

Matrix Elements



Dr. Ricardo Faccio
Centro NanoMat
Facultad de Química
Universidad de la República

Schrödinger equation

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

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

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

$$H_{\mu\nu} = \langle \phi_{\mu} | H | \phi_{\nu} \rangle$$

$$S_{\mu\nu} = \langle \phi_{\mu} | \phi_{\nu} \rangle$$

Kohn-Sham hamiltonian

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

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

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

$$V_{ion}(\mathbf{r}) \rightarrow -Z_{val} / r \quad \text{Local pseudopotential}$$

$$V_{nl} = \sum_{\alpha} |\chi_{\alpha}\rangle \varepsilon_{\alpha} \langle \chi_{\alpha}| \quad \text{Kleinman-Bylander}$$

$$V_H(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') / |\mathbf{r}-\mathbf{r}'| \quad \text{Hartree potential}$$

$$V_{xc}(\mathbf{r}) = v_{xc}(\rho(\mathbf{r})) \quad \text{Exchange \& correlation}$$

Long-range potentials

$$H = T + V_{\text{ion}}(\mathbf{r}) + V_{\text{nl}} + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})$$

Long range



$$V_{\text{na}}(\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + V_{\text{H}}[\rho_{\text{atoms}}(\mathbf{r})] \quad \text{Neutral-atom potential}$$

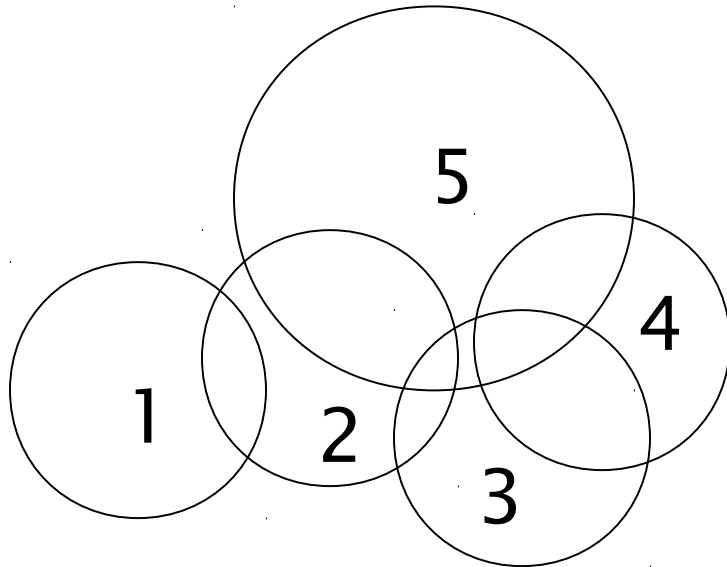
$$\delta V_{\text{H}}(\mathbf{r}) = V_{\text{H}}[\rho_{\text{SCF}}(\mathbf{r})] - V_{\text{H}}[\rho_{\text{atoms}}(\mathbf{r})]$$

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

Two-center integrals Grid integrals



Sparsity



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

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

1 with 1 and 2

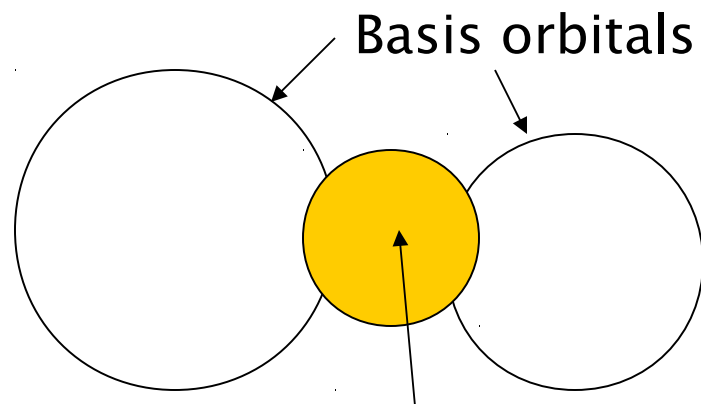
2 with 1, 2, 3, and 5

3 with 2, 3, 4, and 5

4 with 3, 4 and 5

5 with 2, 3, 4, and 5

Non-overlap interactions



KB pseudopotential projector

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

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

$$\phi(\mathbf{r}) = \phi_l(r) Y_{lm}(\hat{\mathbf{r}}) \Rightarrow \phi(\mathbf{k}) = \phi_l(k) Y_{lm}(\hat{\mathbf{k}})$$

