GENERAL REMARKS ON THE TIGHT-BINDING METHOD

1. In cases of practical interest more than one atomic level appears in the expansion (10.7). Leading to a 2×2 secular problem in the case of three p-levels, a 3×3 secular problem for five d-levels etc. Figure 10.6, for example shows the band structure that emerges from a tight-binding calculation based on the 5-fold degenerate atomic 3d levels in nickel. The bands are plotted for three directions of symmetry in the zone, each of which has its characteristic set of degeneracies.[13]

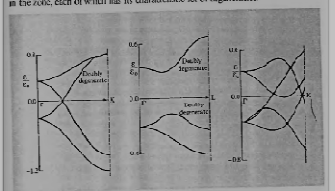
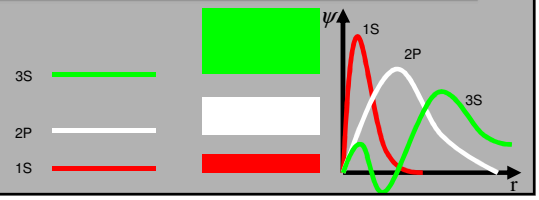


Figure 10.6
A tight-binding calculation of the 3d bands of nickel (fig. C. Fletcher, *Proc. Phys. Soc.* **A65**, 192 (1952)). Energies are given in units of $E_R = 1.349$ eV, so the bands are about 27 volts wide. The lines along which δ is plotted are shown in Figure 10.5. Note the characteristic degeneracies along $\Gamma\Delta$ and $\Gamma\Lambda$ and the absence of degeneracy along $\Gamma\mathrm{K}$. The great width of the bands indicates the inadequacy of so elementary a treatment.

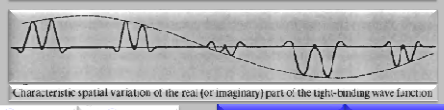
2. A quite general feature of the tight-binding method is the relation between bandwidth and the overlap integrals

$$\gamma_{ij}(\mathbf{R}) = -\int d\mathbf{r}\, \phi_i^*(\mathbf{r})\, \Delta U(\mathbf{r}) \phi_j(\mathbf{r} - \mathbf{R})$$

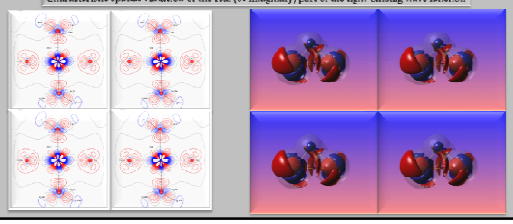
If the γ_{ij} are small, then the bandwidth is correspondingly small. As a rule of thumb, when the energy of a given atomic level increases (i.e., the binding energy decreases) so does the spatial extent of its wave function. Correspondingly, the low-lying bands in a solid are very narrow, but bandwidths increase with mean band energy. In metals the highest band (or bands) are very broad, since the spatial ranges of the highest atomic levels are comparable to a lattice constant, and the tight-binding approximation is then of doubtful validity.



3. Although the tight-binding wave function (10.6) is constructed out of localized atomic levels ϕ, an electron in a tight-binding level will be found, with equal probability, in any cell of the crystal, since its wave function (like any Bloch wave function) changes only by the phase factor $e^{i\mathbf{k}\cdot\mathbf{R}}$ as one moves from one cell to another a distance $\mathbf{R}$ away. Thus as $\mathbf{r}$ varies from cell to cell, there is superimposed on the atomic structure within each cell a sinusoidal variation in the amplitudes of $\mathrm{Re}\,\psi$ and $\mathrm{Im}\,\psi$, as illustrated in Figure 10.7.



