbf{d}}_{ij}) V_{l_\alpha l_\beta \mu}^{(s)}. \quad (5)$$

Here $\boldsymbol{\tau}_i$ and $\boldsymbol{\tau}_j$ are the atomic positions (basis vectors) of atoms i and j within the unit cell, $\mathbf{R}$ is a direct (Bravais) lattice vector, $c_{\alpha\beta\mu}(\hat{\mathbf{d}})$ are direction-cosine factors, l_α, l_β are angular-momentum quantum numbers, $\mu \in \{\sigma, \pi, \delta\}$ labels the bond symmetry, and the superscript (s) indicates the neighbor shell. For an *spd* basis, there are ten independent bond integrals per shell: $V_{ss\sigma}, V_{sp\sigma}, V_{pp\sigma}, V_{pp\pi}, V_{sd\sigma}, V_{pd\sigma}, V_{pd\pi}, V_{dd\sigma}, V_{dd\pi}$, and $V_{dd\delta}$.

B. Design-tensor representation

The linearity of $H_{\alpha\beta}^{\text{SK}}$ in the bond integrals motivates the introduction of a design tensor $M_{b\lambda\alpha\beta}^{(s)}$, where b indexes bonds in shell s and λ indexes the active SK parameters:

$$M_{b\lambda\alpha\beta}^{(s)} = c_{\alpha\beta\mu(\lambda)}(\hat{\mathbf{d}}_b), \quad (6)$$

where the active SK parameters are the subset of the ten independent two-center integrals $V_{ll'\mu}$ that are allowed for the orbital pair and shell being fitted (e.g., only the $ss\sigma, sp\sigma, \dots$, channels that exist for the given l, l'). The index λ is a single composite index that enumerates these active (l_α, l_β, μ) channels—i.e., it packs the (l, l', μ) triplet—so that $V_\lambda^{(s)}$ runs over exactly the active integrals in shell s . The full SK Bloch Hamiltonian can thus be written as

$$H_{\alpha\beta}^{\text{SK}}(\mathbf{k}) = \sum_p \varepsilon_p \Omega_{p,\alpha\beta} + \sum_{s=1}^{N_s} \sum_b e^{i\mathbf{k}\cdot\mathbf{R}_b} \sum_{\lambda} V_\lambda^{(s)} M_{b\lambda\alpha\beta}^{(s)}, \quad (7)$$

where $\Omega_{p,\alpha\beta}$ is a sparse on-site map tensor. The design tensor inherits a pronounced block-sparse structure: a bond connecting atoms i and j produces nonzero entries only in the orbital sub-block $\alpha \in \mathcal{O}_i$, $\beta \in \mathcal{O}_j$. We exploit this by grouping bonds into bond groups $\mathcal{G}_{ij}$ that share the same atom pair and operating on compact sub-blocks, yielding significant speedups for multiatom unit cells.

C. Environment-dependent screening

In the EDTB extension [10], each two-center hopping integral is modulated by an environment-dependent screening factor:

$$\tilde{V}_\lambda^{(s)}(i, j) = V_\lambda^{(s)} \exp(-\gamma_\lambda S_{ij}), \quad (8)$$

where S_{ij} is a bond screening sum and $\gamma_\lambda \geq 0$ is a screening strength parameter. The screening sum

$$S_{ij} = \sum_{k \neq i, j} f_c(d_{ik}) f_c(d_{jk}) \quad (9)$$

runs over all atoms k that are simultaneously close to both bond end points, with f_c a smooth cosine-tapered cutoff function:

$$f_c(d) = \begin{cases} 1, & d \leq r_{\text{taper}}, \\ \frac{1}{2} [1 + \cos(\pi \frac{d - r_{\text{taper}}}{r_{\text{cut}} - r_{\text{taper}}})], & r_{\text{taper}} < d < r_{\text{cut}}, \\ 0, & d \geq r_{\text{cut}}, \end{cases} \quad (10)$$

where r_{cut} is the cutoff radius and $r_{\text{taper}} = 0.8 r_{\text{cut}}$. The physical content of Eq. (8) is transparent: the more atoms surround a bond, the larger S_{ij} becomes, and the more strongly the hopping is screened. This mechanism captures, at the two-center level, the modification of covalent bonding by the local coordination environment.

The screening strengths γ_λ can be parametrized at three levels of granularity: (i) a single global γ shared by all channels (one parameter); (ii) one $\gamma_{l'}$ per angular-momentum pair (up to six parameters for spd); (iii) one γ_μ per independent SK bond integral (up to 10 parameters). The EDTB Bloch Hamiltonian thus reads

$$H_{\alpha\beta}^{\text{EDTB}}(\mathbf{k}) = \sum_p \varepsilon_p \Omega_{p,\alpha\beta} + \sum_{s,b} e^{i\mathbf{k} \cdot \mathbf{R}_b} \times \sum_\lambda V_\lambda^{(s)} e^{-\gamma_{q(\lambda)} S_b} M_{b\lambda\alpha\beta}^{(s)}, \quad (11)$$

where $q(\lambda)$ maps each hopping parameter to the appropriate screening index.

Optionally, on-site energies can be made environment-dependent through coordination-dependent shifts:

$$\tilde{\varepsilon}_\alpha = \varepsilon_\alpha + \eta_\alpha C_i, \quad C_i = \sum_{k \neq i} f_c(d_{ik}), \quad (12)$$

where η_α is a shift parameter and C_i is the effective coordination number of atom i .

D. Distance-dependent hopping functions

The discrete-shell model assigns independent hopping parameters $V_\lambda^{(s)}$ to each shell. For systems with continuously

varying bond lengths we replace the shell-resolved parameters with a Goodwin-Skinner-Pettifor functional form [6]:

$$V_\lambda(r) = V_{0,\lambda} \left(\frac{r_0}{r} \right)^{n_\lambda} \times \exp \left[n_\lambda \left(- \left(\frac{r}{r_c} \right)^{n_c} + \left(\frac{r_0}{r_c} \right)^{n_c} \right) \right], \quad (13)$$

where $V_{0,\lambda}$ is the hopping amplitude at the reference distance r_0 , $n_\lambda > 0$ is a per-channel decay exponent, r_c is the cutoff radius, and $n_c > 0$ is a shared cutoff steepness. As r increases, the exponential factor ensures a rapid and smooth decay to zero and $V_\lambda(r_0) = V_{0,\lambda}$ by construction.

