

# Electron Bands

Richard M. Martin

## OUTLINE

- Kohn-Sham Equations
- Finite vs. extended systems
- Crystals
  - Crystal = Lattice + Basis
  - Translation symmetry: The Bravais Lattice
  - The Reciprocal Lattice and the Brillouin Zone
  - Excitations and the Bloch Theorem
- Energy Bands
  - Equations for Non-interacting Particles at each  $\mathbf{k}$
  - Solution by Matrix Diagonalization
- Bands calculated in a Plane Wave Basis
  - Empirical Pseudopotential Approximation
  - Examples of Bands: Si, GaAs
- Bands calculated in a Atomic-like Basis
  - Empirical Tight binding
  - Examples of Bands: Si, nanotubes

For more complete exposition and many references see  
“Electronic Structure: Basic Theory and Practical Methods”  
Richard M. Martin, Cambridge University Press, 2004  
and  
<http://ElectronicStructure.org>

# Kohn-Sham Equations

The step that has made density functional theory so useful is the Kohn-Sham *ansatz* which leads to independent-particle equations for the electrons in matter. Thus one arrives at the Kohn-Sham Schrödinger-like equations:

$$(H_{eff} - \varepsilon_i)\psi_i(\mathbf{r}) = 0 \quad (1)$$

where the  $\varepsilon_i$  are the eigenvalues,

$$H_{eff}(\mathbf{r}) = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\mathbf{r}). \quad (2)$$

and

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{\partial E_{Hart}}{\partial n_{eff}(\mathbf{r})} + \frac{\partial E_{xc}}{\partial n_{eff}(\mathbf{r})} \quad (3)$$

$$= V_{ext}(\mathbf{r}) + V_{Hart}[n_{eff}] + V_{xc}[n_{eff}]. \quad (4)$$

The only ways that one electron knows about the other electrons is (1) through the exclusion principle and (2) through the effective potential  $V_{eff}(\mathbf{r})$  which is a functional of the density

$$n_{eff}(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2, \quad (5)$$

which depends upon all the electrons. The density and the potential must be solve self-consistently and at the solution  $n_{eff}(\mathbf{r}) = n(\mathbf{r})$  is the density.

The total energy can be written

$$\tilde{E} = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \int V_{Hart}(\mathbf{r})n_{eff}(\mathbf{r})dr + (E_{xc}[n] - \int (V_{xc}n_{eff}(\mathbf{r})dr) \quad (6)$$

# Finite vs. Extended Systems

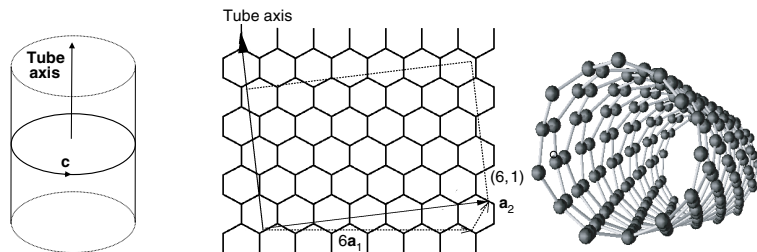
Here we consider the solution of the independent-particle Schrödinger-like equations:

$$(H_{eff} - \varepsilon_i)\psi_i(\mathbf{r}) = 0 \quad (7)$$

where the  $\varepsilon_i$  are the eigenvalues, and we assume the hamiltonian  $H_{eff}(\mathbf{r}) = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(\mathbf{r})$  is given. That is, it as been derived or we have an approximate form. The purpose here is to understand the nature of the solution - not the details.

- Finite systems - atoms, molecules, clusters
  - Boundary conditions determine which states are allowed:  $\psi_i = 0$  at infinity
  - Leads to discrete bound states; unbound continuum states
- Extended systems - crystals, nanotubes, devices with a small system coupled to extended leads, ...
  - Boundary conditions may be “open”, periodic, ...
  - Leads to continuous “bands” of allowed states; and it may lead to forbidden gaps

Figure 1: “Rolling” of a graphene sheet (part of an extended crystal) to form a nanotube (finite circumference, extended length)



# Periodic Crystals

(See, e.g., Ashcroft and Mermin, "Solid State Physics", Chapters 4-8.)