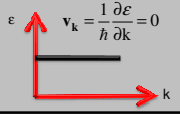
Characteristic spatial variation of the real (or imaginary) part of the tight-binding wave function



A further indication that the tight-binding levels have a running wave or itinerant character comes from the theorem that the mean velocity of an electron in a Bloch level with wave vector $\mathbf{k}$ and energy $\mathcal{E}(\mathbf{k})$ is given by $\mathbf{v}(\mathbf{k}) = (1/\hbar)\,\partial\mathcal{E}/\partial\mathbf{k}$. (See Appendix E.) If $\mathcal{E}$ is independent of $\mathbf{k}$, $\partial\mathcal{E}/\partial\mathbf{k}$ is zero, which is consistent with the fact that in genuinely isolated atomic levels (which lead to zero bandwidth) the electrons are indeed tied to individual atoms. If, however, there is any nonzero overlap in the atomic wave functions, then $\mathcal{E}(\mathbf{k})$ will not be constant throughout the zone. Since a small variation in $\mathcal{E}$ implies a small nonzero value of $\partial\mathcal{E}/\partial\mathbf{k}$, and hence a small but nonzero mean velocity, as long as there is any overlap electrons will be able to move freely through the crystal! Decreasing the overlap only reduces the velocity; it does not eliminate the motion. One can view this motion as a quantum-mechanical tunneling from lattice site to lattice site. The less the overlap, the lower the tunneling probability, and hence the longer it takes to go a given distance.

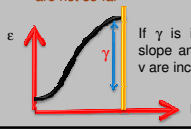
If the distance between atoms are so far

$$\mathbf{v}_\mathbf{k} = \frac{1}{\hbar}\frac{\partial\mathcal{E}}{\partial\mathbf{k}} = 0$$



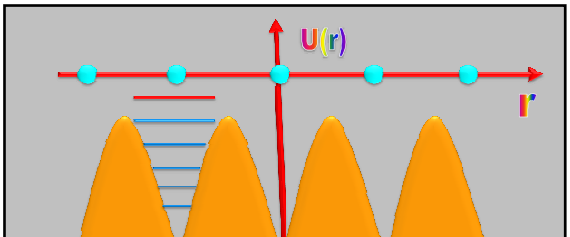
If the distance between atoms are not so far

$$\mathbf{v}_\mathbf{k} = \frac{1}{\hbar}\frac{\partial\mathcal{E}}{\partial\mathbf{k}} \neq 0$$

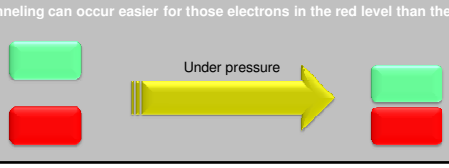


If γ is increased, then slope and consequently v are increased.

$$m^* = \frac{\hbar^2}{2\gamma a^2}$$



Tunneling can occur easier for those electrons in the red level than the others.



4. In solids that are not monatomic Bravais lattices, the tight-binding approximation is more complicated. This problem arises in the hexagonal close-packed metals, which are simple hexagonal with a two-point basis. Formally, one can treat the two-point basis as a molecule, whose wave functions are assumed to be known, and proceed as above, using molecular instead of atomic wave functions. If the nearest-neighbor overlap remains small, then, in particular, it will be small in each "molecule," and an atomic s-level will give rise to two nearly degenerate molecular levels. Thus a single atomic s-level yields two tight-binding bands in the hexagonal close-packed structure.

Alternatively, one can proceed by continuing to construct linear combinations of atomic levels centered at the Bravais lattice points *and* at the basis points, generalizing (10.6) to

$$\psi(\mathbf{r}) = \sum_\mathbf{R} e^{i\mathbf{k}\cdot\mathbf{R}}\{a\phi(\mathbf{r} - \mathbf{R}) + b\phi(\mathbf{r} - \mathbf{d} - \mathbf{R})\}, \qquad (10.26)$$

(where $\mathbf{d}$ is the separation of the two basis atoms). This can be viewed as essentially the first approach, in which, however, approximate molecular wave functions are used, the approximation to the molecular levels being combined with the tight-binding approximation to the levels of the entire crystal.[13]