The screened distance-dependent Bloch Hamiltonian becomes

$$H_{\alpha\beta}^{\text{DD}}(\mathbf{k}) = \sum_p \varepsilon_p \Omega_{p,\alpha\beta} + \sum_b e^{i\mathbf{k} \cdot \mathbf{R}_b} \times \sum_\lambda V_\lambda(d_b) e^{-\gamma_{q(\lambda)} S_b} M_{b\lambda\alpha\beta}. \quad (14)$$

A natural initialization for the distance-dependent fit is obtained from an existing discrete-shell fit: for each channel λ , $V_\lambda^{(1)}$ sets $V_{0,\lambda}$, and the decay exponent n_λ is estimated from the ratio of first- and second-shell hoppings.

E. Multiparameter model for complex geometries

To model systems with chemically distinct environments—surfaces, interfaces, or multispecies systems such as alloys or heterostructures—we generalize the EDTB Hamiltonian to a multiparameter framework. Each atom is assigned an environment label ℓ_i (e.g., “bulk,” “surface,” or a species identifier) and the hopping parameters for a bond connecting atoms i and j are selected as

$$V_{ij}^{(\text{bond})} = \begin{cases} V^{(\ell_i)} & \text{if } \ell_i = \ell_j, \\ \mathcal{M}(V^{(\ell_i)}, V^{(\ell_j)}) & \text{if } \ell_i \neq \ell_j, \end{cases} \quad (15)$$

where $\mathcal{M}$ denotes a mixing operator for interface bonds. We employ by default the geometric mean, $\mathcal{M}_{\text{geo}}(a, b) = \text{sgn}(a+b) \sqrt{|ab|}$, which preserves the sign structure of the SK integrals. Arithmetic and first-label mixing are also available. On-site energies are selected by each atom’s own label and chemical species.

This multiparameter framework enables the construction of Hamiltonians for systems substantially larger than the DFT training cells—for instance, thick slabs, long-period superlattices, or multicomponent heterostructures—by combining a small number of independently or jointly fitted parameter sets, each trained on a manageable unit cell, and assembling them according to the environment labels and mixing rules defined above. Because the screening functions and hopping parameters are transferable across local environments, no additional DFT calculations are required for the target system.

IV. FITTING PROCEDURE

A. Objective function

The model parameters $\mathbf{p}$ are determined by minimizing the root-mean-square eigenvalue error over a uniform

Brillouin-zone mesh:

$$\text{rmse}(\mathbf{p}) = \left[\frac{1}{N_k N_b} \sum_{\mathbf{k}} \sum_{n=1}^{N_b} (\varepsilon_{n\mathbf{k}}^{\text{SK}} - \varepsilon_{n\mathbf{k}}^{\text{PAO}})^2 \right]^{1/2}. \quad (16)$$

The objective in Eq. (16) is evaluated on a uniform Brillouin-zone mesh, chosen explicitly for each system (Pt 12^3 , bulk Si 6^3 , Si slabs $6 \times 6 \times 1$, and graphene 18^2); all these uniform meshes include the Γ point. Because the fit targets the full eigenvalue spectrum over a dense uniform mesh—rather than only high-symmetry eigenvalues—band curvature near the band edges is constrained implicitly. Similarly to other TB fitting implementations [17–19], minimization is performed with the Levenberg-Marquardt algorithm [20,21], which requires the Jacobian matrix $J_{m,j} = \partial r_m / \partial p_j$ of the residual vector. The residual vector $\mathbf{r}(\mathbf{p})$ collects the individual eigenvalue mismatches that the objective in Eq. (16) drives to zero. Each entry is a single band– k -point residual,

$$r_m(\mathbf{p}) = \varepsilon_{n\mathbf{k}}^{\text{SK}}(\mathbf{p}) - \varepsilon_{n\mathbf{k}}^{\text{PAO}}, \quad m \equiv (n, \mathbf{k}), \quad (17)$$

where the composite index m runs over all N_b retained bands and all N_k mesh points, so that $\mathbf{r}$ has length $N_k N_b$ and $\text{rmse}(\mathbf{p}) = \|\mathbf{r}(\mathbf{p})\|_2 / \sqrt{N_k N_b}$. Only the SK eigenvalues $\varepsilon_{n\mathbf{k}}^{\text{SK}}$ depend on the parameters $\mathbf{p}$; the PAO targets $\varepsilon_{n\mathbf{k}}^{\text{PAO}}$ are fixed reference data, which is what makes Eq. (18) an exact analytic Jacobian. The fit target $\varepsilon_{n\mathbf{k}}^{\text{PAO}}$ in Eq. (16) is the PAO band structure of Sec. II B, i.e., the eigenvalues obtained by diagonalizing the reconstructed Bloch PAO Hamiltonian $H(\mathbf{k})$ [Eq. (4)], which is built from $\bar{H}$ [Eq. (3)] via the inverse-Fourier transform and Bloch sum.

B. Analytic Jacobian via the Hellmann-Feynman theorem

The derivative of each eigenvalue with respect to any parameter p_j is computed analytically from the Hellmann-Feynman theorem:

$$\frac{\partial \varepsilon_{n\mathbf{k}}}{\partial p_j} = \langle n\mathbf{k} | \frac{\partial H(\mathbf{k})}{\partial p_j} | n\mathbf{k} \rangle. \quad (18)$$

For on-site energies, $\partial \varepsilon_{n\mathbf{k}} / \partial \varepsilon_p = \sum_{\alpha \in p} |\psi_{n\mathbf{k}}^\alpha|^2$. For hopping parameters,

$$\frac{\partial H_{\alpha\beta}}{\partial V_\lambda^{(s)}} = \sum_b e^{i\mathbf{k} \cdot \mathbf{R}_b} e^{-\gamma_q(\lambda) S_b} M_{b\lambda\alpha\beta}^{(s)}. \quad (19)$$

For screening strengths,

$$\frac{\partial H_{\alpha\beta}}{\partial \gamma_q} = - \sum_{s,b} e^{i\mathbf{k} \cdot \mathbf{R}_b} \sum_{\lambda: q(\lambda)=q} V_\lambda^{(s)} S_b e^{-\gamma_q S_b} M_{b\lambda\alpha\beta}^{(s)}. \quad (20)$$

Analogous expressions hold for the distance-dependent parameters $V_{0,\lambda}$, n_λ , and n_c , obtained via the chain rule applied to Eq. (13).