A crystal is an ordered state of matter in which the positions of the nuclei (and consequently all properties) are repeated periodically in space. It is specified by the positions of the nuclei in the smallest possible repeat unit (primitive unit cell), and the rules that describe the repetition (translations).

The positions and types of atoms in the unit cell is called the basis, and the set of translations generates the entire periodic crystal by repeating the basis. The set of translation vectors is a lattice of points in space called the Bravais lattice. This can be summarized as:

**Crystal structure = Bravais lattice + basis.**

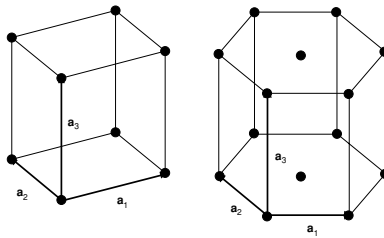
The Bravais lattice is a set of points - each point represents a translation that is as an integral multiple of primitive translation vectors,

$$\mathbf{T}(n_1, n_2, \dots) = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + \dots \quad (8)$$

Examples: (here  $a$  is the unit of length)

- line:  $\mathbf{a}_1 = a$ .
- square:  $\mathbf{a}_1 = (1, 0)a$ ;  $\mathbf{a}_2 = (0, 1)a$ .
- triangular:  $\mathbf{a}_1 = (1, 0)a$ ;  $\mathbf{a}_2 = (\frac{1}{2}, \frac{\sqrt{3}}{2})a$ .
- simple cubic:  $\mathbf{a}_1 = (1, 0, 0)a$ ;  $\mathbf{a}_2 = (0, 1, 0)a$ ;  $\mathbf{a}_3 = (0, 0, 1)a$ .
- face centered cubic  $\mathbf{a}_1 = (\frac{1}{2}, \frac{1}{2}, 0)a$ ;  $\mathbf{a}_2 = (\frac{1}{2}, 0, \frac{1}{2})a$ ;  $\mathbf{a}_3 = (0, \frac{1}{2}, \frac{1}{2})a$ .

Figure 2: Bravais for simple cubic and simple hexagonal crystals



# Periodic Functions and the Reciprocal Lattice

Consider any function  $f(\mathbf{r})$  defined for the crystal, such as the density of the electrons. This function is the same in each unit cell,

$$f(\mathbf{r} + \mathbf{T}(n_1, n_2, n_3)) = f(\mathbf{r}), \quad (9)$$

where  $\mathbf{T}$  is any translation defined above.

## Fourier transforms

A periodic function can be represented by a Fourier transform

$$f(\mathbf{q}) = \frac{1}{\Omega_{crystal}} \int_{\Omega_{crystal}} f(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \quad (10)$$

Since  $f$  is periodic, this can be written:

$$\begin{aligned} f(\mathbf{q}) &= \frac{1}{\Omega_{crystal}} \sum_{n_1, n_2, n_3} \int_{\Omega_{cell}} f(\mathbf{r}) \exp(i\mathbf{q} \cdot (\mathbf{r} + \mathbf{T}(n_1, n_2, n_3))) d\mathbf{r} \\ &= \frac{1}{N_{cell}} \sum_{n_1, n_2, n_3} \exp(i\mathbf{q} \cdot \mathbf{T}(n_1, n_2, n_3)) \times \frac{1}{\Omega_{cell}} \int_{\Omega_{cell}} f(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \end{aligned} \quad (11)$$

Now the first term on the right hand side is 0 all  $\mathbf{q}$  except those for which  $\mathbf{q} \cdot \mathbf{T}(n_1, n_2, n_3) = 2\pi \times \text{integer}$  for all translations  $\mathbf{T}$ . Since  $\mathbf{T}(n_1, n_2, n_3)$  is an integral multiple of the primitive translations  $\mathbf{a}_i$ , it follows that  $\mathbf{q} \cdot \mathbf{a}_i = 2\pi \times \text{integer}$ .

