

Implementation of Density Functional Theory

Outline

- General DFT algorithm
- Basis functions
- Pseudopotentials
- Bloch's Theorem
- k-space integration
- Self-consistency
- Common mistakes and problems
- A simple DFT calculation

Note: Next class is a computer lab!!

DFT Algorithm

START: Get initial ρ

- Atomic charge density
- Previous calc. of ρ
- Previous calc. of ϕ

Use ρ to generate $V_{\text{eff}} = V_{\text{ion}} + V_{\text{Hartree}} + V_{\text{XC}}$

- Choose form of V_{XC} (Perdue+Zunger, etc.)

Solve Kohn-Sham equations $[-\nabla^2 + V_{\text{eff}}]\phi = \epsilon\phi$

- Expand ϕ in basis θ
- Maybe use Pseudopotential for V_{ion}
- Diagonalize matrices on k-point grid

Determine $\rho = \sum \phi_i^* \phi_i$ and check if ρ is the same as last iteration

If Yes

END: Output charge densities, band structure, relaxed atomic positions, total energies, forces on atoms

Self-consistency loop

If No

General DFT Problem

$$\left[-\nabla_i^2 + V_{ion}(\mathbf{r}_i) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{XC}(\rho(\mathbf{r}_i)) \right] \phi_i(\mathbf{r}_i) =$$
$$\left[-\nabla_i^2 + V_{eff}(\mathbf{r}_i, \rho) \right] \phi_i(\mathbf{r}_i) = \varepsilon_i \phi_i(\mathbf{r}_i)$$

$$\rho(\mathbf{r}) = \sum_i^{\text{N electrons}} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r})$$

Before you begin calculation you must choose the

- **Basis functions** θ_α in which to expand ϕ : $\phi = \sum_\alpha a_\alpha \theta_\alpha$
(Plane waves, Gaussians, Muffin-Tin-Orbitals, etc.)
- **Ionic potential** (true or pseudo)

The Basis Functions: Getting Eigenvalue Equation

You expand in a basis to transform a differential equation into an eigenvalue equation using $\phi = \sum a_\alpha \theta_\alpha$.

$$H\phi = \epsilon\phi$$

A differential equation.

H is an operator.

$$H(\sum_\alpha a_\alpha \theta_\alpha) = \epsilon \sum_\alpha a_\alpha \theta_\alpha$$

Substitute in the expansion.

$$\sum_\alpha a_\alpha H_{\beta\alpha} = \epsilon \sum_\alpha a_\alpha S_{\beta\alpha}$$

Multiply both sides by θ_β . S is an overlap matrix.

$$H_{\alpha\beta} = \int d\mathbf{r} \theta_\alpha^*(\mathbf{r}) H \theta_\beta(\mathbf{r})$$

$$S_{\alpha\beta} = \int d\mathbf{r} \theta_\alpha^*(\mathbf{r}) \theta_\beta(\mathbf{r})$$

$$[\mathbf{S}^{-1}\mathbf{H} - \epsilon\mathbf{I}]\mathbf{a} = \mathbf{0}$$

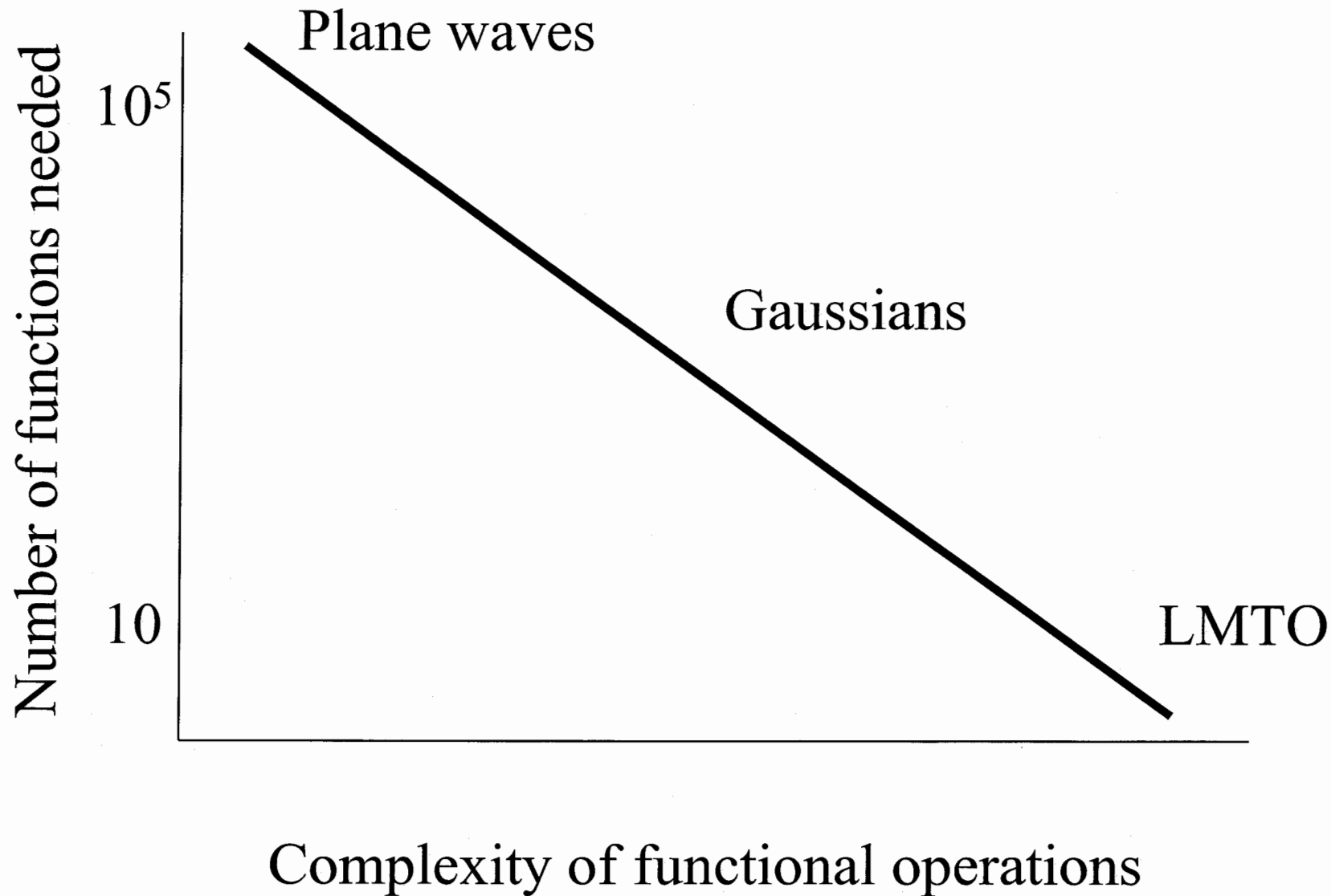
Rewrite as an eigenvalue equation.

