

Electron bands in crystals

Pseudopotentials, Plane Waves, Local Orbitals

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Lecture at Summer School
Hands-on introduction to Electronic Structure
Materials Computation Center
University of Illinois – June, 2005

Crystals and electron bands

Pseudopotentials

Plane Wave Methods

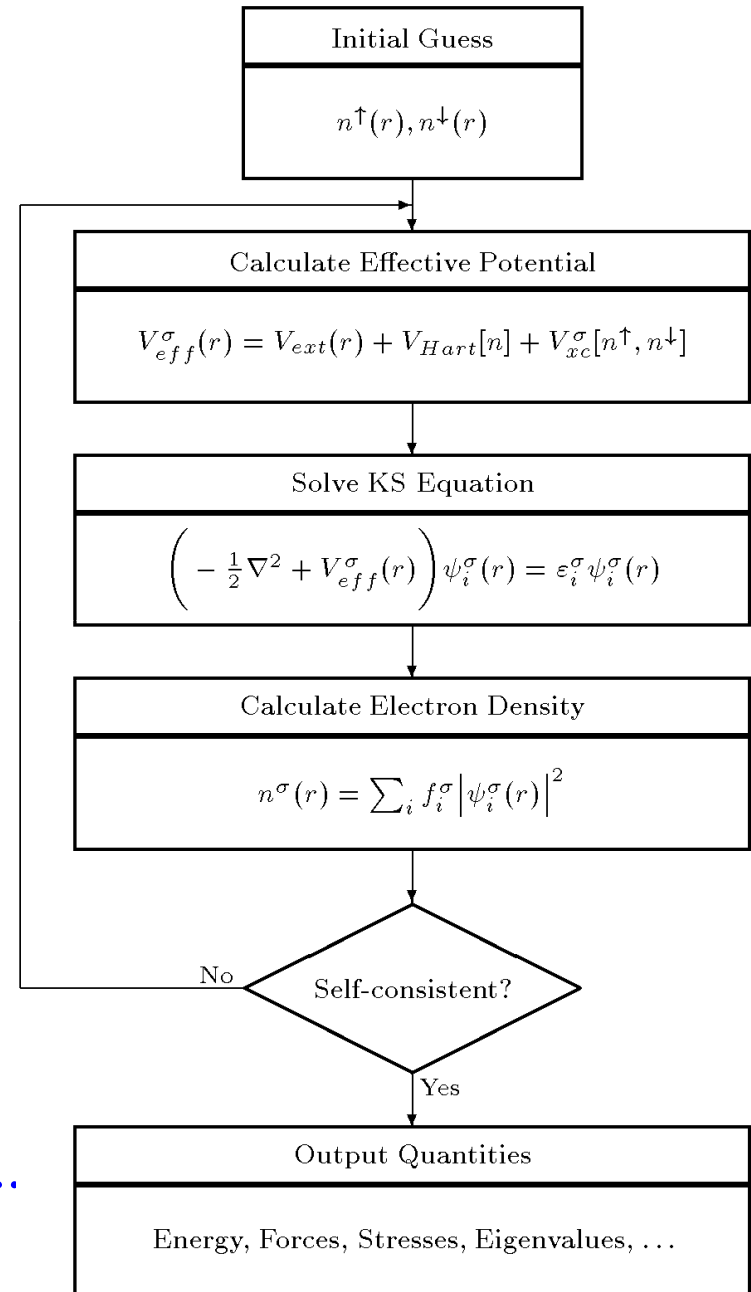
Local Orbital Methods

Reference:

Electronic Structure: Basic Theory and Practical Methods,
Richard M. Martin (Cambridge University Press, 2004)

