

## Interatomic Potential Function:

Given nuclear types  $\{Z_i\}$  and positions  $\{R_i\}$ , there exists an electronic ground state  $|\Psi\rangle_{el}$ , which leads to total energy  $V(R_1, R_2, \dots, R_N)$ .  $V$  is called the interatomic potential. The Born-Oppenheimer approximation states that the nuclei move as if sitting on such an energy surface.

- Molecular dynamics simulation relies heavily on accurate and fast evaluations of  $V$ .

## First Principle Electronic Structure Approach:

Expand  $|\Psi\rangle_{el}$  into plane waves and calculate  $V$  using QM. The electron-electron interactions are usually simplified by the Local Density Approximation (LDA).

- No adjustable parameters
- Universal
- Very accurate ( $< 5\%$ )
- Very expensive (upper limit: 1000 atoms)

## Semi-empirical Interatomic Potential:

Directly fit  $V$  as a function of  $\{R\}$  to experimental and LDA data using physically inspired functional form.

- Affordable developmental cycle
- Very cheap usage
- Not as accurate
- Less transferable, lacks in predictive power

Example: the highly successful Tersoff potential for Si/C/Ge systems (1989).

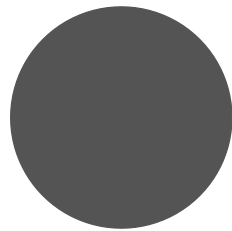
## First Principle Approach:

- Bulk crystalline / liquid / amorphous systems
  - Point defects
  - Surfaces, (grain boundaries)
  - Specialty: electronic and optical properties
- 

## Semi-empirical Approach:

- Polymers; alloy design
- Large defects (grains, dislocations)
- Slow dynamics and non-equilibrium processes
- Specialty: mechanical behavior

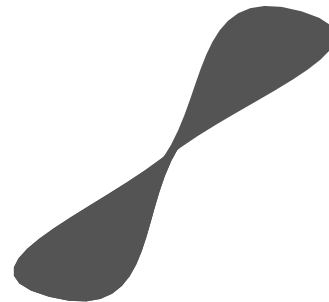
The Tight-Binding (TB) approach is a simplified version of LDA: it deals with electronic wave function  $|\Psi\rangle_{el}$ , but only expanding it in a small set of local orbitals.



