SUMMER SCHOOL ON COMPUTATIONAL MATERIALS SCIENCE
University of Illinois at Urbana-Champaign, June 13-23, 2005

Introduction to the SIESTA method

Some technicalities

Linear-scaling DFT based on Numerical Atomic Orbitals (NAOs)

- Born-Oppenheimer
- DFT
- Pseudopotentials
- Numerical atomic orbitals
- Numerical evaluation of matrix elements

- *relaxations, MD, phonons.*
- *LDA, GGA*
- *norm conserving, factorised.*
- *finite range*

siesta

P. Ordejon, E. Artacho & J. M. Soler , Phys. Rev. B 53, R10441 (1996)

J. M.Soler et al, J. Phys.: Condens. Matter **14**, 2745 (2002)

Matrix equations:

$$\psi_n(\vec{r}) \approx \sum_\mu c_{\mu n}\phi_\mu(\vec{r})$$

unknown

Expand in terms of a finite set of known wave-functions $\phi_\mu(\vec{r})$

$$\hat{h}\psi_n(\vec{r}) = \varepsilon_n\psi_n(\vec{r}) \longrightarrow \sum_\mu c_{\mu n}\hat{h}\phi_\mu(\vec{r}) = \varepsilon_n\sum_\mu c_{\mu n}\phi_\mu(\vec{r})$$

Def. $h_{\nu\mu} \equiv \int \phi_\nu^*(\vec{r})\hat{h}\phi_\mu(\vec{r})d^3\vec{r}$ and $S_{\nu\mu} \equiv \int \phi_\nu^*(\vec{r})\phi_\mu(\vec{r})d^3\vec{r}$

