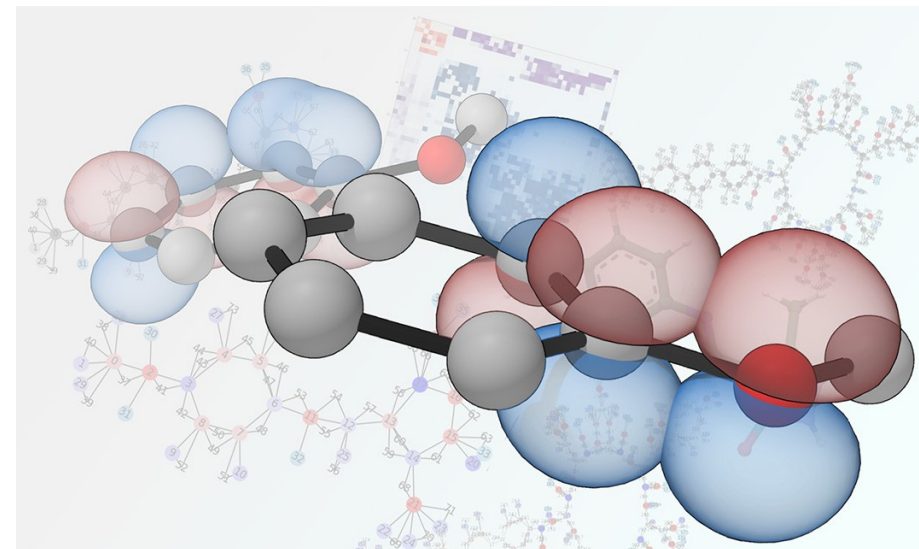


Aula 01 – Density Functional Theory

Prof. Elvis Soares
elvis@peq.coppe.ufrj.br



$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle$$

$$|\Psi\rangle = |\psi\rangle e^{-iEt/\hbar}$$

$$\hat{H} |\psi\rangle = E |\psi\rangle$$

Problema de muitos elétrons

- Hamiltoniano de muitos elétrons

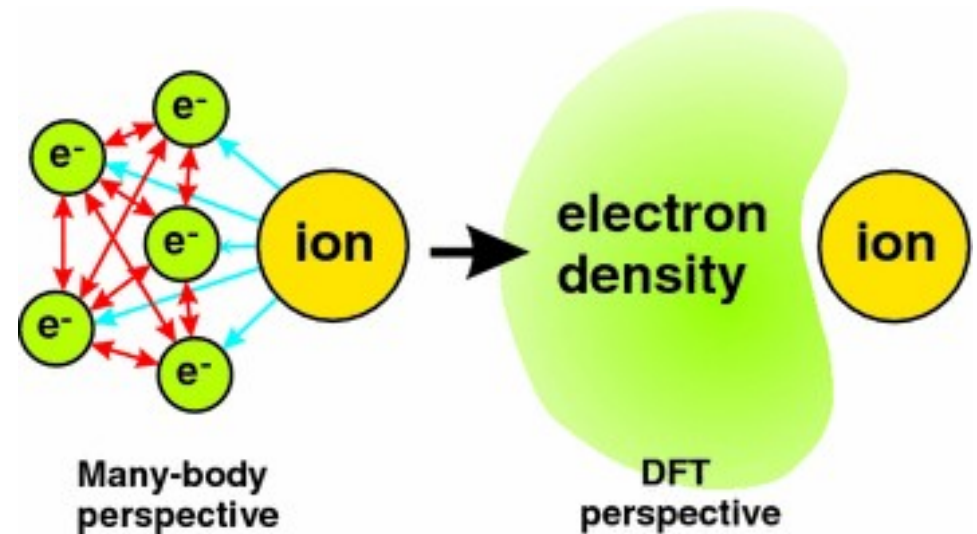
$$\hat{H}_e = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{A=1}^M \sum_{i=1}^N \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{A=1}^M \sum_{B \neq A}^M \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}$$

