Tightbinding Modelling of Semiconductor Nanowires

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Abstract

Tightbinding is an important bridge between the accurate, but computationally expensive density functional theory and the fast, but less accurate molecular dynamics. Tightbinding is appropriate for modelling systems of a few thousand atoms such as semiconductor nanowires. We perform some band structure calculations on bulk Si and the smallest [111] nanowire, extremes of the regime we are interested in, and find reasonable agreement with DFT. Furthermore, we calculate the energetics of an Si dimer, in verifying our implementation of total energy calculations. This will be useful in comparing different nanowire configurations (for instance under strain, or different dopant locations) and other geometry optimizations.
1 Background

Semiconducting nanowires are a promising nanomaterial in that their geometric and electrical properties can be well-controlled during their synthesis. Semiconducting nanowires can be doped to vary the concentration of carriers. Boron doped and phosphorus doped silicon nanowires have been shown to behave as p-type and n-type materials respectively [1]. In addition, the diameters of semiconducting nanowires are determined by the size of the metal catalyst nanoparticles from which they grow [2, 3]. Nanowire length has been shown to correlate linearly with growth time [4] and also depend linearly on the size of the nanoparticles from which they grow [5]. A large variety of nanowires materials including Si, Ge, GaN, InP, and ZnO can be synthesized [6], and many semiconductor industry techniques can be used with nanowires.

The levels of physical and chemical control possible during synthesis suggests the emergence of semiconductor nanowires for a wide variety of possible nanowire applications. Silicon nanowires have been demonstrated to only allow electron flow in one direction and could also be used to create bipolar transistors and complementary inverters [7]. Field effect transistors (FET) and p-n diodes have been assembled out of GaN [8] and InP [9] by forming a p-n junction with a n-type GaN or InP and p-type SiNWs. The junctions with InP, in fact, are photoluminescent, behaving as nanoscale light emitting diodes. Sensors are also feasible as boron-doped Si nanowire surfaces have been modified with molecular receptors to make them sensitive to pH, streptavidin, antibodies, and Ca$^{2+}$ [10]. Nanowires have also been functionalized with redox active molecules and assembled using fluidic-flow directed approaches to form programmable logic arrays [11]. Optical applications are also a possibility as ZnO nanowires were recently shown to exhibit a lasing action under optical excitation [12]. ZnO nanowires can also be used to guide light, similar to optical fiber.

2 Motivation

The purpose of this project is to characterize the bandgap and electronic properties of semiconductor nanowires using tight-binding simulations, which can handle up to a few thousand atoms. We aim to determine size and shape effects of semiconductor nanowires on their elec-
3 TightBinding Method

The tightbinding approach for modelling solids was first described by Slater and Koster [13] when describing the bandstructure of a periodic system and offers an intuitive picture of chemical bonding. The tightbinding approximation is based on a linear combination of atomic orbitals (LCAO) approach to solving the single electron Schrödinger equation

$$\hat{H}_1 |\psi_j(\vec{r})\rangle = \varepsilon_j |\psi_j(\vec{r})\rangle, \ j = 1, \ldots N_{\text{tot}}. \quad (1)$$

$$\hat{H}_1 = \frac{\vec{p}^2}{2m_e} + V(\vec{r}) \quad (2)$$

Here the potential $V(\vec{r})$ includes the interaction due to all the other electrons in the system and nuclei. For a periodic system, the potential $V(\vec{r})$ will have the periodicity of the lattice, $V(\vec{r} + \vec{R}) = V(\vec{r})$ where $\vec{R}$ is a lattice vector. The Hamiltonian will thus, also be periodic $\hat{H}_1(\vec{r} + \vec{R}) = \hat{H}_1(\vec{r})$ and the single electron eigenstates will satisfy the Bloch theorem

$$\psi_{\vec{k}j}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi_{\vec{k}j}(\vec{r}) \quad (3)$$

or the alternative form

$$\psi_{\vec{k}j}(\vec{r}) = e^{i\vec{k} \cdot \vec{R}} u_{\vec{k}j}(\vec{r}) \quad (4)$$

where $u_{\vec{k}j}(\vec{r})$ is periodic with the lattice periodicity.

The Bloch wavefunction $\psi_{\vec{k}j}(\vec{r})$ satisfies the single electron Schrödinger equation

$$\hat{H}_1 \left| \psi_{\vec{k}j}(\vec{r}) \right\rangle = \varepsilon_{\vec{k}j} \left| \psi_{\vec{k}j}(\vec{r}) \right\rangle. \quad (5)$$

The energy eigenvalue $\varepsilon_{\vec{k}j}$ of each level varies smoothly with wavevector $\vec{k}$ and together form the bandstructure of the crystal.

