Potential Energy Surfaces

Formal view 28

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

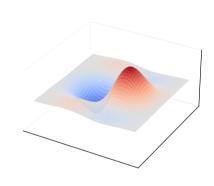
Numbers of electrons
$$\perp$$
 Electronic spin

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

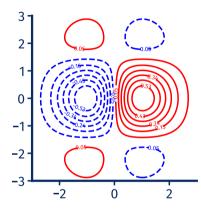
Nuclear coordinates

Nuclear charges

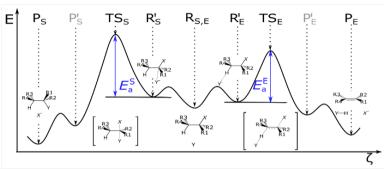
(12)



3D surface



2D contour lines



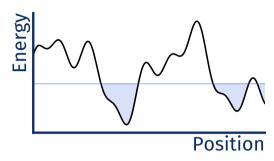
Å Features

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

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

Properties 3

- **U** Curvatures
- Vibrational frequencies
- Normal modes
- Vibrational energy levels
- \sim Barriers
- Tunneling
- Thermalisation
- Thermally accessible regions
- Ensemble of configurations



Landscape

Summary 32

Potential Energy Landscapes

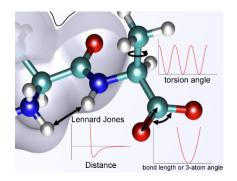
- Key for behaviour for single systems and reactions
- Complex, many minima
- Smooth surface
- High-dimensional

Families of Approximation

Classical Molecular Dynamics

Strong Approximation

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



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

$$(13)$$

$\begin{array}{c|cccc} & \text{Chemical Accuracy} \\ \\ \text{unoccupied } \psi_o(\mathbf{r}') & & & \\ & & \text{exact exchange and exact partial correlation} \\ \text{occupied } \psi_o(\mathbf{r}') & & & \\ & & \text{exact exchange and compatible correlation} \\ \\ \tau(\mathbf{r}) & & & \\ & & \text{meta-generalized gradient approximation} \\ \\ \nabla n(\mathbf{r}) & & & \\ & & \\ & & & \\$

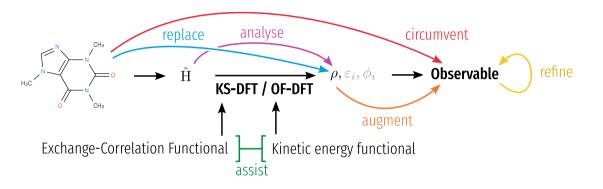
FIGURE 1. Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational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

Hartree World

John Perdew



Michael Willmann, 1691



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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