5. In the heavier elements spin-orbit coupling (see page 169) is of great importance in determining the atomic levels, and should therefore be included in a tight-binding treatment of the broadening of these levels into bands in the solid. In principle the extension is straightforward. We simply include in $\Delta U(\mathbf{r})$ the interaction between the electron's spin and the electric field of all ions except the one at the origin, incorporating that interaction into the atomic Hamiltonian. Once this is done we can no longer use spin-independent linear combinations of atomic orbital wave functions, but must work with linear combinations of both orbital and spin levels. Thus the tight-binding theory of an s-level, when spin-orbit coupling is appreciable, would approximate ϕ not by a single atomic s-level but by a linear combination (with $\mathbf{k}$ dependent coefficients) of two levels with the same orbital wave functions and two opposite spins. The tight binding theory of a d band would go from a 5×5 determinantal problem to a 10×10 one, etc. As mentioned in Chapter 9, effects of spin-orbit coupling, though often small, can frequently be crucial, as when they eliminate degeneracies that would rigorously be present if such coupling were ignored.[14]

6. All the analysis of electronic levels in a periodic potential in this chapter (and the preceding two) has been done within the independent electron approximation, which either neglects the interaction between electrons, or, at best, includes it in some average way through the effective periodic potential experienced by each single electron. We shall see in Chapter 32 that the independent electron approximation can fail when it gives at least one *partially* filled band that derives from well-localized atomic levels with small overlap integrals. In many cases of interest (notably in insulators and for the very low-lying bands in metals) this problem does not arise, since the tight-binding bands are so low in energy as to be completely filled. However, the possibility of such a failure of the independent electron approximation must be kept in mind when narrow tight-binding bands are derived from partially filled atomic shells—in metals, generally the d- and f-shells. One should be particularly aware of this possibility in solids with a magnetic structure.

This failure of the independent electron approximation obscures the simple picture the tight-binding approximation suggests: that of a continuous transition from the metallic to the atomic state as the interatomic distance is continuously increased.[15] If we took the tight-binding approximation at face value, then as the lattice constant in a metal increased, the overlap between all atomic levels would eventually become small, and all bands—even the partially filled conduction band (or bands)—would eventually become narrow tight-binding bands. As the conduction band narrowed, the velocity of the electrons in it would diminish and the conductivity of the metal would drop. Thus, we would expect a conductivity that dropped continuously to zero with the overlap integrals as the metal was expanded.

In fact, however, it is likely that a full calculation going beyond the independent electron approximation would predict that beyond a certain nearest-neighbor separation the conductivity should drop abruptly to zero, the material becoming an insulator (the so-called *Mott transition*).

The reason for this departure from the tight-binding prediction lies in the inability of the independent electron approximation to treat the very strong additional repulsion a second electron feels at a given atomic site when another electron is already there. We shall comment further on this in Chapter 32, but we mention the problem here because it is sometimes described as a failure of the tight-binding method.[16] This is somewhat misleading in that the failure occurs when the tight-binding approximation to the independent electron model is at its best; it is the independent electron approximation itself that fails.

WANNIER FUNCTION

AUGUST 1, 1937 PHYSICAL REVIEW VOLUME 52

The Structure of Electronic Excitation Levels in Insulating Crystals

GREGORY H. WANNIER
Princeton University, Princeton, New Jersey

(Received May 13, 1937)

In this article, a method is devised to study the energy spectrum for an excited electron configuration in an ideal crystal. The configuration studied consists of a single excited electron taken out of a full band of N electrons. The multiplicity of the state is N^2. It is shown that because of the Coulomb attraction between the electron and its hole $N^{1/3}$ states are split off from the bottom of the excited Bloch band; for these states the electron cannot escape its hole completely. The analogy of these levels to the spectrum of an atom or molecule is worked out quantitatively. The bottom of the Bloch band appears as "ionization potential" and the Bloch band itself as the continuum above this threshold energy.