H, S, and a are matrices.

The Basis Functions: Solving Eigenvalue Equation

- $[\mathbf{S}^{-1}\mathbf{H}-\varepsilon\mathbf{I}]\mathbf{a}=\mathbf{0}$ is an **eigenvalue equation**. If we are using M basis functions then $\mathbf{S}^{-1}\mathbf{H}$ is an $M\times M$ matrix.
- By diagonalizing $\mathbf{S}^{-1}\mathbf{H}$ we obtain M eigenvalues ε_{α} and M eigenvectors \mathbf{a}_{α} . The ε_{α} give the energies of the electronic states, the \mathbf{a}_{α} give the wavefunctions $\phi_{\alpha}=\sum_{\alpha\beta}a_{\alpha\beta}\theta_{\beta}$.
- By using only M basis functions we are getting a variational best estimate for the ε_{α} and ϕ_{α} .
- Diagonalization is often bottleneck in large calculations.
 - Standard techniques take time= $O(M^3)$.
 - Iterative techniques take time= $O(M^2\ln M)$.
 - Real space techniques take time= $O(M)$.

The Basis Functions: Number and Complexity



The Basis Functions: Specification

For atomic-like functions (eg, LMTO) one specifies the basis functions by angular momentum states (S, P, D, ...).

For plane wave functions one specifies the basis functions by an energy cutoff E_{MAX} . All plane waves with reciprocal lattice vector \mathbf{G} such that $[(\hbar/2\pi)\mathbf{G}]^2/2m \leq E_{MAX}$ are included.

- *Energy is more accurate the larger the value of E_{MAX} .*
- *G depends on cell size so different cell sizes have different basis.*
- *Use same E_{MAX} in comparable calculations to cancel errors.*

The Pseudopotential: Introduction

- **All-electron** codes take ion potential as $V_{\text{ion}}(r) = -Ze^2/r$ and calculate electronic structure for all the electrons. But core electrons are essentially inert so ...
- **Pseudopotential** codes take ion and core electron potential as $V_{\text{ion}}(r) = V_{\text{PP}}(r)$ and calculate electronic structure for only valence electrons.
- $V_{\text{PP}}(r)$ is chosen so the true wavefunction and potential match for $r > r_c$ (core radius), but so that the potential is “soft” and the wavefunction smooth for $r < r_c$.