The single electron wavefunction can be represented as a superposition of localized or-
localized orbitals $\phi_j(\vec{r} - \vec{R})$

$$\psi_{\vec{k}_j}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}_j \cdot \vec{R}} \phi_j(\vec{r} - \vec{R}) \tag{6}$$

where $N$ is the number of lattice sites.

The localized orbitals can be taken as a linear combination of atomic orbitals like functions $\varphi(\vec{r})$

$$\phi_j(\vec{r}) = \sum_n c_{nj} \varphi_n(\vec{r}) \tag{7}$$

This is equivalent to the single electron wavefunction being expressed as a linear combination of Bloch-sums

$$\psi_{\vec{k}_j}(\vec{r}) = \sum_n c_{nj}(\vec{k}) b_{kn}(\vec{r}) \tag{8}$$

where

$$b_{kn}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \phi_j(\vec{r} - \vec{R}) \tag{9}$$

The $\varphi(\vec{r})$ are considered to be atomic orbitals-like functions of the isolated atoms, and thus this method is often referred to as a linear combination of atomic orbitals (LCAO).

Our Hamiltonian matrix element is thus,

$$H_{nm} = \langle b_n | \hat{H} | b_m \rangle \tag{10}$$

$$= \frac{1}{N} \sum_{\vec{R}, \vec{R}'} e^{-i\vec{k} \cdot (\vec{R} - \vec{R}')} \int \varphi^*_m(\vec{r} - \vec{R}') \hat{H} \varphi_n(\vec{r} - \vec{R}) d\vec{r} \tag{11}$$

$$= \sum_{\vec{R}} e^{-i\vec{k} \cdot \vec{R}} \int \varphi^*_m(\vec{r}) \hat{H} \varphi_n(\vec{r} - \vec{R}) d\vec{r} \tag{12}$$

and the overlap matrix is similarly

$$S_{nm} = \langle b_n | b_m \rangle \tag{13}$$

$$= \sum_{\vec{R}} e^{-i\vec{k} \cdot \vec{R}} \int \varphi^*_m(\vec{r}) \varphi_n(\vec{r} - \vec{R}) d\vec{r} \tag{14}$$
The discretized eigenvalue equation is now

\[ \sum_n H_{nm}(\vec{k})c_{mj}(\vec{k}) = \varepsilon_{kj} \sum_m S_{nm}(\vec{k})c_{mj}(\vec{k}) \]  \hspace{1cm} (15) 

\[ (\mathbf{H}(\vec{k}) - \varepsilon_{kj} \mathbf{S}(\vec{k})) \mathbf{C}_j = 0 \]  \hspace{1cm} (16)

If the \( \varphi_n \) are orthonormal (orthogonal tightbinding) than the overlap matrix \( \mathbf{S}(\vec{k}) = \mathbf{I} \). We thus solve a different eigenvalue equation for each wavevector \( \vec{k} \) to produce the bandstructure of the solid we are studying.

When the two wavefunctions are all centered on the same atom, the integral is called an on-site integral. In Harrison’s approach, the on site energies are the Hartree-Fock term values, estimates of the removal energy of an electron from the corresponding state in the neutral atom in the approximation that the removal does not modify the remaining electronic wavefunctions. When the site-potential function and one of the wavefunctions are centered on one atom and the other wavefunction is centered on a different atom the integral will be called a two center integral. When the two wavefunctions and the site-potential function are all centered on different atoms the integral will be called a three center integral.

For general case where the two atoms are not on the same Cartesian axis, the integrals will depend on the vector \( \vec{R}_{JI} \) between the two atoms. Often times these integrals in Slater Koster notation, \( V_{ll'}_{m} \) as parameters chosen as to fit energies at certain \( k \)-points.

The three center integrals are smaller than the two center integrals and in the two center approximation, we ignore these integrals. Furthermore, we assume the site-potential functions are spherically symmetric and the atomic orbital-like function can be thus, be expressed as as the product of a radial function and a spherical harmonic \( \varphi_n(\vec{r}) = R_L(r)Y^L_M(\theta, \phi) \). The integral becomes similar to what we would have in a diatomic molecule.

The integrals as expressed in Equation 12 can then be decomposed into terms with respect to the vector between atoms \( \vec{R}_{JI} = \vec{R}_J - \vec{R}_I \). Let the direction cosines of this vector be \( l, m, n \). The two center integrals between s and p-atomic orbitals are thus give in Table 1. Other matrix elements can be found be permuting indices. A more general set of expressions has also been derived by Sharma [14].
<table>
<thead>
<tr>
<th>Integral term</th>
<th>Two center integral expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{s,s}$</td>
<td>$V_{ss\sigma}$</td>
</tr>
<tr>
<td>$E_{x,x}$</td>
<td>$lV_{sp\sigma}$</td>
</tr>
<tr>
<td>$E_{x,x}$</td>
<td>$l^2V_{pp\sigma} + (1 - l^2)V_{pp\pi}$</td>
</tr>
<tr>
<td>$E_{x,y}$</td>
<td>$l m_{pp\sigma} - l m_{pp\pi}$</td>
</tr>
<tr>
<td>$E_{x,z}$</td>
<td>$l n_{pp\sigma} - l n_{pp\pi}$</td>
</tr>
</tbody>
</table>

Table 1: Energy integrals for two-center integrals

The integral terms between higher-order terms are found in [13] or alternative expressions have been derived by Sharma [15].

