Band structure calculations in a nutshell

M. R. Benam

Band Structure Calculations- many body problem

- **We have a many-body problem:**

$$H = H_{el} + H_{nuc} + H_{el-nuc}$$

$$H_{el} = \sum_i \frac{-\hbar^2}{2m_i}\nabla^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_j - r_i|}$$

$$H_{nuc} = \sum_M \frac{-\hbar^2}{2M_\mu}\nabla_\mu^2 + \frac{1}{2}\sum_{\mu\neq\mu'}\frac{z_\mu z_{\mu'}}{|R_\mu - R_{\mu'}|}e^2$$

$$H_{el-nuc} = -\sum_{i,\mu'}\frac{z_\mu e^2}{|R_\mu - r_i|}$$

$$H\psi = E\psi$$

Band Structure Calculations - Born-Oppenheimer app.

- **In order to solve this problem, we should change it to a single-electron equation which need simplifications and approximations:**

1- Born-Oppenheimer approximation (1927): take the nuclei to be static

$$H_e \Psi_e = E_e \Psi_e$$

$$\hat{H}_e = \hat{K}_e + \hat{V}_{ne} + \hat{V}_{ee}$$

Band Structure Calculations- IEA &FEA app.

- **……. simplifications and approximations:**

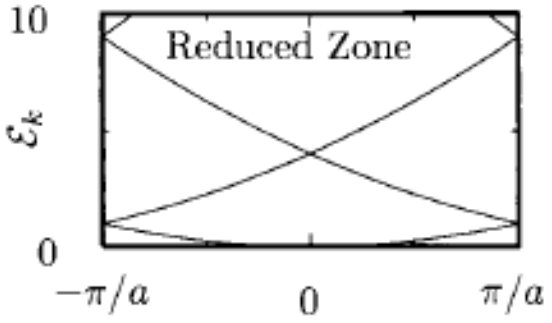
2- Independent Electron Approximation (IEA).

3- Free Electron Approximation(FEA).

This is in fact the free fermi gas where the S.E. is separable to single-electron eq. and the solution:

$$\Psi_k = \left(\frac{1}{\sqrt{V}}\right) e^{ik\cdot r}$$

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m}$$



Band Structure Calculations- Bloch's Theorem

- **Toward more real situations:**

The effect of ions are important. Ignore FEA and for an ideal periodic crystal:

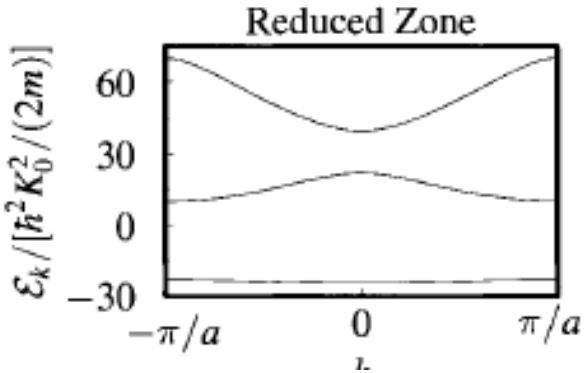
1- the many-body S.E. will separate to N single-electron eq.

2- Now, we only need to solve S.E. in the unit cell:

$$U(\vec{r}+\vec{R}) = U(\vec{r})$$

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + U(r)\right)\psi(r) = \varepsilon\Psi$$

$$\psi_{nk}(r) = e^{ik.r}u_{nk}(r)$$



Band Structure Calculations- Interacting electrons.

- **Toward more real situations: Consider also** Electron-Electron Interactions

Now the All the computational difficulty arises from the Coulomb interaction and the question is:

How one can change interacting electrons to single-electron one?

this give rise to Hartree and Hartree-Fock Equations and finally to Kohn-Sham equations.

$$[\frac{-\hbar^2}{2m_e}\nabla_i^2 + V_{eff}]\psi_{ks}(\vec{r}) = \varepsilon\psi_{ks}(\vec{r})$$

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Band Structure Calculations- solving Kohn-Sham equations

- **Toward more real situations: Consider also** Electron-Electron Interactions

  Now the problem is solving KS eguations:

  1-Pseudopotentials.