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

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

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

Overlap and kinetic matrix elements

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

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

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

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

Real spherical harmonics

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

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

Grid work

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

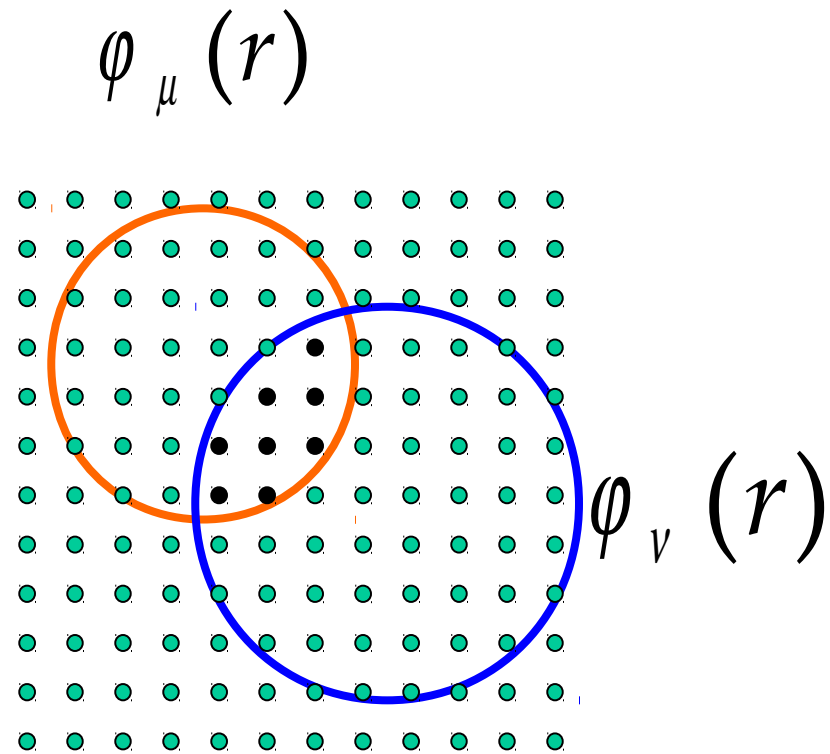
$$\rho_{\mu\nu} = \sum_i c_{i\mu} c_{i\nu}$$

$$\rho(\mathbf{r}) = \sum_{i\mu\nu} \psi_i^2(\mathbf{r}) = \sum_{\mu\nu} \rho_{\mu\nu} \phi_{\mu}(\mathbf{r}) \phi_{\nu}(\mathbf{r})$$

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

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

$$\delta\rho(\mathbf{r}) \rightarrow \delta V_{\text{H}}(\mathbf{r})$$



Poisson equation

$$\nabla^2 V_H(\mathbf{r}) = -4\pi \rho(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_G \rho_G e^{i\mathbf{G}\cdot\mathbf{r}} \Rightarrow V_H(\mathbf{r}) = \sum_G V_G e^{i\mathbf{G}\cdot\mathbf{r}}$$