The analytic Jacobian avoids finite-difference approximations entirely, providing both speed and numerical stability. All derivatives are evaluated from the same eigenvector matrix used for the forward model, at negligible additional cost.

Alternative optimization strategies have been employed for TB parameter fitting, including genetic algorithms [22–24] and active-learning-driven iterative schemes [25]. Derivative-free methods such as genetic algorithms or simulated

annealing are attractive for their ability to explore rugged landscapes and avoid local minima, but they typically require 10^4 – 10^6 objective-function evaluations and scale poorly with the number of parameters. Active-learning approaches [25] iteratively expand the training set by testing model predictions against new DFT calculations, effectively addressing the data-generation problem rather than the optimization itself. Our approach is complementary: the availability of analytic Jacobians makes each Levenberg-Marquardt iteration inexpensive, so convergence is reached in $O(10^2)$ iterations even for 30–40 parameters. We compensate for the susceptibility of gradient-based methods to local minima through multistart optimization, which remains efficient because each individual run is fast.

C. Regularization

To suppress unphysical oscillations in the hopping parameters—a strategy also adopted in recent TB parametrization work [23,26,27]—we optionally augment the residual vector with Tikhonov penalty terms:

$$\tilde{r}_m(\mathbf{p}) = \begin{cases} r_m(\mathbf{p}), & m = 1, \dots, N_k N_b, \\ \alpha w_j p_j, & m = N_k N_b + j, \end{cases} \quad (21)$$

where α is the regularization strength and w_j are parameter-class weights. The first $N_k N_b$ rows are the eigenvalue residuals of Eq. (17); the appended rows add one Tikhonov penalty $\alpha w_j p_j$ per parameter, so the augmented residual vector has length $N_k N_b + N_p$ (N_p is the number of parameters). This is the standard ridge/Tikhonov penalty $\alpha^2 \sum_j w_j^2 p_j^2$ on the parameter norm and it controls the bias-variance trade-off of the fit: $\alpha = 0$ minimizes only the band error (low bias, but high variance, i.e., parameters free to take large, oscillatory, environment-sensitive values), whereas increasing α shrinks the parameters toward zero (higher bias, lower variance), suppressing overfitting at the cost of a slightly larger training RMSE. The per-class weights w_j make this penalty dimensionally consistent and physically targeted: on-site energies, hopping integrals $V_{ll'\mu}$, screening strengths γ , and the Goodwin exponents carry different units and natural magnitudes, so w_j is chosen per parameter class to penalize each on its own scale and to bear down more strongly on the loosely constrained channels. In practice α is kept small enough that the test-set RMSE (Sec. V A) is not degraded, confirming that regularization removes spurious flexibility without sacrificing transferability.

D. Multigeometry training

For a single crystal geometry, the screening parameters γ_λ are partially redundant with the shell-dependent hopping integrals: the uniform coordination in a perfect crystal renders S_{ij} identical for all symmetry-equivalent bonds, so any constant screening can be absorbed into the hoppings. The power of the EDTB formalism emerges when a single shared parameter set is fitted simultaneously to band structures from N_g configurations with different coordination environments [3].