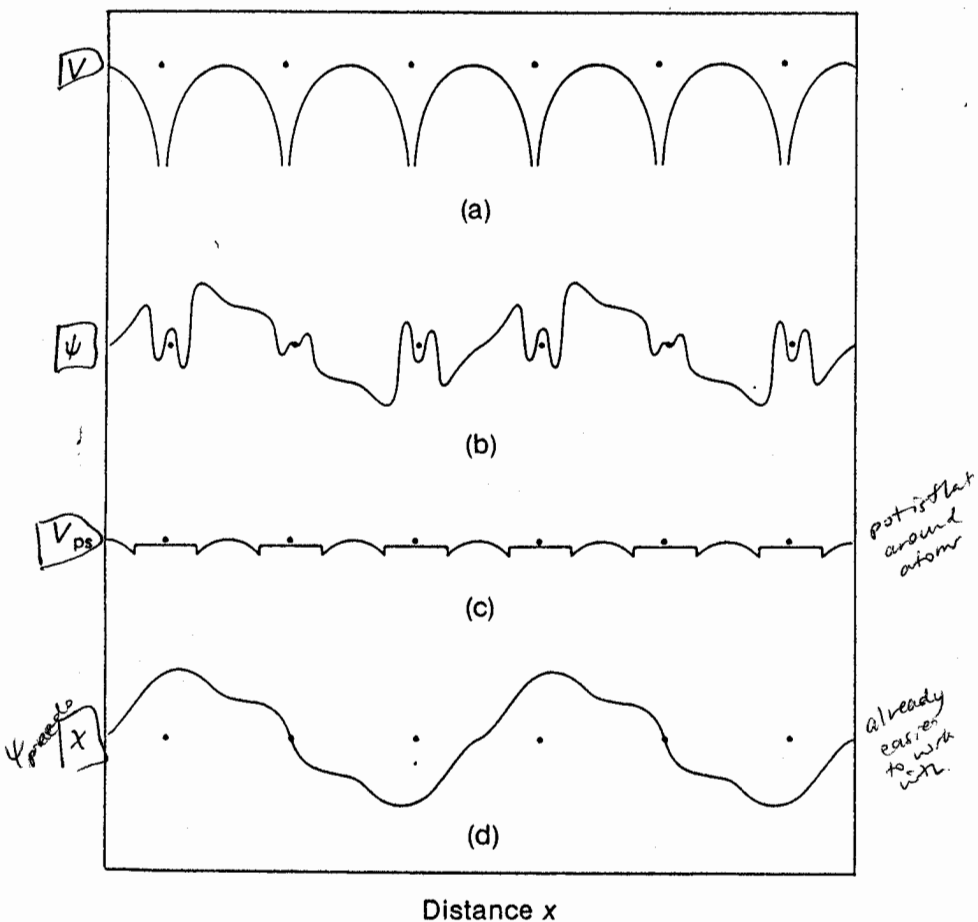


Fig. 2.36a-d. Comparison of (a) a given potential and (b) the associated wave function with (c) a model pseudopotential and (d) the corresponding pseudowave function (from Harrison [13]).

From Madelung, Solid State Theory

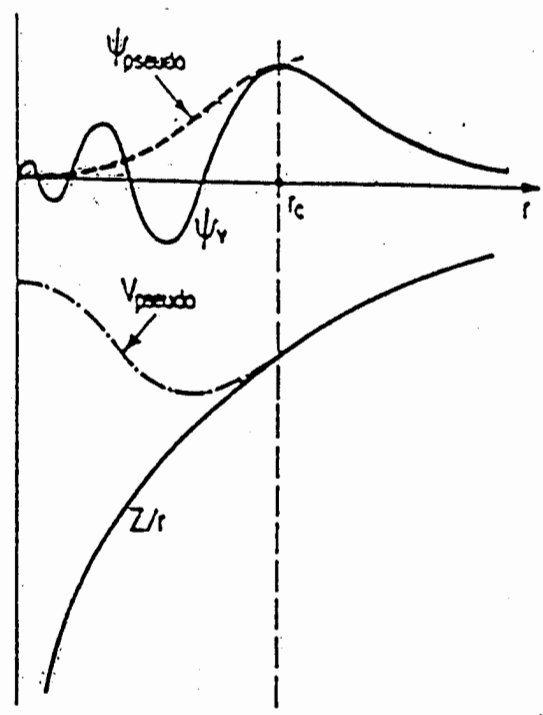


FIG. 5. Schematic illustration of all-electron (solid lines) and pseudoelectron (dashed lines) potentials and their corresponding wave functions. The radius at which all-electron and pseudoelectron values match is designated r_c .

The Pseudopotential: Pro's and Con's

Advantages

- Makes wave functions smoother, requiring fewer plane wave basis functions.
- Uses frozen-core approximation, so calculates electronic structure only for valence electrons.
- Can be fit to empirical data (tunable!)
- Help explains accuracy of “nearly-free” electron picture.

Disadvantages

- Frozen core approximation is not always accurate.
- Not always transferable to varied environments.
- No unique pseudopotential, many methods exist.

Bloch's Theorem: Basic Facts

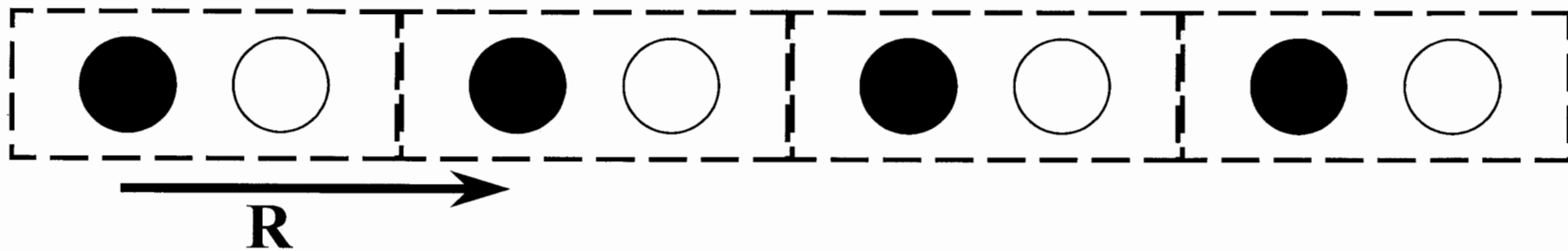
Bloch's theorem is used to treat **infinite periodic systems** (used in studying crystals).

The problem: In an infinite system there are an infinite number of electrons so we need an infinite number of basis functions. This makes the Hamiltonian an infinite matrix which cannot be used for calculation.

The solution: In a periodic system every unit cell is identical in its wave functions, except for a phase. One need only solve a finite problem for an infinite number of different possible phase relationships.

**** This trick, in one form or another, is very common for periodic systems (eg, used for electrons and phonons) ****

Bloch's Theorem: Hand-waving Proof



Let \mathbf{R} be a primitive lattice vector.