$|S\rangle$



$|P_x\rangle$



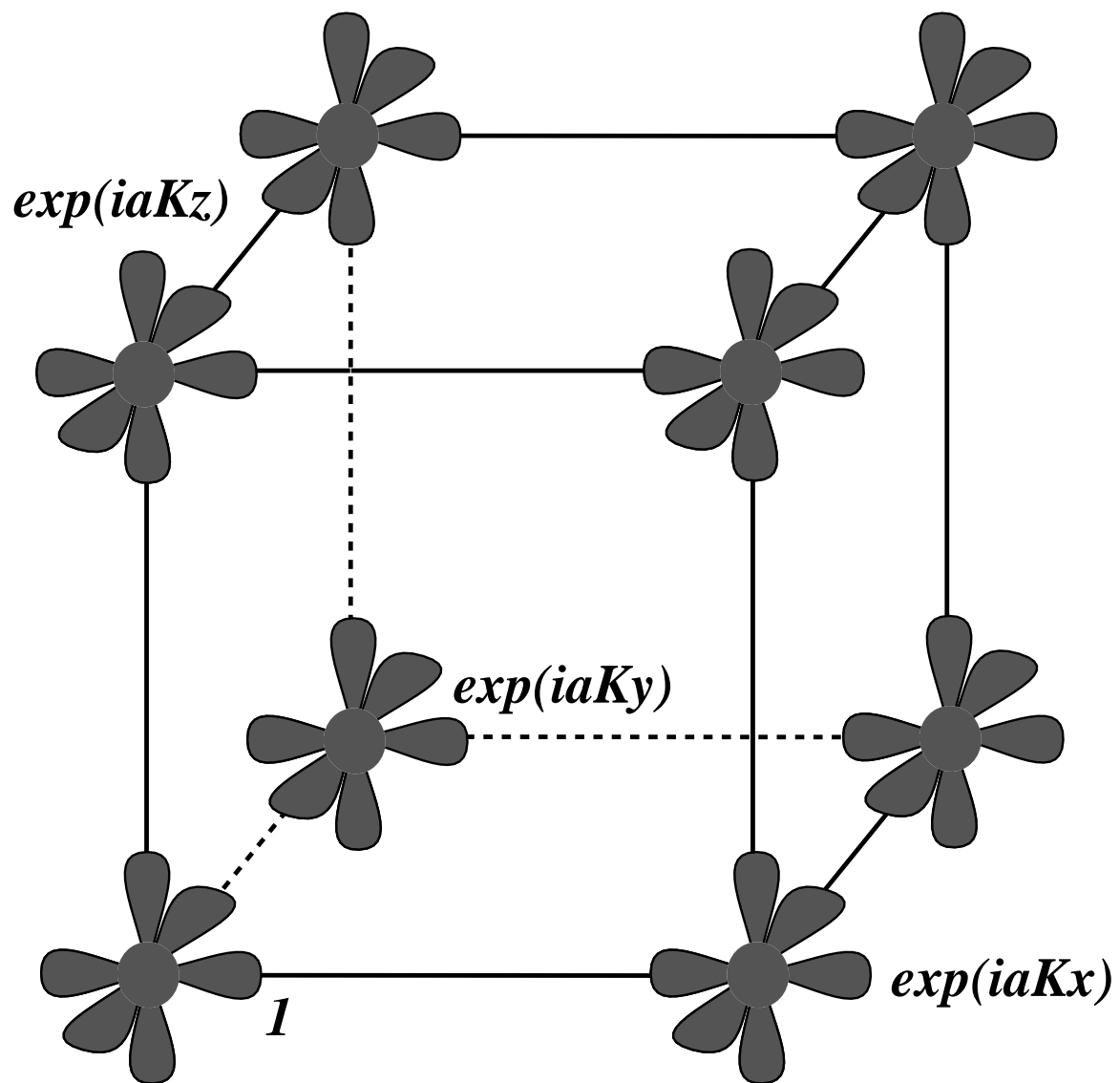
$|P_y\rangle$



$|P_z\rangle$

Valence Orbitals of

Si, C



*Linear Combination*

*of Atomic Orbitals*

The TB total energy  $V(\{R\})$  is written as

$$V = \sum_i^{\text{occ}} \langle \psi_i | \mathcal{H}^{el}(\{R\}) | \psi_i \rangle + V_{rep}(\{R\}), \quad (1)$$

where  $i$  sums over all valence electron eigenstates below the Fermi level.  $V_{rep}$  is the energy residual which does not depend on  $|\Psi\rangle_{el}$ . With  $|\psi_i\rangle$ 's expanded in local orbitals,

$$|\psi_i\rangle = \sum_n^N \sum_{\lambda=1}^4 a_i^{n\lambda} |\phi_{n\lambda}\rangle,$$

$\mathcal{H}^{el}(\{R\})$  is a  $4N \times 4N$  matrix which is to be diagonalized. (1) can be shown to be a first-order or “non-selfconsistent” approximation to the LDA total energy.

- TB is  $10^2$ - $10^3$  times faster than LDA simply because a  $4N \times 4N$   $\mathcal{H}^{el}$  is much easier to diagonalize than a  $40N \times 40N$   $\mathcal{H}^{el}$ , if it is expanded in a plane-wave basis.

---

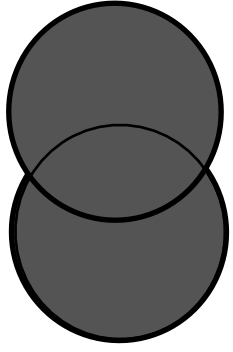
- By symmetry, there are only 4 basic interactions (“hopping integrals”) between  $s$  and  $p$  orbitals:  $ss\sigma$ ,  $sp\sigma$ ,  $pp\sigma$ ,  $pp\pi$ . Once their strengths as a function of distance, for instance,

$$V_{sp\sigma}(r) = \langle \phi_s(0) | \mathcal{H}^{el} | \tilde{\phi}_p(r) \rangle$$

are known, we can construct the entire matrix  $\mathcal{H}^{el}(\{R\})$ .