## This defines the Reciprocal Lattice

If we define the vectors  $\mathbf{b}_i$ ,  $i = 1, d$  which are reciprocal to the the primitive translations  $\mathbf{a}_i$ , i.e.,

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}, \quad (12)$$

then the only non-zero Fourier components of  $f(\mathbf{r})$  are for  $\mathbf{q} = \mathbf{G}$ , where the  $\mathbf{G}$  vectors are a lattice of points in reciprocal space defined by

$$\mathbf{G}(n_1, n_2, n_3) = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3. \quad (13)$$

Finally, the non-zero Fourier transform of the periodic function can be written in terms of the integral over one primitive cell,

$$f(\mathbf{G}) = \frac{1}{\Omega_{cell}} \int_{\Omega_{cell}} f(\mathbf{r}) \exp(i\mathbf{G} \cdot \mathbf{r}) d\mathbf{r} \quad (14)$$

# The Reciprocal Lattice

Figure 3: Face centered cubic (fcc) lattice and its Wigner-Seitz cell (right figure). Note: fcc is reciprocal to the bcc lattice.

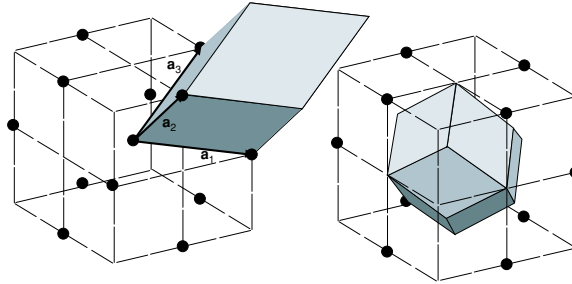
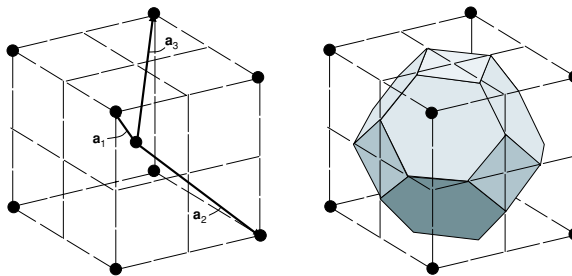


Figure 4: Body centered cubic (bcc) lattice and its Wigner-Seitz cell. Note: bcc is reciprocal to the fcc lattice.



# Wigner-Seitz Cell and First Brillouin Zone

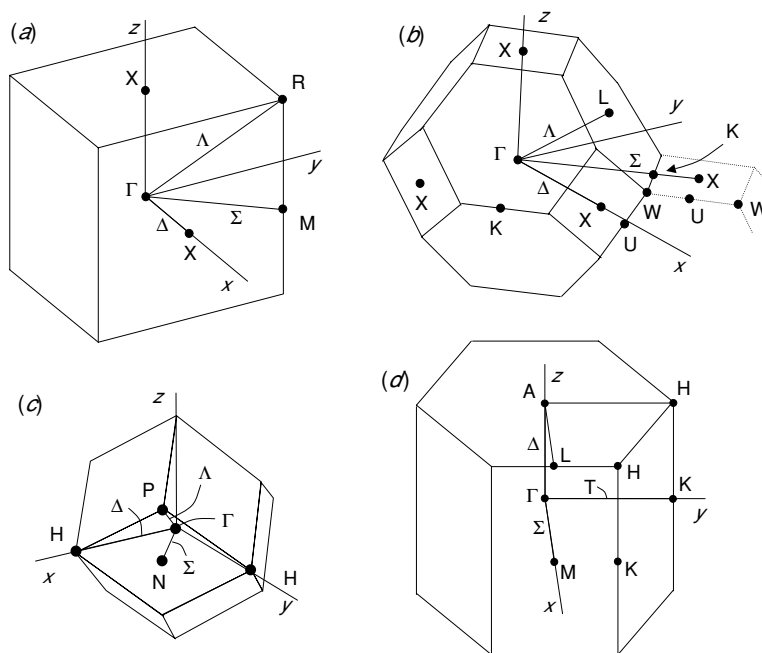
The primitive cell for the crystal can be any one of the infinite set of possible choices of cells that fill all space when translated by the set of all lattice vectors. This holds for the direct and the reciprocal lattices.

Is there a way to make a "best" choice that is unique in some important way?

**Wigner-Seitz Cell:** defined to be the most compact cell possible, i.e., the primitive cell around the origin is set of all points closer to the origin than to any other lattice vector. The Wigner-Seitz Cell can always be constructed by the set of points inside the perpendicular bisecting planes between the origin and all other lattice vectors.