Physics identical in all unit cells \Rightarrow

$$\phi_i(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{f}(\mathbf{R})}u(\mathbf{r}), \text{ where } u(\mathbf{r}+\mathbf{R}) = u(\mathbf{r}) \Rightarrow$$

$$\phi_i(\mathbf{r}+\mathbf{R}+\mathbf{R}') = e^{i\mathbf{f}(\mathbf{R}+\mathbf{R}')} \phi_i(\mathbf{r}) = e^{i\mathbf{f}(\mathbf{R})}e^{i\mathbf{f}(\mathbf{R}')} \phi_i(\mathbf{r}) \Rightarrow$$

$$\mathbf{f}(\mathbf{R}+\mathbf{R}') = \mathbf{f}(\mathbf{R})+\mathbf{f}(\mathbf{R}') \Rightarrow \mathbf{f}(\mathbf{R}) = \mathbf{k}\mathbf{R} \Rightarrow$$

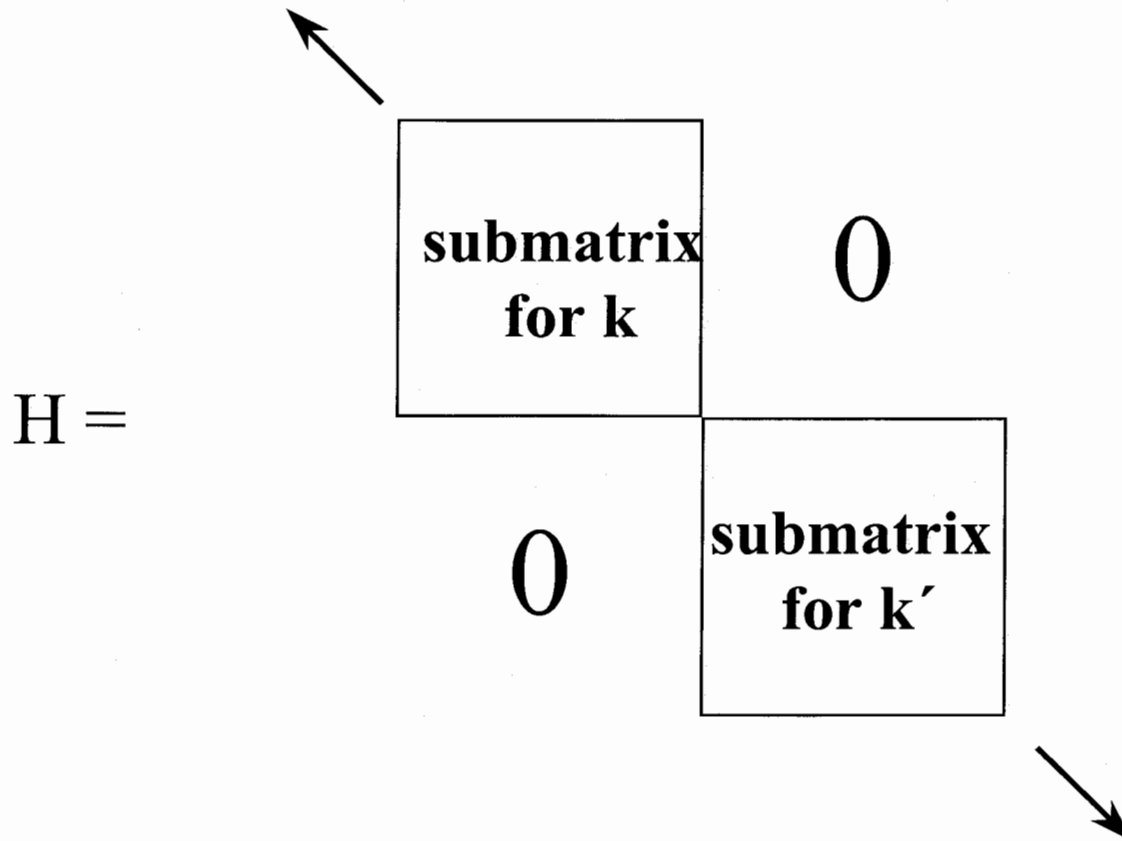
Bloch's Theorem: $\phi_i(\mathbf{r}+\mathbf{R})=e^{i\mathbf{k}\mathbf{R}} \phi_i(\mathbf{r})$, or equivalently,

$\phi_i(\mathbf{r})=e^{i\mathbf{k}\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$ (since $u(\mathbf{r})$ depends on \mathbf{k} and possibly other things, labeled by n).

Note: general index “ i ” \rightarrow wavenumber “ \mathbf{k} ” and branch “ n ”.

Bloch's Theorem: The Simplified Hamiltonian

Take basis functions to be Bloch functions: $\theta_{nk}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} v_{nk}(\mathbf{r})$
 $\Rightarrow H_{nk, n'k'} \sim \delta_{kk'}$ (The Hamiltonian is block diagonal in this basis).



