

PHY 752 Solid State Physics
11-11:50 AM MWF Olin 107

Plan for Lecture 9:

Reading: Chapter 8 in MPM; Electronic Structure

- 1. Linear combination of atomic orbital (LCAO) method**
- 2. Slater and Koster analysis**
- 3. Wannier representation**

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Course schedule for Spring 2015
(Preliminary schedule -- subject to frequent adjustment.)

Lecture date	MPM Reading	Topic	Assign.	Due date
1 Mon: 01/12/2015	Chap. 1 & 2	Crystal structures	#1	01/23/2015
2 Wed: 01/14/2015	Chap. 1 & 2	Some group theory	#2	01/23/2015
Fri: 01/16/2015	No class	NAWH out of town		
Mon: 01/19/2015	No class	MLK Holiday		
3 Wed: 01/21/2015	Chap. 1 & 2	Some group theory	#3	01/23/2015
4 Fri: 01/23/2015	Chap. 1 & 2	Some more group theory	#4	01/26/2015
5 Mon: 01/26/2015	Chap. 7.3	Some more group theory	#5	01/28/2015
6 Wed: 01/28/2015	Chap. 6	Electronic structure; Free electron gas	#6	01/30/2015
7 Fri: 01/30/2015	Chap. 7	Electronic structure; Model potentials	#7	02/02/2015
8 Mon: 02/02/2015	Chap. 8	Electronic structure; LCAO	#8	02/04/2015
9 Wed: 02/04/2015	Chap. 8	Electronic structure; LCAO and tight binding	#9	02/06/2015

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WFU Physics Colloquium

TITLE: Diagnosis and treatment of cancer with radiofrequency electromagnetic fields amplitude modulated at tumor-specific frequencies

SPEAKER: Dr. Boris Pasche,
Department of Cancer Biology
Wake Forest University

TIME: Wednesday February 4, 2015 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

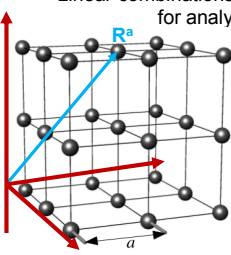
Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

In the past century, there have been many attempts to treat cancer with low levels of electric and magnetic fields. We have developed noninvasive biofeedback examination

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Linear combinations of atomic orbitals (LCAO) methods for analyzing electronic structure



Bloch wave:

$$\Psi_{nk}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{nk}(\mathbf{r})$$
 where $u_{nk}(\mathbf{r})$ is a periodic function.

Let $\mathbf{R}^a = \boldsymbol{\tau}^a + \mathbf{T}$
 where $\boldsymbol{\tau}^a$ is the basis vector and \mathbf{T} is the lattice translation vector.

Bloch wave identity: $\Psi_{nk}(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}} \Psi_{nk}(\mathbf{r})$

LCAO basis functions with Bloch symmetry:

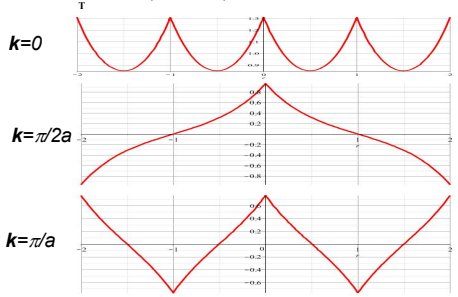
$$\Phi_{\mathbf{k}}^{nlm}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot(\mathbf{r} + \mathbf{T})} \phi_{nlm}^a(\mathbf{r} - \boldsymbol{\tau}^a - \mathbf{T})$$

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LCAO methods -- continued

LCAO basis functions with Bloch symmetry:

$$\Phi_{\mathbf{k}}^{nlm}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi_{nlm}^a(\mathbf{r} - \boldsymbol{\tau}^a - \mathbf{T})$$
 Example for $\phi_{nlm}(\mathbf{r}) = \phi_{100}(\mathbf{r}) = Ce^{-\gamma r}$