  2- Linear Combination of Atomic Orbital or Tight – Binding.

  3-Linear Muffin – Tin Orbital.

  4- Linear Augmented Plane Wave.

  ……..

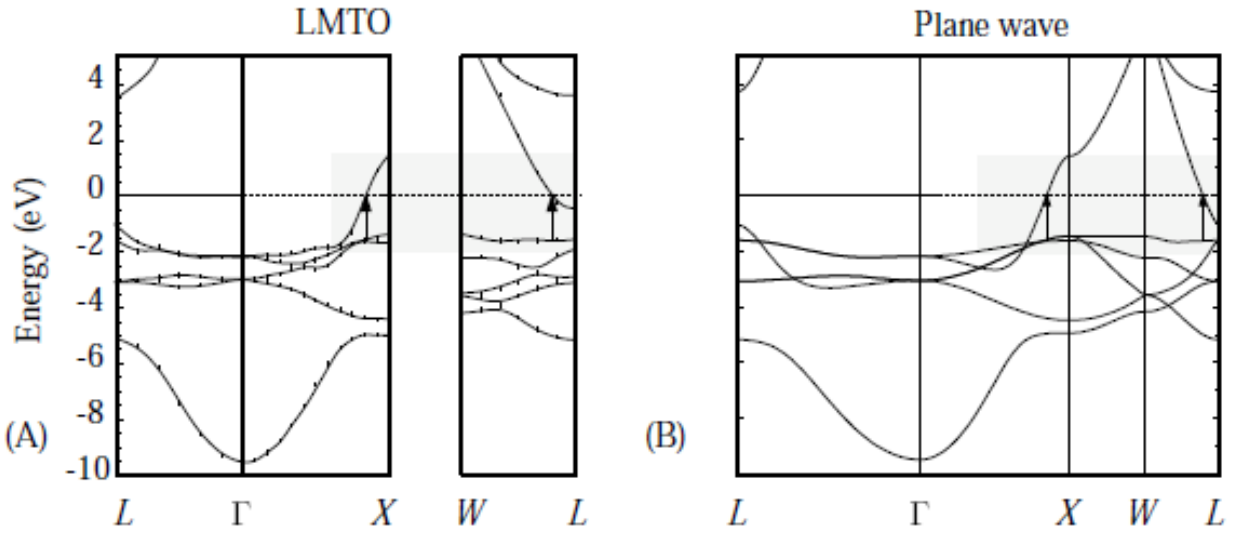
Band Structure Calculations- solving Kohn-Sham equations

- **Toward more real situations: Consider also** Electron-Electron Interactions

  Now the problem is solving KS eguations:

SIESTA code uses PAO orbitals

Band Structure Calculations- solving Kohn-Sham equations



Band Structure Calculations- k-point sampling

- **We need evaluate integrals over the allowed values of k in the Brillouin zone :**

$$g = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{\text{BZ}} g(\mathbf{k})\, d\mathbf{k}.$$

- **Integrals can be approximated by evaluating the function to be integrated at a set of discrete k-points:**

$$\int_{1}^{1} f(x)\, dx \cong \sum_{j\ 1}^{n} c_j f(x_j),$$

- **In the limit of using a very large number of points, these numerical methods converge to the exact result for the integral.**

Band Structure Calculations- k-point sampling-Monkhorst-Pack method

- **Most packages offer the option of choosing k points based on the Monkhorst and Pack (1976) method.**
- **To use this method, all that is needed is to specify how many k points are to be used in each direction in reciprocal space.**
- **For calculations with supercells that have the same length along each lattice vector, it is natural to use the same number of k points in each direction.**
- **If M k points are used in each direction, it is usual to label the calculations as using M×M×M k points.**

Band Structure Calculations- k-point sampling- Monkhorst-Pack method

- **It is clear that we should expect that a calculation using M×M×M k points will give a more accurate result than a calculation with N×N×N k points if M >N.**

- **How many k points we should choose?**

Band Structure Calculations- How many k points we should choose?

