Some internals of the SIESTA method (part 2)

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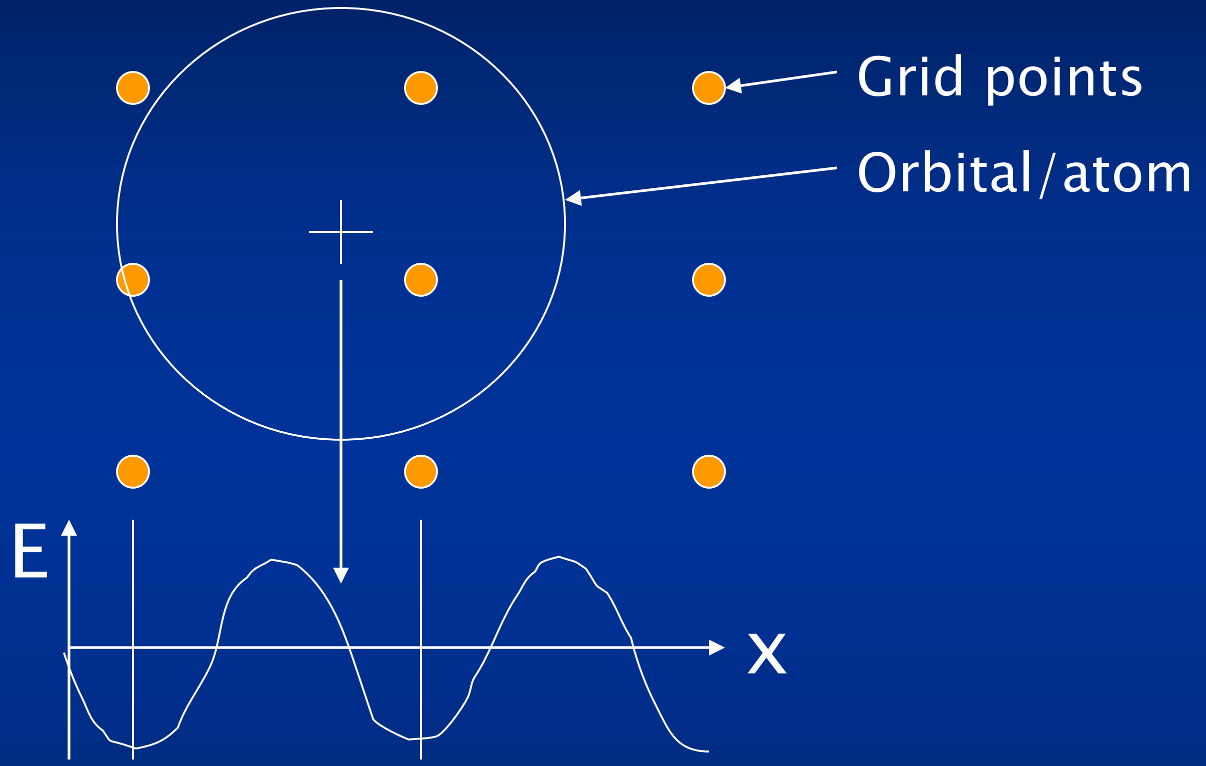
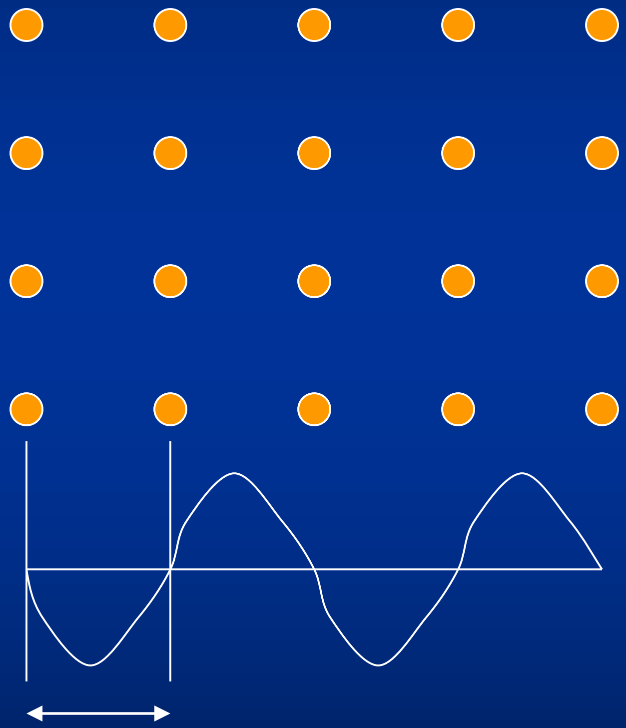
Egg-box effect