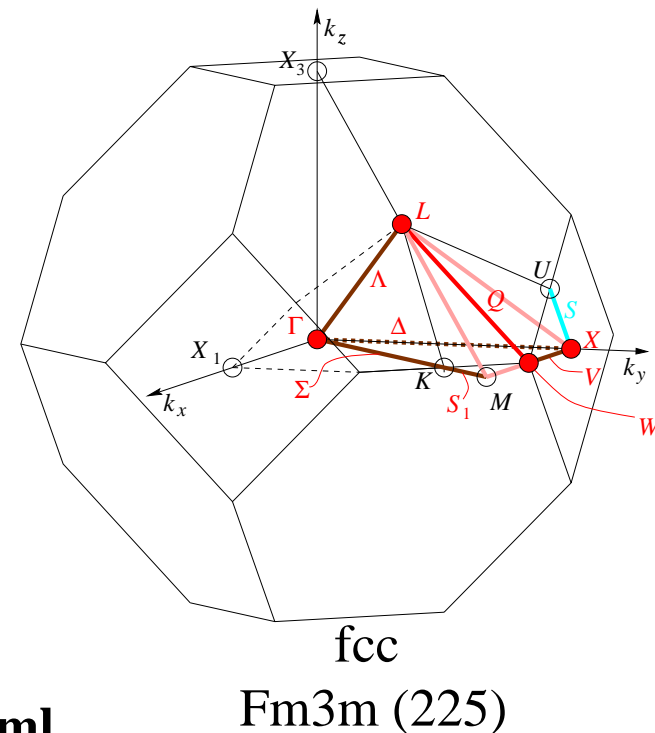
Solving Kohn-Sham Equations

- Structure, types of atoms
- Guess for input
- Solve KS Eqs.
- New Density and Potential
- Self-consistent?
- Output:
 - Total energy, force, stress, ...
 - Eigenvalues