Energia do estado fundamental por função de onda

$$E_0 = \frac{\langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

- Energia do estado fundamental por densidade eletrônica

$$E_0 = E[\rho(\mathbf{r})]$$



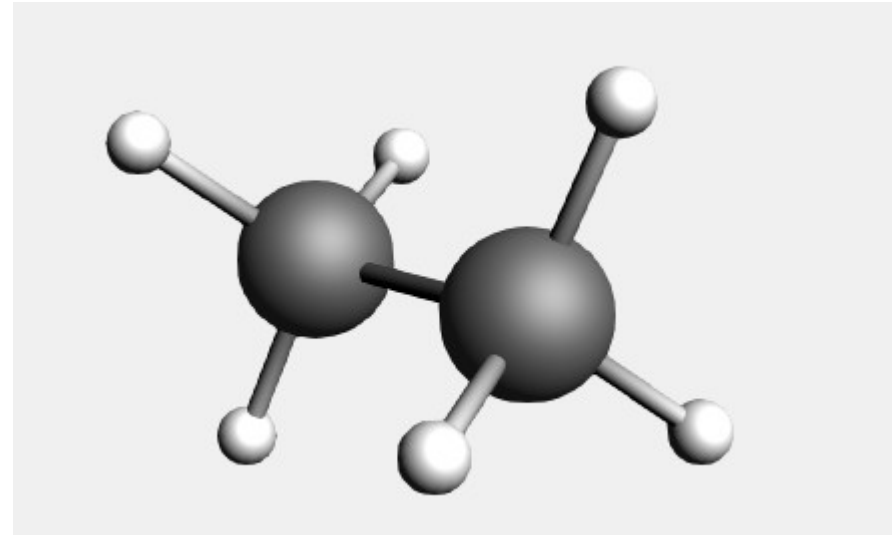
Density Functional Theory

Funcional de Hohenberg-Kohn

$$E[\rho(\mathbf{r})] = E_{HK}[\rho(\mathbf{r})] + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

Potencial Externo

$$V_{\text{ext}}(\mathbf{r}) = - \sum_{A=1}^M \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}$$



Método de Kohn-Sham

Funcional de Hohenberg-Kohn

$$E_{HK}[\rho(\mathbf{r})] = \sum_i \langle \psi_i | -\frac{1}{2} \nabla_i^2 | \psi_i \rangle + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho(\mathbf{r})]$$

