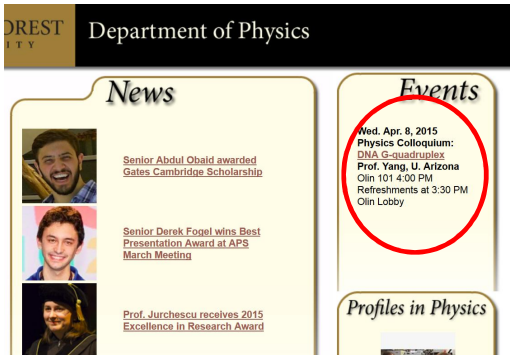
PHY 752 Solid State Physics
11-11:50 AM MWF Olin 107

Plan for Lecture 29:

- Chap. 22 in Marder & pdf file on "Maximally Localized Wannier Functions"
  - Electromagnetic properties of insulators
  - Modern theory of polarization

22	Fri: 03/20/2015	Chap. 16	Electron Transport	#21	03/23/2015
23	Mon: 03/23/2015	Chap. 17	Electron Transport	#22	03/25/2015
24	Wed: 03/25/2015	Chap. 17 & 18	Electron Transport		
25	Fri: 03/27/2015	Chap. 18	Microscopic picture of transport	#23	03/30/2015
26	Mon: 03/30/2015	Chap. 19	Semiconductor devices	#24	04/01/2015
27	Wed: 04/01/2015	Chap. 20	Models of dielectric functions	#25	04/06/2015
	Fri: 04/03/2015	Good Friday	No class		
28	Mon: 04/06/2015	Chap. 21	Optical properties of solids	#26	04/08/2015
29	Wed: 04/08/2015	Chap. 22	Modern theory of polorization	#27	04/10/2015
30	Fri: 04/10/2015				04/13/2015
31	Mon: 04/13/2015				04/15/2015
32	Wed: 04/15/2015				04/17/2015
33	Fri: 04/17/2015				04/20/2015
34	Mon: 04/20/2015				
35	Wed: 04/22/2015				
36	Fri: 04/24/2015				
	Mon: 04/27/2015		Presentations I		
	Wed: 04/29/2015		Presentations II		
	Fri: 05/01/2015		Presentations III & Take home exam		



Electromagnetic properties of insulating materials

Some references:

- "Maximally localized Wannier functions: Theory and applications", Marzari et al., RMP **84,** 1419 (2012)
- "Macroscopic polarization in crystalline dielectrics: the geometric phase approach", Resta, RMP **66**, 899 (1994)
- "Electric polarization as a bulk quantity and its relation to surface charge", Vanderbilt and King-Smith, PRB **48**, 4442 (1993)

REVIEWS OF MODERN PHYSICS, VOLUME 84, OCTOBER–DECEMBER 2012

Maximally localized Wannier functions: Theory and applications

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Notion of an electric dipole moment

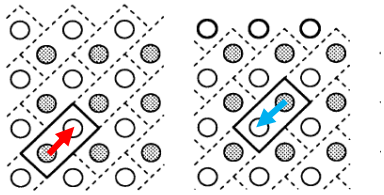
$$\mathbf{d} = -e\sum_j \langle\psi_j|\mathbf{r}|\psi_j\rangle$$

summing over eigenstates of the system

When the system is a periodic solid and the eigenstates are Bloch waves, $|\psi_{n\mathbf{k}}(\mathbf{r})\rangle$, this definition is problematic.

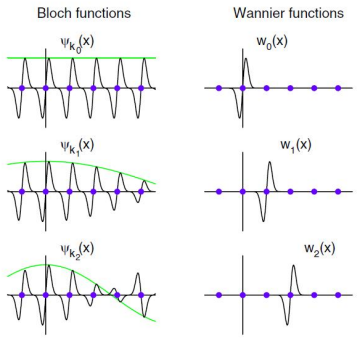
➔"Modern" theory of polarization can be formulated in terms of Wannier functions or in terms a Berry-phase expression. All of the formulations define the polarization modulo e**R**/V, where **R** is a lattice translation and V is the volume of the unit cell.