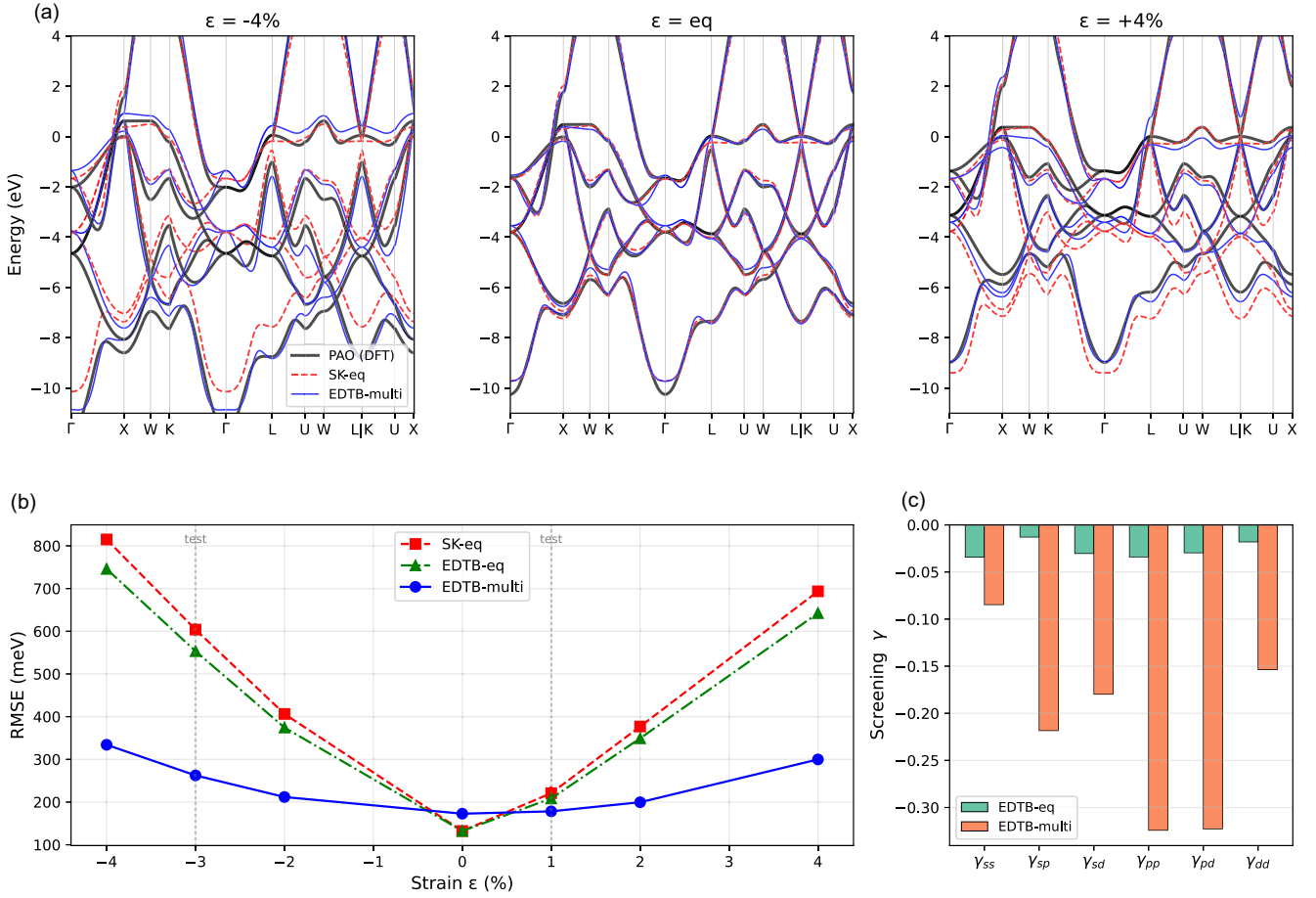


FIG. 1. FCC platinum volume-scan results. (a) Band structures at $\epsilon = -4\%$ (left), equilibrium (center), and $+4\%$ (right); black: PAO reference; red dashed: SK-eq; blue: EDTB-multi. (b) RMSE vs strain for the three models; gray lines mark the test volumes. (c) Fitted screening strengths $\gamma_{ll'}$ for EDTB-eq (green) and EDTB-multi (orange).

The combined residual vector is

$$\tilde{\mathbf{r}}(\mathbf{p}) = \begin{pmatrix} w_1 \mathbf{r}^{(1)}(\mathbf{p}) \\ \vdots \\ w_{N_g} \mathbf{r}^{(N_g)}(\mathbf{p}) \end{pmatrix}, \quad (22)$$

where w_g are per-geometry weights. The Jacobian is assembled by vertical concatenation of the per-geometry Jacobians.

We employ the following fitting protocol: (1) a standard SK fit (without screening) at the equilibrium geometry to obtain initial two-center parameters; (2) a multigeometry EDTB fit initialized with the stage-1 parameters and small random screening values. Multistart optimization (multiple independent Levenberg-Marquardt runs from random initial points) is used to guard against local minima.

V. APPLICATIONS

A. FCC platinum

As a first demonstration, we consider FCC platinum with an *spd* basis (nine orbitals per atom) and three neighbor shells and an equilibrium lattice parameter $a_0 = 3.93$ Å. The PAO Hamiltonian is constructed with PAOFLOW from

a 12^3 k mesh. Self-consistent DFT calculations are performed at seven isotropic volumes spanning strains $\epsilon \in \{-4\%, -3\%, -2\%, 0\%, +1\%, +2\%, +4\%\}$. Five volumes ($\epsilon = -4\%, -2\%, 0\%, +2\%, +4\%$) constitute the training set; two ($\epsilon = -3\%, +1\%$) are held out for blind testing. These two volumes are never seen by the optimizer and therefore provide a genuine out-of-sample test of transferability beyond the *training manifold*—the set of coordination environments S_{ij} and bond lengths spanned by the training geometries. We expect the model to transfer to environments lying within or near this span; the $\epsilon = -3\%$ and $+1\%$ volumes interpolate within the sampled bond-length range and thus probe exactly this regime.

We compare three models, all sharing the same orbital basis: (i) SK-eq: a standard SK fit trained only at equilibrium (34 parameters: four on-site energies, 30 hoppings); (ii) EDTB-eq: an EDTB fit with per- ll' screening, also trained at equilibrium only (40 parameters); (iii) EDTB-multi: an EDTB fit trained simultaneously on all five training volumes (40 parameters). Figure 1(a) compares the band structures and shows how, at $\epsilon = \pm 4\%$, visible deviations appear in the SK-eq d -band manifold, while the EDTB-multi model tracks the PAO reference closely across the entire Brillouin

TABLE I. Per-volume RMSE (meV) for FCC platinum. “Train” and “test” indicate whether the volume was used in the multigeometry fit.

Strain	Type	SK-eq	EDTB-eq	EDTB-multi
−4%	Train	815	746	334
−3%	Test	604	553	262
−2%	Train	406	375	212
eq	Train	132	132	173
+1%	Test	221	208	178
+2%	Train	377	349	200
+4%	Train	694	642	300
Combined (RMS)		519	478	244
Test only		455	418	224
No. parameters		34	40	40

zone. Figure 1(b) shows the RMSE vs strain data from Table I while Fig. 1(c) displays the screening γ ’s for the two EDTB fitting procedures. The fitted screening strengths from the multigeometry fit display a clear angular-momentum hierarchy ($|\gamma_{pp}| \approx |\gamma_{pd}| > |\gamma_{sp}| > |\gamma_{sd}| > |\gamma_{dd}| > |\gamma_{ss}|$), with the largest values for p – p and p – d interactions, which are the most sensitive to coordination changes. These physically meaningful screening strengths emerge only when the optimizer is forced to fit multiple volumes simultaneously.

Table I reports the RMSE at each volume. At equilibrium, all three models achieve comparable accuracy (~ 130 – 170 meV). Away from equilibrium, the models diverge sharply: the SK-eq RMSE reaches 815 meV at -4% strain, while the EDTB-multimodel maintains sub-350 meV accuracy across the entire $\pm 4\%$ range. The combined RMSE is reduced from 519 meV (SK-eq) to 244 meV—a factor of 2 improvement. Crucially, the two test volumes show the same trend (test RMSE reduced from 455 meV to 224 meV), confirming genuine transferability rather than overfitting. We stress that this halving of the error occurs on volumes that were entirely excluded from the fit: the test-only RMSE drops from 455 meV (SK-eq) to 224 meV (EDTB-multi) (Table I),

so the improvement reflects genuine extrapolation onto unseen coordination environments rather than a denser fit of the training data. This blind out-of-sample agreement is the central quantitative evidence that the fitted parameters remain robust within the training manifold defined above.