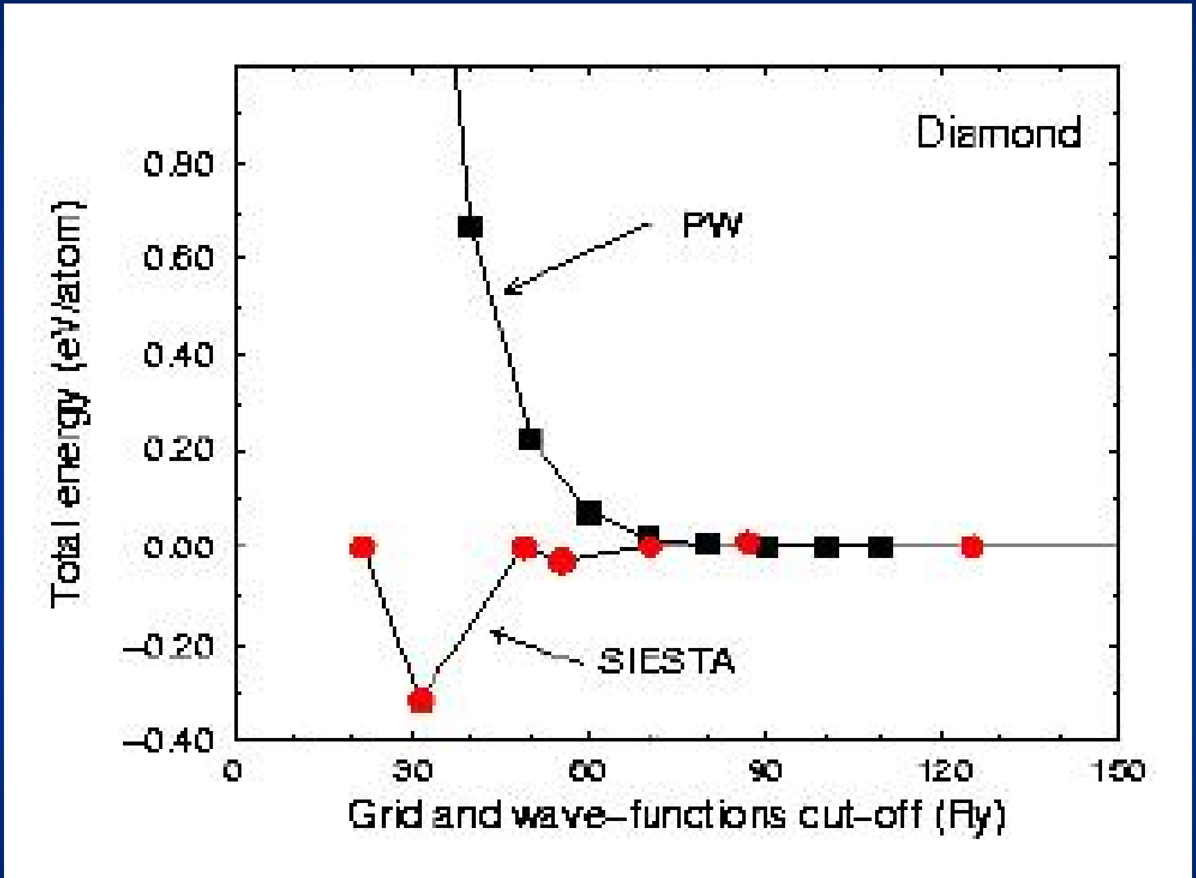
- Affects more to forces than to energy
- Grid-cell sampling

Grid fineness: 'mesh cutoff'