$$\sum_\mu h_{\nu\mu}c_{\mu n} = \varepsilon_n\sum_\mu S_{\nu\mu}c_{\mu n}$$

$$\underset{\sim}{H}C_n = \varepsilon_n\underset{\sim}{S}C_n$$

$\rho(\vec{r}) = \sum \rho^{atom}(\vec{r})$

Initial guess

$\rho(\vec{r}) = \sum_{\mu,\nu} \rho_{\mu,\nu} \phi_\mu \phi_\nu$

$V_H(\vec{r}), V_{xc}(\vec{r})$

Mixing $\rho^{out}_{\mu,\nu}, \rho^{in}_{\mu,\nu}$

Self-consistent iterations

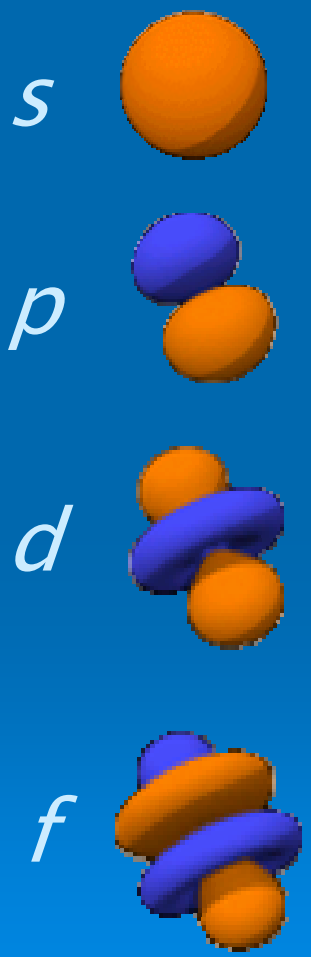
$\rho^{out}_{\mu,\nu}$

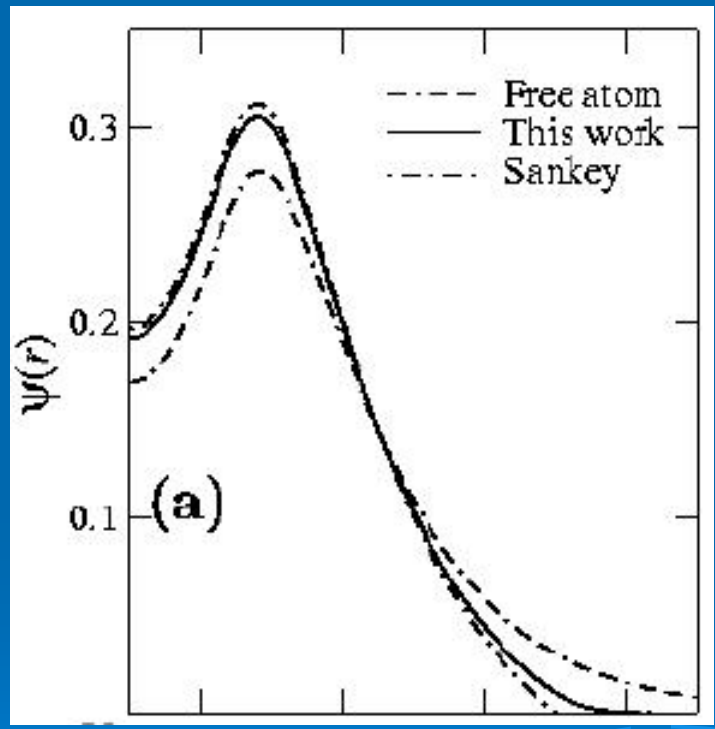
$\hat{H}\psi = \varepsilon\psi$

$\rho^{out}_{\mu,\nu} - \rho^{in}_{\mu,\nu} <$

Total energy
Charge density
Forces

Basis Set: Atomic Orbitals





Strictly localised
(zero beyond a cut-off radius)

Long-range potentials

$$H = T + V_{ion}(r) + V_{nl} + V_H(r) + V_{xc}(r)$$

Long range

$$V_{na}(r) = V_{ion}(r) + V_H[\rho_{atoms}(r)]$$

Neutral-atom potential

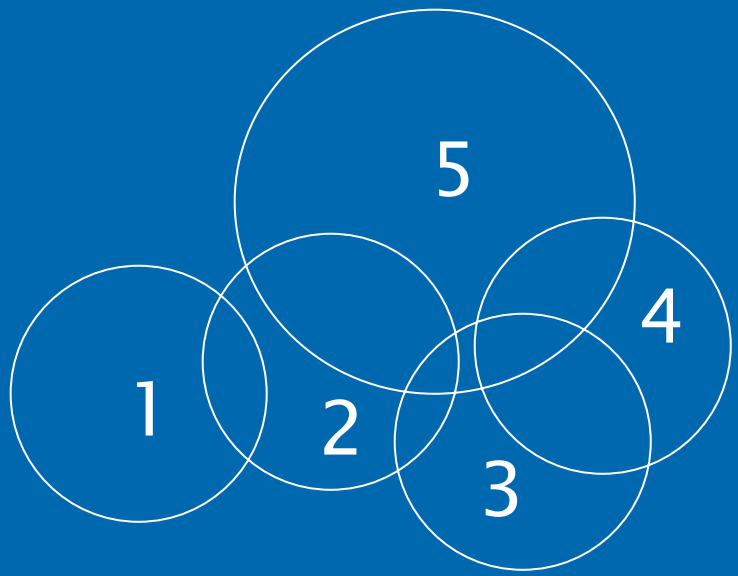
$$\delta V_H(r) = V_H[\rho_{SCF}(r)] - V_H[\rho_{atoms}(r)]$$

$$H = T + V_{nl} + V_{na}(r) + \delta V_H(r) + V_{xc}(r)$$

Two-center integrals

Grid integrals

Sparsity

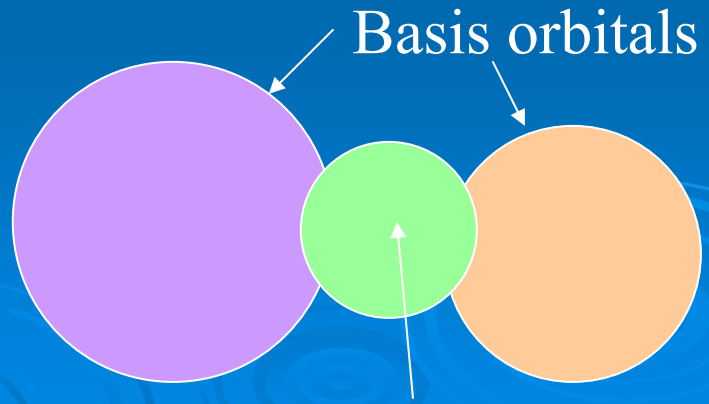


1 with 1 and 2
2 with 1,2,3, and 5
3 with 2,3,4, and 5
4 with 3,4 and 5
5 with 2,3,4, and 5