A key advantage of the EDTB parametrization is that the resulting Hamiltonian is fully compatible with the PAOFLOW postprocessing pipeline. To illustrate this, we augment the EDTB-multi model with *ad hoc* atomic spin-orbit coupling (SOC),

$$H_{\text{SOC}} = \sum_{i,l} \xi_l^{(i)} \mathbf{L}_i \cdot \mathbf{S}_i, \quad (23)$$

using $\xi_p = 0.553$ eV for the dominant p -channel contribution in Pt [28]. The SOC doubles the Hilbert-space dimension and lifts band degeneracies throughout the Brillouin zone, as seen in Figs. 2(a) and 2(b) for the band structure and density of states.

Having a fully SOC Hamiltonian allows us to calculate, for instance, the intrinsic spin Hall conductivity (SHC) from the Kubo formula [4,5,29],

$$\sigma_{xy}^z = \frac{e}{\hbar} \sum_n \int_{\text{BZ}} \frac{d^3k}{(2\pi)^3} f_{n\mathbf{k}} \Omega_{n,xy}^z(\mathbf{k}), \quad (24)$$

where $\Omega_{n,xy}^z(\mathbf{k})$ is the spin Berry curvature. Figure 2(c) shows the resulting SHC as a function of Fermi energy. These results are in good agreement with first-principles relativistic calculations [4,5,30,31], demonstrating that the EDTB model augmented with *ad hoc* SOC captures the essential physics of spin-orbit-driven transport.

B. Silicon surfaces

The silicon EDTB model uses an *spd* basis (nine orbitals/atom) with three neighbor shells. The model is trained simultaneously on four geometries: bulk diamond Si (6^3 k mesh, weight $w = 2.0$) and three unrelaxed, unpassivated eight-atom slabs for the (001), (110), and (111) surfaces ($6 \times 6 \times 1$ k mesh, $w = 1.0$ each). The elevated bulk weight ensures accurate bulk band structure reproduction, while the

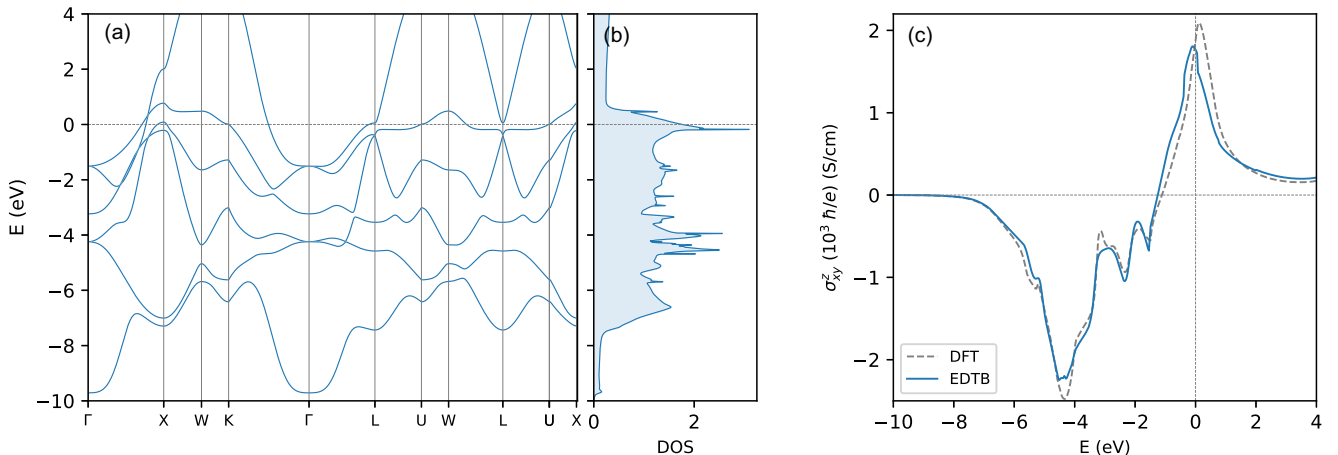


FIG. 2. EDTB model for FCC Pt with *adhoc* SOC, processed through the full PAOFLOW pipeline. (a) Band structure showing SOC-induced splittings. (b) Density of states. (c) Intrinsic spin Hall conductivity $\sigma_{xy}^z(E)$.

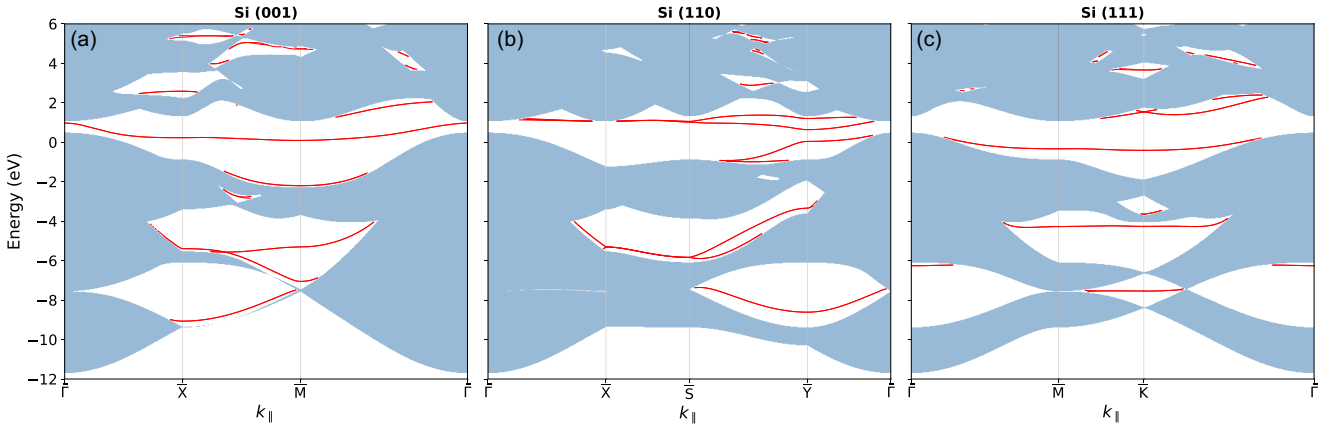


FIG. 3. Projected bulk band structure (blue shaded) and surface states (red) for three silicon surfaces: (a) Si(001), (b) Si(110), and (c) Si(111) 40-atom unrelaxed, unpassivated slabs.

surface slabs provide the coordination variation needed to constrain the screening. The total parameter count is 40 (34 SK + 6 screening).