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

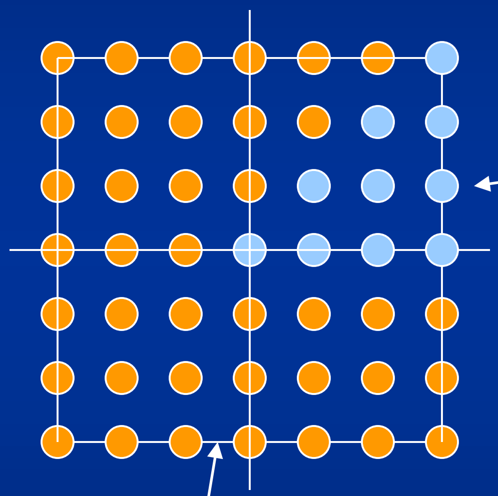
Grid fineness convergence



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

K-point sampling

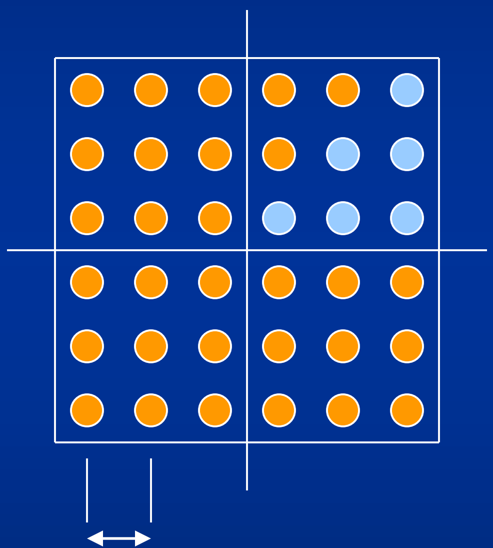
Regular k-grid



Inequivalent points

First Brillouin Zone

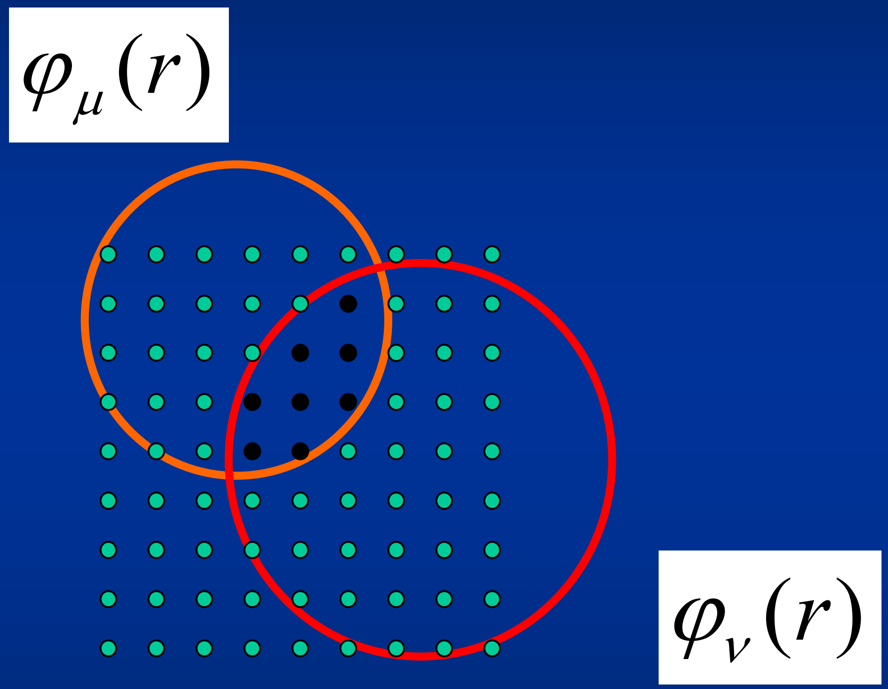
Monkhorst-Pack



$\Delta k \;\Rightarrow\; L_c = \pi / \Delta k$

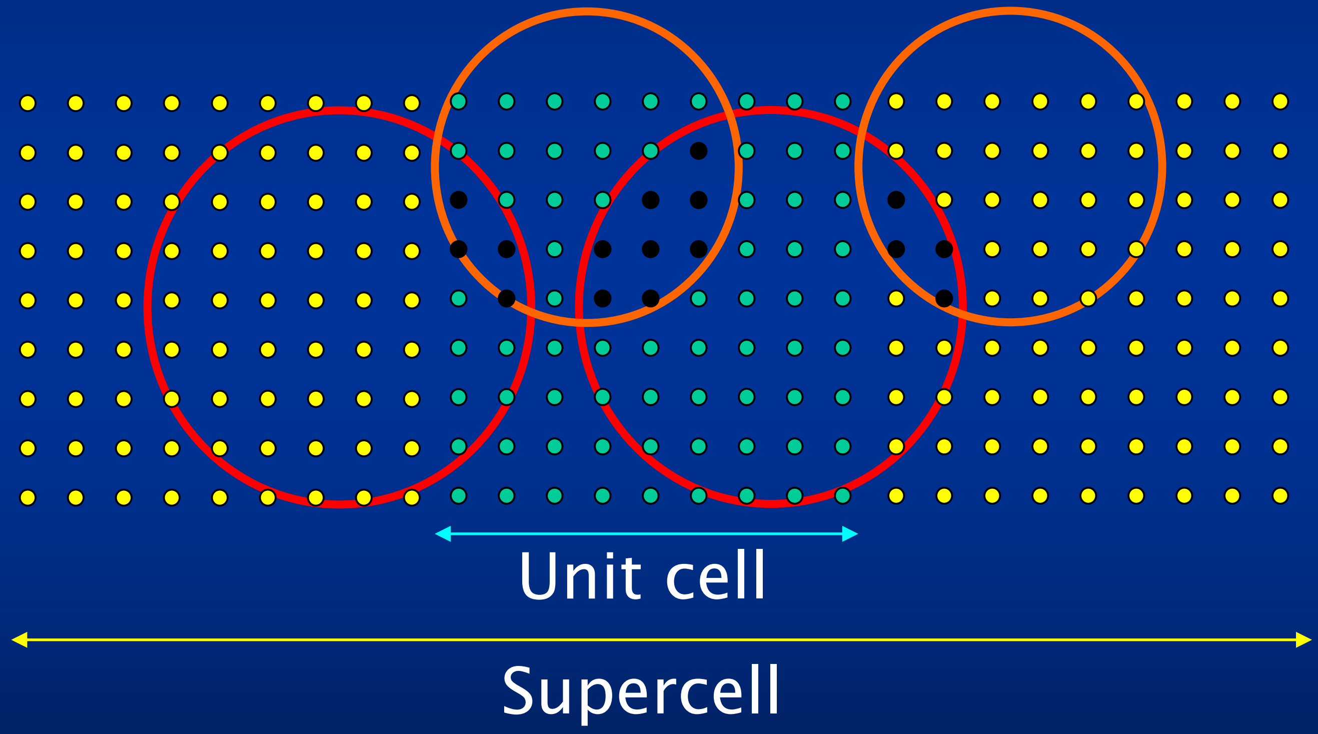
L_c = ‘length cutoff’

Internal supercell



SIESTA uses periodic boundary conditions

Internal supercell



Poisson equation

$$\nabla^2 V_H(r) = -\,4\pi\,\rho(r)$$

$$\rho(r) = \sum_G \rho_G\, e^{iGr} \;\Rightarrow\; V_H(r) = \sum_G V_G\, e^{iGr}$$

$$V_G = -\,4\pi\,\rho_G \,/\, G^2$$

$$\rho(r) \xrightarrow{\text{FFT}} \rho_G \rightarrow V_G \xrightarrow{\text{FFT}} V_H(r)$$