$S_{\mu\nu}$ and $H_{\mu\nu}$ are sparse

$\rho_{\mu\nu}$ is not strictly sparse but only a sparse subset is needed

Non-overlap interactions



Two-center integrals

Convolution theorem

$$S(\mathbf{R}) \equiv \langle \phi_1 | \phi_2 \rangle = \int \phi_1(\mathbf{r})\, \phi_2(\mathbf{r}-\mathbf{R})\, d\mathbf{r}$$

$$\phi(\mathbf{k}) = \frac{1}{(2\pi)^{2/3}} \int \phi(\mathbf{r})\, e^{-i\mathbf{k}\mathbf{r}}\, d\mathbf{r}$$

$$S(\mathbf{R}) = \int \phi_1(\mathbf{k})\, \phi_2(\mathbf{k})\, e^{i\mathbf{k}\mathbf{R}}\, d\mathbf{k}$$

Grid work

$$\psi_i(r) = \sum_\mu c_{i\mu}\varphi_\mu(r)$$

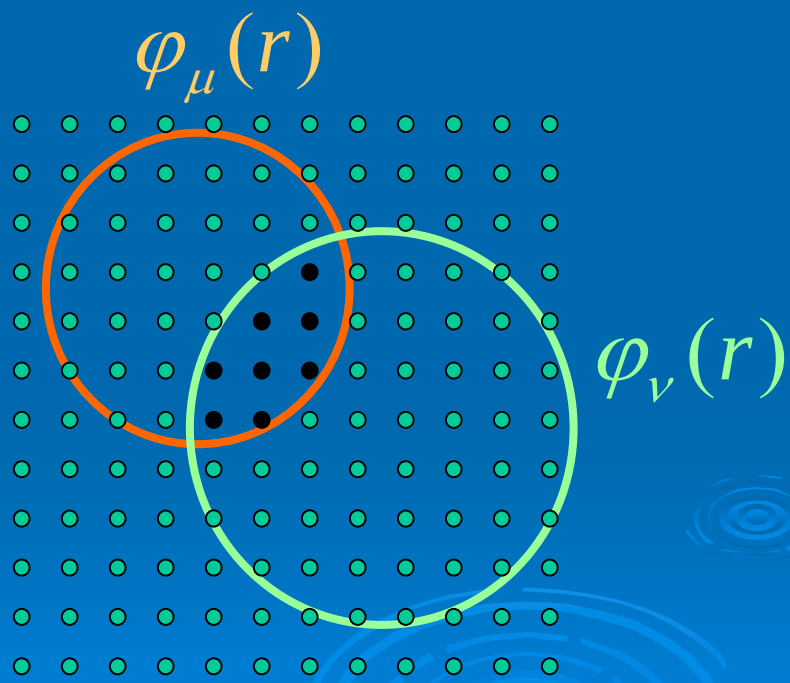
$$\rho_{\mu\nu} = \sum_i c_{i\mu}c_{i\nu}$$

$$\rho(r) = \sum_i \psi_i^2(r) = \sum_{\mu\nu} \rho_{\mu\nu}\varphi_\mu(r)\varphi_\nu(r)$$

