

Electronic Structure of Condensed Matter Fudan University - April 2010

Understanding electrons in solids The three types of descriptions

Understanding electrons in solids The three basic methods

Instructor: Richard M. Martin
University of Illinois
Stanford University

rmartin@illinois.edu

and

rmartin42@gmail.com

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The three ideas and three methods

- **LCAO - Representation of the eigenfunctions as linear combination of atomic-like orbitals**
 - The dominant functions having the same s-p-d character as in the atom --- additional radial functions and higher angular momentum to improve the description
 - Good way to understand bands – get simple approximations
- **Plane waves - Representation of the eigenfunctions in terms of a general independent of the atoms**
 - Good way to describe nearly free electron bands
 - Advantage for computation – very simple algorithms – the same for all problems
 - BUT one must use pseudopotentials that put in the atoms
- **Augmented methods – expansion in spherical harmonics near the nucleus – smooth functions (e.g., plane waves) between the atoms**
 - The “best of both worlds” - atomic-like and band-like
 - Good way to describe localized states like d electrons
 - General algorithms, but difficult

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Local atomic-like orbitals (LCAOs)

The good thing about LCAOs

They are atomic-like

Incorporate the fact that states are atomic-like near each atom

The bad thing about LCAOs

They are atomic-like

The “tail” of an orbital does not have the character of the molecular or solid state

The good thing about LCAOs

A very small basis is sufficient to give a semi-quantitative understanding of electronic states

A larger (but still small) carefully-chosen basis is very efficient for accurate calculations of electronic states

The obvious basis for a molecule where the eigenstates are localized to the molecule - widely used in chemistry

Gaussians are not atomic-like but they are advantageous because all integrals are analytic

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Independent-Particle Eqs in Localized Bases

14.1 Localized atom-centered orbitals

A local orbital basis is a set of orbitals $\chi_\alpha(\mathbf{r} - \mathbf{R}_I)$, each associated with an atom at position \mathbf{R}_I . In order to simplify notation, we will let m denote both α and site I , so that $m = 1, \dots, N_{\text{basis}}$ labels all the states in the basis, which can also be written $\chi_m(\mathbf{r} - \mathbf{R}_m)$.

Any state can be expressed as a linear combination of basis orbitals

$$\Psi_i = \sum_m c_{im} \chi_m(\mathbf{r} - \mathbf{R}_m) \quad (\text{LCAO})$$

Matrix elements $H_{mm'} = \langle \chi_m | H | \chi_{m'} \rangle = \int \chi_m(\mathbf{r} - \mathbf{R}_m) H \chi_{m'}(\mathbf{r} - \mathbf{R}_{m'})$

Localized functions are not orthogonal $S_{mm'} = \langle \chi_m | \chi_{m'} \rangle = \int \chi_m(\mathbf{r} - \mathbf{R}_m) \chi_{m'}(\mathbf{r} - \mathbf{R}_{m'})$

Leads to matrix equation: $\sum_{m'} (H_{mm'} - \epsilon_i S_{mm'}) c_{im'} = c_{im}$

The problem separates into two parts:

The Schrodinger equation is determined by the matrix elements

The actual form in real space is determined by the functions $\chi_m(\mathbf{r} - \mathbf{R}_m)$

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Expressions in a crystal

14.1 Localized atom-centered orbitals

A local orbital basis is a set of orbitals $\chi_\alpha(\mathbf{r} - \mathbf{R}_I)$, each associated with an atom at position \mathbf{R}_I . In order to simplify notation, we will let m denote both α and site I , so that $m = 1, \dots, N_{\text{basis}}$ labels all the states in the basis, which can also be written $\chi_m(\mathbf{r} - \mathbf{R}_m)$.

$\chi_m(\mathbf{r} - \mathbf{R}_m) \rightarrow \chi_m(\mathbf{r} - (\tau_m + \mathbf{T}))$, where \mathbf{T} is a translation vector.

