Calculation of matrix elements

José M. Soler

Universidad Autónoma de Madrid

Schrödinger equation

$$H\psi_i(r) = E_i\psi_i(r)$$

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

$$\sum_\nu (H_{\mu\nu} - E_i S_{\mu\nu})c_{i\nu} = 0$$

$$H_{\mu\nu} = < \phi_\mu \mid H \mid \phi_\nu >$$

$$S_{\mu\nu} = < \phi_\mu \mid \phi_\nu >$$

Kohn-Sham hamiltonian

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

$T = -(1/2)\ \Box^2$

$V_{PS} = V_{ion}(r) + V_{nl}$

$V_{ion}(r)\ \Box\ -Z_{val}\ /\ r$ Local pseudopotentiual

$V_{nl} = \Box_{\Box}\ |\Box_{\Box}>\ \Box_{\Box}\ <\Box_{\Box}|$ Kleinman-Bylander

$V_H(r) = \Box dr'\ \Box(r')\ /\ |r-r'|$ Hartree potential

$V_{xc}(r) = v_{xc}(\Box(r))$ Exchange & correlation

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

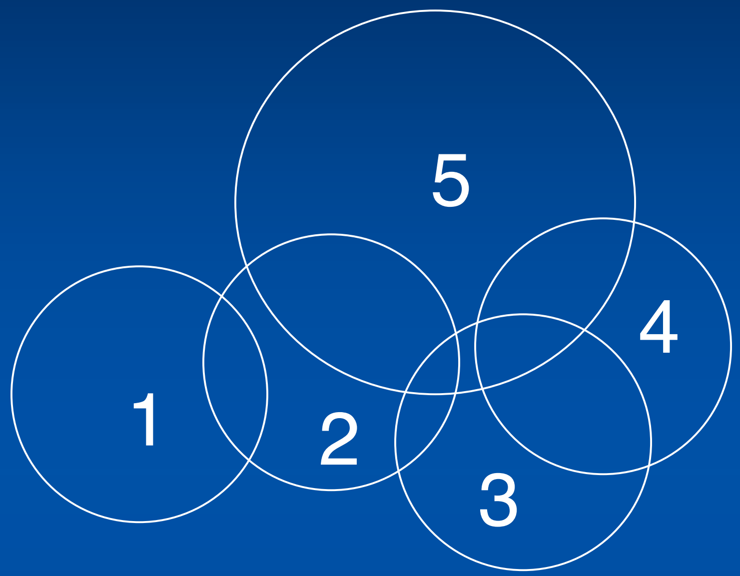
$$\delta V_H(r) = V_H[\rho_{SCF}(r)] - V_H[\rho_{atoms}(r)]$$

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

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

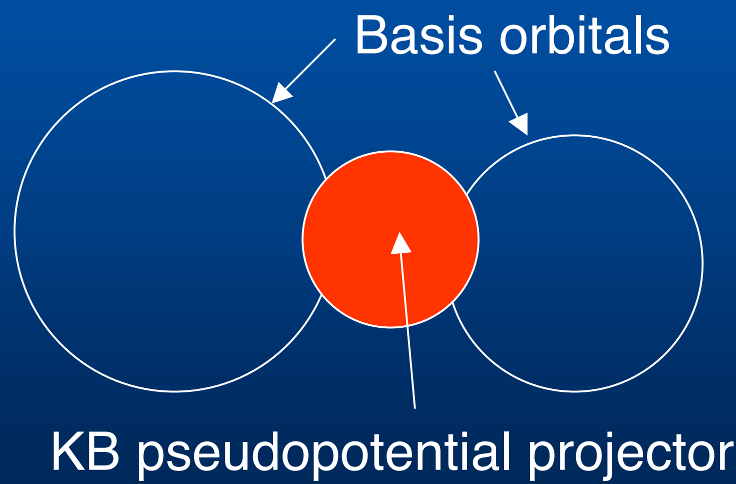
4 with 3,4 and 5

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

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

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

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

Atomic orbitals

$$S(\mathbf{R}) = \int \varphi_{l_1}(\mathbf{k})\,\varphi_{l_2}(\mathbf{k})\,e^{i\mathbf{kR}}\,d\mathbf{k}$$