$k=0$

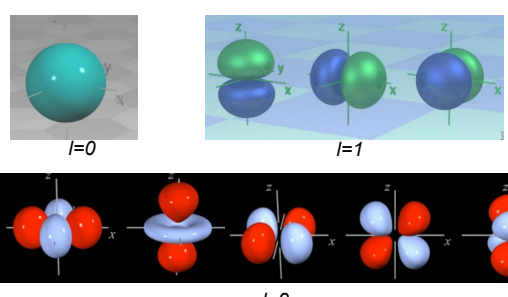
$k=\pi/2a$

$k=\pi/a$

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LCAO methods -- continued – angular variation

<http://winter.group.shef.ac.uk/orbitron/>



$l=0$

$l=1$

$l=2$

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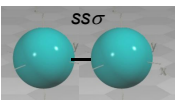
LCAO methods -- continued -- angular variation

While, for atoms the "z" axis is an arbitrary direction, for diatomic molecules and for describing bonds, it is convenient to take the "z" axis as the bond direction.

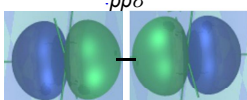
Atom		Bond		
	<i>symbol</i>		<i>symbol</i>	
$l=0$	$m=0$	s	$l=0$ $\lambda=0$	σ
$l=1$	$m=0$	p	$l=1$ $\lambda=0$	σ
	$m=\pm 1$	p	$l=1$ $\lambda=1$	π
$l=2$	$m=0$	d	$l=2$ $\lambda=0$	σ
	$m=\pm 1$	d	$l=2$ $\lambda=1$	π
	$m=\pm 2$	d	$l=2$ $\lambda=2$	δ

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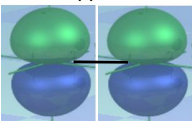
LCAO methods -- continued -- bond types



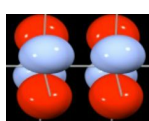
$ss\sigma$



$pp\sigma$



$pp\pi$



$dd\pi$

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PHYSICAL REVIEW VOLUME 94, NUMBER 6 JUNE 15, 1954

Simplified LCAO Method for the Periodic Potential*

J. C. SLATER AND G. F. KOSTER†
Massachusetts Institute of Technology, Cambridge, Massachusetts
 (Received February 17, 1954)

The LCAO, or Bloch, or tight binding, approximation for solids is discussed as an interpolation method, to be used in connection with more accurate calculations made by the cellular or orthogonalized plane-wave methods. It is proposed that the various integrals be obtained as disposable constants, so that the tight binding method will agree with accurate calculations at symmetry points in the Brillouin zone for which these calculations have been made, and that the LCAO method then be used for making calculations throughout the Brillouin zone. A general discussion of the method is given, including tables of matrix components of energy for simple cubic, face-centered and body-centered cubic, and diamond structures. Applications are given to the results of Fletcher and Wohlfarth on Ni, and Howarth on Cu, as illustrations of the fcc case. In discussing the bcc case, the splitting of the energy bands in chromium by an antiferromagnetic alternating potential is worked out, as well as a distribution of energy states for the case of no antiferromagnetism. For diamond, comparisons are made with the calculations of Herman, using the orthogonalized plane-wave method. The case of such crystals as InSb is discussed, and it is shown that their properties fit in with the energy band picture.

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LCAO methods -- continued – Slater-Koster analysis

LCAO basis functions with Bloch symmetry:

$$\Phi_{\mathbf{k}}^{\alpha nm}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k} \cdot (\mathbf{r}^a + \mathbf{T})} \phi_{nlm}^{\alpha}(\mathbf{r} - \mathbf{r}^a - \mathbf{T})$$

Approximate Bloch wavefunction:

$$\Psi_{\alpha\mathbf{k}}(\mathbf{r}) = \sum_{\alpha nm} X_{\alpha\mathbf{k}}^{\alpha nm} \Phi_{\mathbf{k}}^{\alpha nm}(\mathbf{r})$$

In this basis, we can estimate the electron energy by variationally computing the expectation value of the Hamiltonian:

$$E_{\alpha\mathbf{k}} = \frac{\langle \Psi_{\alpha\mathbf{k}} | H | \Psi_{\alpha\mathbf{k}} \rangle}{\langle \Psi_{\alpha\mathbf{k}} | \Psi_{\alpha\mathbf{k}} \rangle}$$