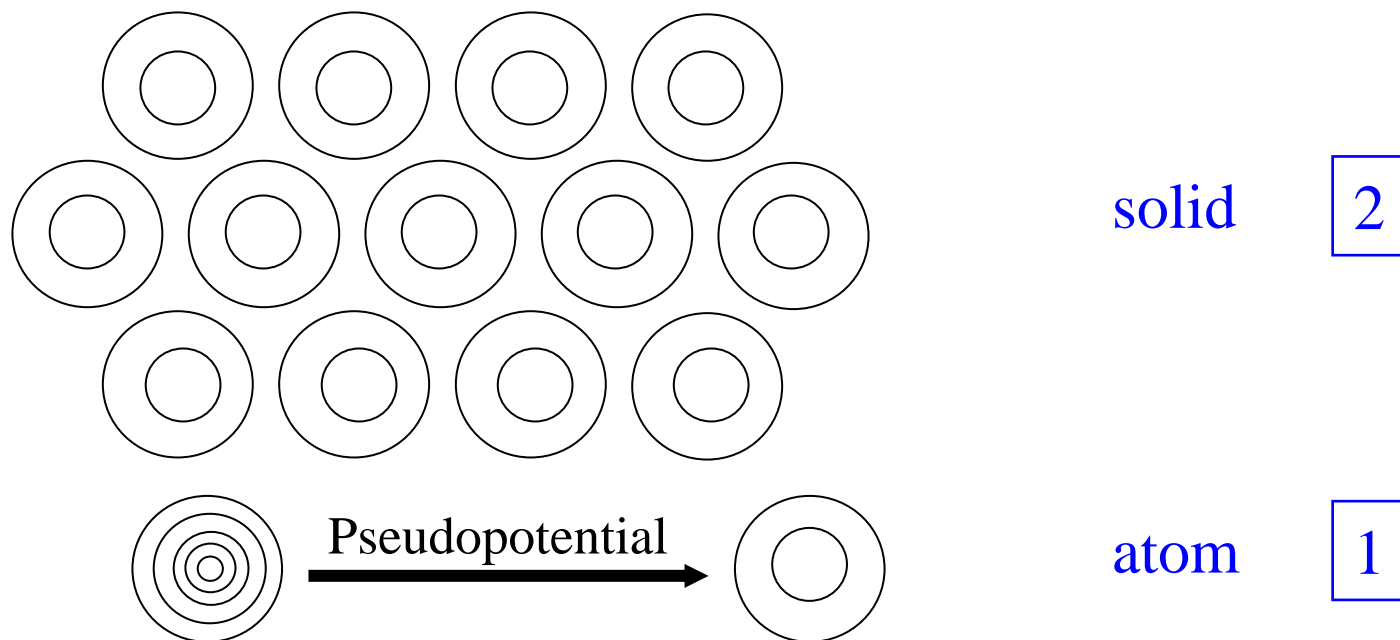
Structure

- **“External Potential” for electrons determined by structure**
 - Lattice periodicity
 - Positions of atoms in primitive cell
 - Chemical identity of each atom – atomic number
- **Symmetry**
 - Translation symmetry
 - Lattice – Reciprocal lattice
 - Bloch Theorem
 - States labeled by k in Brillouin Zone (BZ)
- **See Notes and examples in Lab**
 - Example fcc crystals
- **Useful Web site**
 - BZ with labels for all 230 space groups
http://www.cryst.ehu.es/cryst/get_kvec.html



Pseudopotentials

- **Pseudopotential Method** – replace each potential



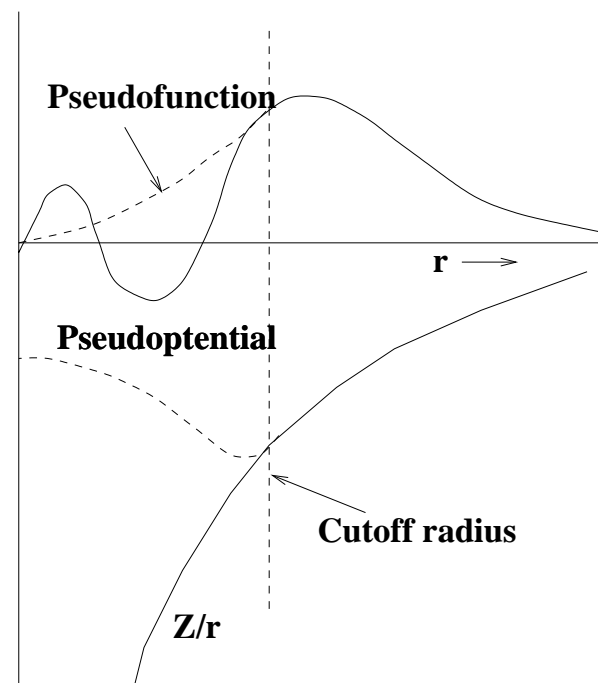
- **1** Generate **Pseudopotential** in atom (spherical) – **2** use in solid
- **Pseudopotential** can be constructed to be weak
 - Can be chosen to be smooth
 - Solve Kohn-Sham equations in solid directly in Fourier space

Pseudopotentials

- **Norm-Conserving Pseudopotential (NCPP)**
 - Hamann, Schluter, Chaing



- **Generate weak pseudopotential** in atom with same scattering properties for valence states as the strong all-electron potential
- **Conditions**
 - Potential same for $r > R_c$
 - Pseudofunction “norm-conserving” for $r < R_c$
- **Codes available for generating potentials**



Pseudopotentials

- **Web Site:** <http://www.tddft.org/programs/octopus/pseudo.php>

News | Download | Developers | Pseudopotentials | Contributors | Info

Pseudopotentials

Octopus uses non-local, norm-conserving Troullier-Martins pseudopotentials. You can generate them with **José Luis Martins'** atomic **program**, or use the pseudopotentials distributed from this web page.

Obviously you will use the pseudopotential at your own risk, and we do not feel responsible for any (bad) result that could outcome from the use of these files. I suppose that you are grown-up and understand that ;))

Just click on an element

Not everything works, but part does!