$$\psi(\mathbf{r}) = \varphi_l(r)\,\mathrm{Y}_{lm}(\hat{\mathbf{r}}) \quad \Rightarrow \quad \psi(\mathbf{k}) = \varphi_l(k)\,\mathrm{Y}_{lm}(\hat{\mathbf{k}})$$

$$\varphi_l(k) = (-i)^l \sqrt{2/\pi} \int_0 r^2 dr\; j_l(r)\,\varphi_l(r)$$

$$e^{i\mathbf{kR}} = \sum_{l=0} \sum_{m=-l}^{+l} 4\pi i^l j_l(kR)\,\mathrm{Y}^*{}_{lm}(\hat{\mathbf{k}})\,\mathrm{Y}_{lm}(\hat{\mathbf{R}})$$

$$S(\mathbf{R}) = \sum_{l=0}^{l_1+l_2} \sum_{m=-l}^{+l} S_{lm}(R)\,\mathrm{Y}_{lm}(\hat{\mathbf{R}})$$

Overlap and kinetic matrix elements

$$S(\mathbf{R}) = \sum_{l=0}^{l_1+l_2} \sum_{m=-l}^{+l} S_{lm}(R)\, Y_{lm}(\hat{\mathbf{R}})$$

$$S_{lm}(R) = G_{l_1 m_1 l_2 m_2 lm} \int_0^{k_{\max}} k^2 dk\ j_l(kR)\, \phi_1(k)\, \phi_2(k)$$

$$T_{lm}(R) = G_{l_1 m_1 l_2 m_2 lm} \int_0^{k_{\max}} \frac{1}{2} k^4 dk\ j_l(kR)\, \phi_1(k)\, \phi_2(k)$$

- K^2_{max} = 2500 Ry
- Integrals by special radial-FFT
- $S_{lm}(R)$ and $T_{lm}(R)$ calculated and tabulated once and for all

Real spherical harmonics

$$Y_{lm}(\theta,\phi) = C_{lm} P_l^m(\cos\theta) \times \begin{cases} \sin(m\phi) & \text{if } m < 0 \\ \cos(m\phi) & \text{if } m \geq 0 \end{cases}$$