In a crystal, all matrix elements between states separated by \mathbf{T} :

$$H_{m,m'}(\mathbf{T}) = \int d\mathbf{r} \chi_m^*(\mathbf{r} - \tau_m) \hat{H} \chi_{m'}(\mathbf{r} - (\tau_{m'} + \mathbf{T})), \quad (14.1)$$

$$S_{m,m'}(\mathbf{T}) = \int d\mathbf{r} \chi_m^*(\mathbf{r} - \tau_m) \chi_{m'}(\mathbf{r} - (\tau_{m'} + \mathbf{T})). \quad (14.2)$$

The Bloch theorem for the eigenstates can be derived by defining a basis state with wavevector \mathbf{k} ,

$$\chi_{m\mathbf{k}}(\mathbf{r}) = A_m \sum_{\mathbf{T}} e^{i\mathbf{k} \cdot \mathbf{T}} \chi_m(\mathbf{r} - (\tau_m + \mathbf{T})), \quad (14.3)$$

The following slides have many details. The parts that are most important are the secular equations on the previous slide, the form of the matrix elements. The Slater-Koster form is perhaps the simplest way in the entire course to understand bands qualitatively, and it will be used in exercises. ⁵

Expressions in a crystal - II

Thus the matrix elements and Schrodinger Eq can be written:

$$H_{m,m'}(\mathbf{k}) = \int d\mathbf{r} \chi_{m\mathbf{k}}^*(\mathbf{r}) \hat{H} \chi_{m'\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k} \cdot \mathbf{T}} H_{m,m'}(\mathbf{T}), \quad (14.4)$$

and

$$S_{m,m'}(\mathbf{k}) = \int d\mathbf{r} \chi_{m\mathbf{k}}^*(\mathbf{r}) \chi_{m'\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k} \cdot \mathbf{T}} S_{m,m'}(\mathbf{T}). \quad (14.5)$$

Since the hamiltonian conserves \mathbf{k} , an eigenfunction of the Schrödinger equation in a basis always can be written in the form

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_m c_m(\mathbf{k}) \chi_{m\mathbf{k}}(\mathbf{r}), \quad (14.6)$$

and the secular equation for wavevector \mathbf{k} is

$$\sum_{m'} [H_{m,m'}(\mathbf{k}) - \varepsilon_i(\mathbf{k}) S_{m,m'}(\mathbf{k})] c_{i,m'}(\mathbf{k}) = 0. \quad (14.7)$$

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Atomic-like functions

14.2 Matrix elements with atomic orbitals

Much can be gained from consideration of the symmetries of the basis orbitals and the crystal or molecule. This is the basis for tight-binding approaches (Sec. 14.4) and continues to be essential in full calculations (Ch. 15). An appropriate choice for basis functions is a set of atomic-like functions centered on the atom sites. On each site κ , j the basis functions can be written as radial functions multiplied by spherical harmonics,

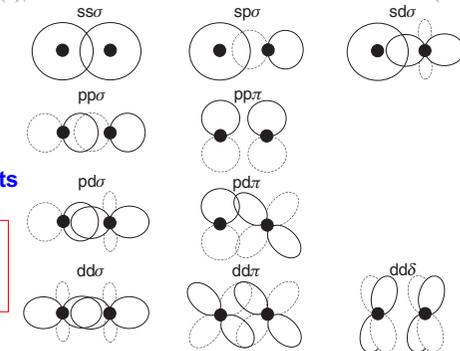
$$\chi_\alpha(\mathbf{r}) \rightarrow \chi_{nlm}(\mathbf{r}) = \chi_{nl}(r) Y_{lm}(\hat{\mathbf{r}}), \quad (14.8)$$

Schematic pictures of overlaps

and

2-center matrix elements

The figures are very useful for understanding the matrix elements



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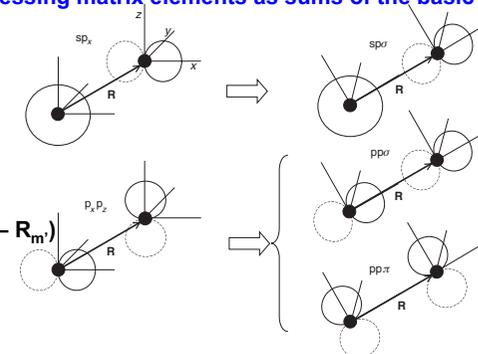
Two-center Matrix elements