Froyen and Harrison came up with universal parameters describing the coupling between neighboring s- and p-like states using the similarity between nearest-neighbor LCAO bands and free-electron bands for solids in a diamond structure [16].

\[ V_{l'm} = \eta_{l'm} \frac{h^2}{m_e a^2}, \tag{17} \]

4 Bulk Semiconductors

The bandstructure for Si using the Harrison universal scheme is shown in 1 at the experimental lattice constant of $a = 5.43$. We use the Hartree-Fock term values for valence levels and prefactors $\eta_{ss\sigma} = -1.32$, $\eta_{sp\sigma} = 1.43$, $\eta_{pp\sigma} = 2.22$, $\eta_{pp\pi} = -0.63$ [17].

As can be seen, the band gap is overestimated at 1.75 eV and the band gap is also direct.
Chadi et al showed that such an sp$^3$ tightbinding model for zincblende or diamond materials that the conduction bands will necessarily rise from $\Gamma$ to $X$ [18].

In order to accurately reproduce the lowest conduction bands for indirect band gap materials, interatomic interactions beyond nearest neighbors or the addition of excited atomic states can be used. A popular parameterization for addressing this issue has been using an ad-hoc $s^*$ basis to depress the states below as introduced by Vogl [19]. This popular parameterization uses an excited $s^*$ state to depress the lower, unoccupied energy levels of neighboring atoms and presses the indirect conduction band minimum down.
As can be seen in Figure 6, the $sp^3s^*$ tightbinding scheme produces an indirect bandgap of 1.12 eV as desired, and also at the correct k-point.

5 Nanowire Modelling

A variety of methods can be used to fit tightbinding bands such as simulated annealing or genetic algorithm [20, 21]. Using the $sp^3s^*$ Vogl model, we use a genetic algorithm to perform a fit on the $V_{ssa}$ and $V_{spa}$ matrix elements where one of the s-like orbitals is on the Hydrogen atom. We obtain $\eta_{ssa} = -11.22$ and $\eta_{spa} = -18.15$. We use $\varepsilon_s = -16.32$ for the Hydrogen onsite energy from the universal model described in [19].
Figure 3: Nanowire growing in the [111] direction. Its diameter is 6.75 Å

Figure 4: Vogl Tightbinding bands of Si nanowire compared to GGA+U

The band gap using the more accurate DFT is 3.89 eV and the bandgap is indirect, while the band gap using the tightbinding model is 3.25 eV and also indirect (thought at a different k point). Since the tightbinding model fairly accurately represents the bandstructure for the most extreme cases of the systems we are interested in (for both bulk Si and a small nanowire), the model should also accurately represent the regime in between these two extremes.
6 Atomistic Simulations

Tightbinding methods can also be used for atomistic simulations through calculations of total energy and atomic forces.

The total energy $U(\vec{R})$ in the tightbinding approach is calculated as

$$U(\vec{R}) = U_{el}(\vec{R}) + U_{rep}(\vec{R})$$

where the electronic energy $U_{el}(\vec{R})$ is the sum of one-electron energies $\varepsilon_{kj}$ for the occupied states

$$U_{el}(\vec{R}) = \sum_{j}^{occ} \varepsilon_{j}$$

and $U_{rep}(\vec{R})$ is given by a repulsive pair potential

$$U_{rep}(\vec{R}) = \sum_{I} \sum_{J > I} \chi(|\vec{R}_{IJ}|).$$

For a periodic system, we average the energy over different $k$ points

$$U_{el}(\vec{R}) = \frac{1}{N_{k}} \sum_{\vec{k}} \sum_{j}^{occ} \varepsilon_{\vec{k}j}$$

where $N_{k}$ is the number of wavevectors $\vec{k}$, which are meshed over the Brillouin zone with mesh-size chosen depending on the necessary precision.