$$l = 1,\ m = -1, 0, +1 \quad \rightarrow \quad p_y, p_z, p_x$$

Grid work

$$ø_i(r) = □_{ì}\, c_{iì}\, ö_{ì}(r)$$

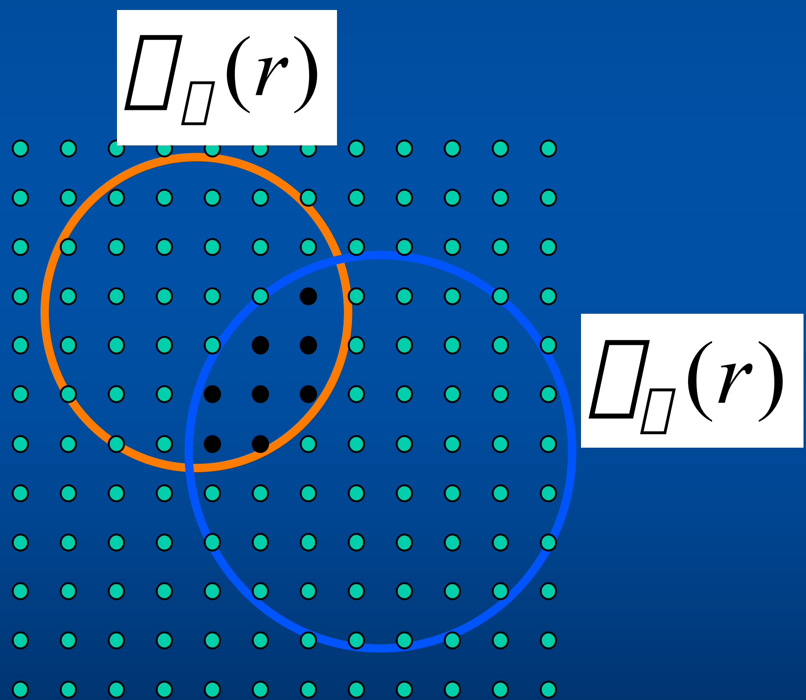
$$ñ_{ìí} = □_{i}\, c_{iì}\, c_{ií}$$

$$ñ(r) = □_{i}\, ø_i^2(r) = □_{ìí}\, ñ_{ìí}\, ö_{ì}(r) ö_{í}(r)$$

$$ñ(r)\ □\ V_{xc}(r)$$

$$äñ(r) = ñ_{SCF}(r)\, □\, ñ_{atoms}(r)$$

$$äñ(r)\ □^{FFT}\ äV_H(r)$$



Poisson equation

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

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

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

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

GGA

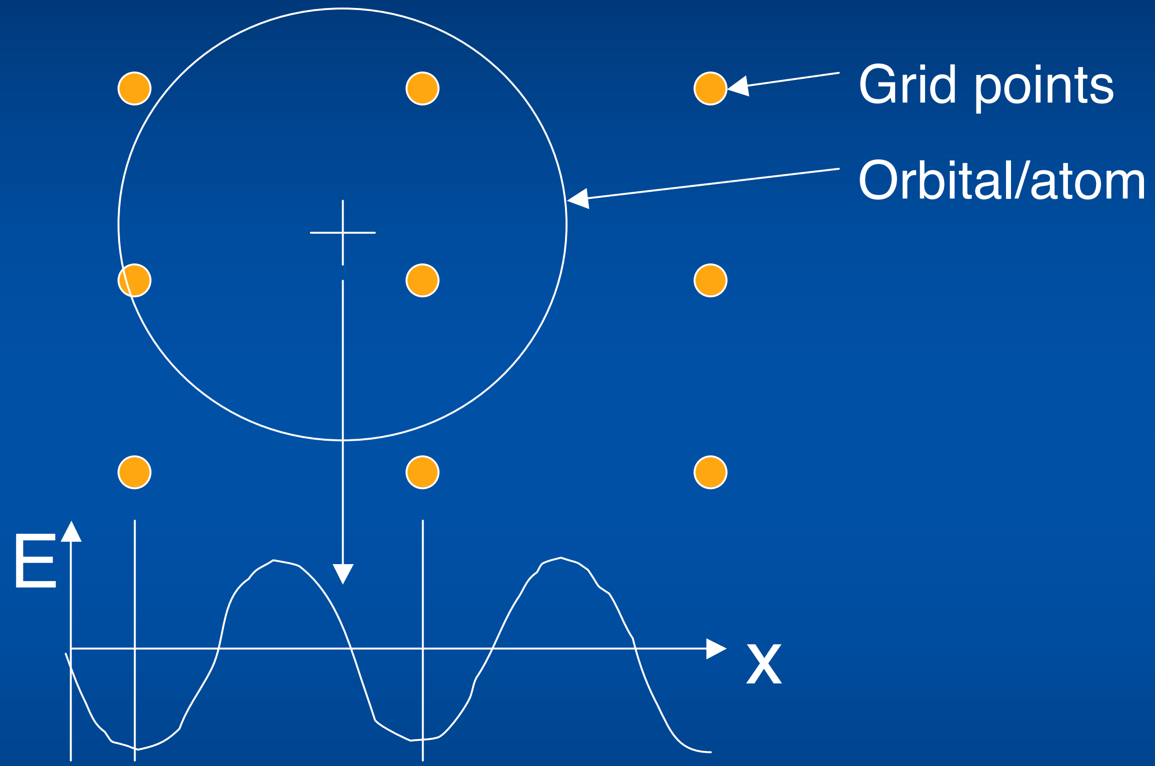
$$v_{xc}(r) = \frac{\delta E_{GGA}[\rho(r'), |\nabla \rho(r')|]}{\delta \rho(r)}$$