- **A sample calculations of the Total Energy of fcc- Cu:**

M	E/atom (eV)	No. of k Points in IBZ	τ_M/τ_1
1	1.8061	1	1.0
2	3.0997	1	1.1
3	3.6352	4	2.3
4	3.7054	4	2.6
5	3.7301	10	5.2
6	3.7541	10	6.0
7	3.7676	20	10.4
8	3.7671	20	11.2
9	3.7680	35	16.9
10	3.7676	35	17.1
11	3.7662	56	31.2
12	3.7665	56	28.5
13	3.7661	84	40.0
14	3.7659	84	39.7

Band Structure Calculations- How many k points we should choose?

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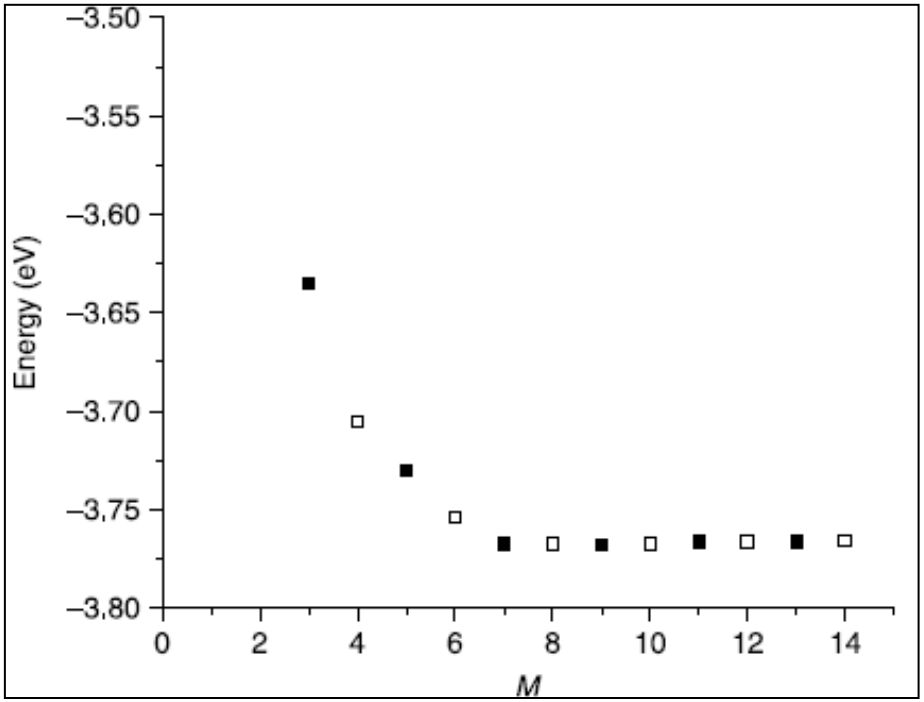


Band Structure Calculations- How many k points we should choose?

- **If there are symmetries then the integrals in reciprocal space do not need to be evaluated using the entire BZ, instead they can just be evaluated in a reduced portion of the zone that can then be extended without approximation to fill the entire BZ using symmetry. This reduced region in k space is called:**