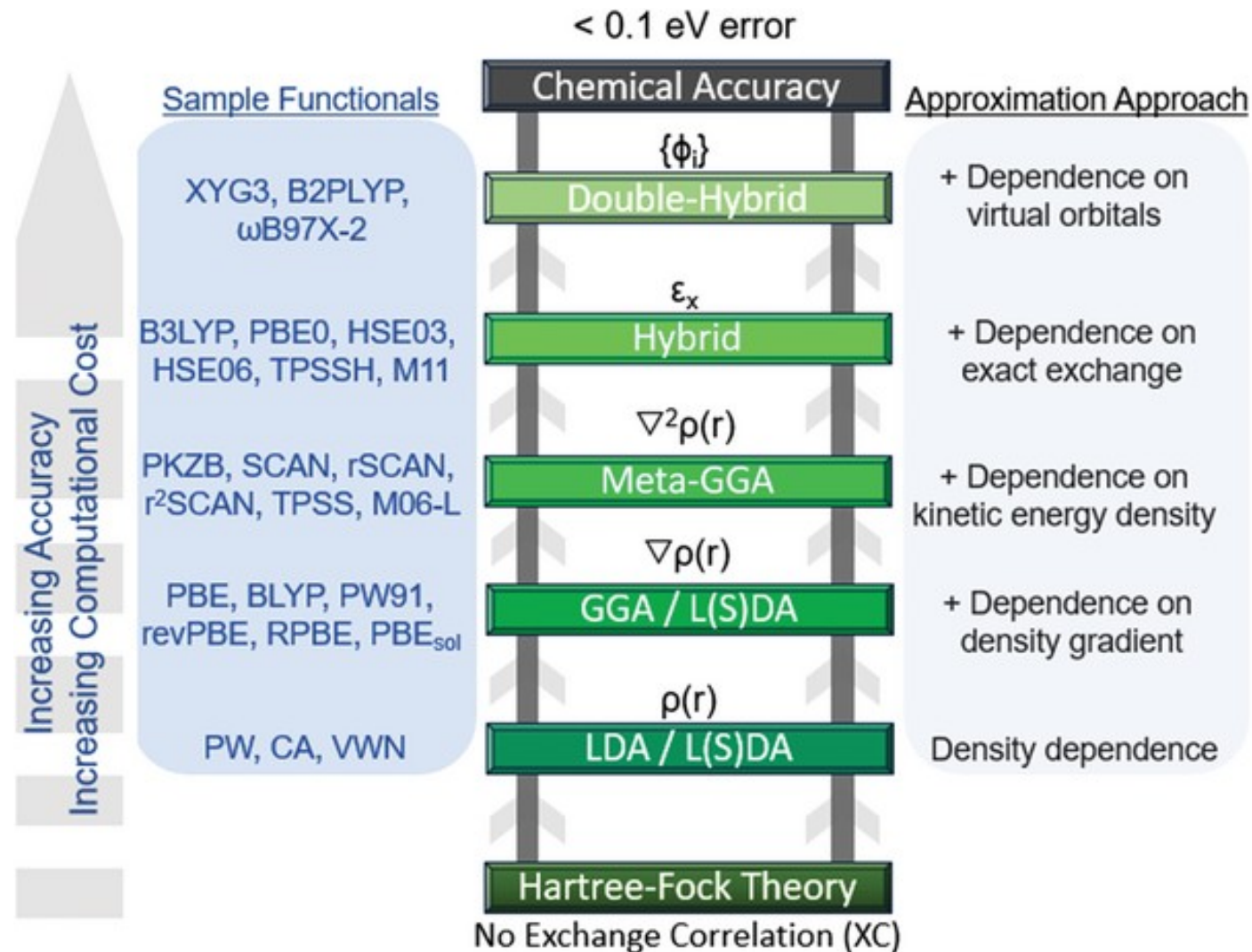
Densidade e orbitais de Kohn-Sham

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2$$

Equações de Kohn-Sham

$$\left[-\frac{1}{2} \nabla^2 + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