Terms in this expansion have the form:

$$\sum_{\mathbf{T}} e^{i\mathbf{k} \cdot (\mathbf{r}^a - \mathbf{r}^b + \mathbf{T})} \langle \phi_{n'l'm'}^{\alpha}(\mathbf{r} - \mathbf{r}^b) | H | \phi_{nlm}^{\alpha}(\mathbf{r} - \mathbf{r}^a - \mathbf{T}) \rangle$$

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LCAO methods – Slater-Koster analysis -- continued

$$\sum_{\mathbf{T}} e^{i\mathbf{k} \cdot (\mathbf{r}^a - \mathbf{r}^b + \mathbf{T})} \langle \phi_{n'l'm'}^{\alpha}(\mathbf{r} - \mathbf{r}^b) | H | \phi_{nlm}^{\alpha}(\mathbf{r} - \mathbf{r}^a - \mathbf{T}) \rangle$$

Notation in Slater-Koster paper

$$\mathbf{k} \cdot (\mathbf{r}^a - \mathbf{r}^b + \mathbf{T}) = l\xi + m\eta + n\zeta$$

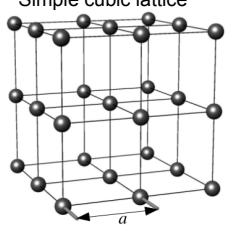
$$\langle \phi_{n'l'm'}^{\alpha}(\mathbf{r} - \mathbf{r}^b) | H | \phi_{nlm}^{\alpha}(\mathbf{r} - \mathbf{r}^a - \mathbf{T}) \rangle:$$

$E_{s,s}$	$(ss\sigma)$
$E_{s,z}$	$l(sp\sigma)$
$E_{z,z}$	$l^2(pp\sigma) + (1-l^2)(pp\pi)$
$E_{z,y}$	$lm(pp\sigma) - lm(pp\pi)$
$E_{z,x}$	$ln(pp\sigma) - ln(pp\pi)$
$E_{s,xy}$	$\sqrt{3}lm(sd\sigma)$

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LCAO methods – Slater-Koster analysis -- continued

Simple cubic lattice



on site NN
 $(s/s) = E_{s,s}(000) + 2E_{s,z}(100)(\cos\xi + \cos\eta + \cos\zeta)$

NNN
 $+ 4E_{s,z}(110)(\cos\xi\cos\eta + \cos\eta\cos\zeta + \cos\xi\cos\zeta) + \dots$

$$(\mathbf{r}^a - \mathbf{r}^b + \mathbf{T}) = ap\hat{x} + aq\hat{y} + ar\hat{z}$$

$$l = \frac{p}{\sqrt{p^2 + q^2 + r^2}} \quad m = \frac{q}{\sqrt{p^2 + q^2 + r^2}} \quad n = \frac{r}{\sqrt{p^2 + q^2 + r^2}}$$

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LCAO methods – summary

LCAO basis functions with Bloch symmetry:

$$\Phi_{\mathbf{k}}^{\alpha nlm}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{T})} \phi_{nlm}^{\alpha}(\mathbf{r}-\mathbf{T})$$

Approximate Bloch wavefunction:

$$\Psi_{\alpha\mathbf{k}}(\mathbf{r}) = \sum_{nlm} X_{\alpha\mathbf{k}}^{nlm} \Phi_{\mathbf{k}}^{\alpha nlm}(\mathbf{r})$$

In this basis, we can estimate the electron energy by variationally computing the expectation value of the Hamiltonian:

$$E_{\alpha\mathbf{k}} = \frac{\langle \Psi_{\alpha\mathbf{k}} | H | \Psi_{\alpha\mathbf{k}} \rangle}{\langle \Psi_{\alpha\mathbf{k}} | \Psi_{\alpha\mathbf{k}} \rangle}$$

Terms in this expansion have the form:

$$\sum_{\mathbf{T}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{T})} \langle \phi_{n'l'm'}^{\alpha}(\mathbf{r}-\mathbf{T}') | H | \phi_{nlm}^{\alpha}(\mathbf{r}-\mathbf{T}) \rangle$$

and also $\sum_{\mathbf{T}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{T})} \langle \phi_{n'l'm'}^{\alpha}(\mathbf{r}-\mathbf{T}') | \phi_{nlm}^{\alpha}(\mathbf{r}-\mathbf{T}) \rangle$

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LCAO methods – summary

LCAO basis functions with Bloch symmetry:

$$\Phi_{\mathbf{k}}^{\alpha nlm}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{T})} \phi_{nlm}^{\alpha}(\mathbf{r}-\mathbf{T})$$

Is there a “best choice” for atom-centered functions?