The multigeometry training yields screening strengths of significantly larger magnitude compared to bulk-only fitting—in particular, the *sd* and *pd* screening strengths increase by more than an order of magnitude, indicating that *d*-orbital hybridization at the surface is substantially modified by the reduced coordination.

To build thick slabs larger than the DFT training cells, we adopt a dual-parameter approach: each atom is classified as “bulk” or “surface” based on its coordination and the Hamiltonian matrix elements are constructed using the fitted EDTB parameters with the local S_{ij} values. For bonds bridging different environments, hopping parameters are mixed using the geometric-mean rule. We apply this model to 40-atom slabs for each surface orientation.

Figure 3 shows the results for all three low-index surfaces. The projected bulk bands (shaded regions) correctly reproduce the expected bulk gaps and slab states in the projected gaps are observed for all orientations. While the unrelaxed, unpassivated slab geometries preclude quantitative comparison with experiment, this calculation demonstrates that the EDTB multigeometry framework combined with dual-parameter slab construction provides a fast, physically transparent approach to modeling surface electronic structure.

C. Si/Ge [001] superlattices

As a test of the multiparameter framework for binary heterostructures, we consider Si/Ge [001] superlattices. An EDTB model is first fitted to a 16-atom Si_8Ge_8 training cell using an *spd* basis (nine orbitals/atom) with three neighbor shells and per- ll' screening. Each atom in the prediction superlattice is classified as Si_{bulk} , Ge_{bulk} , or interface (any atom with a cross-species nearest neighbor) and the multiparameter Hamiltonian is assembled using geometric-mean mixing at the interface.

Realistic band offsets are introduced through rigid on-site energy shifts applied to the Ge orbitals: $\Delta\epsilon_p^{\text{Ge}} = \text{VBO}_{\text{target}} = 1.05$ eV and $\Delta\epsilon_s^{\text{Ge}} = \text{CBO}_{\text{target}} = 0.0$ eV, chosen to reproduce

the valence band alignment of Ge strained to the Si lattice constant [32]. Layer-resolved projected densities of states for the 32-atom $\text{Si}_{16}\text{Ge}_{16}$ superlattice [Fig. 4(a)] display a valence band offset $\text{VBO} = \text{VBM}_{\text{Si}} - \text{VBM}_{\text{Ge}} \approx 0.5$ eV and a conduction band offset $\text{CBO} = \text{CBM}_{\text{Si}} - \text{CBM}_{\text{Ge}} \approx 0.2$ eV,

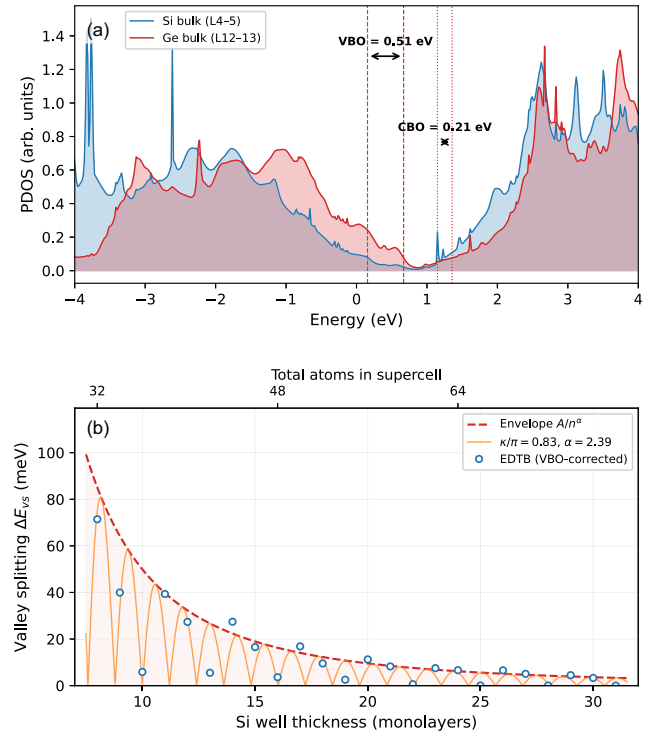


FIG. 4. Band offsets and valley splitting in Si/Ge [001] superlattices. (a) Layer-resolved PDOS for bulklike Si (blue) and Ge (red) layers of the $\text{Si}_{16}\text{Ge}_{16}$ superlattice, with extracted VBM (dashed) and CBM (dotted) positions indicating the valence band offset (VBO ≈ 0.5 eV) and conduction band offset (CBO ≈ 0.2 eV). (b) Valley splitting ΔE_{vs} vs Si well thickness for Si_n/Ge_8 ($n = 8\text{--}31$ ML). Open circles: EDTB data; solid curve: fit to Eq. (25); dashed line: power-law envelope. The oscillation period $\kappa/\pi \approx 0.83$ matches the bulk Si Δ -valley position.

consistent with the expected type-II band alignment at the strained Si/Ge [001] interface. The spatial separation of Si-like and Ge-like electronic states confirms that the multiparameter framework correctly propagates the on-site energy differences into the superlattice Hamiltonian.

An important observable in Si/Ge heterostructures is the valley splitting ΔE_{vs} —the energy difference between the two lowest conduction-band states at Γ that descend from the bulk Si Δ -valley pair folded onto the zone center by the [001] periodicity. We compute ΔE_{vs} for a systematic series of Si_n/Ge_8 superlattices with Si well thickness $n = 8\text{--}31$ monolayers (ML) in steps of 1 ML, covering systems up to 78 atoms. The Ge barrier is fixed at 8 ML; when the total monolayer count is not divisible by 4, additional Ge monolayers are appended to close the supercell, with negligible effect on the splitting.