Bloch's Theorem: Summary of Essentials

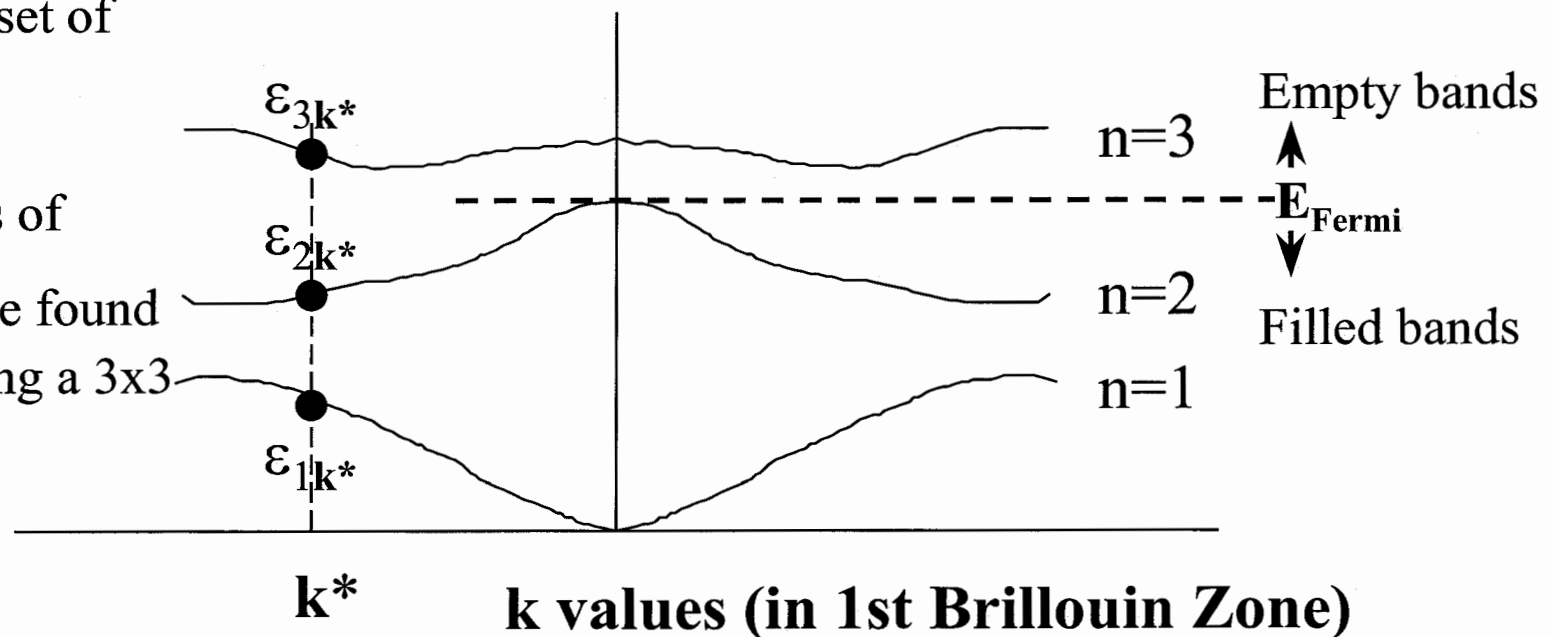
By using Bloch states we block diagonalize the Hamiltonian, reducing the diagonalization problem from a single infinite matrix to an infinite number of $M \times M$ matrices, where M is the number of basis functions (labeled by n) being used for each \mathbf{k} . The problem is now solved by doing calculations at only a finite number of \mathbf{k} values. The results give the band structure

Energies are calculated for a discrete set of \mathbf{k} points.

Energy of Eigenstates

$M=3$ basis functions

These 3 values of $\epsilon_{n\mathbf{k}^*}$ would be found by diagonalizing a 3×3 matrix at \mathbf{k}^* .



Bloch's Theorem: Plane Wave Bloch Basis States

$\phi_{\mathbf{nk}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}u_{\mathbf{nk}}(\mathbf{r})$ is a Bloch state Kohn-Sham orbital.

Since $u_{\mathbf{nk}}(\mathbf{r})$ has the periodicity of the lattice we can expand $u_{\mathbf{nk}}(\mathbf{r})$ in plane waves as $u_{\mathbf{nk}}(\mathbf{r}) = \sum_{\mathbf{G}} a_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}$, where \mathbf{G} is a reciprocal lattice vector.

$$\Rightarrow \phi_{\mathbf{nk}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \sum_{\mathbf{G}} a_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} = \sum_{\mathbf{G}} a_{\mathbf{G}} e^{i\mathbf{k}\mathbf{r}} e^{i\mathbf{G}\mathbf{r}} = \sum_{\mathbf{G}} a_{\mathbf{G}} \theta_{\mathbf{G}}(\mathbf{r})$$

Here $\theta_{\mathbf{G}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} e^{i\mathbf{G}\mathbf{r}}$ is a plane wave Bloch basis state.

k-space Integration: The Problem

There are a number of important quantities that require knowing all the eigenvalues $\varepsilon_{n\mathbf{k}}$ below E_{Fermi} .

$$E_{\text{band}} = \int d\mathbf{k} \sum_n \varepsilon_{n\mathbf{k}} \left\{ \forall \varepsilon_{n\mathbf{k}} \leq E_{\text{Fermi}} \right\}$$

$$\rho(\mathbf{r}) = \int d\mathbf{k} \sum_n \phi_{n\mathbf{k}}^*(\mathbf{r}) \phi_{n\mathbf{k}}(\mathbf{r}) \left\{ \forall \varepsilon_{n\mathbf{k}} \leq E_{\text{Fermi}} \right\}$$

Since we can only calculate the $\varepsilon_{n\mathbf{k}}$ for a finite number of k-points, how do we choose these points to get the most accurate values for the above integrals.

k-space Integration: The Solution

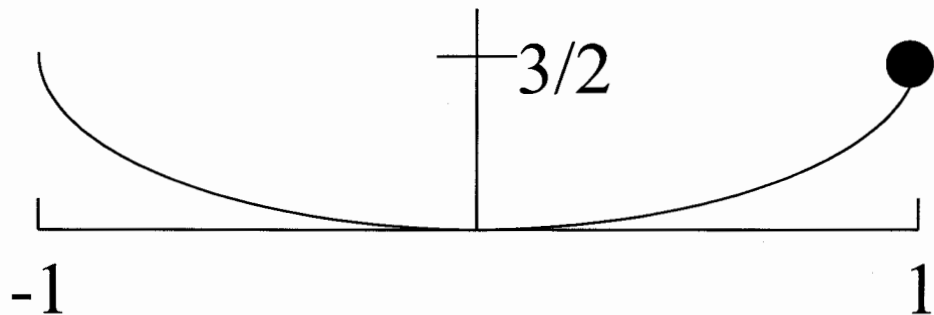
- **Symmetry:** O in crystal point group $\Rightarrow \phi_{nk} = \phi_{nO(k)}$, $\varepsilon_{nk} = \varepsilon_{nO(k)}$ so you use just the k -points in the irreducible wedge.
 - Can reduce number of k -points by up to a factor of 48.
 - High-symmetry structures go faster.
- **Monkhorst-Pack method:** Create a grid of k -points over the first Brillouin zone by uniformly dividing up the reciprocal lattice vectors. Shift grid by $1/2$ a division along each direction. Keep only the symmetry inequivalent k -points.
- **Metal vs. Insulator:** The sharp discontinuities in band occupation for metals make convergence much slower as a function of number of k -points.