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

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

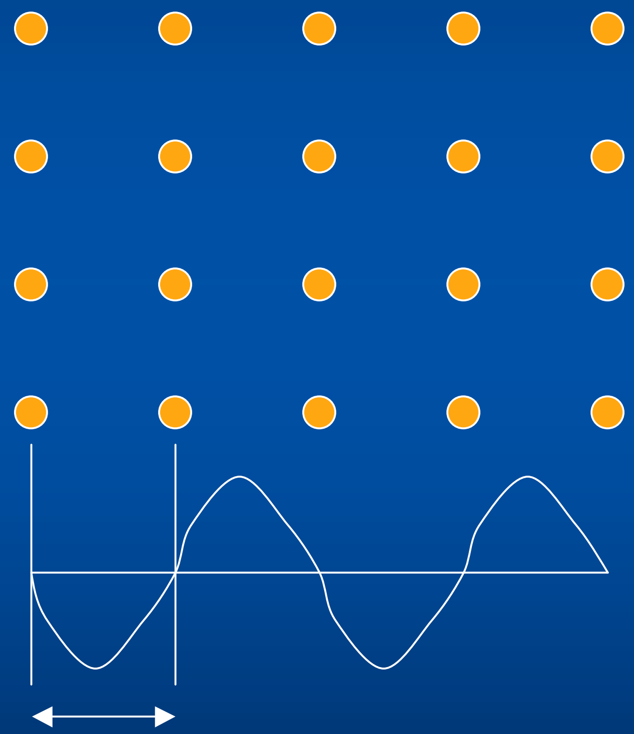
$$\Rightarrow \quad v_{xc}(r_i) \equiv \frac{\partial E_{xc}}{\partial \rho_i}$$

Egg-box effect



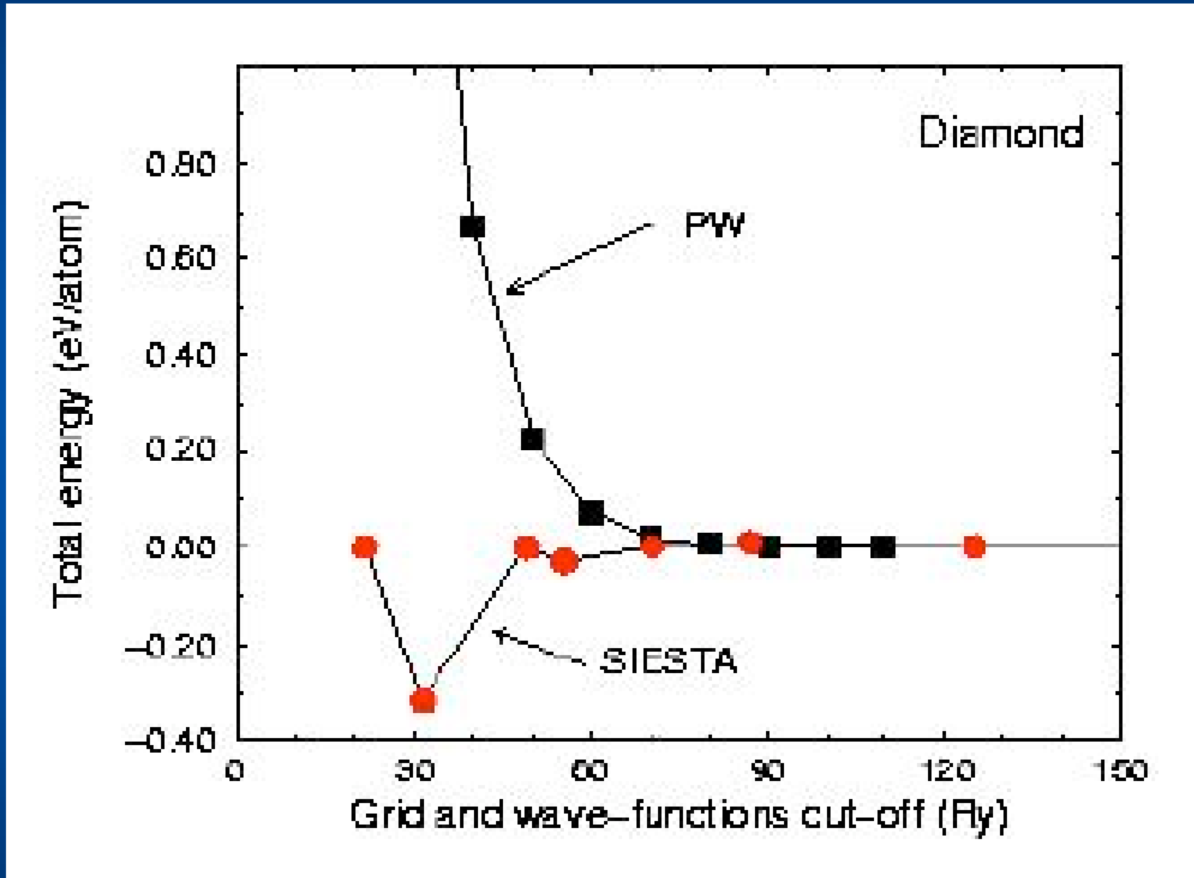
- Affects more to forces than to energy
- Grid-cell sampling