Ambiguity of polarization



P_1 P_2

Notion of Wannier functions formed from Bloch eigenstates: $\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$,



Construction of Wannier function from Bloch states

$$|\mathbf{R}n\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{R}}|\psi_{n\mathbf{k}}\rangle.$$

Inverse transform: $|\psi_{n\mathbf{k}}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}|\mathbf{R}n\rangle$

Non-uniqueness of Wannier functions; suppose a Bloch function is multiplied by an arbitrary phase:

$$|\tilde{\psi}_{n\mathbf{k}}\rangle = e^{i\varphi_n(\mathbf{k})}|\psi_{n\mathbf{k}}\rangle,$$

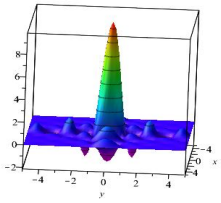
➔ constructed Wannier function would change

Simple example of Wannier function

Simple plane wave in a cubic unit cell of length a

$$|\psi_{n\mathbf{k}}(\mathbf{r})\rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$|\mathbf{R}n\rangle = \frac{8\sqrt{V}}{(2\pi)^3} \frac{\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi y}{a}\right)\sin\left(\frac{\pi z}{a}\right)}{xyz}$$



In addition to the arbitrary phase problem, it is often the case that there are multiple or entangled bands needed to form the Wannier states.

➔Turning problem into an advantage – notion of maximally localized Wannier functions

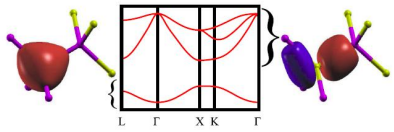


FIG. 3 (color online). MLWFs constructed from the s band (left) or from the three p bands (right) of GaAs.

Some details:

Normalization of Bloch waves:

$$\langle \psi_{n\mathbf{k}} | \psi_{m\mathbf{k}'} \rangle = \frac{(2\pi)^3}{V} \delta_{nm} \delta^3(\mathbf{k} - \mathbf{k}').$$

Orthogonality of Wannier functions:

$$\langle \mathbf{R}n | \mathbf{R}'m \rangle = \delta_{\mathbf{R}\mathbf{R}'} \delta_{nm}.$$

Notion of maximally localized Wannier function is to use the non-uniqueness to choose the phase in order to maximize the localization of the Wannier function

Wannier function in the center cell (**R**=0):

$$|0n\rangle = \frac{V}{(2\pi)^3}\int d\mathbf{k}\,|\psi_{nk}\rangle$$

First, the localization functional

$$\Omega = \sum_n [\langle 0n|r^2|0n\rangle - \langle 0n|\mathbf{r}|0n\rangle^2] = \sum_n [\langle r^2\rangle_n - \bar{\mathbf{r}}_n^2]$$

Practical calculation of localization function

$$\langle \mathbf{R}n|\mathbf{r}|\mathbf{0}m\rangle = i\frac{V}{(2\pi)^3}\int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{R}}\langle u_{n\mathbf{k}}|\nabla_{\mathbf{k}}|u_{m\mathbf{k}}\rangle$$

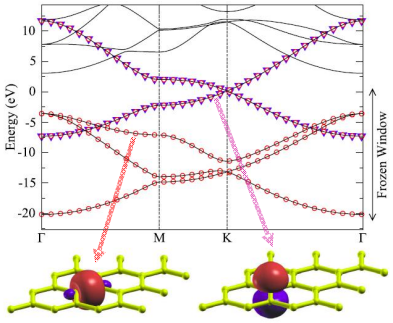
and

$$\langle \mathbf{R}n|r^2|\mathbf{0}m\rangle = -\frac{V}{(2\pi)^3}\int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{R}}\langle u_{n\mathbf{k}}|\nabla_{\mathbf{k}}^2|u_{m\mathbf{k}}\rangle.$$

Actually these expressions must be evaluated using finite differences in **k**. The localization function is minimized by means of a unitary transformation on the phase of the Bloch functions:

$$|\mathbf{R}n\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{R}}\sum_{m=1}^{J} U_{mn}^{(\mathbf{k})}|\psi_{m\mathbf{k}}\rangle.$$

Some examples Graphene



Wannier functions used to evaluate polarization

Wannier function in central cell:

$$|\mathbf{0}n\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\,|\tilde{\psi}_{n\mathbf{k}}\rangle.$$

To find their centers of charge, we note that

$$\mathbf{r}|\mathbf{0}n\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\,(-i\nabla_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}})|\tilde{u}_{n\mathbf{k}}\rangle.$$