SCIENTIFIC HIGHLIGHT OF THE MONTH

An Introduction to Maximally-Localized Wannier Functions

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Abstract

The electronic ground state of a periodic system is usually described in terms of extended Bloch orbitals, simultaneous eigenstates of the periodic Hamiltonian and of the direct lattice translations. An alternative representation in terms of localized orbitals has been introduced by Gregory Wannier in 1937; besides its theoretical relevance in several areas of solid-state theory, it has gained recent prominence due to its connection with the Berry phase theory of bulk polarization, the interest in linear-scaling approaches, and with the development of general algorithms to derive Wannier functions in the framework of first-principles electronic structure calculations. The connection between the Bloch representation and the Wannier representation is realized by families of transformations in a continuous space of unitary matrices, carrying a large degree of arbitrariness. A few years ago we have developed a localization algorithm that allows one to iteratively transform the extended Bloch orbitals of a first principles calculation into a unique set of *maximally localized* Wannier functions (MLWFs), extending and encompassing Boys formulation for molecules to the solid-state case. The localization algorithm is independent of the single-particle electronic structure approach adopted, or the choice of basis set, and it is straightforwardly applied to extended or periodic solids and to isolated systems. Additionally, a novel disentanglement procedure allows to extract a maximally-connected manifold of *any* chosen dimension from a given energy window, leading to the extension of the original algorithm to the case of systems without gaps (e.g., metals) and removing the limitation to isolated groups of bands separated by gaps from higher and lower manifolds. In this Highlight we will outline and summarize the main results of the theory and algorithm underlying the maximally-localized Wannier-functions representation, and review some of the applications that have since appeared in the literature.

wannier90: User Guide

Version 1.1

21st December 2007

The present release of wannier90 was written by Arash A. Mostofi (Imperial College London, UK), Jonathan R. Yates (University of Cambridge, UK), and Young-Su Lee (KIST, S. Korea). wannier90 is based on routines written in 1996-7 for isolated bands by Nicola Marzari and David Vanderbilt, and for entangled bands by Ivo Souza, Nicola Marzari, and David Vanderbilt in 2000-1.

Acknowledgements: Stefano de Gironcoli (SISSA, Trieste, Italy) for the PWSCF interface; Michel Posternak (EPFL, Switzerland) for the original plotting routines.

WANNIER FUNCTION

We conclude this chapter with a demonstration that the Bloch functions for *any* band can always be written in the form (10.4) on which the tight-binding approximation is based. The functions ϕ that play the role of the atomic wave functions are known as *Wannier functions*. Such Wannier functions can be defined for any band, whether or not it is well described by the tight-binding approximation; but if the band is not a narrow tight-binding band, the Wannier functions will bear little resemblance to any of the electronic wave functions for the isolated atom.

To establish that any Bloch function $\psi_{n\mathbf{k}}(\mathbf{r})$ can be written in the form (10.4), we first note that considered as a function of $\mathbf{k}$ for fixed $\mathbf{r}$, $\psi_{n\mathbf{k}}(\mathbf{r})$ is periodic in the reciprocal lattice. It therefore has a Fourier series expansion in plane waves with wave vectors in the reciprocal of the reciprocal lattice, i.e., in the direct lattice. Thus for any fixed $\mathbf{r}$ we can write

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \psi_n(\mathbf{r} - \mathbf{R})$$

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} f_n(\mathbf{R}, \mathbf{r}) e^{i\mathbf{R}\cdot\mathbf{k}}$$

where the coefficients in the sum depend on $\mathbf{r}$ as well as on the "wave vectors" $\mathbf{R}$, since for each $\mathbf{r}$ it is a different function of $\mathbf{k}$ that is being expanded.