**First Brillouin Zone:** the Wigner-Seitz Cell of the reciprocal lattice.

Figure 5: Examples of Brillouin Zones with labels for points in the zone.



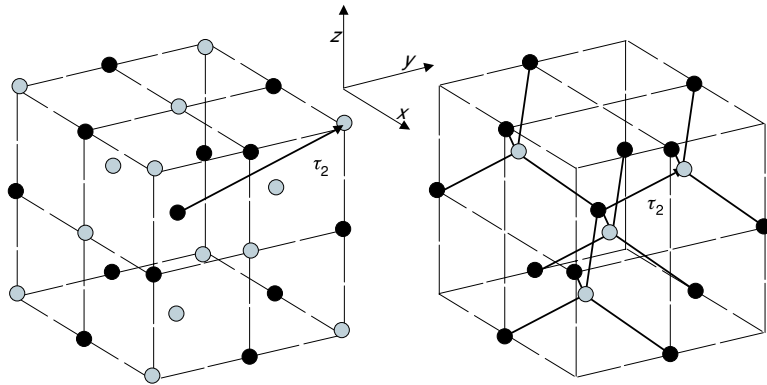
# Basis of Atoms in a Primitive Cell

The basis describes the positions of atoms in each unit cell relative to the chosen origin. If there are  $N_{atom}$  atoms per primitive cell, then the basis is specified by the atomic position vectors  $\tau_\kappa$ ,  $\kappa = 1, N_{atom}$ .

NaCl and ZnS are two examples of crystals with an fcc Bravais lattice and a basis of two atoms per cell. For the case of NaCl, one can choose one atom at the origin, since there is inversion symmetry and cubic rotational symmetry around each atomic site:  $\tau_1 = (0, 0, 0)$  and the second basis vector chosen to be  $\tau_2 = (\frac{1}{2}, 0, 0)a$  or any one of the 6 equivalent choices.

The basis for the Zinc Blende structure can be chosen in a symmetric way,  $\tau_1 = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8})a$ , and  $\tau_2 = -(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})a$ , which is appropriate for diamond since this is a center of inversion symmetry. One can also choose the origin at one atom, which is a center of tetrahedral symmetry,  $\tau_1 = (0, 0, 0)a$ , and  $\tau_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a$  or any of the equivalent choices. (It is easy to show that in terms of the primitive lattice vectors, the  $\tau_2^L = [\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$ , etc.

Figure 6: Examples of crystals with a basis of more than one atom per cell: NaCl (left) and ZnS (right).





# Excitations and the Bloch Theorem

Excitations of the electrons in the crystal are *not* required to have the periodicity of the crystal. For example, in any independent-particle theory the energies to add or subtract electrons are the eigenvalues of the independent particle Schrödinger equation (e.g., Kohn-Sham equations),

$$\hat{H}\psi_{i,\mathbf{k}}(\mathbf{r}) = \left[ -\frac{\hbar^2}{2m_e}\nabla^2 + V(\mathbf{r}) \right] \psi_{i,\mathbf{k}} = \varepsilon_i(\mathbf{k})\psi_{i,\mathbf{k}}(\mathbf{r}), \quad (15)$$

where  $V(\mathbf{r})$  is periodic, i.e.,  $V(\mathbf{r})$  is the same in each cell.

**The Bloch theorem.** As indicated in Eq. 15, each eigenfunction can be labelled by a wavevector  $\mathbf{k}$  and can be written

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) \times u_{i,\mathbf{k}}(\mathbf{r}), \quad (16)$$

where  $u_{i,\mathbf{k}}(\mathbf{r})$  is a periodic function of  $\mathbf{r}$ . Thus each excitation has a periodic part and a phase that varies from cell to cell. Here  $\mathbf{k}$  is a continuous variable giving rise to a continuum of eigenstates for each band  $i = 1, 2, 3, \dots$

**The Role of the Brillouin Zone (BZ).** All independent eigenstates can be classified in terms of wavevectors  $\mathbf{k}$  restricted to the BZ; all other  $\mathbf{k}$  outside the BZ are identical and are not independent. Examples of BZs for important cases are shown in Fig. 6.