2-center matrix elements can always be written in terms of direction cosines – prove by expressing matrix elements as sums of the basic forms on previous slide

Overlap

Kinetic energy

$$-1/2 \int \chi_m(\mathbf{r} - \mathbf{R}_m) \Delta \chi_{m'}(\mathbf{r} - \mathbf{R}_{m'})$$



Each matrix element can be expressed as simple functions of the angles multiplied by a function of the distance between the centers – next slide

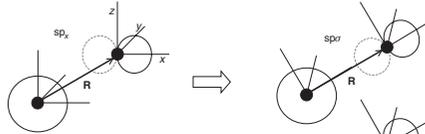
Potential matrix elements in general more complicated – lower symmetry - often called “3-center”

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Two-center Matrix elements II

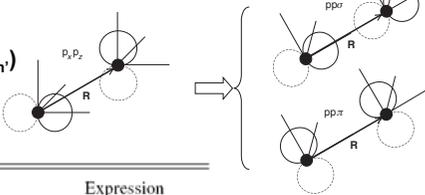
2-center matrix elements can always be written in terms of direction cosines – prove by expressing matrix elements as sums of the basic forms on previous slide

Overlap



Kinetic energy

$$-1/2 \int \chi_m(\mathbf{r} - \mathbf{R}_m) \Delta \chi_{m'}(\mathbf{r} - \mathbf{R}_{m'})$$



Element		Expression
$K_{s,s}$	$\hat{\mathbf{R}} \equiv \{x, y, z\}$	$K_{ss\sigma}$
K_{s,p_x}		$x^2 K_{sp\sigma}$
K_{p_x,p_x}		$x^2 K_{pp\sigma} + (1 - x^2) K_{pp\pi}$
K_{p_x,p_z}		$xz(K_{pp\sigma} - K_{pp\pi})$

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Slater-Koster Formulation – Tight-binding

If all matrix elements are approximated as having the 2-center form, then the hamiltonian and overlaps are completely determined by the angular momenta considered and forms of the matrix elements as a function of distance

$$\sum_{m'} (H_{mm'} - \epsilon_i S_{mm'}) c_{im'} = c_{im}$$

In a crystal

$$\sum_{m'} [H_{m,m'}(\mathbf{k}) - \epsilon_i(\mathbf{k}) S_{m,m'}(\mathbf{k})] c_{i,m'}(\mathbf{k}) = 0. \quad (14.7)$$

with

$$H_{m,m'}(\mathbf{k}) = \int d\mathbf{r} \chi_{mk}^*(\mathbf{r}) \hat{H} \chi_{m'k}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k} \cdot \mathbf{T}} H_{m,m'}(\mathbf{T}), \quad (14.4)$$

etc.

Tight-binding approximation – consider matrix elements as parameters – fit to experiment or to a theoretical calculation

Very useful !

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Two-center Matrix elements III

2-center matrix elements for H and S have the simple form

Element		Expression
$K_{s,s}$	$\hat{\mathbf{R}} \equiv \{x, y, z\}$	$K_{ss\sigma}$
K_{s,p_x}		$x^2 K_{sp\sigma}$
K_{p_x,p_x}		$x^2 K_{pp\sigma} + (1 - x^2) K_{pp\pi}$
K_{p_x,p_z}		$xz(K_{pp\sigma} - K_{pp\pi})$

Functions of distance |R|

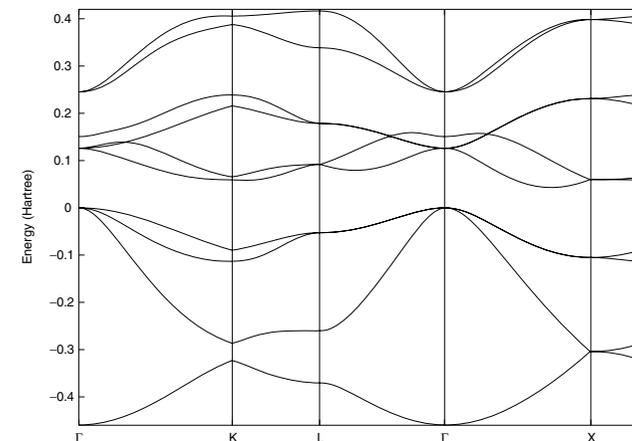
Each matrix element can be expressed as simple functions of the angles multiplied by a function of the distance between the centers