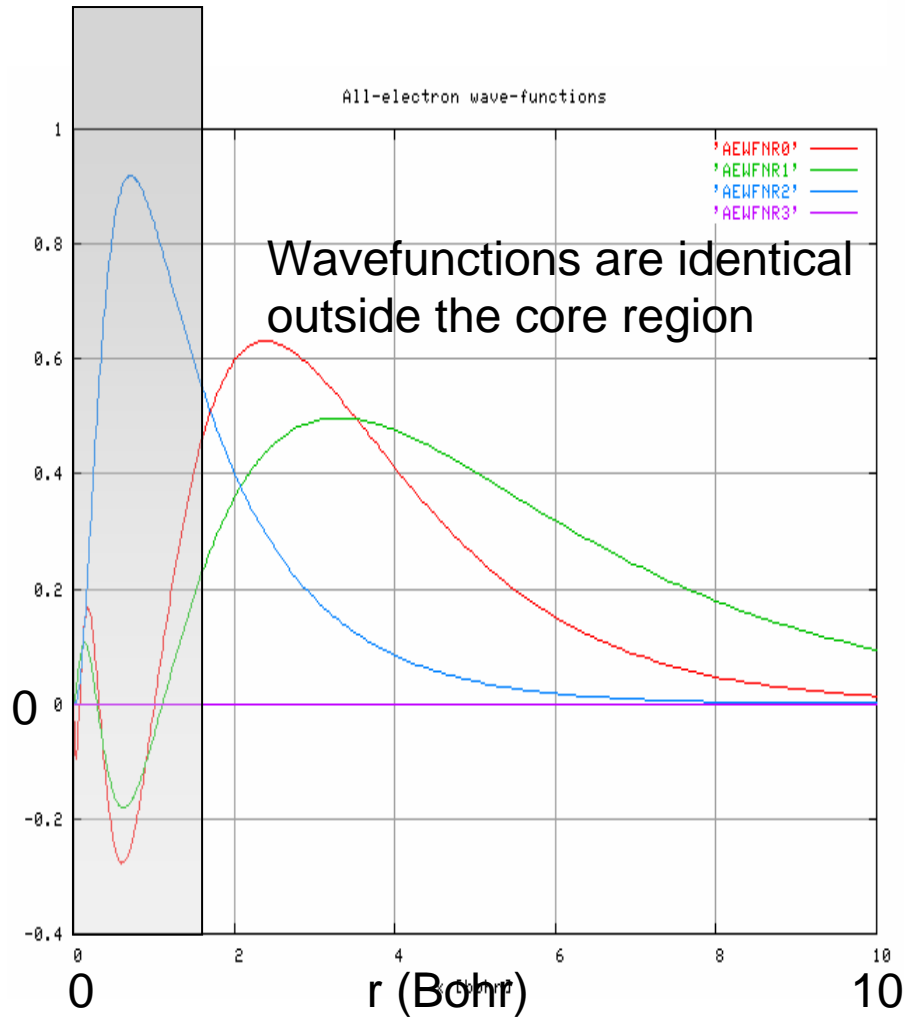
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Use with care!

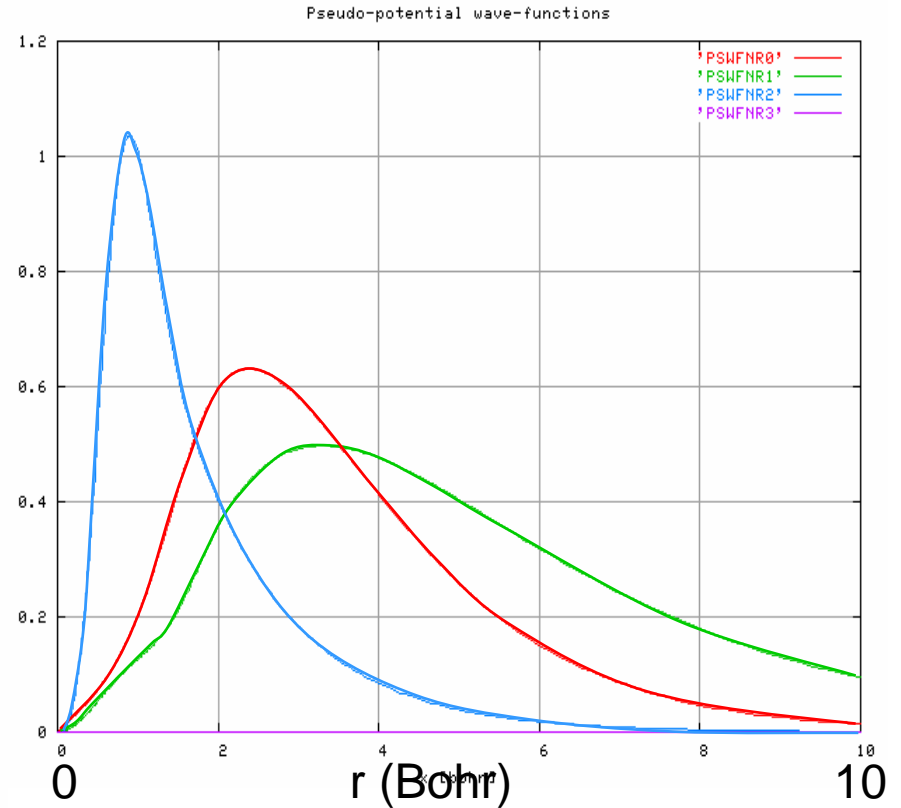
Always Test!