**Expansion of the eigenfunctions in a basis.** One way to express the eigenfunctions is a Fourier expansion, which is an expansion in a plane wave basis. Since  $u$  is periodic this can be written

$$u_{i,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{G}}(\mathbf{k}) \frac{1}{\sqrt{\Omega_{cell}}} \exp(i\mathbf{G} \cdot \mathbf{r}). \quad (17)$$

Another approach is to write each  $u_{i,\mathbf{k}}(\mathbf{r})$  as a sum of localized atomic-like functions centered on the atoms in each unit cell. This gives rise to a representation of the form

$$u_{i,\mathbf{k}}(\mathbf{r}) = \sum_m c_{i,m}(\mathbf{k}) \phi(\mathbf{r} - \mathbf{R}_m), \quad (18)$$

where  $\phi(\mathbf{r} - \mathbf{R}_m)$  is an atomic like function centered on an atom at position  $\mathbf{R}_m$ .

# Calculations of Bands in Plane Wave Basis

Using the formulas above we find the matrix equation for the Schrödinger equation in plane waves:

$$\sum_{\mathbf{G}'} H_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) c_{i,\mathbf{G}'}(\mathbf{k}) = \varepsilon_i(\mathbf{k}) c_{i,\mathbf{G}}(\mathbf{k}) \quad (19)$$

where

$$H_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) = \frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G},\mathbf{G}'} + V(\mathbf{G} - \mathbf{G}') \quad (20)$$

This is a hermitian matrix equation in  $\mathbf{G}, \mathbf{G}'$ , and the solution by standard diagonalization techniques leads to the bands of eigenvalues  $\varepsilon_i(\mathbf{k})$  and the periodic part of their eigenstates  $u_{i,\mathbf{k}}(\mathbf{r})$ .

## Plane Wave Empirical Pseudopotential Calculations

We now have the equations to solve *any* independent particle problem in a crystal.

What is the problem?

- Works only if the number of plane waves is feasible.
  - Only for hydrogen! Core electrons too difficult for other elements!
  - Or if we use pseudopotentials to eliminate core electrons
- Works only if we have a way of getting the potential  $V(\mathbf{r})$  or  $V(\mathbf{G})$ 
  - Density functional theory provides ways to find  $V$  - approximate, but well tested in many classes in many materials
  - Models and Empirical Approximations for  $V$  show us the general character of solutions

# Sum of Spherical Potentials

Often the potential is given by a sum of spherical potentials in real space. This is always true for the bare proton potentials or the bare ionic pseudopotentials. Often it is also a good approximation to take the entire potential as a sum of spherical potentials. An example which is often rather close to the final potential is to assume  $V(\mathbf{r})$  to be a sum of neutral atom potentials. In any case where the potential is a sum of spherical potentials,

$$V(\mathbf{r}) = \sum_{i=1}^{N_{type}} \sum_{j=1}^{N_{atom}(i)} \sum_{\mathbf{T}} V_{atom}^i(|\mathbf{r} - \vec{\tau}_{i,j} - \mathbf{T}|), \quad (21)$$

then the Fourier transform can be written,

$$V(\mathbf{G}) = \frac{1}{\Omega_{cell}} \int_{\Omega_{cell}} V(\mathbf{r}) \exp(i(\mathbf{G} \cdot \mathbf{r})) d\mathbf{r} = \sum_{i=1}^{N_{type}} S_i(\mathbf{G}) V_{atom}^i(|\mathbf{G}|), \quad (22)$$

where the **structure factor** for each type of atom is

$$S_i(\mathbf{G}) = \frac{1}{N_{atom}(i)} \sum_{j=1}^{N_{atom}(i)} \exp(i(\mathbf{G} \cdot \vec{\tau}_{i,j})) \quad (23)$$

and the **form factor** for each type of atom is

$$V_{atom}^i(|\mathbf{G}|) = \frac{N_{atom}(i)}{\Omega_{cell}} \int_{all\ space} V_{atom}^i(|\mathbf{r}|) \exp(i(\mathbf{G} \cdot \mathbf{r})) d\mathbf{r}. \quad (24)$$

This is an approximation to the true potential which is not a sum of spherical potentials. However, it is often a good approximation. Furthermore, in the full Kohn-Sham calculations the bare ionic potential due to the rigid spherical nuclei and cores are spherical and this form is used in that case.