$$\rho(r) \rightarrow V_{xc}(r)$$

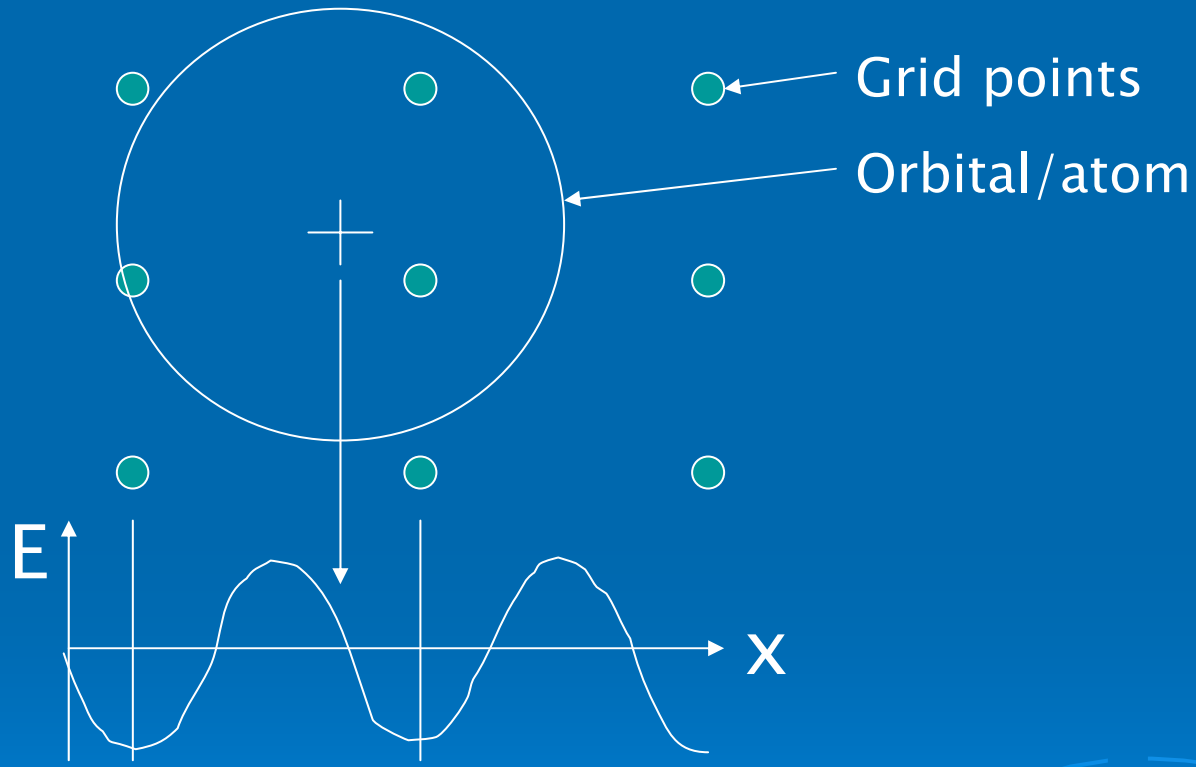
$$\delta\rho(r) = \rho_{SCF}(r) - \rho_{atoms}(r)$$

$$\delta\rho(r) \xrightarrow{FFT} \delta V_H(r)$$



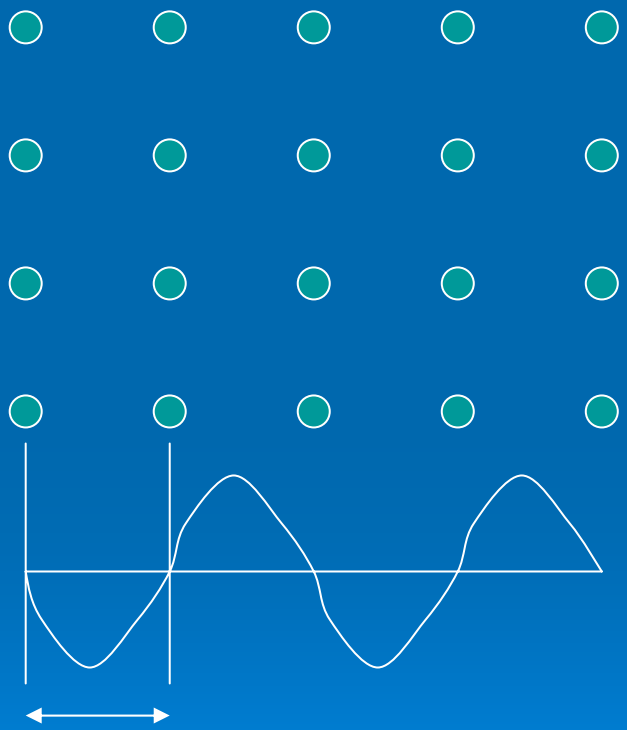
$$H_{\mu\nu} = \langle \varphi_\mu(r) | V | \varphi_\nu(r) \rangle = \int \varphi_\mu(r) V(r) \varphi_\nu(r)$$