Introduction to the Wannier representation

PHYSICAL REVIEW B VOLUME 56, NUMBER 20 15 NOVEMBER 1997-II

Maximally localized generalized Wannier functions for composite energy bands

Nicola Marzari and David Vanderbilt
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08855-0849
(Received 10 July 1997)

We discuss a method for determining the optimally localized set of generalized Wannier functions associated with a set of Bloch bands in a crystalline solid. By “generalized Wannier functions” we mean a set of localized orthonormal orbitals spanning the same space as the specified set of Bloch bands. Although we minimize a functional that represents the total spread $\sum_{\mathbf{r}} \langle r^2 \rangle_{\mathbf{r}} = \langle r^2 \rangle_{\mathbf{r}}^2$ of the Wannier functions in real space, our method proceeds directly from the Bloch functions as represented on a mesh of k points, and carries out the minimization in a space of unitary matrices U_{nk}^{lm} describing the rotation among the Bloch bands at each k point. The method is thus suitable for use in connection with conventional electronic-structure codes. The procedure also returns the total electric polarization as well as the location of each Wannier center. Sample results for Si, GaAs, molecular C-H₂, and LiCl will be presented. (S0163-1829/97/02944-5)

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Wannier representation of electronic states

Note: This formulation is based on the relationship between the Bloch and Wannier representations and does not necessarily imply an independent computational method.

Bloch wave: $\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$ Bloch wave identity: $\Psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}} \Psi_{n\mathbf{k}}(\mathbf{r})$

Orthonormality: $\langle \Psi_{n\mathbf{k}}(\mathbf{r}) | \Psi_{n'\mathbf{k}'}(\mathbf{r}) \rangle = \delta_{nn'} \delta^3(\mathbf{k}-\mathbf{k}')$

Wannier function in lattice cell \mathbf{T} , associated with band n is given by

$$W_n(\mathbf{r}-\mathbf{T}) = \frac{V}{(2\pi)^3} \int d^3k e^{-i\mathbf{k}\cdot\mathbf{T}} \Psi_{n\mathbf{k}}(\mathbf{r})$$

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Wannier representation of electronic states -- continued

Wannier function in lattice cell \mathbf{T} , associated with band n is given by

$$W_n(\mathbf{r} - \mathbf{T}) = \frac{V}{(2\pi)^3} \int d^3k e^{-i\mathbf{k} \cdot \mathbf{T}} \Psi_{n\mathbf{k}}(\mathbf{r})$$

Note that:

$$\langle W_n(\mathbf{r} - \mathbf{T}) | W_{n'}(\mathbf{r} - \mathbf{T}') \rangle = \delta_{nn'} \delta_{\mathbf{T}\mathbf{T}'}$$

Comment: Wannier functions are not unique since the Bloch function may be multiplied by a \mathbf{k} -dependent phase, which may generate a different function $W_n(\mathbf{r}-\mathbf{T})$.

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Example from RMP **84**, 1419 (2012) by Mazari, Mostofi, Yates, Souza, and Vanderbilt

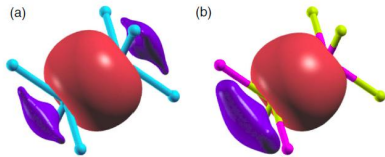


FIG. 2 (color online). Maximally localized Wannier functions (MLWFs) constructed from the four valence bands of Si (a) and GaAs [(b): Ga at upper right, As at lower left], displaying the character of σ -bonded combinations of sp^3 hybrids. Isosurfaces of different shades of gray correspond to two opposite values for the amplitudes of the real-valued MLWFs.

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