- Net charge compensated by uniform background
- Spurious interactions between ‘images’

GGA

$$v_{xc}(r) = \frac{\delta E_{GGA}[\rho(r'), |\nabla\rho(r')|]}{\delta\rho(r)}$$

$$= V_{GGA}\left(\rho(r), |\nabla\rho(r)|, \nabla^2\rho(r), \nabla\rho(r)\bullet\nabla|\nabla\rho(r)|\right)$$

$$\frac{\partial\rho}{\partial x} \equiv \frac{\rho_{i+1}-\rho_{i-1}}{x_{i+1}-x_{i-1}} \quad \Rightarrow \quad E_{xc} \equiv E_{GGA}\left(\rho_1, \rho_2, \ldots\right)$$

$$\Rightarrow v_{xc}(r_i) \equiv \frac{\partial E_{xc}}{\partial\rho_i}$$

Forces and stress tensor

Analytical: e.g.

$$\frac{\partial \langle \phi_\mu | V | \phi_\nu \rangle}{\partial \mathbf{r}_\nu} = \int \phi_\mu(\mathbf{r}-\mathbf{r}_\mu)\, V(r)\, \frac{\partial \phi_\nu(\mathbf{r}-\mathbf{r}_\nu)}{\partial \mathbf{r}_\nu}\, d^3\mathbf{r}$$