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

FFT

FFT

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

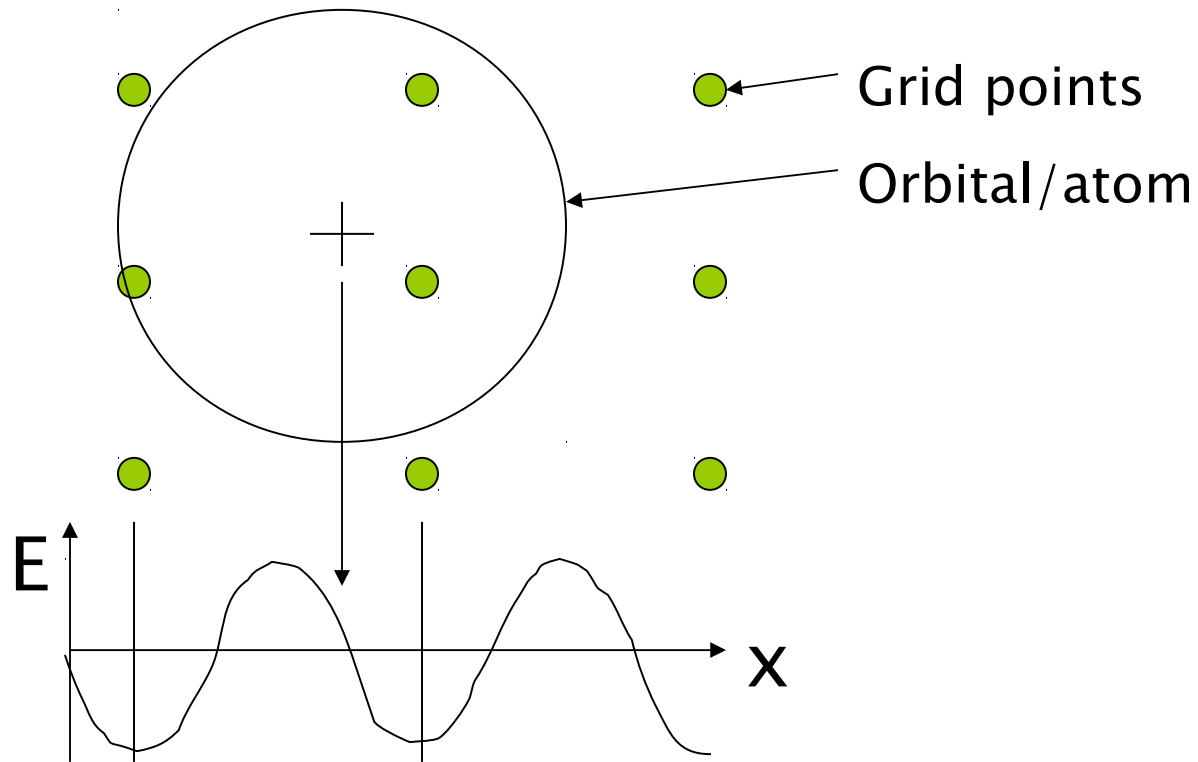
GGA

$$\begin{aligned}v_{xc}(r) &= \frac{\delta E_{GGA}[\rho(r'), |\nabla \rho(r')|]}{\delta \rho(r)} \\&= V_{GGA}(\rho(r), |\nabla \rho(r)|, \nabla^2 \rho(r), \nabla \rho(r) \bullet \nabla |\nabla \rho(r)|)\end{aligned}$$

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

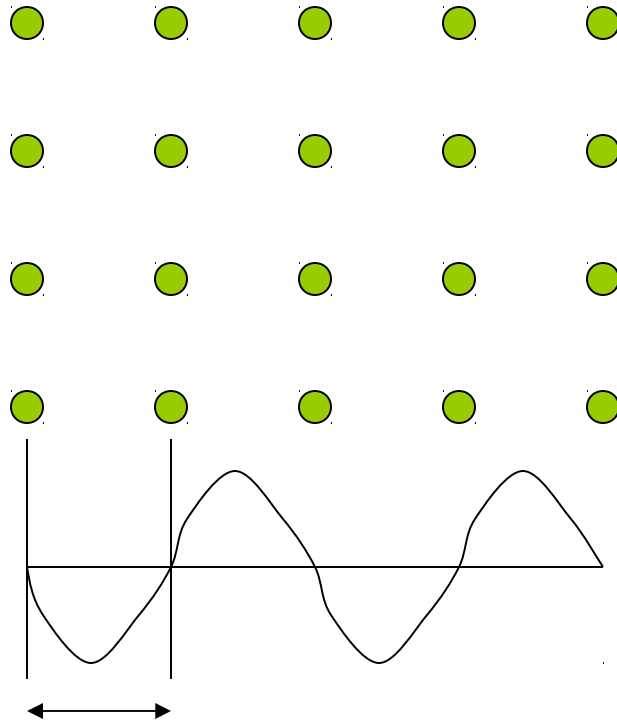
$$\Rightarrow v_{xc}(r_i) \equiv \frac{\partial E_{xc}}{\partial \rho_i}$$