The Fourier coefficients in (10.27) are given by the inversion formula[17]

$$f_n(\mathbf{R}, \mathbf{r}) = \frac{1}{v_\Omega} \int d\mathbf{k}\, e^{-i\mathbf{R}\cdot\mathbf{k}} \phi_{n\mathbf{k}}(\mathbf{r}). \tag{10.28}$$

Equation (10.26) is of the form (10.4), provided that the function $f_n(\mathbf{R}, \mathbf{r})$ depends on $\mathbf{r}$ and $\mathbf{R}$ only through their difference, $\mathbf{r} - \mathbf{R}$. But if $\mathbf{r}$ and $\mathbf{R}$ are both shifted by the Bravais lattice vector $\mathbf{R}_m$, then f is indeed unchanged as a direct consequence of (10.28) and Bloch's theorem, in the form (8.5). Thus $f_n(\mathbf{R}, \mathbf{r})$ has the form:

$$f_n(\mathbf{R}, \mathbf{r}) = \phi_n(\mathbf{r} - \mathbf{R}) \tag{10.29}$$

Unlike tight-binding atomic functions $\phi_i(\mathbf{r})$, the Wannier functions $\phi_n(\mathbf{r} - \mathbf{R})$ at different sites (or with different band indices) are orthogonal (see Problem 3, Eq. (10.33)). Since the complete set of Bloch functions can be written as linear combinations of the Wannier functions, the Wannier functions $\phi_n(\mathbf{r} - \mathbf{R})$ for all n and $\mathbf{R}$ form a complete orthogonal set. They therefore offer an alternative basis for an exact description of the independent electron levels in a crystal potential.

The similarity in form of the Wannier functions to the tight-binding functions leads one to hope that the Wannier functions will also be localized—i.e., that when $\mathbf{r}$ is very much larger than some length on the atomic scale, $\phi_n(\mathbf{r})$ will be negligibly small. To the extent that this can be established, the Wannier function is often an ideal tool for discussing phenomena in which the spatial localization of electrons plays an important role. Perhaps the most important areas of application are these:

1. Attempts to derive a transport theory for Bloch electrons. The analog of free electron wave packets, electronic levels in a crystal that are localized in both $\mathbf{r}$ and $\mathbf{k}$, are conveniently constructed with the use of Wannier functions. The theory of Wannier functions is closely related to the theory of when and how the semiclassical theory of transport by Bloch electrons (Chapters 12 and 13) breaks down.

2. Phenomena involving localized electronic levels, due, for example, to attractive impurities that bind an electron. A very important example is the theory of donor and acceptor levels in semiconductors (Chapter 28).

3. Magnetic phenomena, in which localized magnetic moments are found to exist at suitable impurity sites.

Theoretical discussions of the range of Wannier functions are in general quite subtle.[18] Roughly speaking, the range of the Wannier function decreases as the band gap increases (as one might expect from the tight binding approximation, in which the bands become narrower as the range of the atomic wave functions decreases). The various "breakdown" and "breakthrough" phenomena we shall mention in Chapter 12 that occur when the band gap is small find their reflection in the fact that theories based on the localization of the Wannier functions become less reliable in this limit.

Wannier functions [338, 759, 763] are orthonormal localized functions that span the same space as the eigenstates of a band or a group of bands. Extensive reviews of their properties have been given by Wannier [338], Blount [759], and Nenciu [339]. Here we consider properties relevant to understanding the electronic properties of materials and to present-day practical calculations.

The eigenstates of electrons in a crystal are extended throughout the crystal with each state having the same magnitude in each unit cell. This has been shown in the independent-particle approximation Sec. 4.3 using the fact that the hamiltonian $\hat{H}$ in (4.22) commutes with the translations operations $\hat{T}_\mathbf{n}$ in (4.23). Thus eigenstates of hamiltonian $\hat{H}$ are also eigenstates of $\hat{T}_\mathbf{n}$, leading to the Bloch theorem, Eqs. (4.33) or (12.11),

$$\psi_i^\mathbf{k}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_i^\mathbf{k}(\mathbf{r}). \tag{21.1}$$

which here is taken to be normalized in one cell. Since the overall phase of each eigenstate is arbitrary, any Bloch function is subject to a "gauge transformation"

$$\psi_i^\mathbf{k}(\mathbf{r}) \to \tilde{\psi}_i^\mathbf{k}(\mathbf{r}) = e^{i\phi_i(\mathbf{k})} \psi_i^\mathbf{k}(\mathbf{r})$$

which leaves unchanged all physically meaningful quantities.[1]