The force on atom $I$ is the negative derivative of the total energy $U(\vec{R})$ with respect to its nucleus position $\vec{R}_{I}$

$$\vec{F}_{I}(\vec{R}_{I}) = -\frac{dU(\vec{R})}{d\vec{R}_{I}}.$$

The contribution of the repulsive pair potential can be calculated analytically, while the electronic contribution from $U_{el}(\vec{R})$ can be calculated using the Hellman-Feynman theorem

$$\vec{F}_{el}(\vec{R}_{I}) = -\frac{dU_{el}(\vec{R})}{d\vec{R}_{I}} = -\sum_{j}^{occ} \frac{d\varepsilon_{j}}{d\vec{R}_{I}} \vec{C}_{j} + \sum_{j}^{occ} \vec{C}_{j} \left[ \frac{d}{d\vec{R}_{I}} (\vec{H} - \varepsilon_{j} \vec{S}) \right] \vec{C}_{j}$$
7 Nonorthogonal tightbinding

While the atomic orbitals on the same atom are indeed orthogonal, for different atoms, they are generally not orthogonal. The use of orthogonal tightbinding is generally justified that the atomic like orbitals can be orthogonalized while preserving symmetry properties by Löwdin’s method [22].

However, the orthogonal matrix elements do not transfer between different structures as the orthogonalization of the atomic orbitals depends on the particular structure. In addition, the orthogonalized functions have a wider range since the orthogonalization process mixes functions from nearby atoms. Higher order nearest-neighbors must thus be included in order to account for the nonorthogonality of atomic orbitals [23].

Explicitly including the nonorthogonality of the atomic orbitals should thus lead to a more transferable tightbinding scheme. In extended Hückel theory [24], an explicit atomic basis is used and the overlap matrix elements are calculated explicitly. Van schilfgaarde and Harrison have proposed a nonorthogonality scheme within the tightbinding framework [25].

The overlap matrix \( S \) is obtained from extended Hückel theory

\[
S_{ll'm'} = \frac{2V_{ll'm'}}{K(\varepsilon_l + \varepsilon_{l'})}
\]  

(24)

The matrix elements \( H_{ll'm'} \) in the non-orthogonal atomic basis are related to those in the orthogonal basis \( V_{ll'm'} \) by

\[
H_{ll'm'} = V_{ll'm'} \left( 1 + \frac{1}{K} + S_2^2 \right)
\]  

(25)

where \( S_2 \) is the nono-orthogonality between two \( sp^3 \)

\[
S_2 = \frac{(S_{ss\sigma} - 2\sqrt{3}S_{sp\sigma} - 3S_{pp\sigma} + S_{pp\pi})}{4}
\]  

(26)

8 Menon Subbaswamy Scheme

The Menon Subbaswamy scheme has been used to model small \( Si_n \) clusters with \( n \) between 3-10 [26]. This model or variations of it have also been used to simulate \( C_{60} \) [27] and Ge clusters [28].
We use this particular non-orthogonal tightbinding scheme as a reference for our implementation of tightbinding molecular dynamics.

In this particular scheme, the matrix elements are taken to decrease exponentially

\[ V_{ll'm}(d) = V_{ll'm}(d_0)e^{-\alpha(d-d_0)} \]  

(27)

The four \( V_{ll'm}(d_0) \) parameters have the values \( V_{ss\sigma}(d_0) = -2.37 \text{ eV}, \ V_{sp\sigma}(d_0) = 2.52 \text{ eV}, \ V_{pp\sigma}(d_0) = 3.32 \text{ eV}, \ V_{pp\pi}(d_0) = -1.07. \)

The repulsive potential also depends exponentially on distance

\[ \chi(d) = \chi_0e^{-\beta(d-d_0)} \]  

(28)

where \( \beta \) is fixed to \( \beta = 4\alpha. \)

The parameters for Silicon are

<table>
<thead>
<tr>
<th>A priori parameters</th>
<th>Adjustable parameters</th>
</tr>
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<tbody>
<tr>
<td>( \varepsilon_s ) (eV)</td>
<td>( \varepsilon_p ) (eV)</td>
</tr>
<tr>
<td>-13.55</td>
<td>-6.52</td>
</tr>
</tbody>
</table>
Interactions with up to third nearest neighbors are included in this model. Though the valence bands in this particular tightbinding model are not well-representated, only the conduction bands are important for computing ground state energies and forces.

Next, we check the total energy calculations for an Si dimer.
Figure 6: Energy versus dimer distance

We obtain a bond length of 2.29 Å and binding energy of 2.57 eV/atom, compared with an experimental value of 2.24 Å and 1.56 eV/atom.

9 Conclusion

We have use the tightbinding model for the analysis of semiconductor nanowires. We perform some electronic structure calculations on bulk Si and the smallest [111] nanowire, extremes of the regime we are interested in, and find reasonable agreement with the more accurate, but more computationally expensive DFT. Furthermore, we calculate the energetics of an Si dimer, in verifying our implementation of total energy calculations. This will be useful in comparing different nanowire configurations and other geometry optimizations.

References