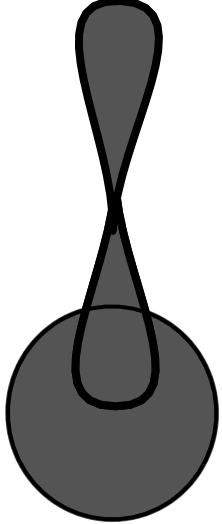


**F O U R**



***ss $\sigma$***

**B A S I C**

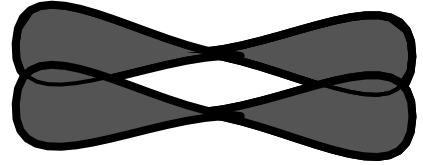


***sp $\sigma$***

**I N T E R A C T I O N S**



***pp $\sigma$***



***pp $\pi$***

There exist two approaches in constructing a TB model:

- The so-called *ab-initio* TB model actually use certain atomic orbital wave functions  $\phi_\lambda(x)$ , and evaluate  $V_{ss\sigma}(r)$  etc. explicitly using LDA. It requires few adjustable parameters, and the construction is relatively straightforward.

---

- But despite their conceptual clarity, the models are often not very accurate. The fundamental reason is that one does not know the optimal local orbitals.

- The so-called empirical TB model does not explicitly use  $\phi_\lambda(x)$ ; as one believes them to be “renormalized” instead of “rigid” orbitals. The  $V_{ss\sigma}(r)$  etc. are fitted to physically inspired functional forms in order to reproduce the target properties from experiments or LDA calculations.

---

- As one is allowed more freedom in this approach, more accurate and transferable model could be constructed. But freedom comes with a price, since one must justify his number of free parameters: anomalies will occur if it is comparable to the number of fitted properties.

- The real merit test is to see how much the model can predict outside its fitting database, and to what accuracy.
- Due to the large database requirements and multi-dimensional optimization tasks, this approach has a long developmental cycle.
- But once they are built, all TB models run equally fast independent of model complexity, since the bottleneck is always matrix diagonalization. Thus it pays to have a carefully built model.

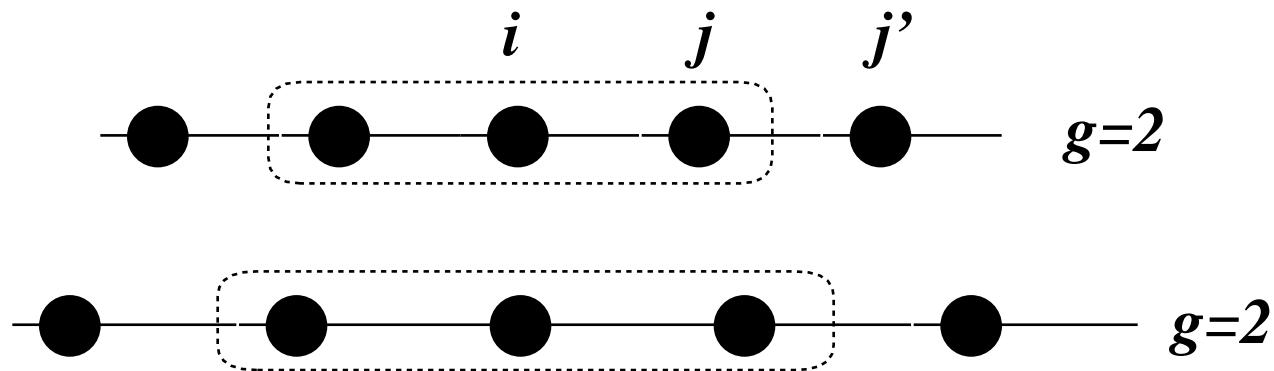
- The Environment Dependent TB model for pure C (Si) developed at Ames Lab (1996) has been applied to point defect energies, lattice anharmonicity, liquid and amorphous systems, C<sub>60</sub> and Si 7 × 7 surface reconstructions, and recently low-energy Si cluster problems, all demonstrating good transferability.