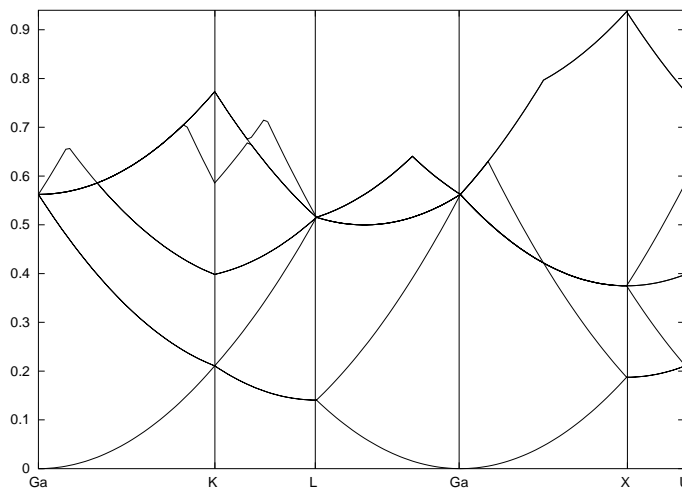
# Model Potentials and Empirical Pseudopotentials

The programs used in our lab exercises use potentials that are sums of spherical atomic-like potentials. These are useful because:

- This is a very good approximation in many cases and gives one a feeling for bands. It is very useful for describing bands, optical properties, etc. See book by Cohen and Chelikowsky.)
- Empirical potentials can be a starting point for large calculations not feasible in *ab initio* methods. Calculations for “quantum dots of many thousands of atoms have been done by Wang, et al (see references) using the same potentials as in our lab.

The programs used in the lab include empirical potentials for Si, Ga, As, (from S. B. Zhang, et al) and various model cases: “El” (i.e., no potential or “empty lattice”). Examples of results:

Figure 7: Free electron bands for an fcc crystal with potential set equal to zero and the lattice constant of Si. Only the lowest 8 bands are shown. Energies are in Hartrees (1 Ha = 27.2 eV).



# Localized atomic-like Basis

Using the formulas above we find the matrix equation for the Schrödinger equation in terms of the basis  $\phi_m(\mathbf{r} - \mathbf{R}_m)$ :

$$\sum_{m'} H_{m,m'}(\mathbf{k}) c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k}) c_{i,m}(\mathbf{k}), \quad (25)$$

where

$$H_{m,m'}(\mathbf{k}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} H_{m,m'}(\mathbf{T}), \quad (26)$$

with  $H_{m,m'}(\mathbf{T})$  denoting the matrix elements of the hamiltonian of a state  $m$  in the cell at the origin and state  $m'$  in the cell labeled by translation vector  $\mathbf{T}$ ,

$$H_{m,m'}(\mathbf{T}) = \int d\mathbf{r} \chi_m^*(\mathbf{r} - \tau_m) \hat{H} \chi_{m'}[\mathbf{r} - (\tau_{m'} + \mathbf{T})]. \quad (27)$$

This is a hermitian matrix equation in  $m, m'$ . If the localized states are orthonormal (always possible in principle by transformation to Wannier functions), and the solution by standard diagonalization techniques leads to the bands of eigenvalues  $\varepsilon_i(\mathbf{k})$  and the periodic part of their eigenstates  $u_{i,\mathbf{k}}(\mathbf{r})$ .

In general, localized functions are not orthogonal. This is the case if the functions on neighboring sites are atomic-like and the shortest-range, most-transferable functions are in general non-orthogonal. This is the case in codes like SIESTA and GAUSSIAN. Then the overlap matrix is given by

$$S_{m,m'}(\mathbf{T}) = \int d\mathbf{r} \chi_m^*(\mathbf{r} - \tau_m) \chi_{m'}(\mathbf{r} - (\tau_{m'} + \mathbf{T})). \quad (28)$$

and the solution is a generalized eigenvalue problem

$$\sum_{m'} [H_{m,m'}(\mathbf{k}) - \varepsilon_i(\mathbf{k}) S_{m,m'}(\mathbf{k})] c_{i,m'}(\mathbf{k}) = 0. \quad (29)$$

# Localized Basis Calculations

We now have the equations to solve *any* independent particle problem in a crystal. The Kohn-Sham equations can be solved in this way as an alternative to plane waves. These methods are now widely used, especially in chemistry, and are very efficient for large problems like nanostructures.