Grid fineness: energy cutoff



$\square x \quad \square \quad k_c=\square/\square x \quad \square \quad E_{cut}=h^2k_c^2/2m_e$

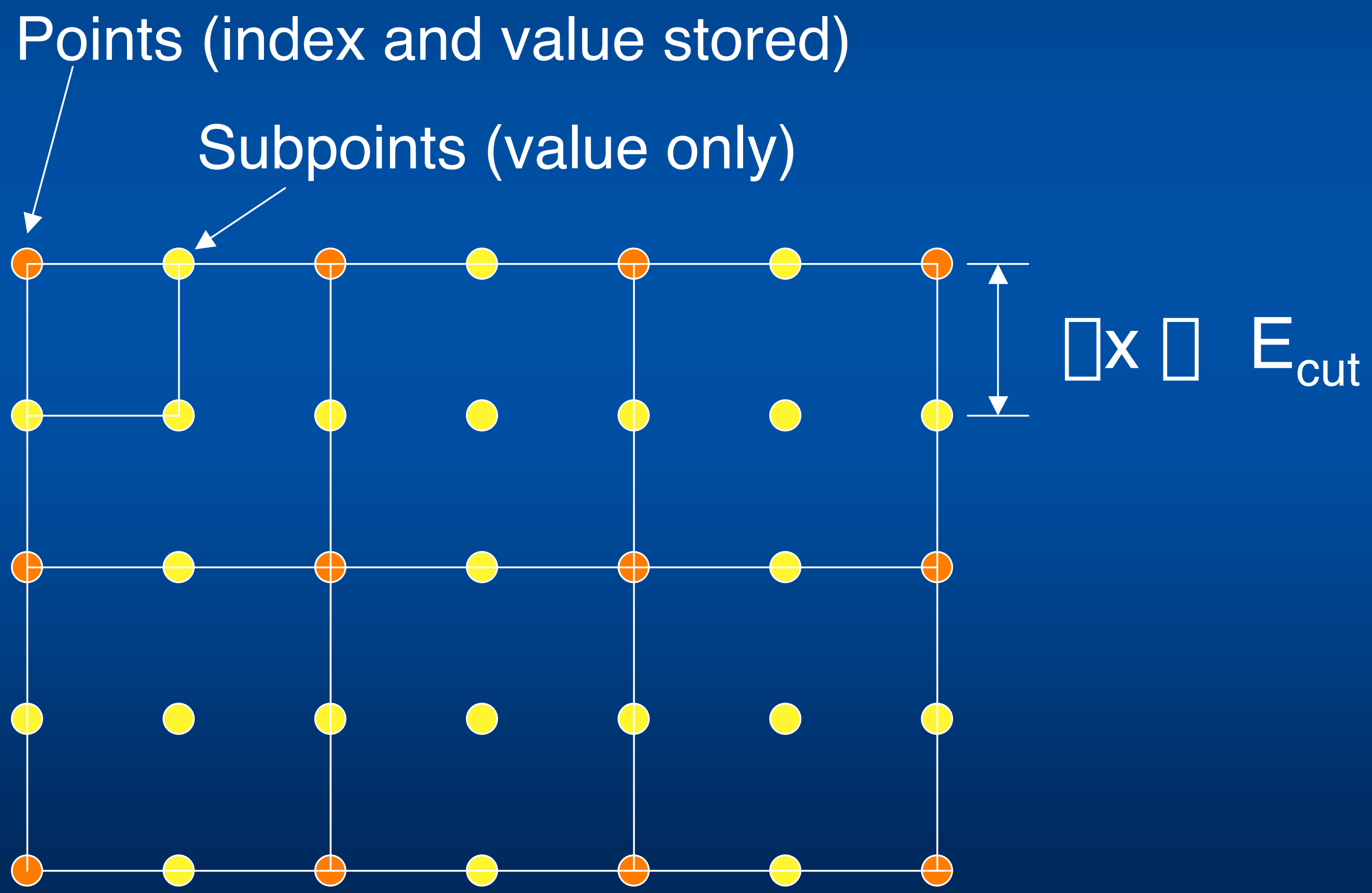
Grid fineness convergence



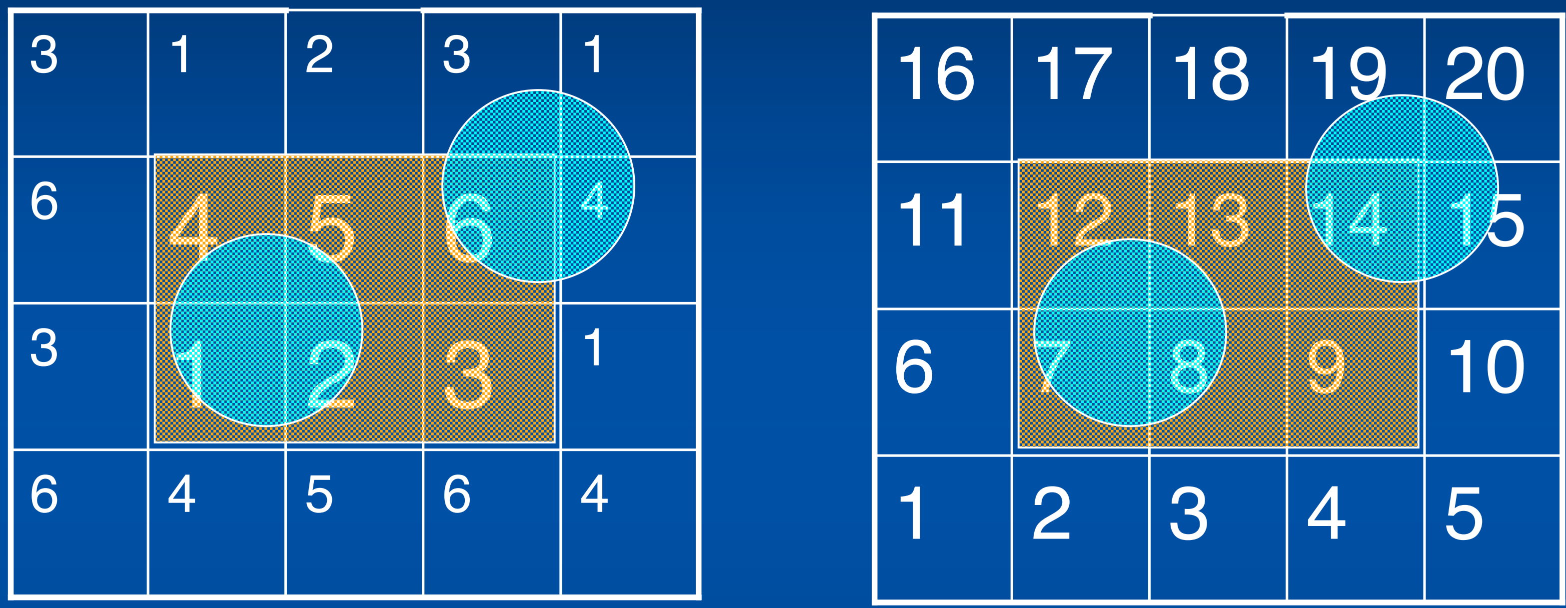
$$E_{cut} = (\pi / \Delta x)^2$$

Points and subpoints

Sparse storage: $(i, \square_i)$



Extended mesh



1 □ 7 □ (+1,+5,+6) 8,12,13 □ 2,4,5

6 □ 14 □ (+1,+5,+6) 15,19,20 □ 4,3,1

Forces and stress tensor

Analytical: e.g.

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

$$= -\int \phi_{\beta}(\mathbf{r} - \mathbf{r}_{i})\, V(\mathbf{r})\, \nabla \phi_{\alpha}(\mathbf{r} - \mathbf{r}_{\alpha})\, d^3\mathbf{r}$$

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

Calculated only in the last SCF iteration