Egg-box effect



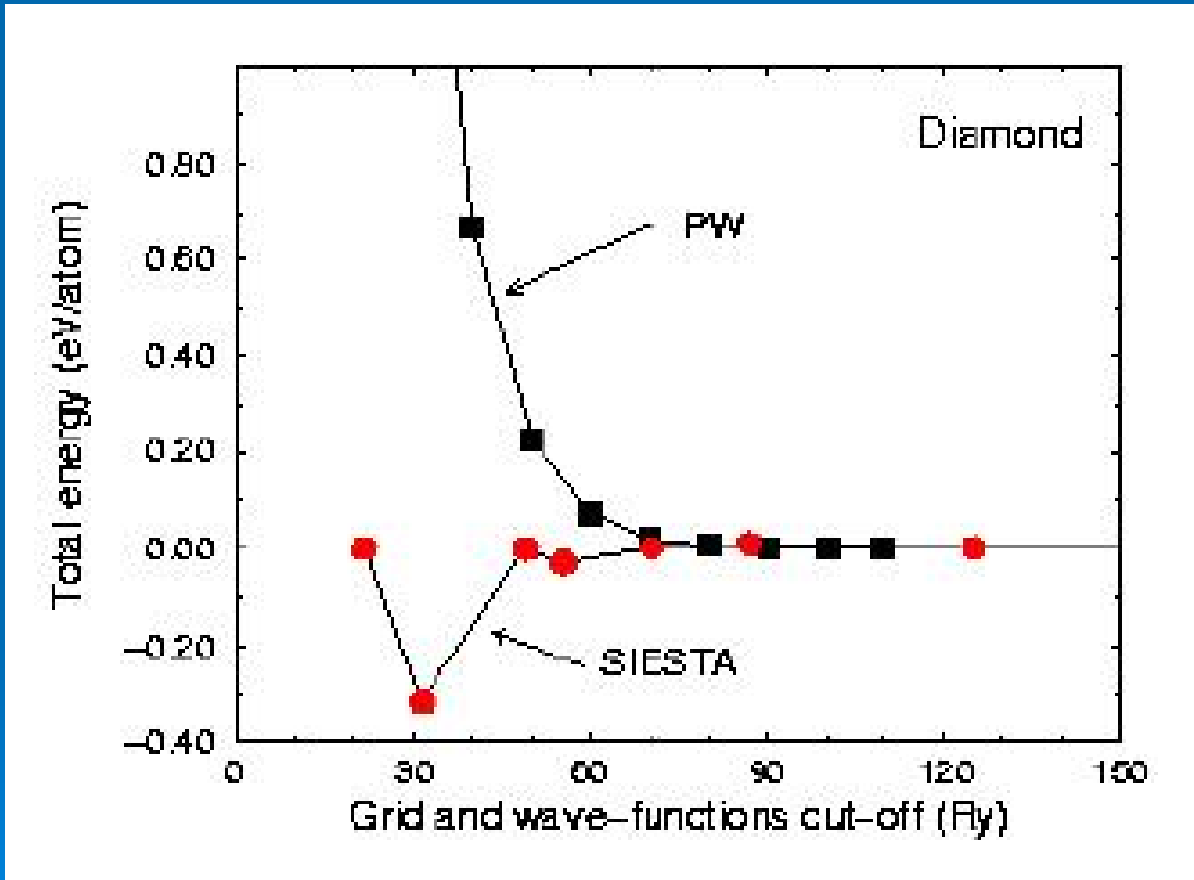
- Affects more to forces than to energy
- Grid-cell sampling

Grid smoothness: *energy cutoff*



$$\Delta x \Rightarrow k_c = \pi/\Delta x \Rightarrow E_{cut} = \hbar^2 k_c^2 / 2m_e$$

Grid smoothness: *convergence*



$$E_{cut} = (\pi / \Delta x)^2$$

Boundary conditions

- Isolated object (atom, molecule, cluster):
  - Open boundary conditions (defined at infinity)
- 3D Periodic object (crystal):
  - Periodic Boundary Conditions
- Mixed:
  - 1D periodic (chains)
  - 2D periodic (slabs)