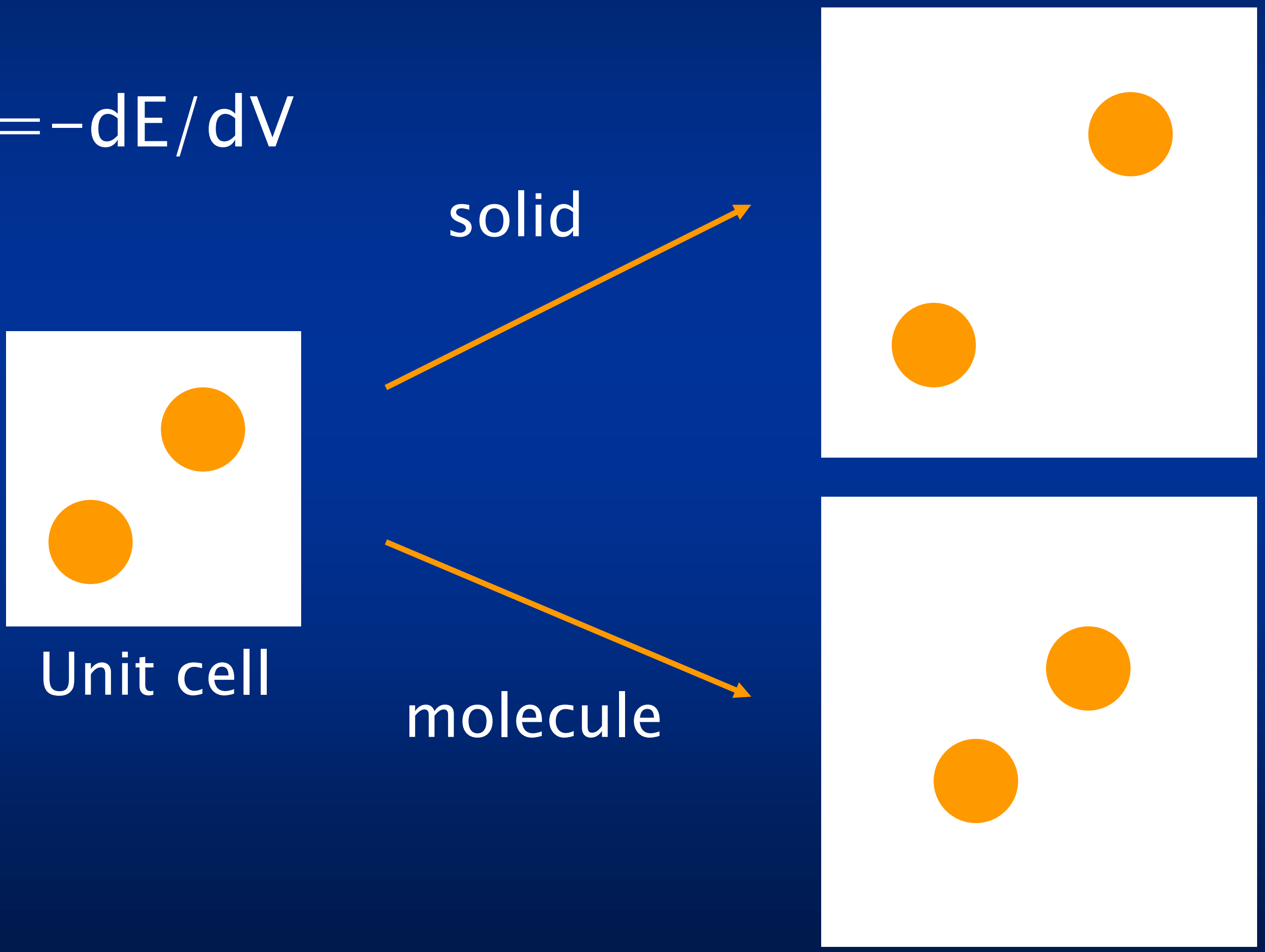
$$= -\int \phi_\mu(\mathbf{r}-\mathbf{r}_i)\, V(\mathbf{r})\, \nabla \phi_\nu(\mathbf{r}-\mathbf{r}_\nu)\, d^3\mathbf{r}$$

$$\frac{\partial T_{\mu\nu}}{\partial \varepsilon_{xy}} = \frac{\partial T_{\mu\nu}}{\partial x_{\mu\nu}}\, y_{\mu\nu} \quad \text{with} \quad \mathbf{r}_{\mu\nu} \equiv \mathbf{r}_\nu - \mathbf{r}_\mu$$