Potential matrix elements in general more complicated – lower symmetry – often called “3-center”

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Examples of results - I

Silicon – fitted scheme with 5 functions per atom (s, 3p, s*) (where s* denotes a second s state) i.e., a 10x10 matrix.)



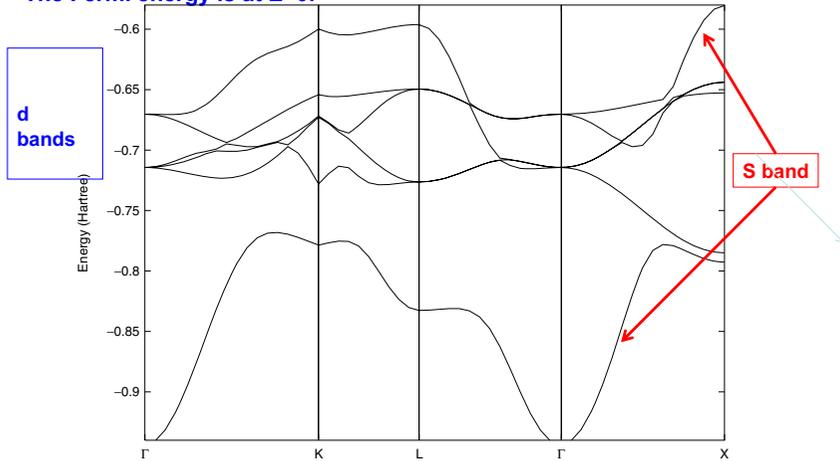
If the smallest possible basis is used (s,p with 4 states per atom), the conduction band will not have the correct shape with the minimum on the line (called Δ) between Γ and X.

(Fig. 14.6 calculated by N. Romero)

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Examples of results - II

Nickel – simple Harrison scheme with 9 functions per atom (s, 3p, 5d)
 Note the 5 narrow d bands and the one s band that crosses the d bands.
 The Fermi energy is at $E=0$.



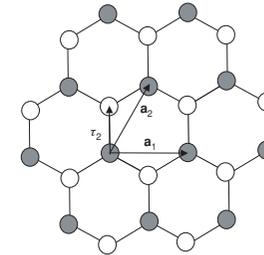
(Fig. 14.7 calculated by N. Romero)

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Simple examples - graphene

π bands of graphene (single sheet of graphite)

Two atoms per cell
 - both carbon



σ states form strong s-p bonds in the plane

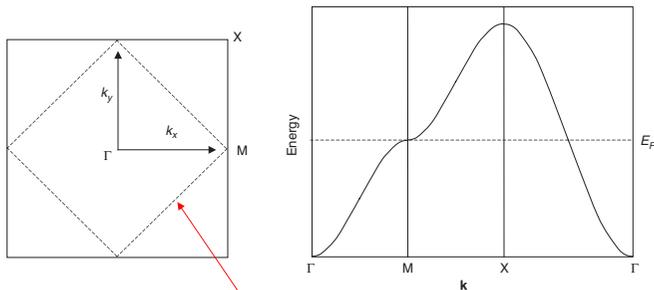
π states are perpendicular to plane – interaction of two states in the same plane is the same in all direction – i.e., s-like in the plane

See next slide

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Simple examples – square lattice

Square lattice – s band – assume states are orthonormal and the only non-zero matrix element of H is for nearest-neighbors



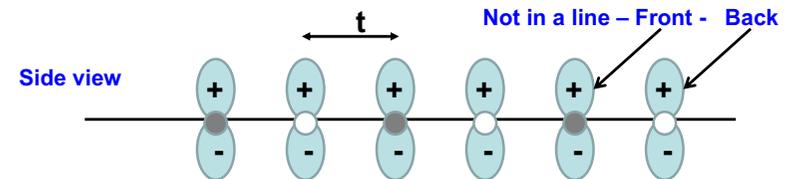
Fermi Surface for one electron per site - a half-filled band