What is the problem?

- Must choose the basis - not as straightforward as in plane waves
- Gaussian Basis
  - Advantage - all integrals analytic
  - Disadvantage - Many Gaussians needed to represent atomic-like functions
  - Highly developed in codes like GAUSSIAN, GAMES, CRYSTAL, . . .
- Numerical radial orbital Basis
  - Advantage - represent atomic-like functions accurately with few functions on a radial grid all integrals
  - Disadvantage - Complicated to calculate all the needed integrals
  - Used in codes like SIESTA

# Tight-binding Slater-Koster Approach

- Tight-binding Models and Empirical Approximations for the matrix elements  $H_{m,m'}(\mathbf{T})$  show us the general character of solutions
  - Models can be fit to describe any bands - very useful but require many parameters
  - Models can be made to approximate classes of materials with a few parameters, for example, Harrison's "universal model" which are meant to give approximate bands all elements
  - Here we assume orthonormal orbitals for simplicity - not essential
- One- and two-center approximation
  - If we assume only one- or two-centers are involved, the matrix elements have the same symmetry as for an atom (spherical symmetry) or a diatomic molecule (angular momentum about the axis is conserved).
  - Orbitals are labelled by angular momentum, : s, p, d, ...
  - All interatomic matrix elements are labelled by angular momentum about the axis between the atoms:
    - m=0:  $ss\sigma, sp\sigma, sd\sigma, pd\sigma, dd\sigma, \dots$
    - m=1:  $pp\pi, pd\pi, dd\pi, \dots$
    - m=2:  $dd\delta, \dots$
  - The code TBPW has as two types of algorithms: 1) a hard-coded set of formulas valid for s,p,d states and 2) a general rotation matrix formulation valid for any angular momentum. See the documentation and the book by R. Martin for a description.
- Examples
  - Si bands with parameters fitted by Vogl, et al..
  - C nanotubes. The structures, Brillouin zones, and bands of the "zig-zag" and "armchair" nanotubes are illustrated in the figure (the same as Fig. 14.9 of Martin). The bands are calculated using the tight-binding model of Xu et al..

## References

- [1] R. M. Martin, *Electronic Structure: Basic Theory and Methods*, Cambridge University Press, Cambridge, U.K., 2004.
- [2] N.W. Ashcroft and N.D. Mermin, *Solid State Physics*, W.B. Saunders Company, Philadelphia, 1976.
- [3] C. Kittel, *Introduction to Solid State Physics*, John Wiley and Sons, New York, 1996.
- [4] M. L. Cohen and J. R. Chelikowsky, *Electronic Structure and Optical Properties of Semiconductors*, 2nd ed., Springer-Verlag, Berlin, 1988.
- [5] W. E. Pickett, ‘Pseudopotential methods in condensed matter applications’, *Computer Physics Reports* 9:115, 1989.
- [6] S. B. Zhang, C.-Y. Yeh, and A. Zunger, ‘Electronic structure of semiconductor quantum films’, *Phys. Rev. B* 48:11204–11219, 1993.
- [7] W. A. Harrison, *Electronic Structure and the Properties of Solids*, Dover, New York, 1989.
- [8] W. A. Harrison, *Elementary Electronic Structure*, World Publishing, Singapore, 1999.
- [9] P. Vogl, H. P. Hjalmarson, and J. D. Dow, ‘A semi-empirical tight-binding theory of the electronic structure of semiconductors’, *Europhys. Lett.* 44:365, 1983.
- [10] C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho, ‘A transferable tight-binding potential for carbon’, *J. Phys.: Condens. Matter* 4:6047, 1992.



Figure 8: Bands for Si using an empirical pseudopotential. Only the lowest 8 bands are shown. Energies are in Hartrees ( $1 \text{ Ha} = 27.2 \text{ eV}$ ).