Calculated only in the last SCF iteration

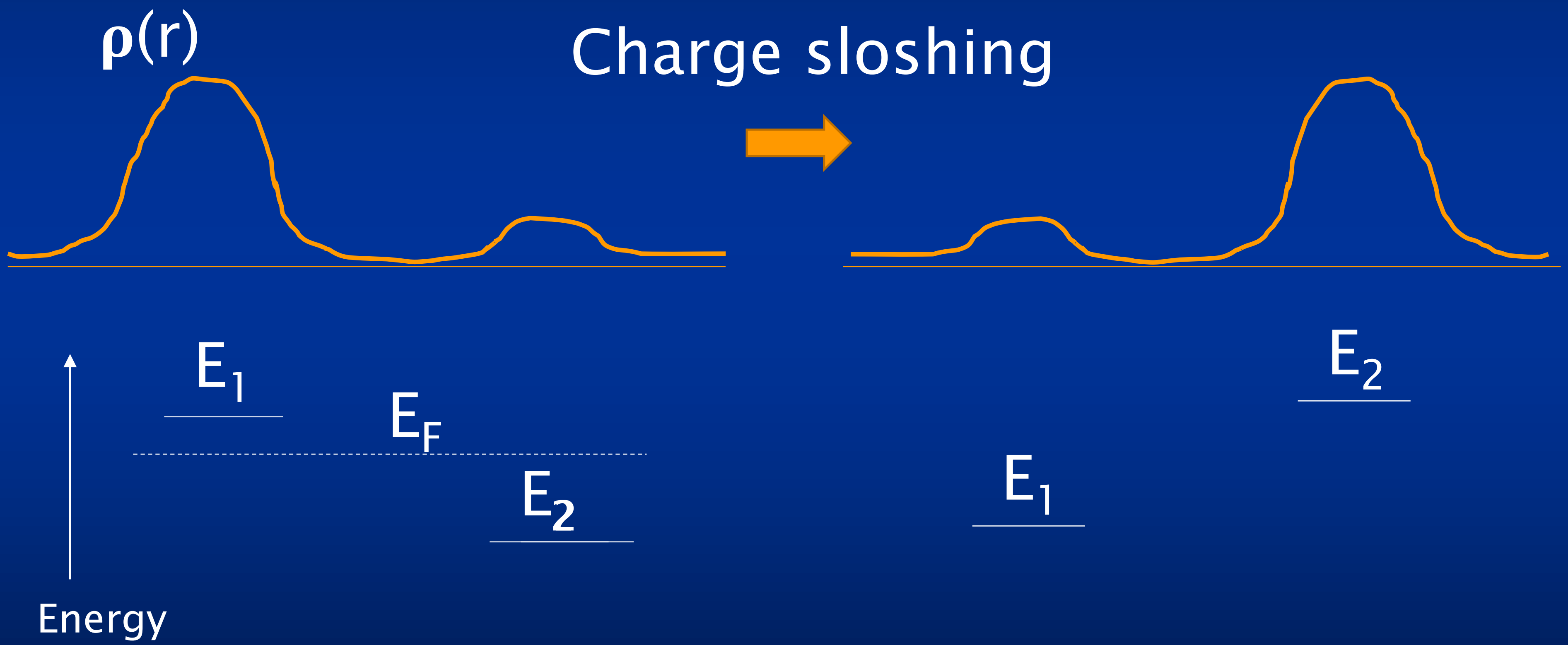
'Molecular' vs 'solid' pressure

$P = -dE/dV$



Selfconsistency convergence

SCF cycle: $\boldsymbol{\rho}(r) \rightarrow v(r) \rightarrow \boldsymbol{\rho}(r)$



Moderated by electronic temperature

Pulay mixing

$$\rho_n(\mathrm{r}) \rightarrow \rho_{new}(\mathrm{r})$$

$$\delta\rho_n(\mathrm{r}) = \rho_{new}(\mathrm{r}) - \rho_n(\mathrm{r})$$

$$\rho_{n+1}(\mathrm{r}) = \sum_{k=n-m}^{n} c_k \rho_k(\mathrm{r})$$

$$\delta\rho_{n+1}(\mathrm{r}) = \sum_{k=n-m}^{n} c_k \delta\rho_k(\mathrm{r}) = min$$