Performing an integration by parts and applying $\langle\mathbf{0}n|$ on the left, the center of charge is given by

$$\mathbf{r}_n = \langle\mathbf{0}n|\mathbf{r}|\mathbf{0}n\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\langle\tilde{u}_{n\mathbf{k}}|i\nabla_{\mathbf{k}}|\tilde{u}_{n\mathbf{k}}\rangle. \qquad (88)$$

Polarization of system depends on position weighted sum of both electronic charges and on ionic charges:

$$\mathbf{P} = \frac{e}{V}\left(\sum_{\tau} Z_\tau \mathbf{r}_\tau - \sum_n \mathbf{r}_n\right)$$

$$\mathbf{P}_{\mathrm{el}} = -\frac{e}{(2\pi)^3}\sum_n \int_{\mathrm{BZ}} d\mathbf{k}\langle\tilde{u}_{n\mathbf{k}}|i\nabla_{\mathbf{k}}|\tilde{u}_{n\mathbf{k}}\rangle,$$

$$= -e\left\langle \mathbf{0}n\left|\mathbf{r}\right|\mathbf{0}n\right\rangle$$

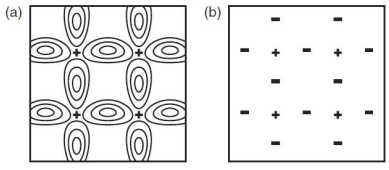


FIG. 21. Illustration of mapping from physical crystal onto equivalent point-charge system with correct dipolar properties. (a) True system composed of point ions (+) and charge cloud (contours). (b) Mapped system in which the charge cloud is replaced by quantized electronic charges (−). In the illustrated model there are two occupied bands, i.e., two Wannier functions per cell.

Note that we previously noticed that the Bloch functions and the corresponding Wannier functions are not unique, but we can shown that r_n is unique up to a lattice translation (thanks to Vanderbilt and King-Smith)

We assume the Bloch waves have the symmetry:

$$\psi_{n,\mathbf{k}+\mathbf{G}} = \psi_{n\mathbf{k}} \ .$$

Consider the transformed Bloch wave:

Now we construct a new set of Bloch functions

$$\overline{\psi}_{n\mathbf{k}} = e^{i\theta_n(\mathbf{k})}\psi_{n\mathbf{k}} \tag{12}$$

with a different phase choice. But note that Eq. (11) applied to both ψ and $\overline{\psi}$ implies that θ_n must return to itself, modulo 2π, as the Brillouin zone is crossed, i.e.,

$$\theta_n(\mathbf{k}+\mathbf{G}) = \theta_n(\mathbf{k}) + \mathbf{G}\cdot\mathbf{R}_n \tag{13}$$

for some lattice vector $\mathbf{R}_n$.

Recall that $\mathbf{P}_e$ can be written, Eq. (8),

$$\mathbf{P}_e = -\frac{e}{\Omega}\sum_{n=1}^{M}\mathbf{r}_n, \tag{14}$$

where

$$\mathbf{r}_n = \langle W_n|\mathbf{r}|W_n\rangle, \tag{15}$$

$$\begin{aligned}\overline{\mathbf{r}}_n &= \frac{\Omega}{N(2\pi)^3}\sum_{\mathbf{R}\mathbf{R}'}\int_{\mathrm{BZ}} d\mathbf{k}\ \overline{W}_n^*(\mathbf{r}-\mathbf{R})e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} \\ &\qquad \times i\nabla_{\mathbf{k}}\overline{W}_n(\mathbf{r}-\mathbf{R}')e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}')} \\ &= \langle W_n|\mathbf{r}|W_n\rangle - \frac{\Omega}{N(2\pi)^3}\sum_{\mathbf{R}}\int_{\mathrm{BZ}} d\mathbf{k}\ \nabla_{\mathbf{k}}\theta_n(\mathbf{k}) \\ &= \mathbf{r}_n - \mathbf{R}_n \end{aligned} \tag{16}$$

from which it immediately follows that $\overline{\mathbf{P}}_e = \mathbf{P}_e + e\mathbf{R}/\Omega$, where $\mathbf{R}$ is the sum of $\mathbf{R}_n$ over occupied bands.

Vanderbilt and King-Smith note that with this definition of the polarization, the surface charge of a polar material is consistent with

$$\sigma = \overline{\mathbf{P}}\cdot\hat{\mathbf{n}} \ .$$