---

- Its most distinctive feature is that all interactions are coordination number dependent; and are also explicitly screened.

Coordination number is conventionally defined as the number of nearest neighbors for a given atom, thus linear chain has 2, diamond cubic has 4, bcc has 8, fcc has 12, etc.

Coordination number should be scale-independent:



→ What makes  $j$  a first neighbor to  $i$ ?

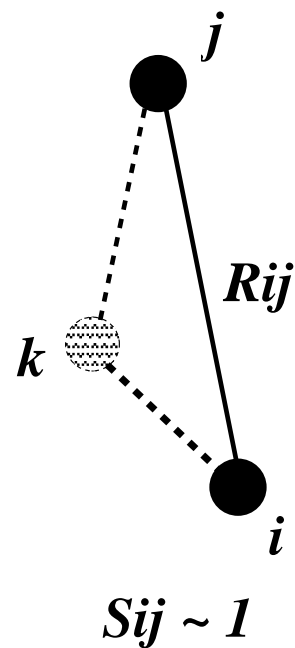
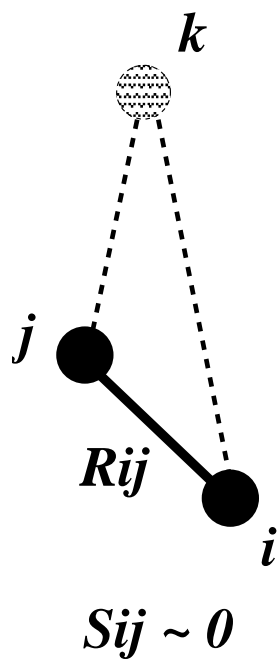
•  $j$  is a first neighbor to  $i$  simply because there are no atoms “standing in between”.  $j'$  is second neighbor to  $i$  must, on the other hand, mean that there is at least one atom  $k$  which significantly screens  $r_{ij'}$ . Thus coordination number  $g_i$  of atom  $i$ , *should* be related to screenings as

$$g_i = \sum_{j \neq i} (1 - S_{ij}),$$

where  $S_{ij}$  is the average screening factor between  $i$  and  $j$ .  $S_{ij}$  should be small for first neighbors, and close to 1 for second neighbors.

A symmetric and scale-independent form for the screening factor between atoms  $i$  and  $j$  could be

$$S_{ij} = \tanh \left( \sum_{k \neq i, j} \beta_1 \exp \left[ -\beta_2 \left( \frac{R_{ik} + R_{jk}}{R_{ij}} \right)^{\beta_3} \right] \right),$$





- We are developing a hybrid Si/C ED-TB potential to describe solid-state chemistry; this model must reproduce all results of original pure C and Si models on either end of the composition axis, so it is a “superset” of the pure element models.
- A generic parameter table is set up which fully specifies A-B interactions screened by either A or B, and screening of A-A interactions by B; most of the entries are taken to be the averages of pure A and pure B models; only the most critical ones will be fit. Nevertheless, a workable ED-TB model involves at least 40 free parameters.

A comprehensive property database has been generated using LDA which, in addition to the pure Si and C data, includes six SiC bulk phases,

- Ground state: 3C-SiC (zinc-blend),  $g \simeq 4.41$
- 2H-SiC (wurzite), polymorph to 3C,  $g \simeq 4.35$
- NaCl structure,  $g \simeq 6.25$
- NiAs structure,  $g_{\text{Si}} \simeq 7.17$ ,  $g_{\text{C}} \simeq 6.24$
- anti-NiAs structure, Si $\rightleftharpoons$ C of above
- CsCl structure,  $g \simeq 10.39$

and

- ten point defect configurations in 8,16,32-atom cells, both relaxed and unrelaxed
- 25% and 75% stoichiometry configurations

Properties to be generated as fitting targets include,

- electronic band structures
- cohesive energy *vs* volume curves
- elastic constants
- frozen phonon energies
- some of the point defect formation energies