The computed valley splitting [Fig. 4(b)] oscillates rapidly with well width and decays with a power-law envelope, consistent with established results [33,34]. A nonlinear least-squares fit to

$$\Delta E_{vs}(n) = \frac{A}{n^\alpha} |\cos(\kappa n + \varphi)| \quad (25)$$

yields envelope exponent $\alpha = 2.4 \pm 0.4$ and oscillation wave vector $\kappa/\pi = 0.83 \pm 0.01$ ($R^2 = 0.80$). The oscillation period matches the position of the bulk Si Δ -valley minimum at $\sim 0.85 (2\pi/a)$ along Γ -X, confirming that the EDTB model correctly captures the zone-folding origin of the splitting. The power-law exponent $\alpha \approx 2.4$ reflects the rapid suppression of intervalley coupling with increasing well width, in qualitative agreement with the expected trend for sharp-interface heterostructures [33].

This application demonstrates that the multiparameter EDTB framework extends naturally to binary heterostructures: the combination of a single prefit on a small training geometry, environment-based labeling, and targeted on-site shifts provides a lightweight approach to modeling band offsets and valley splittings without additional DFT calculations for each superlattice period. The monolayer-resolution sweep over 24 well widths completes in under two minutes on a single core, illustrating the efficiency of the approach for systematic parameter-space exploration.

D. Twisted bilayer graphene

The most demanding application targets twisted bilayer graphene (TBG), where the electronic structure depends sensitively on the interlayer coupling, which varies continuously across the moiré unit cell as the local stacking interpolates between AA and AB regions. We construct an EDTB model with *spd* basis (nine orbitals/atom) fitted simultaneously to nine training geometries: monolayer graphene, five AB-stacked bilayers at interlayer separations $d = 3.00, 3.20, 3.35, 3.50$, and 3.70 Å, and three AA-stacked bilayers at $d = 3.00, 3.35$, and 3.70 Å. All DFT calculations use PBE with a $18^2 \times 1$ k grid.

The critical ingredient is the distance-dependent Goodwin hopping form of Eq. (13) with reference distance $r_0 = 1.42$ Å and cutoff $r_c = 5.29$ Å, which enables continuous interpolation of the interlayer coupling. The complete parameter set (four on-site energies, 10 amplitudes $V_{0,\lambda}$, 10 exponents

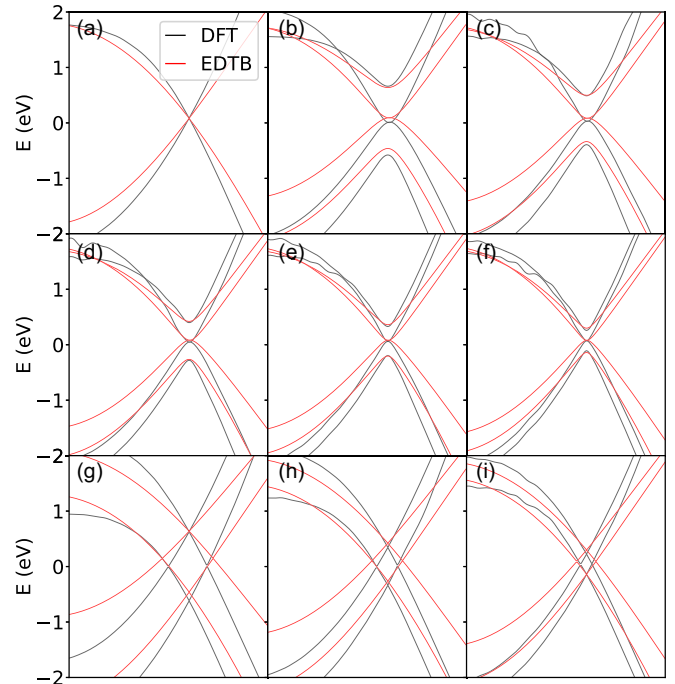


FIG. 5. EDTB (red) vs DFT (black) near the K point for the nine training geometries. (a) Monolayer; (b)–(f) AB bilayer; (g)–(i) AA bilayer.

n_λ , one cutoff steepness n_c , six screening constants γ_{ll} —31 parameters) is determined by a simultaneous Levenberg-Marquardt fit. Besides some deviation away from the Dirac cone region, the model reproduces the Dirac-cone dispersion, band splitting, and the distinct electronic signatures of AB and AA stacking across the full range of interlayer separations (Fig. 5).

To demonstrate scalability, we compute band structures for three commensurate TBG supercells: (6,5) with $\theta = 6.01^\circ$ (364 atoms), (10,9) with $\theta = 3.48^\circ$ (1084 atoms), and (20,19) with $\theta = 1.70^\circ$ (4324 atoms). The corresponding Hilbert-space dimensions are $n_{\text{awf}} = 3276, 9756$, and $38\,916$. In the three geometries the graphene atoms in the individual planes are not relaxed.

Solving the eigenvalue problem for Hamiltonians of such large dimensions is not practical using traditional dense eigensolvers. We adopt a strategy that exploits the intrinsic sparseness of the EDTB Hamiltonian using on-the-fly bond enumeration with the fitted distance-dependent and screening parameters with no reparametrization required. At each of the 80 k points along the moiré Brillouin-zone path, the 40 eigenvalues nearest the shift-invert target $\sigma = 0.0$ eV (Dirac point) are extracted via the implicitly restarted Lanczos algorithm [35,36]. This approach reduces the memory footprint from ~ 11 GB (dense) to ~ 250 MB (sparse) for the largest system.