The basic model the metallic bands near the Fermi energy in Hi-Tc superconductors

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Simple examples - graphene

π bands of graphene -- tight-binding nearest neighbor matrix element t



π states are perpendicular to plane – interaction of two states in the same plane is the same in all direction – i.e., s-like in the plane
 – assume states are orthonormal and the only non-zero matrix element of H is for nearest-neighbors

With this assumption there are only matrix elements between connecting states on white and black atoms

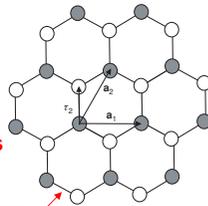
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Simple examples – graphene continued

π bands of graphene (single sheet of graphite)

Two atoms per cell - both carbon

Only matrix elements between white and black atoms



Matrix element t for each bond

Expressions for bands

$$|\hat{H}(\mathbf{k}) - \varepsilon(\mathbf{k})| = \begin{vmatrix} -\varepsilon(\mathbf{k}) & H_{12}(\mathbf{k}) \\ H_{21}^*(\mathbf{k}) & -\varepsilon(\mathbf{k}) \end{vmatrix} = 0, \quad (14.14)$$

where

$$H_{12}(\mathbf{k}) = t \left[e^{ik_x a / \sqrt{3}} + 2e^{-ik_x a / 2\sqrt{3}} \cos\left(k_y \frac{a}{2}\right) \right], \quad (14.15)$$

where a is the lattice constant. This is readily solved to yield the bands [204]

$$\varepsilon(\mathbf{k}) = \pm |H_{12}(\mathbf{k})| = \pm t \left[1 + 4 \cos\left(k_x \frac{\sqrt{3}a}{2}\right) \cos\left(k_y \frac{a}{2}\right) + 4 \cos^2\left(k_y \frac{a}{2}\right) \right]^{1/2}. \quad (14.16)$$

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Simple examples – graphene continued II

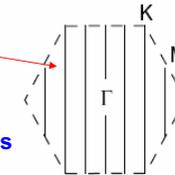
π bands of graphene – repeating expression in tight binding approx.

$$\varepsilon(\mathbf{k}) = \pm |H_{12}(\mathbf{k})| = \pm t \left[1 + 4 \cos\left(k_x \frac{\sqrt{3}a}{2}\right) \cos\left(k_y \frac{a}{2}\right) + 4 \cos^2\left(k_y \frac{a}{2}\right) \right]^{1/2}. \quad (14.16)$$

The most remarkable feature of the graphene bands is that they touch at the corners of the hexagonal Brillouin zone, e.g. the point denoted K ($k_x = 2\pi/\sqrt{3}a, k_y = 0$) shown in the BZ in Fig. 14.9. This and other aspects are brought out in Exercise 14.19. Note also that the bands are symmetric in $\pm\varepsilon$. Since there is one π electron per atom, the band is half-filled and the bands touch with finite slope at the Fermi energy, i.e. a Fermi surface consisting of points. It is this unusual feature that gives rise to the grand array of possibilities for the electronic structure of nanotubes.

Brillouin Zone

Two bands since there are two sates per cell --- but the bands touch at the six points labeled K



Zero gap. Graphene has “Fermi points” (instead of a normal metal Fermi surface)

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Exercise in homework

Work out the matrix elements and the bands yourself

The result should be given for $\mathbf{k} = (k_x, k_y)$ in the plane - but this depends upon the definition of the x and y directions. For the exercise take the x and y directions as shown in the figure.