Fe – s,p,d valence wavefunctions – $r \psi(r)$

All electron functions



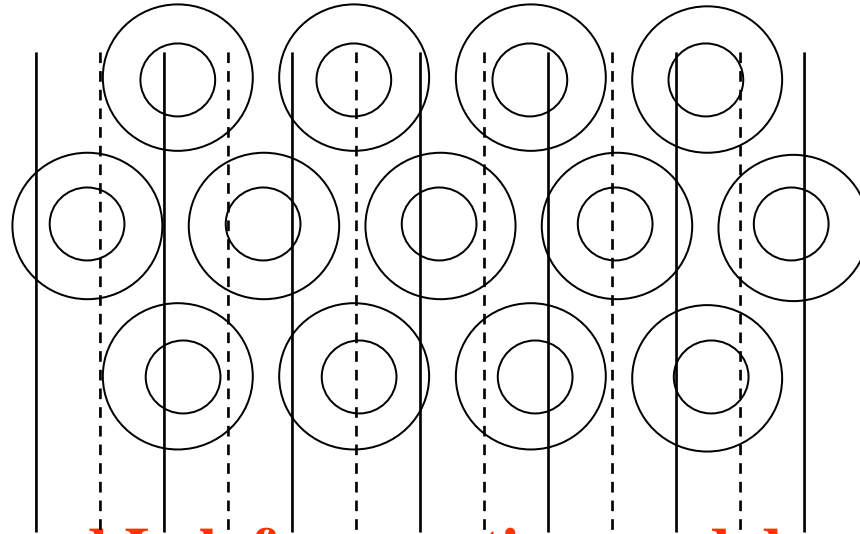
Pseudo functions



From <http://www.tddft.org/>

Plane Waves

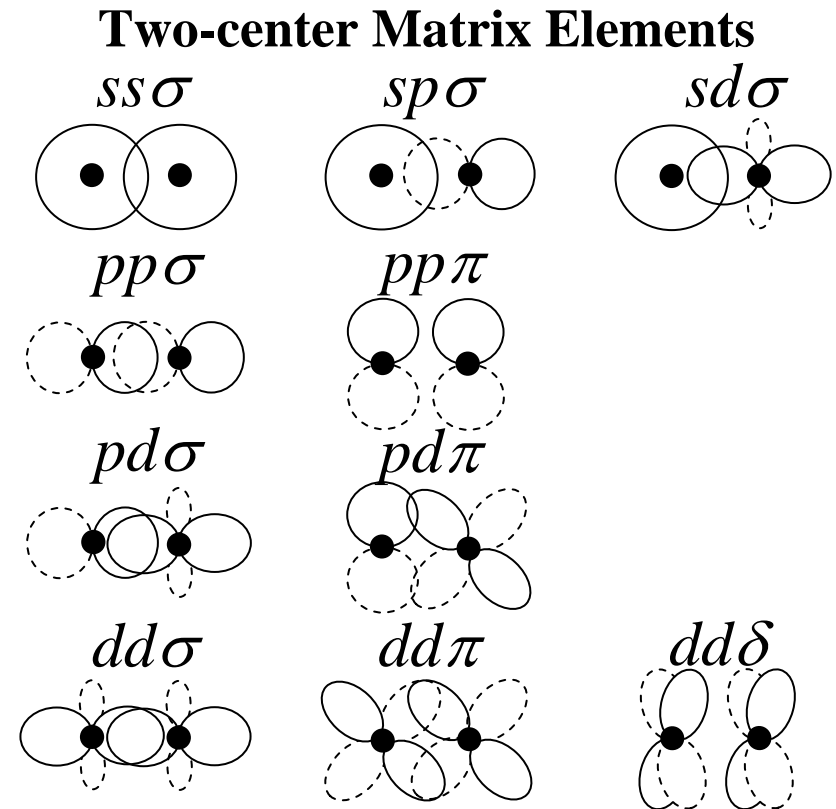
- **Pseudopotential method with plane waves**