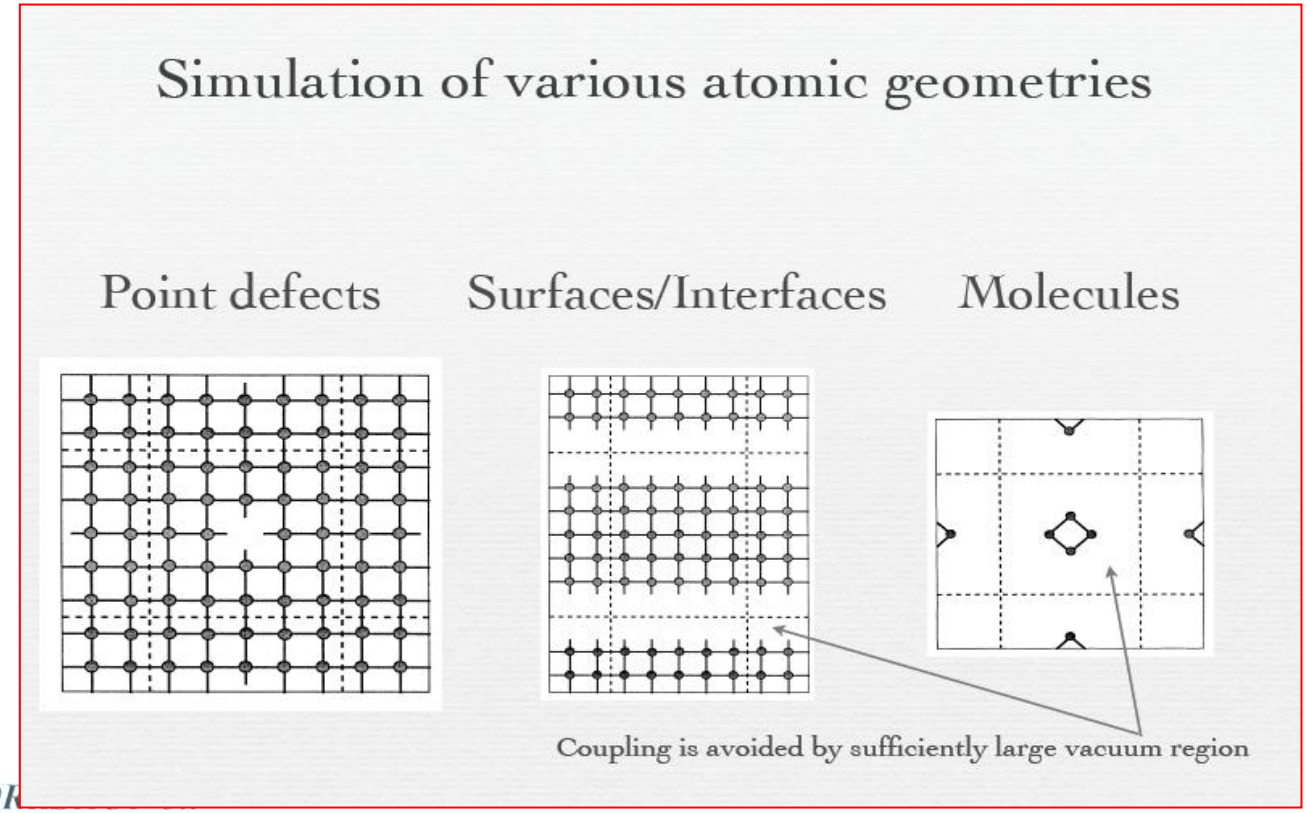
Irreducible Brillouin Zone (IBZ).

Band Structure Calculations- **How many k points we should choose?**

SIESTA code uses Monkhorst-Pack method

Band Structure Calculations- **Supper cell Approximation.**

- **In order to use PBC and Bloch Theorem we should use Supper cell App.**



Band Structure Calculations- Supper cell Approximation.

- **Now, we have an infinite crystal of repeated Suppercells.**
- **A primitive cell is a supercell that contains the minimum number of atoms necessary to fully define a periodic material with infinite extent.**
- **Increasing the volume of a supercell reduces the number of k points needed to achieve convergence because volume increases in real space correspond to volume decreases in reciprocal space.**

Thank you for your attention!