If you choose to use the formulas in the book, You should know that there is a mistake in one edition of the book – you need to work it out yourself!

where

$$H_{12}(\mathbf{k}) = t \left[e^{ik_x a / \sqrt{3}} + 2e^{-ik_x a / 2\sqrt{3}} \cos\left(k_y \frac{a}{2}\right) \right], \quad (14.15)$$

where a is the lattice constant. This is readily solved to yield the bands [204]

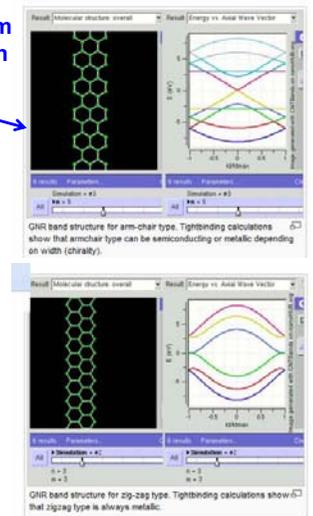
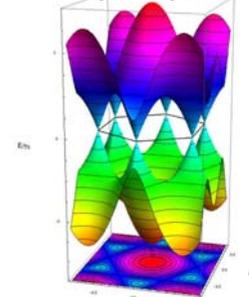
$$\varepsilon(\mathbf{k}) = \pm |H_{12}(\mathbf{k})| = \pm t \left[1 + 4 \cos\left(k_x \frac{\sqrt{3}a}{2}\right) \cos\left(k_y \frac{a}{2}\right) + 4 \cos^2\left(k_y \frac{a}{2}\right) \right]^{1/2}. \quad (14.16)$$

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Graphene planes and “ribbons”

Two examples of “ribbons” cut from graphene sheets – bands for $\varepsilon(\mathbf{k})$ in one dimension

Infinite plane – Dirac points where bands touch with linear band slopes at points



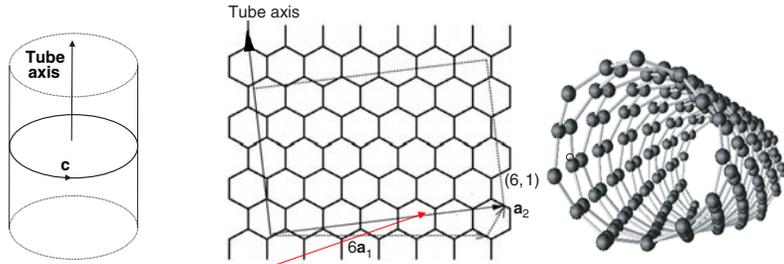
Tight-binding calculations from

http://en.wikipedia.org/wiki/Graphene#Electronic_properties

Carbon nanotubes

Rolled up sheets of graphene – π bands form states near Fermi energy

Model: π bands are the same as in graphene – the only difference is that the only allowed states are those that satisfy the boundary condition for the tube $\psi(r+L) = \psi(r)$



Vector L indicates points that are brought together in rolling

Bands depend on how sheet is rolled

Can be chiral, non-chiral, metals, insulators,

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Accurate Kohn-Sham Calculations

The LCAO method can be very accurate if a large basis with many atom-centered states are used

The main computational difficulties are:

- Calculation of the density and generation of the new potential in the iterations to the self-consistent solution
- Calculation of the matrix elements

Useful codes:

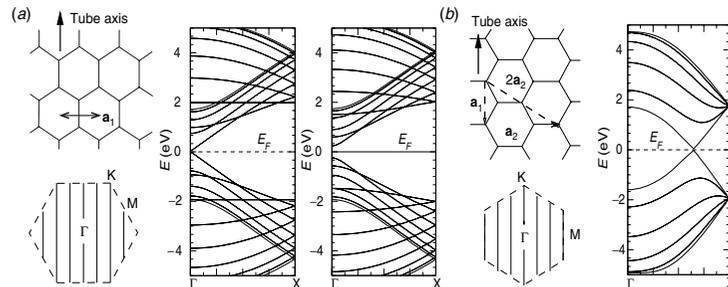
SIESTA – very efficient – designed for solids
- includes molecular dynamics, etc.

Many Gaussian based codes designed for molecules – GAUSSIAN, ...

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Carbon nanotubes – two examples

Rolled up sheets of graphene – π bands form states near Fermi energy



“Zig-zag” zero-gap metal or narrow gap semiconductor

“Armchair” metallic because states allowed by rolled tube always include the zero-gap states

Works very well for large diameter tubes

– there are important corrections for very small diameter tubes

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Why are Gaussians so useful?