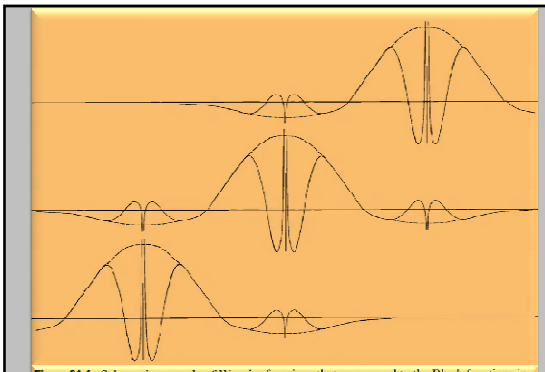


Figure 21.1. Schematic example of Wannier functions that correspond to the Bloch functions in Fig. 4.11. These are for a band made of 3s atomic-like states and the smooth functions derive the smooth part of the wavefunction as illustrated in Fig. 11.2.

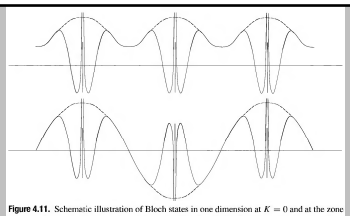


Figure 4.11. Schematic illustration of Bloch states in one dimension at $K = 0$ and at the zone boundary $k = \pi/a$. The envelope is the smooth function that multiplies a periodic array of atomic-like 3s functions, chosen to be the same as in Fig. 11.2.

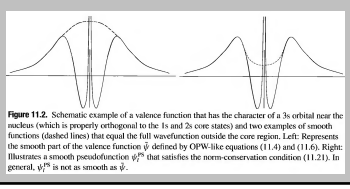


Figure 11.2. Schematic example of a valence function that has the character of a 3s orbital near the nucleus (which is properly orthogonal to the 1s and 2s core states) and two examples of smooth functions (dashed lines) that equal the full wavefunction outside the core region. Left: Represents the smooth part of the valence function $\tilde{\psi}$ defined by OPW-like equations (11.4) and (11.6). Right: Illustrates a smooth pseudofunction ψ_i^{PS} that satisfies the norm-conservation condition (11.21). In general, ψ_i^{PS} is not as smooth as $\tilde{\psi}$.

Wannier functions are Fourier transforms of the Bloch eigenstates. For one band i the function associated with the cell labeled by the lattice point $\mathbf{T}_m$ is

$$w_i(\mathbf{r} - \mathbf{T}_m) = \frac{\Omega_{\text{cell}}}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{T}_m} \psi_i^\mathbf{k}(\mathbf{r}) = \frac{\Omega_{\text{cell}}}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{T}_m)} u_i^\mathbf{k}(\mathbf{r}), \tag{21.3}$$

as shown schematically in Fig. 21.1. The function w_i associated with a different cell $\mathbf{T}_{m'}$ is the same function, except it is translated by $\mathbf{T}_{m'} - \mathbf{T}_m$. Conversely, Eq. (21.3) leads to

$$\psi_i^\mathbf{k}(\mathbf{r}) = \sum_m e^{-i\mathbf{k}\cdot\mathbf{T}_m} w_i(\mathbf{r} - \mathbf{T}_m). \tag{21.4}$$

The transformation (21.3) assumes that the Bloch functions $\psi_i^\mathbf{k}(\mathbf{r})$ are periodic in reciprocal space, i.e. the "periodic gauge" where

$$\psi_i^\mathbf{k}(\mathbf{r}) = \psi_i^{\mathbf{k}+\mathbf{G}}(\mathbf{r}) \tag{21.5}$$

for all reciprocal lattice vectors $\mathbf{G}$. This is clearly obeyed by the Bloch functions given by (21.4).