Figure 6 shows the results. For the (6,5) supercell, folded Dirac cones are clearly resolved. At $\theta = 3.48^\circ$ [(10,9)], increased interlayer hybridization produces a dense manifold of flat bands with reduced bandwidth. For the (20,19) supercell at $\theta = 1.70^\circ$ —approaching the magic angle—the spectrum near the Fermi level is dominated by nearly flat bands with

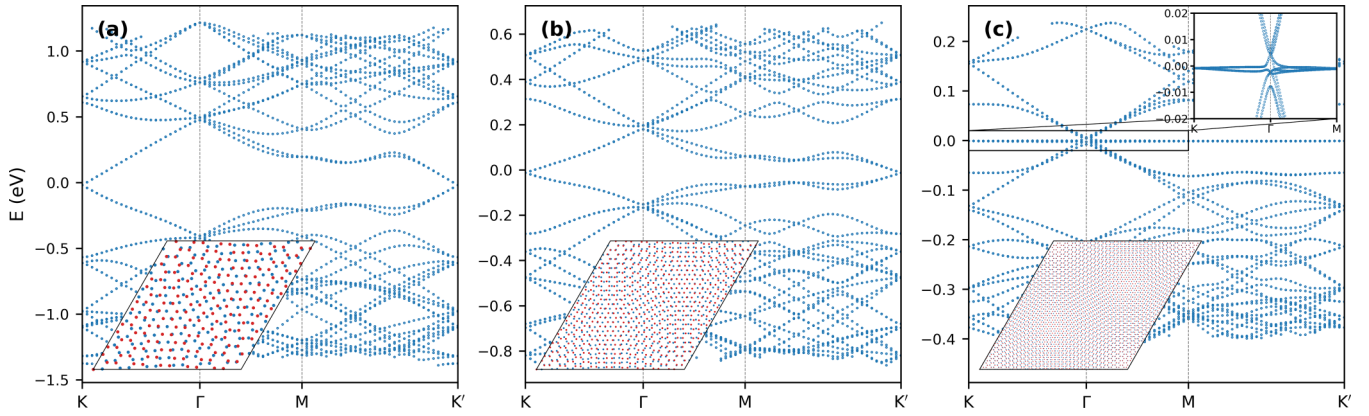


FIG. 6. Sparse Lanczos band structure of TBG along $K\text{--}\Gamma\text{--}M\text{--}K'$ for three supercells: (a) (6,5), $\theta = 6.01^\circ$, 364 atoms; (b) (10,9), $\theta = 3.48^\circ$, 1084 atoms; (c) (20,19), $\theta = 1.70^\circ$, 4324 atoms. 40 eigenvalues nearest $E = 0.0$ eV are plotted per k point. Insets in (a), (b), and (c) on the bottom left show the moiré unit cell; the inset in (c) on the top right is a magnified view of the low-energy region around $E = 0.0$ eV, resolving the nearly flat band manifold of $\sim 10\text{--}20$ meV bandwidth.

bandwidth $\sim 10\text{--}20$ meV, consistent with the expected flattening of the low-energy spectrum in the small-angle regime [37].

The scalability of the sparse EDTB approach is summarized in Table II. The sparsity of the Hamiltonian—arising from the finite hopping cutoff—yields memory and time scaling that is approximately linear in N_{at} for fixed numbers of target eigenvalues, making systems with $n_{\text{awf}} \sim 10^5$ accessible on a single workstation.

These results connect naturally to a substantial body of earlier tight-binding work on TBG. The band-folding picture of the low-energy spectrum and the progressive flattening of the lowest bands with decreasing twist angle were established already by Moon and Koshino [38], who employed a p_z -orbital Slater-Koster model with distance-dependent $V_{pp\sigma}$ and $V_{pp\pi}$ transfer integrals—of the same exponential form adopted here—to compute the spectra of rigidly twisted, unrelaxed bilayers across a range of commensurate angles. Our EDTB results reproduce the same phenomenology (folded Dirac cones, a van Hove-dominated intermediate regime, and a nearly flat low-energy manifold near the magic angle), but now from a single transferable *spd* parameter set fitted to PAO eigenvalues rather than a p_z -only model tuned to graphite. More recently, our findings are in agreement with the local-environment tight-binding study of Pathak *et al.* [39], who showed that the low-energy flat bands of TBG—including the magic-angle flattening—can be reproduced without invoking geometric relaxation, i.e., for rigidly twisted layers. Our unrelaxed supercell calculations are entirely consistent with this picture, as resolved in the magnified low-energy inset of Fig. 6(c). We emphasize, moreover, how economical

the present parametrization is by comparison: Pathak *et al.* fit their model to a training set of 72 distinct deformed bilayer-graphene configurations (shifted, strained, sheared, and randomly displaced primitive cells), whereas our EDTB model is fit to only nine training geometries (monolayer graphene, five AB-stacked bilayers, and three AA-stacked bilayers at a few interlayer separations) with a total of 31 parameters. This result provides strong evidence both for the transferability of the PAO-derived EDTB parametrization and for the quantitative validity of the present TBG results.

VI. CONCLUSIONS

We have presented a comprehensive framework for constructing environment-dependent tight-binding models from *ab initio* pseudoatomic orbital Hamiltonians. The method builds upon the Slater-Koster two-center approximation, augmented with bond-screening functions that capture the influence of the local atomic environment on the electronic structure. By fitting to the eigenvalue spectrum of the PAO Hamiltonian, our approach avoids the gauge ambiguities inherent in Wannier-function-based downfolding while preserving the symmetry and orbital character of the *ab initio* representation. The resulting models are remarkably compact: Pt has 40 parameters, Si 40, the Si/Ge per-species sets ~ 40 , and TBG 31—i.e., $O(30\text{--}40)$ numbers per model. This method enables large-scale simulations of the electronic, optical, and transport properties of materials systems with DFT accuracy at a fraction of the computational cost.

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TABLE II. TBG supercell sizes and memory requirements.

(n, m)	θ (deg)	N_{at}	n_{awf}	Sparse (MB)	Dense (GB)
(3,2)	13.17	76	684	0.1	0.004
(6,5)	6.01	364	3,276	2	0.08
(10,9)	3.48	1,084	9,756	6	0.7
(20,19)	1.70	4,324	38,916	25	11

Copilot (Claude Opus 4.6 [40], Anthropic), an AI-powered programming assistant integrated into the Visual Studio Code development environment.

All scientific decisions—including model design, choice of physical approximations, parameter selection, interpretation of results, and writing of the paper—were made by the author.

DATA AVAILABILITY

The complete EDTB fitting and Hamiltonian construction code is implemented as a module within the PAOFLOW package at [41] (and `pip install paoflow`) and the code, corresponding data and EDTB parameters sets needed to reproduce the presented results are available at [42].

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