Funcionais de Correlação e Troca



Base

Orbitais de Kohn-Sham

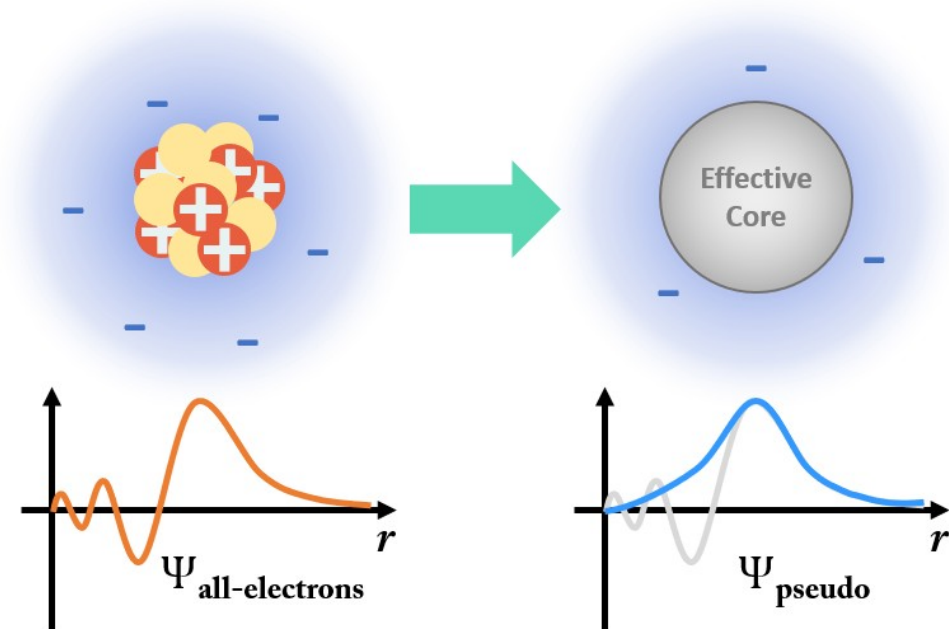
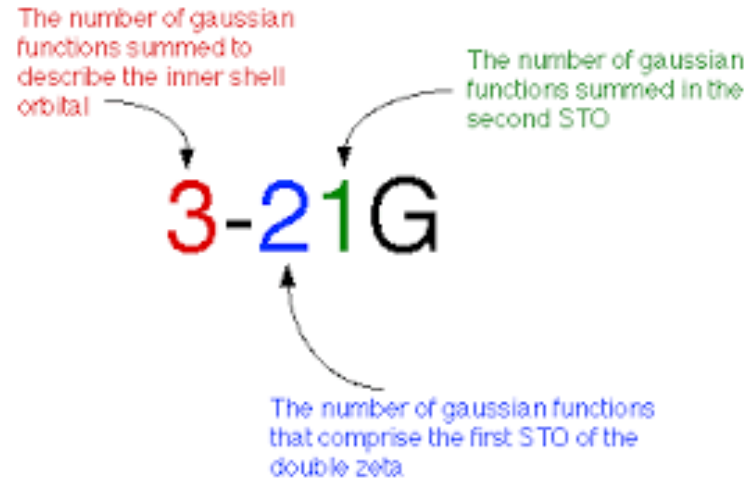
$$|\psi_i\rangle = \sum_{\mu=1}^B c_{\mu i} |\phi_{\mu}\rangle$$