*Integrals may not always increase in accuracy with more k -points!
These k values are different from the plane wave k 's defining the basis!*

k-space Integration: Example

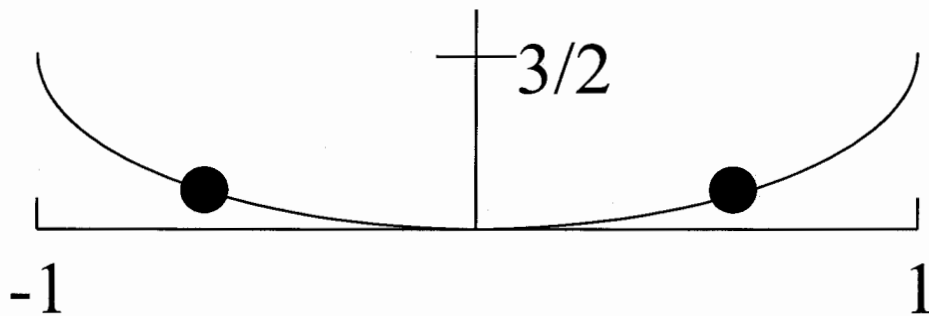
$$F(k) = \frac{3}{2}k^2$$

$$\int_{-1}^1 F(k) = 1$$



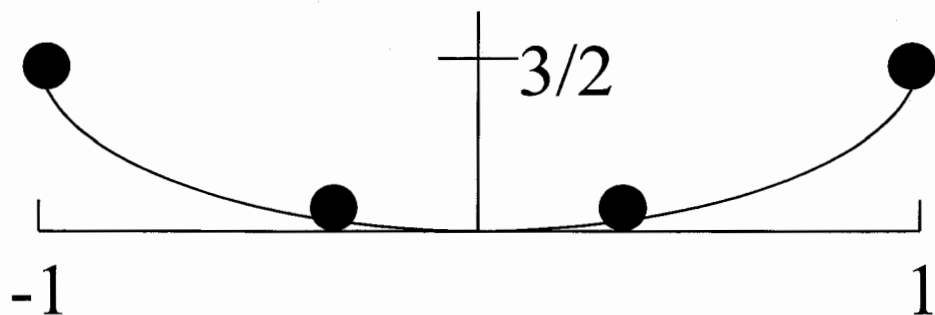
$$M-P=1, \Delta L=2/(M-P)=2$$

$$E = w_i \varepsilon_i \Delta L \\ = 1 \times F(1) \times 2 = 3$$



$$M-P=2, \Delta L=2/(M-P)=1$$

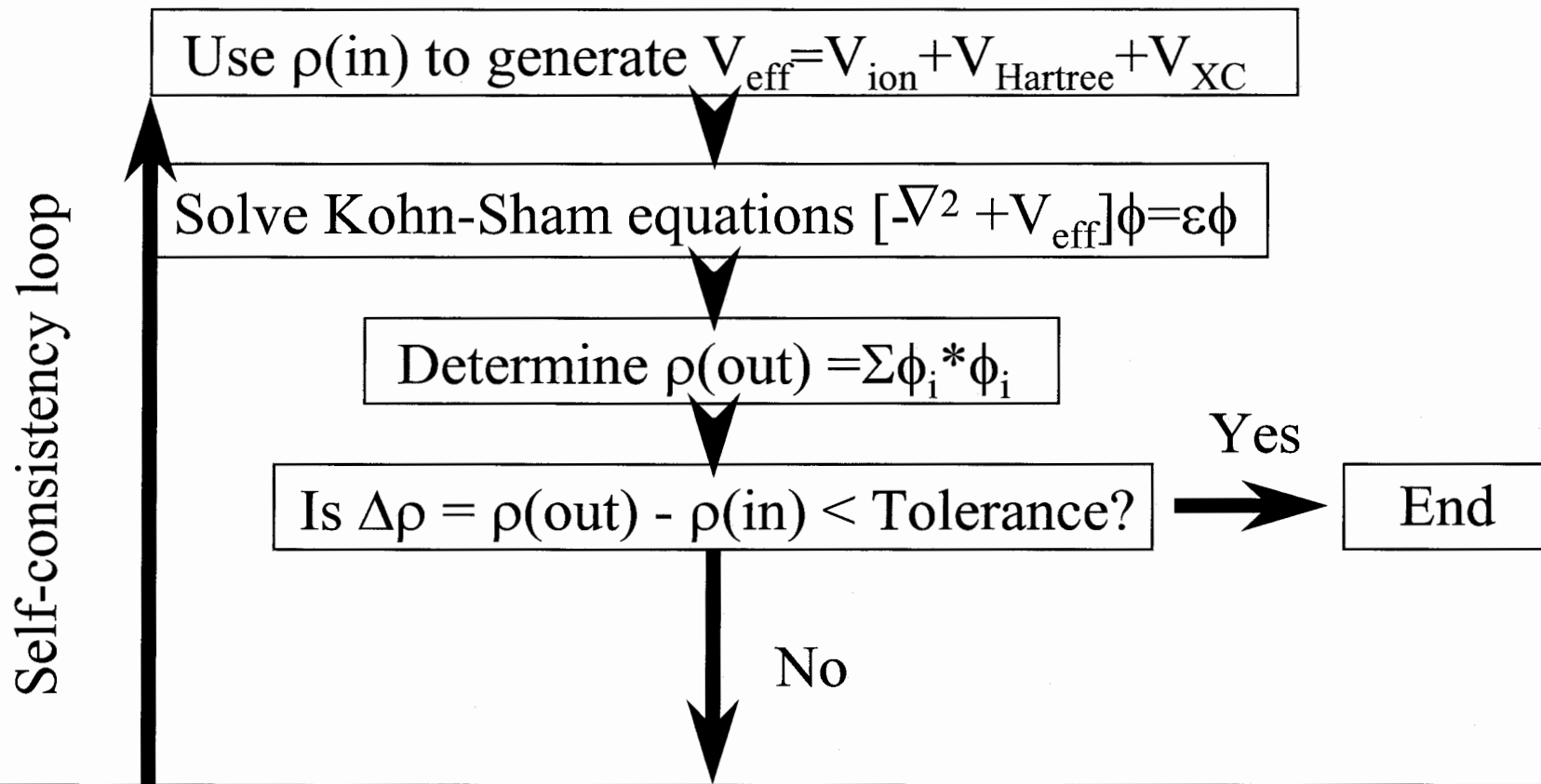
$$E = \sum w_i \varepsilon_i \Delta L \\ = 2 \times F(1/2) \times 1 = 3/4$$



