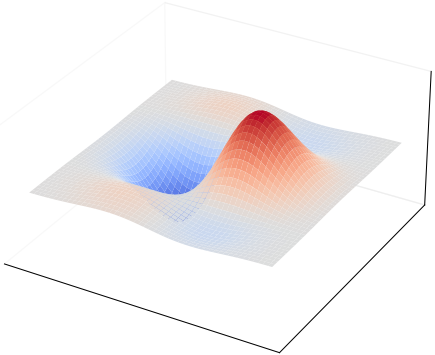
Potential Energy Surfaces

Formal view

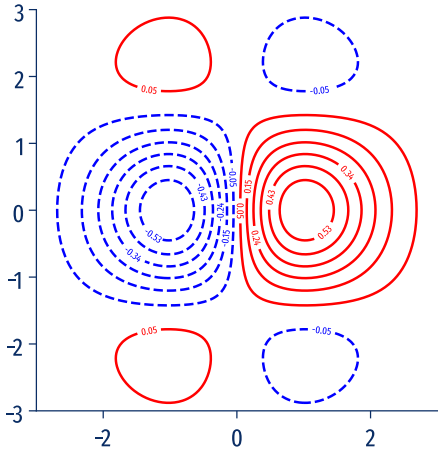
We seek the total energy as a function of nuclear positions, nuclear charges, and the electronic configuration of a system.

$$\text{System} \;\Rightarrow\; \hat{H}(\mathbf{R}_I, Z_I, n, \sigma) \;\Rightarrow\; \Psi \;\Rightarrow\; E(\mathbf{R}_I \mid Z_I, n, \sigma) \tag{12}$$

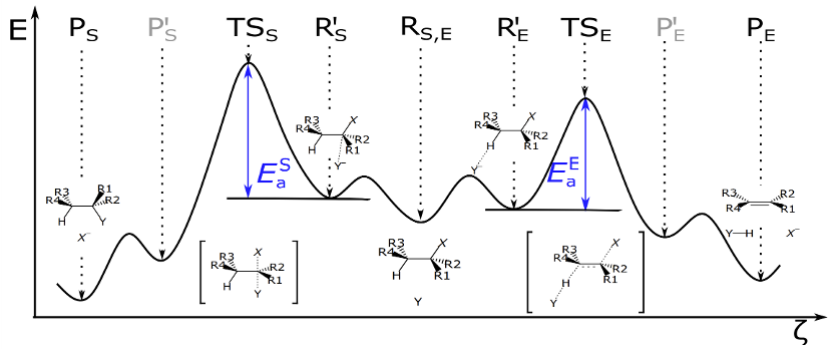
Contour surfaces



3D surface



2D contour lines



Features

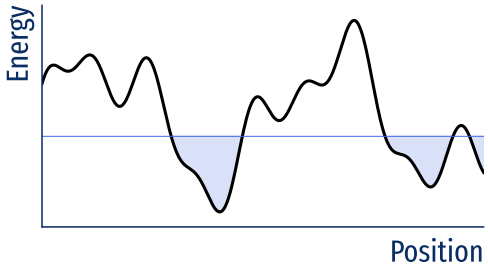
- Minima: (Meta-)stable, ensembles
- Saddle points: Barriers / access
- Attractive basins

https://doi.org/10.1088/2632-2153/aba822

Curvatures
- Vibrational frequencies
- Normal modes
- Vibrational energy levels

Barriers
- Tunneling
- Thermalisation

Thermally accessible regions
Ensemble of configurations



Landscape

Summary

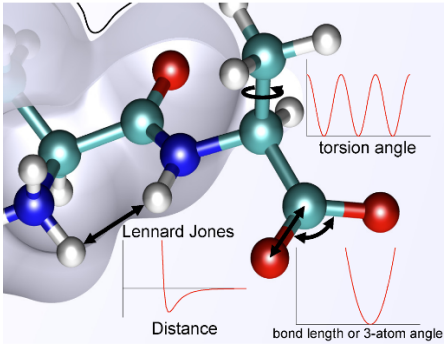
Potential Energy Landscapes

- 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



$$E = \sum_{\text{bonds}} K_b(b - b_0)^2 + \sum_{\text{angles}} K_\theta(\theta - \theta_0)^2 +$$
$$\sum_{\text{dihedrals}} K_\phi\big(1 + \cos(n\phi - \delta)\big) +$$
$$\sum_{\text{improper}} K_\varphi(\varphi - \varphi_0)^2 +$$
$$\sum_{\text{Urey–Bradley}} K_u(u - u_0)^2 +$$
$$\sum_{i<j} 4\varepsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] +$$
$$\sum_{i<j} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \tag{13}$$

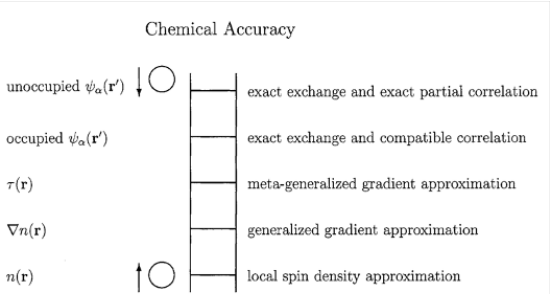
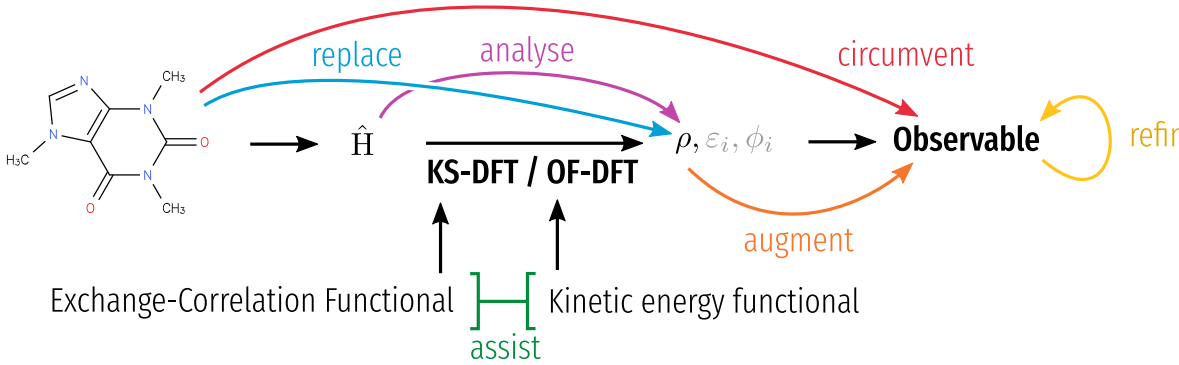


FIGURE 1. Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. However, at present their safety can be guaranteed only on the two lowest rungs.

John Perdew



Michael Willmann, 1691


replace
analyse
circumvent
$\hat{H}$
KS-DFT / OF-DFT
$\rho, \varepsilon_i, \phi_i$
Observable
refir
augment
Exchange-Correlation Functional
Kinetic energy functional
assist

Summary

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