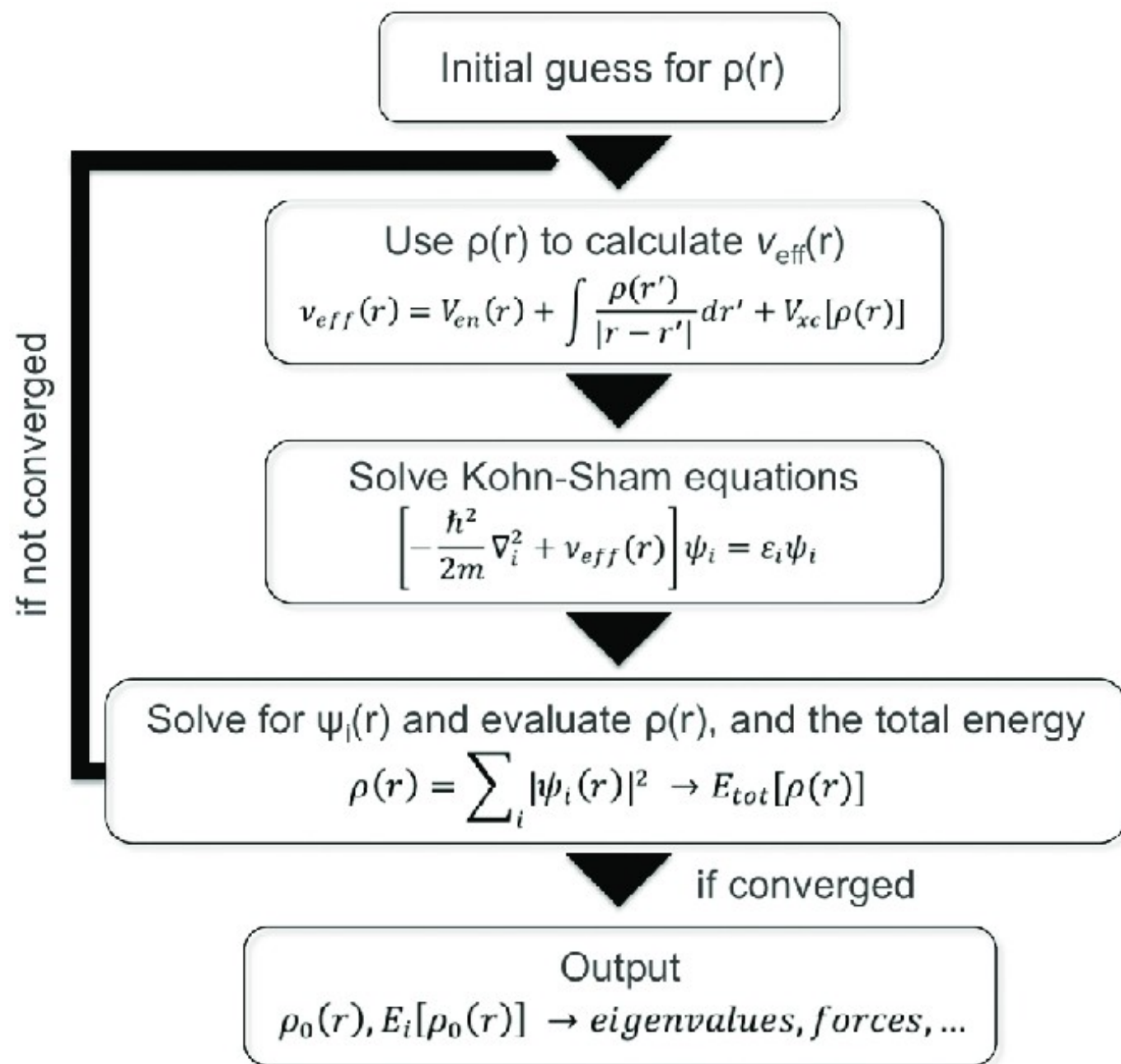
- Base de ondas planas

$$|\phi_{\mu}\rangle = \sum_{i=1}^n d_{i\mu} |\mathbf{k}_i\rangle$$

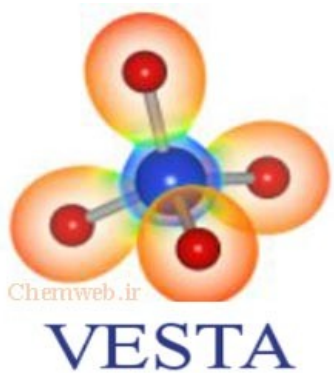
- Bases gaussianas

$$|\phi_{\mu}\rangle = \sum_{i=1}^n d_{i\mu} |\text{GTO}_i\rangle$$





Ferramentas Computacionais



Cálculos de Força

Teorema de Hellmann-Feynman

$$\frac{\partial E}{\partial \mathbf{R}_A} = \langle \Psi_0 | \frac{\partial \hat{H}_e}{\partial \mathbf{R}_A} | \Psi_0 \rangle$$

Força no átomo A

$$\mathbf{F}_A = -\frac{\partial E}{\partial \mathbf{R}_A}$$

Derivada do Hamiltoniano

$$\frac{\partial \hat{H}_e}{\partial \mathbf{R}_A} = \frac{\partial}{\partial \mathbf{R}_A} \left[-\sum_{A=1}^M \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} + \frac{1}{2} \sum_{A=1}^M \sum_{B \neq A}^M \frac{Z_A Z_B}{|\mathbf{R}_B - \mathbf{R}_A|} \right]$$

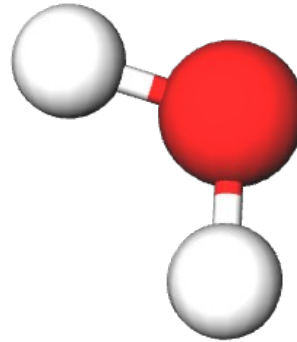
Em DFT

$$\frac{\partial E}{\partial \mathbf{R}_A} = \frac{\partial}{\partial \mathbf{R}_A} \left[-\sum_{A=1}^M \int \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \sum_{A=1}^M \sum_{B \neq A}^M \frac{Z_A Z_B}{|\mathbf{R}_B - \mathbf{R}_A|} \right]$$

