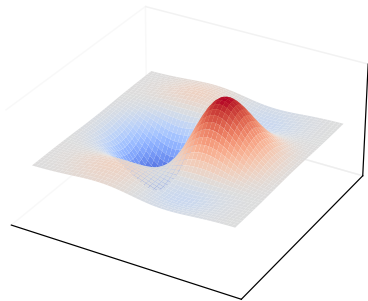


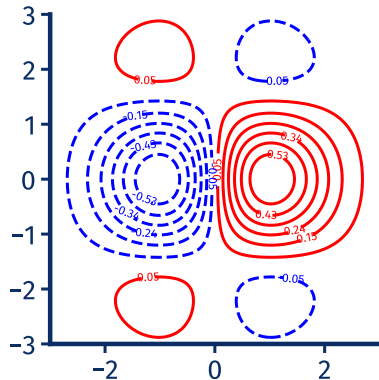
Potential Energy Surfaces

We seek the total energy as a function of nuclear positions, nuclear charges, and the electronic configuration of a system.

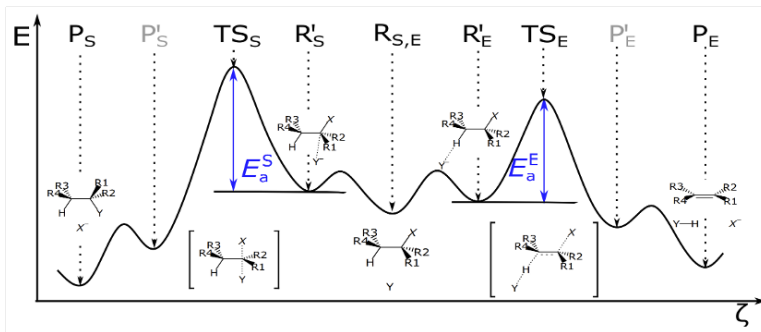
$$\begin{array}{c}
 \text{Numbers of electrons} \quad \text{Electronic spin} \\
 \text{System} \Rightarrow \hat{H}(\underbrace{\mathbf{R}_I}_{\text{Nuclear coordinates}}, \underbrace{Z_I}_{\text{Nuclear charges}}, \underbrace{n, \sigma}_{\text{Electronic spin}}) \Rightarrow \Psi \Rightarrow \underbrace{E(\mathbf{R}_I \mid Z_I, n, \sigma)}_{\text{Energy}} \quad (12)
 \end{array}$$



3D surface



2D contour lines



Features

- Minima: (Meta-)stable, ensembles
- Saddle points: Barriers / access
- Attractive basins

U Curvatures

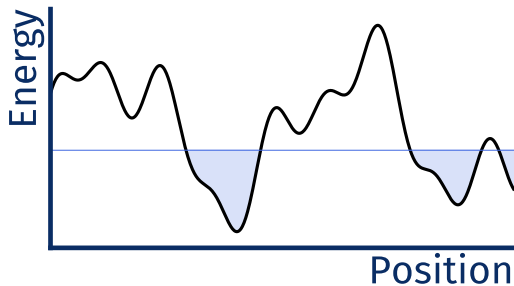
- Vibrational frequencies
- Normal modes
- Vibrational energy levels

~ Barriers

- Tunneling
- Thermalisation

🔑 Thermally accessible regions

- Ensemble of configurations



Landscape

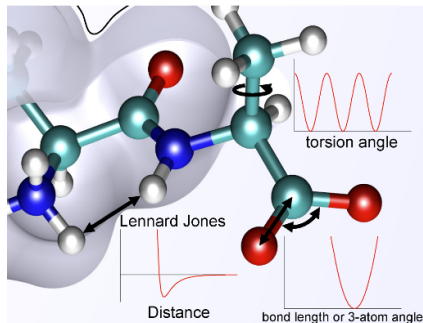
Potential Energy Landscapes

- Key for behaviour for single systems and reactions
- Complex, many minima
- Smooth surface
- High-dimensional

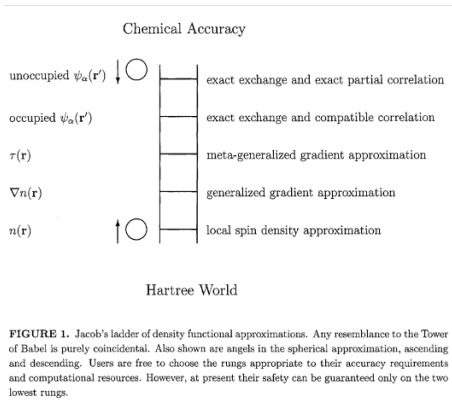
Families of Approximation

💡 Strong Approximation

- Typically fixed bonds
- No quantum effects
- Fitted to *ab initio* reference



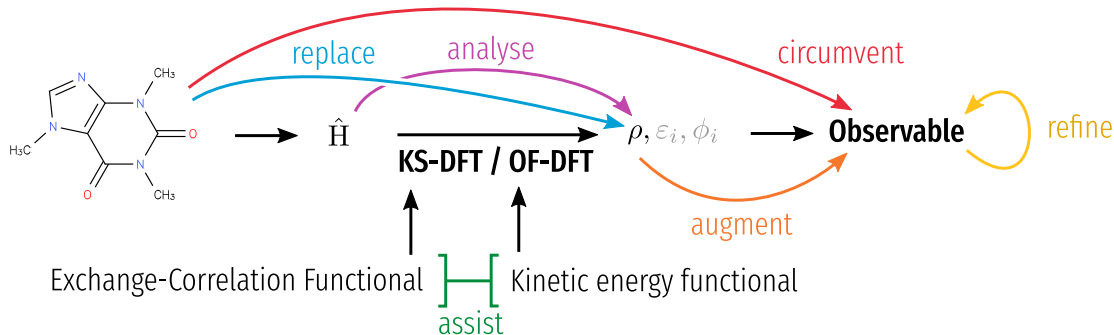
$$\begin{aligned}
 E = & \sum_{\text{bonds}} K_b(b - b_0)^2 + \sum_{\text{angles}} K_\theta(\theta - \theta_0)^2 + \\
 & \sum_{\text{dihedrals}} K_\phi(1 + \cos(n\phi - \delta)) + \\
 & \sum_{\text{improper}} K_\varphi(\varphi - \varphi_0)^2 + \\
 & \sum_{\text{Urey-Bradley}} K_u(u - u_0)^2 + \\
 & \sum_{i < j} 4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \\
 & \sum_{i < j} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}
 \end{aligned} \tag{13}$$



John Perdew



Michael Willmann, 1691



Concepts

- Strong approximation (constant topology): Classical force fields
- First principles (bottom-up approach from physical effects: quantum chemistry)
- Surrogate model of quantum chemistry: machine learning force fields