Egg-box effect



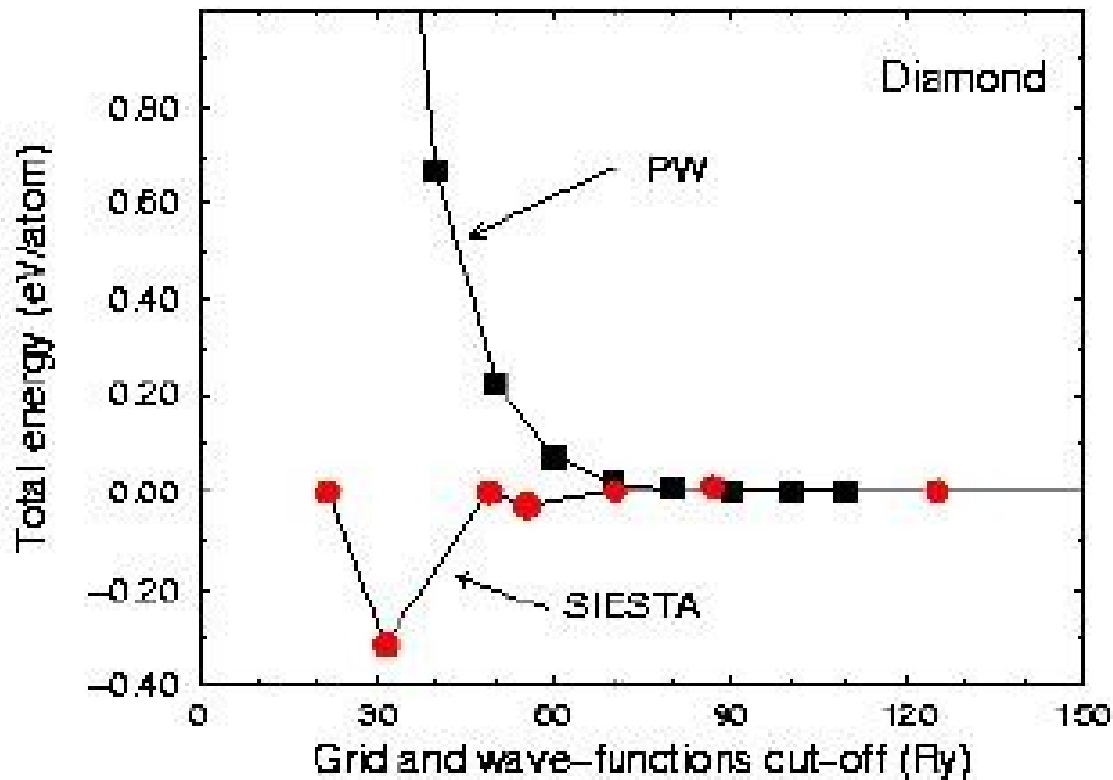
- Affects more to forces than to energy
- Grid-cell sampling