The needed integrals always have the form

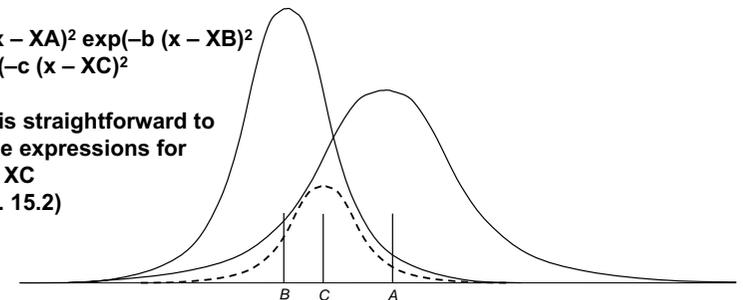
$$\int \chi_{m'}(r - R_{m'}) \chi_{m''}(r - R_{m''}) \chi_m(r - R_m) \chi_{m'''}(r - R_{m'''})$$

These integrals can easily be evaluated for gaussians multiplied by any polynomial.

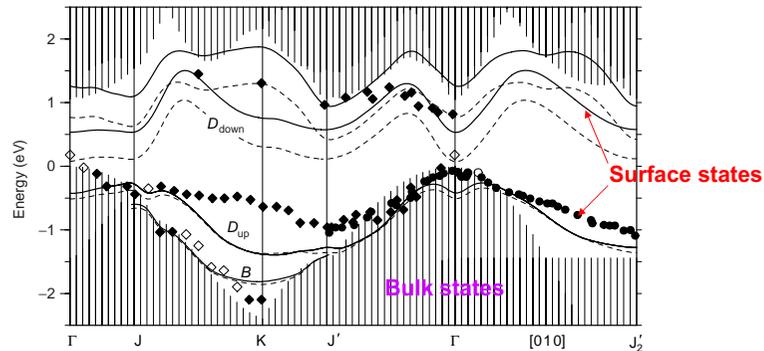
The reason is simple: The product of two gaussians is a gaussian

$$\exp(-a(x - XA)^2) \exp(-b(x - XB)^2) = g \exp(-c(x - XC)^2)$$

where it is straightforward to derive the expressions for g, c, and XC (see Sec. 15.2)



Example of Gaussian basis calculation



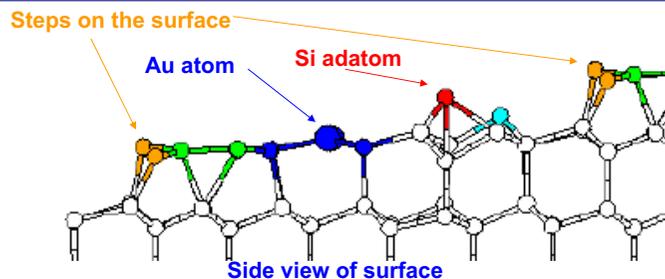
Gaussian basis code by Rohlfing (Fig 15.2 in text) has been applied to the bands of many materials – excellent agreement with plane waves

Here is an example of states at a surface of Ge. This shows both LDA results (the famous zero gap) and “GW” calculations (discussed later) done with the same basis.

Au “wires” on Si (557) surface

SIESTA local orbital calculation (numerical modified atomic orbitals)

Most stable structure predicted from theory
in very good agreement with experiment done later
[I. K. Robinson, et al., PRL 88, 096104 (2002)]



After the finding structure, plane wave calculations were used to calculate electronic bands (very close to bands from SIESTA) – Novel large coupling to the electron spin effect predicted – PRL 93, 146803 (2004)

Conclusions

Atomic-like (LCAO) bases are very useful

A very small number of states is sufficient to understand important aspects of bands

Tight binding approximations leads to very simple algebra and description of bands

Examples – Si, Ni, graphene, nanotubes,

Useful codes available (SIESTA (free) , GAUSSIAN, GAMESS free) ,

Simple code - TBPW from my group, free