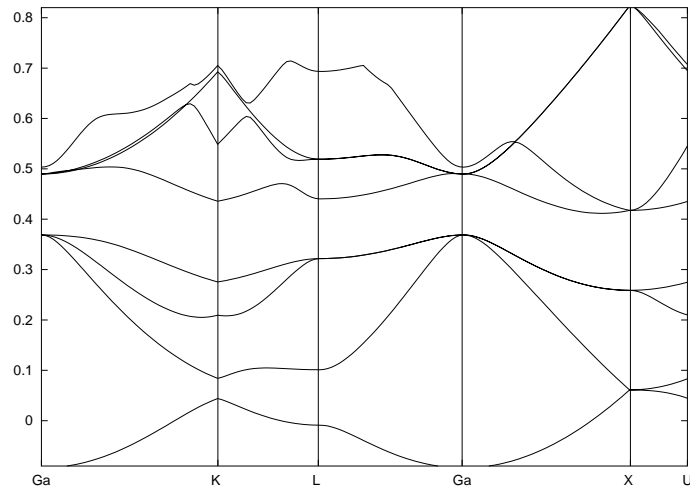


Figure 9: Bands for GaAs using empirical pseudopotentials. Only the lowest 8 bands are shown.

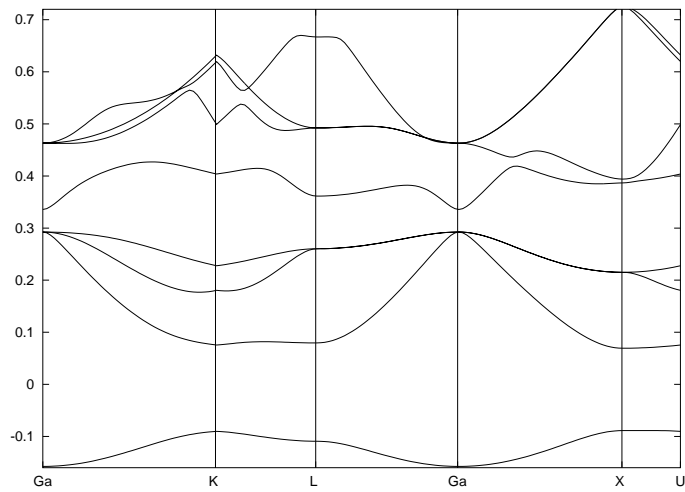


Figure 10: Bands for Si calculated with the Slater–Koster parameters determined by Vogl and coworkers. The higher bands are not reliable and only the lowest 8 bands are shown.

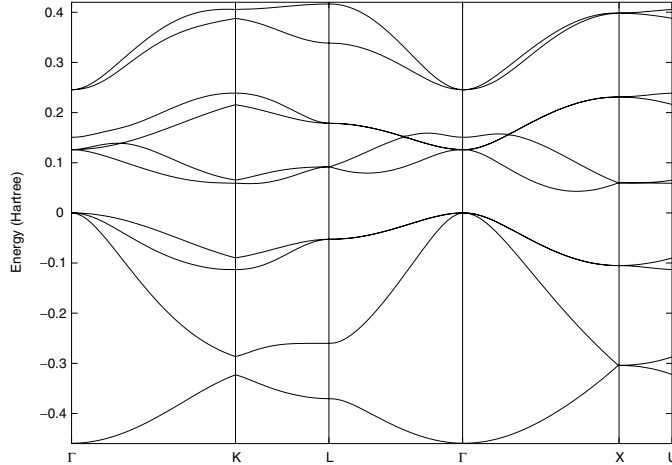


Figure 11: Structures, Brillouin zones, and bands of the “zig-zag” (a) and “armchair” (b) nanotubes. The bands are calculated using the tight-binding model of Xu et al.. The zig-zag tubes shown are denoted  $(13, 0)$  and  $(12, 0)$ ; the latter is insulating and the former has a small gap that is due to curvature. The armchair  $(n, n)$  tubes are always metallic since the lines of allowed states with  $k$  along the tube always include  $\Gamma$  and one of the K points. (b) Illustrates the bands for a  $(3, 3)$  tube. In each case the bands of the tube are plotted in the one-dimensional BZ denoted  $\Gamma \rightarrow X$ . Provided by J. Kim.