$$M-P=3, \Delta L=2/(M-P)=2/3$$

$$E = \sum w_i \varepsilon_i \Delta L \\ = [2 \times F(1/3) \times 2/3 + \\ 1 \times F(1) \times 2/3] = 11/9$$

Mixing and self-consistency



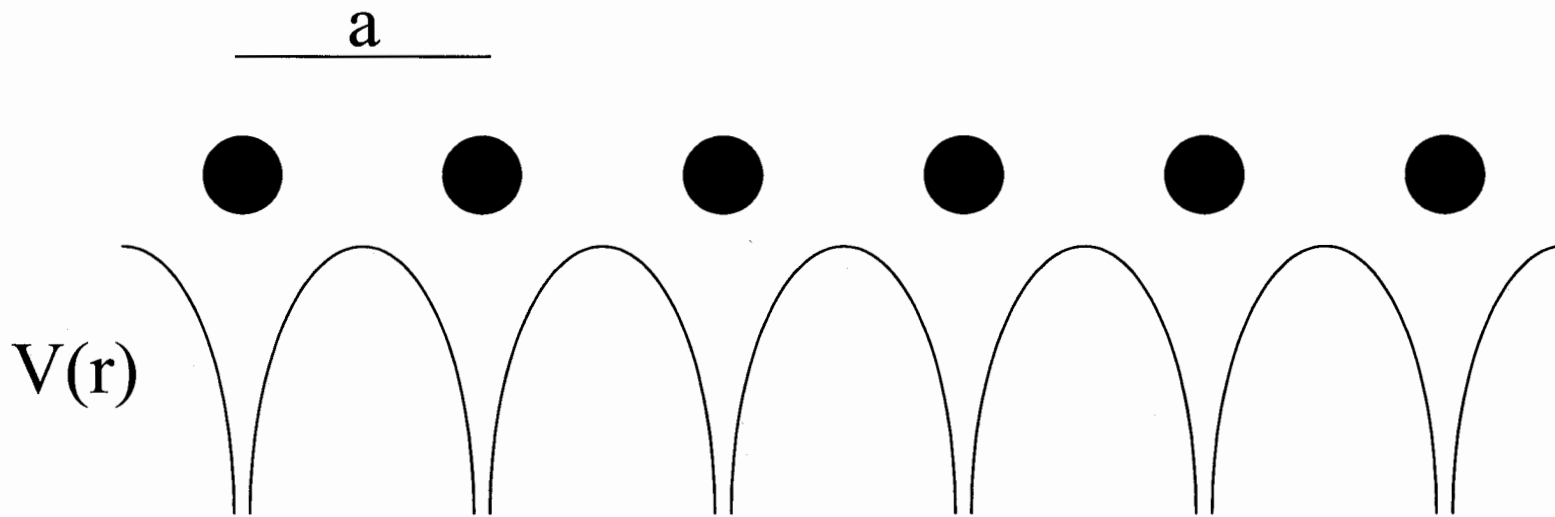
Mix $\rho^{(m)}(\text{in})$, $\rho^{(m)}(\text{out})$ to get $\rho^{(m+1)}(\text{in})$:

- $\rho^{(m+1)}(\text{in}) = (1-\alpha)\rho^{(m)}(\text{in}) + \alpha\rho^{(m)}(\text{out})$ converges only for small α .
- There exist many more efficient schemes (eg, Broyden).
- Self-consistency can usually be obtained in ~ 10 iterations.