- **See Notes and Lab for equations and descriptions - TBPW**
 - **Examples with approximate empirical pseudopotentials**
- **Full self-consistent calculations – ABINIT, other codes**
 - **Method of choice for many reasons -
Simplicity and the speed of Fast Fourier Transforms**
 - **Forces, phonons, response functions, ...**
 - **Simulations – solids, liquids,**

Localized orbitals

- Intuitive appeal of atomic-like states
 - Gaussian basis widely used in chemistry
 - Numerical radial orbitals used in SIESTA
- More efficient than plane waves
 - Very useful for complicated problems
 - Localized, non-periodic problems
- Tight-binding
 - Simple understanding
 - Interpolation of bands calculated by other methods
 - Very fast and applicable to very large systems



Localized Orbitals & Tight binding

- **Localized orbitals**

- Full methods – Calculate all quantities – done in SIESTA
- Tight binding – Take matrix elements as parameters
- Very useful – qualitative – quantitative

Define localized orbitals $\chi_m^*(\mathbf{r} - \tau_m)$ centered at site τ_m , where $m = 1, 2, \dots$ labels all the orbitals. Then

$$H_{m,m'} = \int d\mathbf{r} \chi_m^*(\mathbf{r} - \tau_m) \hat{H} \chi_{m'}(\mathbf{r} - \tau_{m'}), \quad (1)$$

and the overlap matrix is given by

$$S_{m,m'} = \int d\mathbf{r} \chi_m^*(\mathbf{r} - \tau_m) \chi_{m'}(\mathbf{r} - \tau_{m'}). \quad (2)$$

Localized Orbitals & Tight binding

In a crystal one can define basis states with wavevector \mathbf{k} ,

$$\chi_{m\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \chi_m(\mathbf{r} - (\tau_m + \mathbf{T})). \quad (1)$$

The solution can be written

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_m c_m(\mathbf{k}) \chi_{m\mathbf{k}}(\mathbf{r}), \quad (2)$$

and the secular equation for wavevector \mathbf{k} is

$$\sum_{m'} \left[H_{m,m'}(\mathbf{k}) - \varepsilon_i(\mathbf{k}) S_{m,m'}(\mathbf{k}) \right] c_{i,m'}(\mathbf{k}) = 0. \quad (3)$$