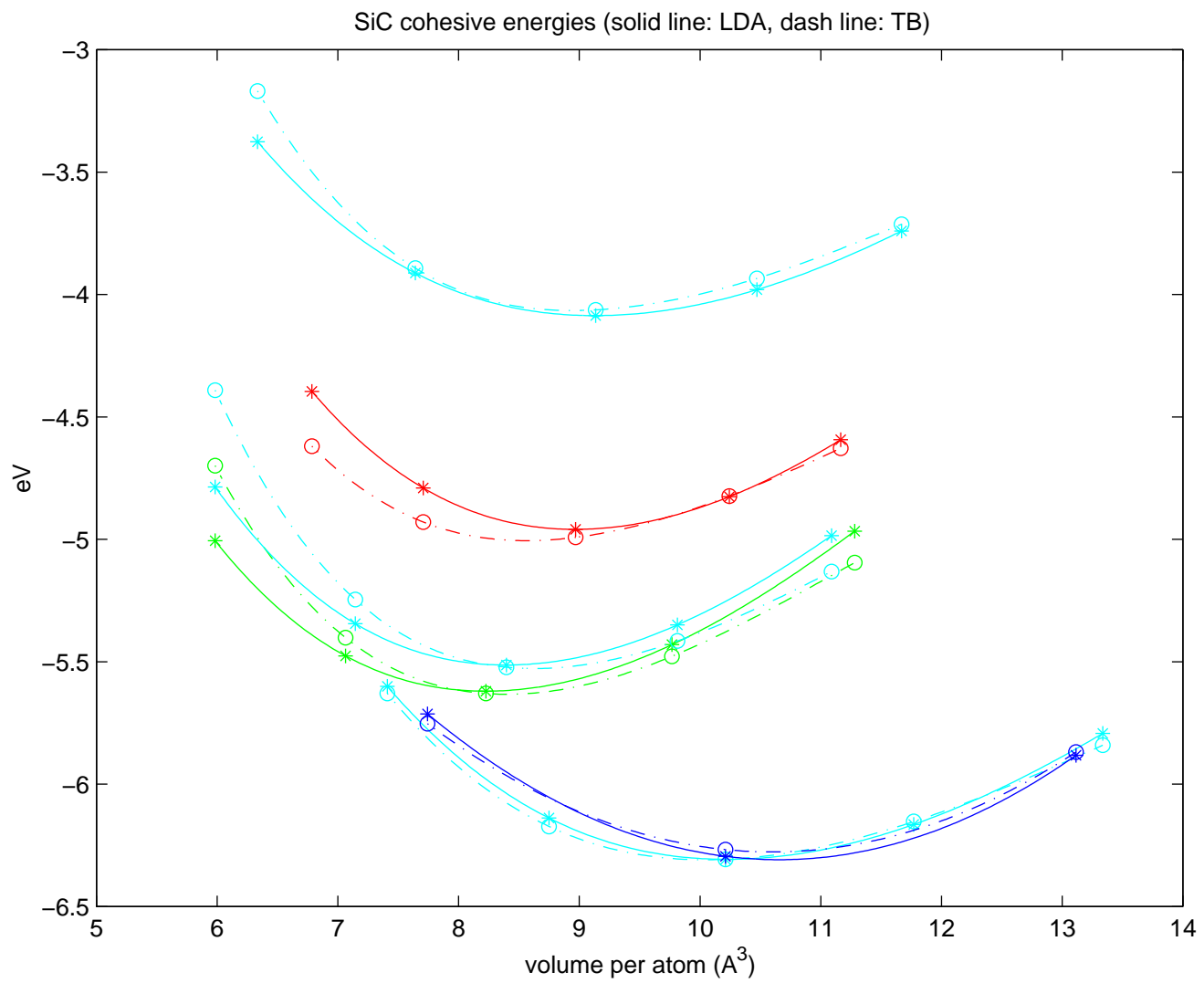
The results are checked against experiments and other published LDA calculations whenever possible. Except for the defect formation energies, the differences are found to be always within 5%.