Otimização da Geometria

Cálculo de Equilíbrio das posições

$$\mathbf{R}_A^{n+1} = \mathbf{R}_A^n + \alpha \mathbf{F}_A^n$$

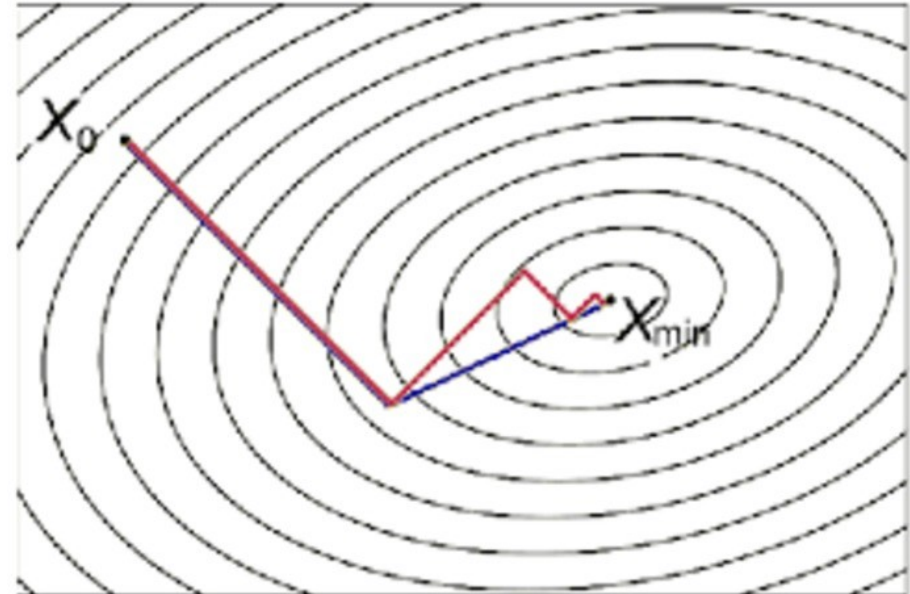


Força no átomo A

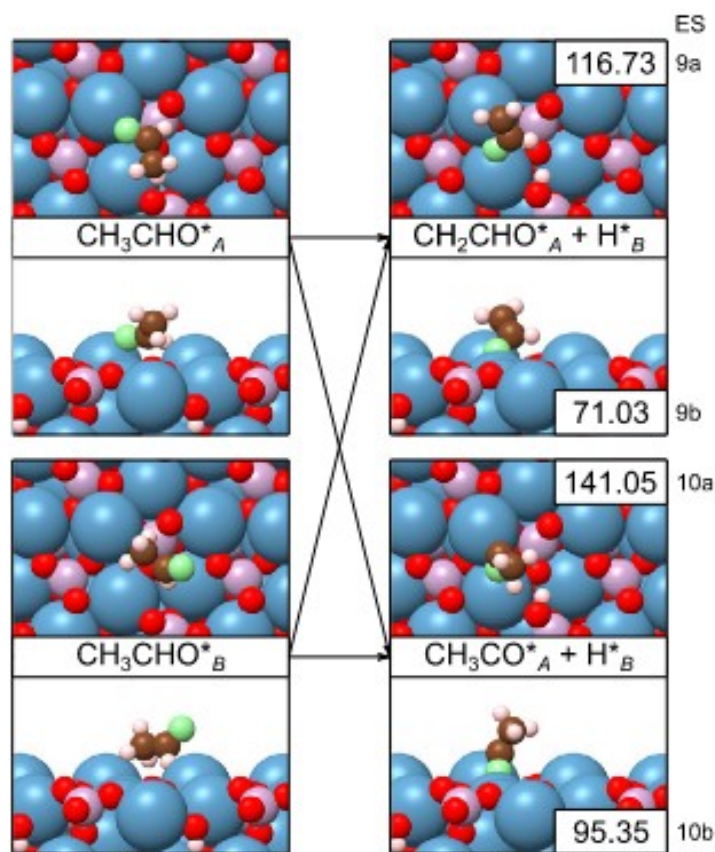
$$\mathbf{F}_A = -\frac{\partial E}{\partial \mathbf{R}_A}$$

Diferentes Métodos:

- RMM-DIIS
- Gradiente Conjugado
- FIRE



Onde chegamos



Brasil, H., Bittencourt, A. F. B., Yokoo, K. C. E. S., Mendes, P. C. D., Verga, L. G., Andriani, K. F., Landers, R., Da Silva, J. L. F., & Valença, G. P. (2021). Synthesis modification of hydroxyapatite surface for ethanol conversion: The role of the acidic/basic sites ratio. *Journal of Catalysis*, 404, 802–813. <https://doi.org/10.1016/j.jcat.2021.08.050>

2.3. Theoretical calculations

All total energy calculations were based on spin-polarized DFT [45,46] adopting the semilocal Perdew–Burke–Ernzerhof (PBE) formulation for the exchange–correlation functional [47]. The semi-empirical D3 van der Waals (vdW) correction proposed by Grimme [48] was used to improve the description of long-range vdW interactions. We employed the Vienna *ab initio* simulation package (VASP), version 5.4.1, which implements the all-electron projected augmented-wave (PAW) method [49–52]. The electron–ion interactions were described by the PAW projectors provided within VASP along with a plane-wave cutoff energy of 489 eV, which is 12.5% higher than the largest recommended value considering all chemical elements (C, Ca, H, O, and P).

The initial geometries of the isolated gas-phase molecules were obtained from the PubChem database [53] and optimized using a 20 Å cubic box. The clean hexagonal HAP(0001) surface was modeled using a repeated slab geometry with a thickness of four layers (one formula unit, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, per layer and Ca/P ratio of 1.67), and a vacuum region of 15 Å. To search for the lowest energy configurations, 30 distinct structures were built for each adsorbed system using a 1×1 surface unit cell with $a_0 = b_0 = 9.497 \text{ Å}$ (88 atoms within the unit cell). The adsorption structures were built by symmetrically placing adsorbates on both sides of the slab with respect to its center of inversion. As a result, dipole correction was no longer required. Once the lowest energy configurations were identified, the optimized adsorbed structures were placed on the surface 2×2 unit cell ($a_0 = b_0 = 18.995 \text{ Å}$, 352 atoms within the unit cell) for a final structure optimization. All optimized structures were calculated allowing all atoms to relax through the conjugate gradient algorithm. The total energy convergence criterion was set to 10^{-5} eV with a force convergence of 0.025 eV Å^{-1} on each atom. Only the Γ -point was employed for the Brillouin zone integration.