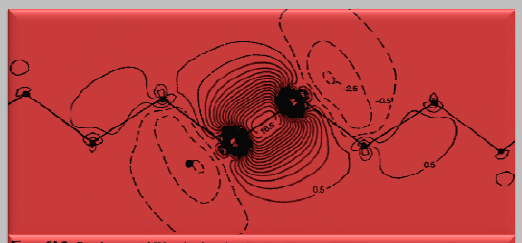


Figure 21.2. Bond-centered Wannier function for Si calculated [694] by requiring the phases of the Bloch functions to have real, positive amplitude at one of the four equivalent band centers. Note the similarity to Fig. 21.4. The decay of the orbital on a log scale is shown in Fig. 21.3.

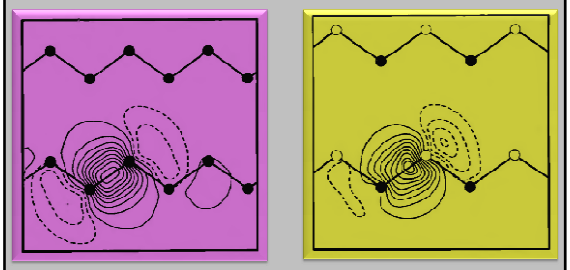
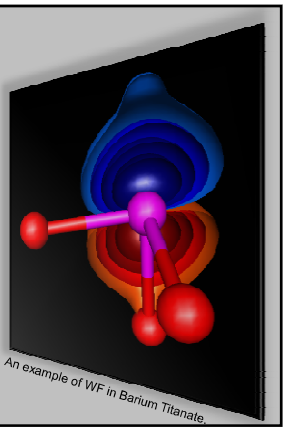


Figure 21.4. "Maximally localized" Wannier functions for Si (left) and GaAs (right) from [762]. Each figure shows one of the four equivalent functions found for the four occupied valence bands. Provided by N. Marzari.

The **Wannier functions** are a complete set of orthogonal functions used in solid-state physics. They were introduced by Gregory Wannier.[1]

[1]The structure of electronic excitation levels in insulating crystals," G. H. Wannier, Phys. Rev. 52, 191 (1937)

The **Wannier functions** for different lattice sites in a crystal are orthogonal, allowing a convenient basis for the expansion of electron states in certain regimes. Wannier functions have found widespread use, for example, in the analysis of binding forces acting on electrons; they have proven to be in general localized, at least for insulators, in 2006[2]. Specifically, these functions are also used in the analysis of excitons and condensed Rydberg matter.



An example of WF in Barium Titanate.

Although Wannier functions can be chosen in many different ways,[3] the original,[1] simplest, and most common definition in solid-state physics is as follows. Choose a single band in a perfect crystal, and denote its Bloch states by

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

where $u_{\mathbf{k}}(\mathbf{r})$ has the same periodicity as the crystal. Then the Wannier functions are defined by

$$\phi_{\mathbf{R}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{\mathbf{k}}(\mathbf{r})$$

Where

R is any lattice vector (i.e., there is one Wannier function for each Bravais lattice vector);

N is the number of primitive cells in the crystal;

The sum on **k** includes all the values of **k** in the Brillouin zone (or any other primitive cell of the reciprocal lattice) that are consistent with periodic boundary conditions on the crystal. This includes *N* different values of **k**, spread out uniformly through the Brillouin zone. Since *N* is usually very large, the sum can be written as an integral according to the replacement rule:

$$\sum_{\mathbf{k}} \rightarrow \frac{N}{\Omega} \int_{BZ} d^3\mathbf{k}$$

where "BZ" denotes the Brillouin zone, which has volume Ω .