---

We then use nonlinear optimization and/or simulated annealing algorithms to fit our ED-TB model to the family of target properties.

The fitting is currently ongoing, but candidate models can already reproduce the target properties on a level that is much better than the Tersoff potential.





SiC cohesive energies of Tersoff potential (circles) compared with LDA (solid lines)

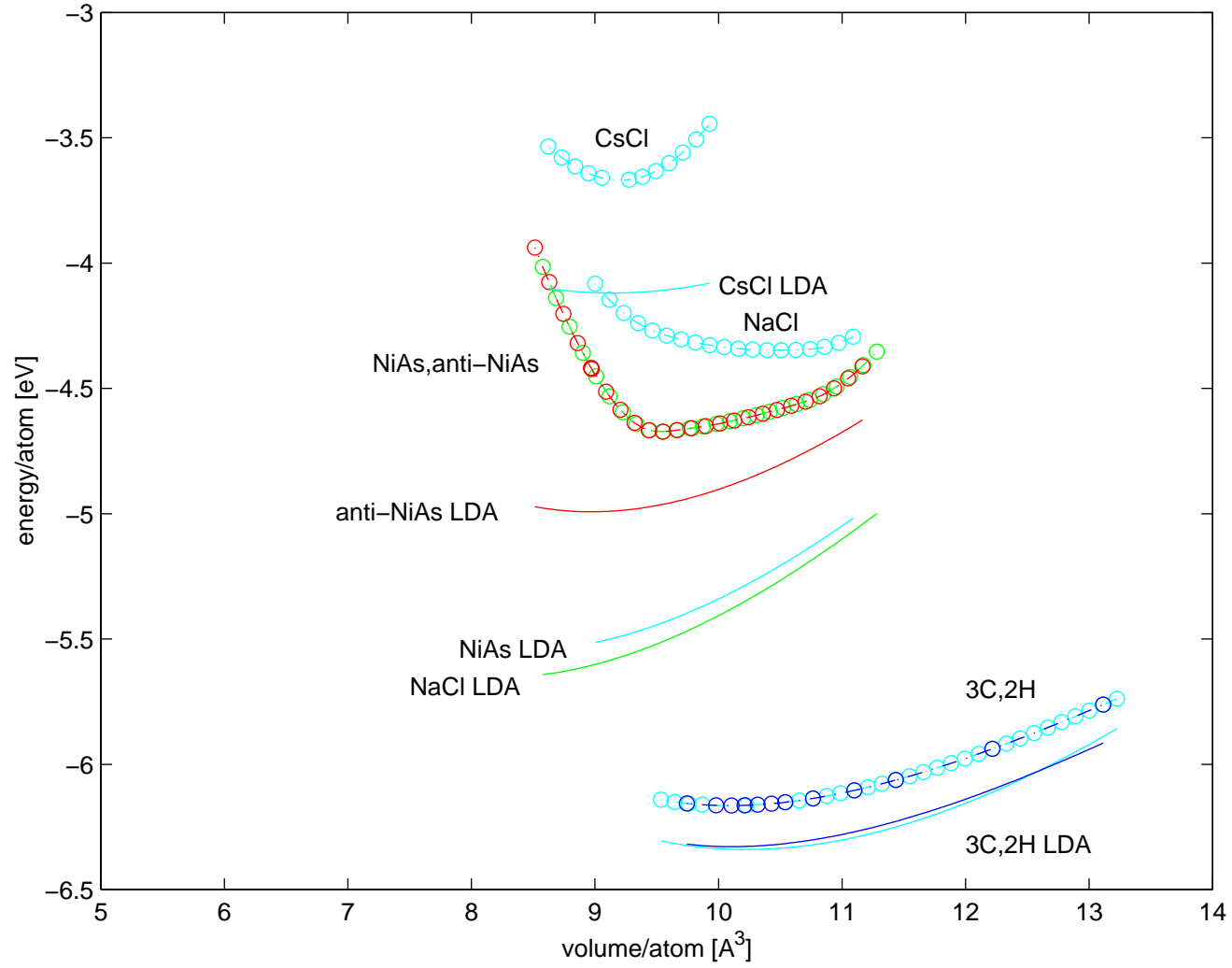


Table I: Equilibrium 3C-SiC Properties

Target	LDA result	TB rel. error
$a$ [ $\text{\AA}$ ]	4.34	2.2%
$V_{\text{coh}}$ [eV]	-6.34	-3.8%
$B$ [GPa]	224.6	-1.8%
$C_{11} - C_{12}$ [GPa]	264	-10.5%
$C_{44}^0$ [GPa]	273.3	-8.4%
TO( $\Gamma$ ) [meV]	97.9	10.7%
LO( $\Gamma$ ) [meV]	-	same
LA(X) [meV]	78.3	6.9%
LO(X) [meV]	103.8	-5.1%
TA(X) [meV]	46.0	-1.4%
TO(X) [meV]	94.8	-2.9%



Table II: 8-atom cell, unrelaxed, defect formation energies (C-rich)

Target	LDA result	TB rel. error
$V_{\text{Si}}$ [eV]	7.0	5.4%
$V_{\text{C}}$ [eV]	3.9	-3.1%
$\text{Si}_{\text{C}}$ [eV]	6.4	-6.2%
$\text{C}_{\text{Si}}$ [eV]	3.4	10.7%

Table III: Phase minima energy differences

Target	LDA result	TB rel. error
2H-3C [meV]	12.2	293%
NaCl-3C [meV]	686.9	0.0%
NiAs-NaCl [meV]	106.8	-5.3%
NiAs-aNiAs [meV]	554.0	11.8%
aNiAs-CsCl [meV]	873.0	-2.9%

- As C is more electro-negative than Si:  $E_{s,p}^0(\text{C}) < E_{s,p}^0(\text{Si})$ , electrons will flow from Si to C, which raises  $E_{s,p}(\text{C})$  and lowers  $E_{s,p}(\text{Si})$  such that equilibrium is reached. By then the Si-C bonds have become dipolar.