See Notes and Lab for examples – TBPW code

Total energy and force in tight binding

The total energy can always be written

$$E_{tot} = \sum_i \varepsilon_i f(\varepsilon_i) + F[n]. \quad (1)$$

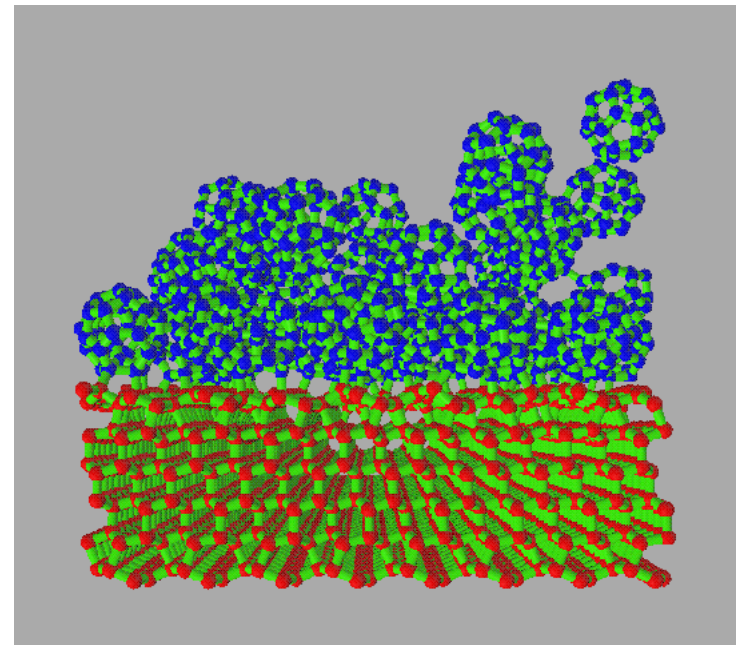
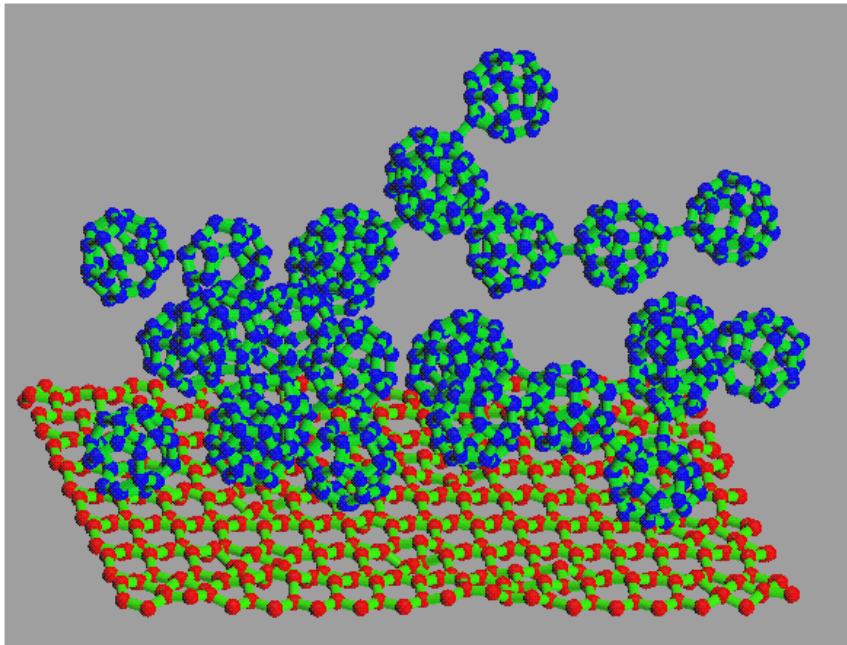
where ε_i are eigenvalues, f is the Fermi function, and $F[n]$ is the repulsive sum of nuclei interactions and double counting corrections. $F[n]$ can be approximated as 2-body terms,

$$E_{tot} = \sum_i \varepsilon_i f(\varepsilon_i) + \sum_{I < J} f(|\mathbf{R}_I - \mathbf{R}_J|). \quad (2)$$

- Key Points
 - Adjustable parameters in hamiltonian, overlap and f terms
 - Can vary from “quick and dirty” to quite accurate
 - Very fast calculations – bands, energy, forces,

Deposition of C₂₈ Buckyballs on Diamond

Example using tight-binding and “Order-N” methods



- Simulations with ~ 5000 atoms, TB Hamiltonian from Xu, et al. (A. Canning, G.~Galli and J .Kim, Phys.Rev.Lett. 78, 4442 (1997)).

Conclusions

- **Solution of the independent-particle Kohn-Sham equations is the essential step in DFT calculations**
 - Most-time-consuming part
- **All DFT calculations share many common features**
 - Structure of nuclei, must specify external potential
- **Differences**
 - Basis – Plane wave, localized, . . .
 - All-electron, pseudopotential
 - Diagonalization of matrix vs iterative solution
- **Many features can be illustrated by simple examples and a pedagogical code TBPW**
 - Lab with TBPW
- **Full calculations illustrated by ABINIT, SIESTA**