Common Mistakes and Problems

- **Convergence errors:** not enough basis functions (E_{MAX} too small), not enough k-points in integrals (Monkhorst-Pac grid too small).
- **Pseudopotentials not accurate:** cores overlap, core electrons need to be valence (eg, Sr[Kr core]), very new environment.
- **Incompatible calculations:** results with different pseudopotentials, E_{MAX} , k-points, convergence criteria for position relaxations (energy vs. force).
- **Magnetic effects:** must use spin-polarized density functional theory.
- **Incorrect initial positions and/or symmetry:** codes will not break initial symmetry or move over barriers to find global energy minima (eg, bcc Cu will not relax to fcc Cu).

Simple DFT Calculation Example



a = primitive lattice vector

L = total length of system (the true infinite crystal exists in the limit of L going to infinity)

$V(r)$ = periodic attractive pseudopotential.

G = reciprocal lattice vectors = $n2\pi/a$

$z = 1$ = number of valence electrons per atom

Simple DFT Calculation Example

Mokhorst-Pack mesh: For simplicity do a 1 k-point calculation (use only $k=\pi/a$).

Initial charge density: Assume ρ is uniform $\Rightarrow \rho(r) = z/a$.

Now get basis functions, construct **H**, **S** and solve Kohn-Sham equations.

Simple DFT Calculation Example

The basis functions

Take $E_{\max} = [(h/2\pi)(\pi/a)]^2/2m = 0.137 \text{ H} = 3.73 \text{ eV}$

Include all G such that $[(h/2\pi)(k+G)]^2/2m \leq E_{\max}$

$\Rightarrow G = -2\pi/a, 0$

(note that using $(k+G)$ and not just G is a cheat to simplify)

Expand Kohn-Sham orbitals as
$$\phi_{nk}(r) = \sum_{\alpha=1}^2 a_{\alpha} \theta_{\alpha}(r)$$

where

$$\theta_1(r) = \frac{1}{\sqrt{L}} e^{i(-\pi/a)r} = |1\rangle$$

$$\theta_2(r) = \frac{1}{\sqrt{L}} e^{i(\pi/a)r} = |2\rangle$$

Simple DFT Calculation Example

The Hamiltonian

$$S_{IJ} = \langle I|J \rangle = \delta_{IJ} \Rightarrow \mathbf{S} \text{ is the identity matrix}$$

$$H_{IJ} = \langle I|H|J \rangle = \langle I|T + V_{\text{eff}}|J \rangle \text{ where}$$

$$T = -\frac{[\hbar / 2\pi]^2 \nabla^2}{2m}$$

$$V_{\text{eff}} = V_{\text{ion}} + V_{\text{Hartree}} + V_{\text{XC}}$$

Simple DFT Calculation Example

Calculating a term $H_{IJ} = \langle I|H|J\rangle$. The kinetic energy.

$$\begin{aligned} T_{12} &= \int dr \theta_1^*(r) \frac{(\hbar / 2\pi)^2 \nabla^2}{2m} \theta_2(r) \\ &= \frac{-1}{L} \int dr e^{i(\pi/a)r} \frac{(\hbar / 2\pi)^2 \nabla^2}{2m} e^{i(\pi/a)r} \\ &= \frac{1}{L} \frac{(\hbar / 2\pi)^2}{2m} (\pi / a)^2 \int dr e^{i(2\pi/a)r} \\ &= 0 \end{aligned}$$

T is a diagonal 2x2 matrix.

Simple DFT Calculation Example

Warning: Assumptions here might be impossible physically or mathematically. This is just to make the Hamiltonian simple.

- Assume that all terms in $\langle I|H|J\rangle$ are dominated by the pseudopotential terms $\langle I|V_{PP}|J\rangle$.
- Take $\langle I|V_{PP}|I\rangle = 0$.
- Write $\langle I|V_{PP}|J\rangle = V_{PP}(G_J - G_I)$
- Assume $V_{PP}(G)$ is real so $V_{PP}(-G) = V_{PP}(G)$.

$$H = \begin{pmatrix} 0 & V_{PP}(2\pi/a) \\ V_{PP}(2\pi/a) & 0 \end{pmatrix}$$

Simple DFT Calculation Example

Diagonalize the 2x2 matrix $\mathbf{H}(k=0)$.

Eigenvectors and eigenvalues:

$$\mathbf{e}_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}; \varepsilon_1 = V_{PP}(2\pi/a)$$

$$\mathbf{e}_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}; \varepsilon_2 = -V_{PP}(2\pi/a)$$

Since $V_{PP}(2\pi/a) < 0$ the lowest energy state is given by

$$\phi_{n=1, k=\pi/a}(r) = \frac{1}{\sqrt{2}} (1\theta_{1\pi/a} + 1\theta_{2\pi/a}) = \sqrt{\frac{2}{L}} \cos\left(\frac{\pi}{a}r\right)$$

Simple DFT Calculation Example

Calculate the new density

Since there is $z=1$ electron per atom only the lowest energy band is occupied band and the density is given by

$$\begin{aligned}\rho(\mathbf{r}) &= \int d\mathbf{k} \sum_n \phi_{n\mathbf{k}}^*(\mathbf{r}) \phi_{n\mathbf{k}}(\mathbf{r}) \left\{ \forall \varepsilon_{n\mathbf{k}} \leq E_{Fermi} \right\} \\ &\approx \phi_{n=1, k=\pi/a}(\mathbf{r}) \phi_{n=1, k=\pi/a}(\mathbf{r}) \\ &= \frac{2}{L} \cos^2\left(\frac{\pi}{a} r\right)\end{aligned}$$

This $\rho(\text{out})$ is quite different from the uniform $\rho(\text{in})$ we used. Mix $\rho(\text{in})$ and $\rho(\text{out})$ to get a new ρ , calculate new V_{eff} , and start next iteration. Continue until self-consistency...