- The essential features of this process can be captured in a TB model by adding a term

$$V' = V + \frac{1}{2} \sum_{m,n} u_{mn} (Q_m - 4)(Q_n - 4) \quad (2)$$

to the total energy  $V$ , where

$$Q_n = \sum_i^{\text{occ}} \sum_{\lambda=1}^4 |\langle \phi_{n\lambda} | \psi_i \rangle|^2$$

is the Mulliken charge on atomic site  $n$ .

- In (2), diagonal summations  $u_{nn}(Q_n - 4)^2/2$  are the on-site Hubbard repulsions, with  $u_{nn} > 0$  stabilizing the charge transfer. For  $m$  far from  $n$ , there should be

$$\lim_{r_{mn} \rightarrow \infty} u_{mn} = \frac{1}{r_{mn}};$$

as only long-ranged Coulomb interactions survive, for  $E_{xc}$  is short-ranged. For intermediate  $r_{mn}$ ,  $u_{mn}$  should smoothly turn over from  $1/r$  to plateau behavior at  $r = 0$ , similar to pseudo-potentials.

- $u$  should be positive definite for stable systems.

One can show from (2) that,

$$V' = \sum_i^{\text{occ}} \langle \psi_i | \mathcal{H}^{el'} | \psi_i \rangle + V_{rep} - \frac{1}{2} \sum_{m,n}^N u_{mn} (Q_m - 4)(Q_n - 4), \quad (3)$$

where the new electronic Hamiltonian  $\mathcal{H}^{el'}(\{R\})$  includes a generalized Madelung potential on its diagonals

$$\langle \phi_{n\lambda} | \mathcal{H}^{el'} | \phi_{n\lambda} \rangle = \langle \phi_{n\lambda} | \mathcal{H}^{el} | \phi_{n\lambda} \rangle + \sum_m^N u_{mn} (Q_m - 4), \quad (4)$$

with  $u_{mn}$  going asymptotically as  $1/r$ .

Eqns (3,4) as such must be solved iteratively, with the same charge-mixing algorithms as in LDA.