Grid fineness: energy cutoff



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

Grid fineness convergence

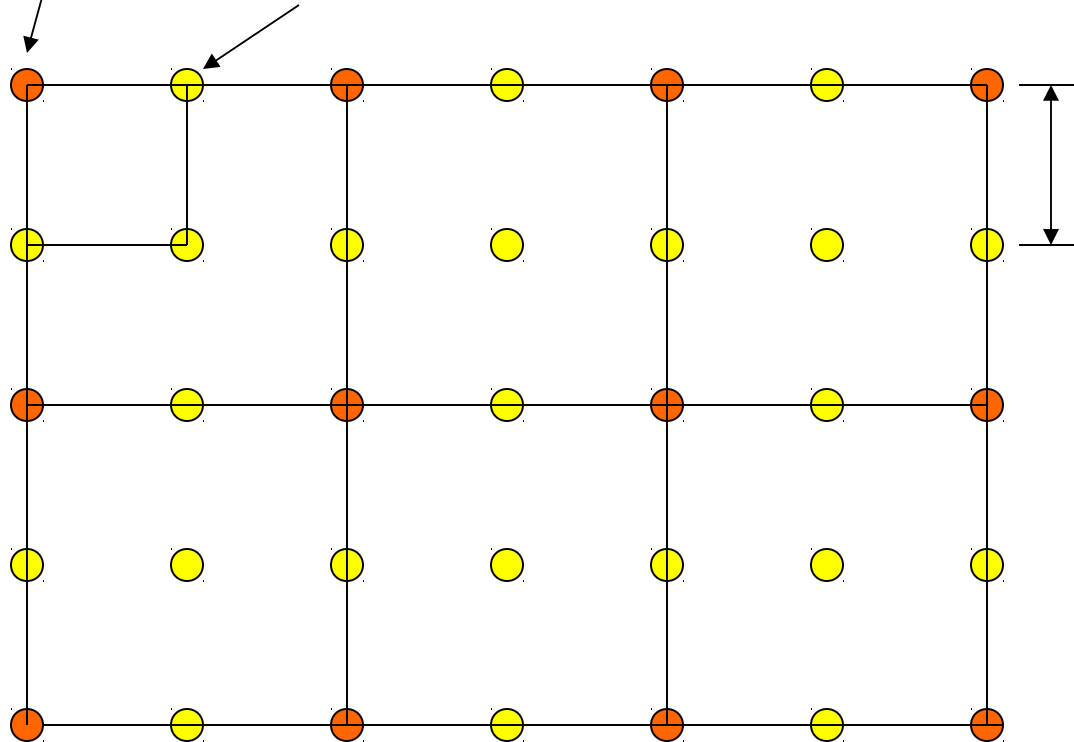


$$E_{cut} = (\pi / \Delta x)^2$$

Points and subpoints

Sparse storage: (i, ϕ_i)
Points (index and value stored)

Subpoints (value only)



$$\Delta x \Rightarrow E_{\text{cut}}$$

Extended mesh

3	1	2	3	1
6	4	5	6	4
3	1	2	3	1
6	4	5	6	4

16	17	18	19	20
6	7	8	9	
1	2	3	4	5

$$\begin{array}{lcl}
 1 \rightarrow 7 & \xrightarrow{+1, +5, +6} & 8, 12, 13 \rightarrow 2, 4, 5 \\
 6 \rightarrow 14 & \xrightarrow{+1, +5, +6} & 15, 19, 20 \rightarrow 4, 3, 1
 \end{array}$$

Forces and stress tensor

Analytical: e.g.

$$\begin{aligned}\frac{\partial \langle \phi_\mu | V | \phi_\nu \rangle}{\partial \mathbf{r}_\nu} &= \int \phi_\mu (\mathbf{r} - \mathbf{r}_\mu) V(r) \frac{\partial \phi_\nu (\mathbf{r} - \mathbf{r}_\nu)}{\partial \mathbf{r}_\nu} d^3 \mathbf{r} \\ &= - \int \phi_\mu (\mathbf{r} - \mathbf{r}_\nu) V(\mathbf{r}) \nabla \phi_\nu (\mathbf{r} - \mathbf{r}_\nu) d^3 \mathbf{r} \\ \frac{\partial T_{\mu\nu}}{\partial \varepsilon_{xy}} &= \frac{\partial T_{\mu\nu}}{\partial x_{\mu\nu}} y_{\mu\nu} \quad \text{with} \quad \mathbf{r}_{\mu\nu} \equiv \mathbf{r}_\nu - \mathbf{r}_\mu\end{aligned}$$

Calculated only in the last SCF iteration