On the basis of this definition, the following properties can be proven to hold: For any lattice vector **R'** ,

$$\phi_{\mathbf{R}}(\mathbf{r}) = \phi_{\mathbf{R}+\mathbf{R}'}(\mathbf{r}+\mathbf{R}')$$

In other words, a Wannier function only depends on the quantity (**r**-**R**). As a result, these functions are often written in the alternative notation

$$\phi(\mathbf{r}-\mathbf{R}) := \phi_{\mathbf{R}}(\mathbf{r})$$

The Bloch functions can be written in terms of Wannier functions as follows:

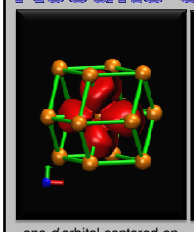
$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_{\mathbf{R}}(\mathbf{r})$$

where the sum is over each lattice vector **R** in the crystal.

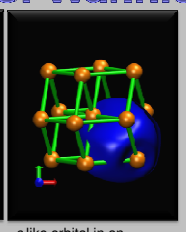
The set of wavefunctions $\phi_{\mathbf{R}}$ is an orthonormal basis for the band in question.

It is generally assumed that the function $\phi_{\mathbf{R}}$ is localized around the point **R**, and rapidly goes to zero away from that point. However, quantifying and proving this assertion can be difficult, and is the subject of ongoing research.[2]

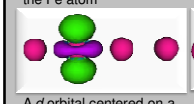
Results of Wannier Method



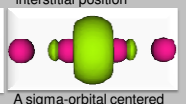
one *d* orbital centered on the Fe atom



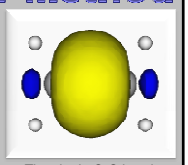
s like orbital in an interstitial position



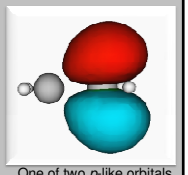
A *d* orbital centered on a Pt atom



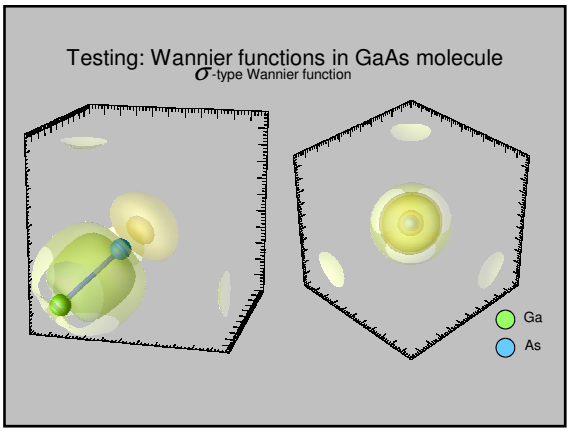
A sigma-orbital centered between a Pt-Pt pair

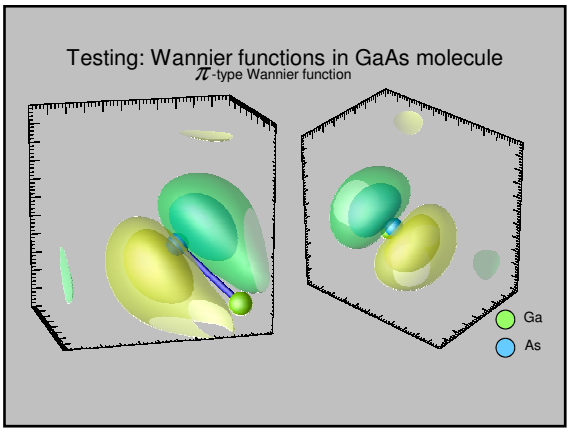


The single C-C bond



One of two *p*-like orbitals


Testing: Wannier functions in GaAs molecule
σ-type Wannier function
Ga
As


Testing: Wannier functions in GaAs molecule
π-type Wannier function
Ga
As