

Density Functional Theory in Catalysis

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Overview

1 Introduction

- What is a Chemical Reaction?
- The Born Oppenheimer Approximation
- What Problem Does DFT Solve?

2 Theory

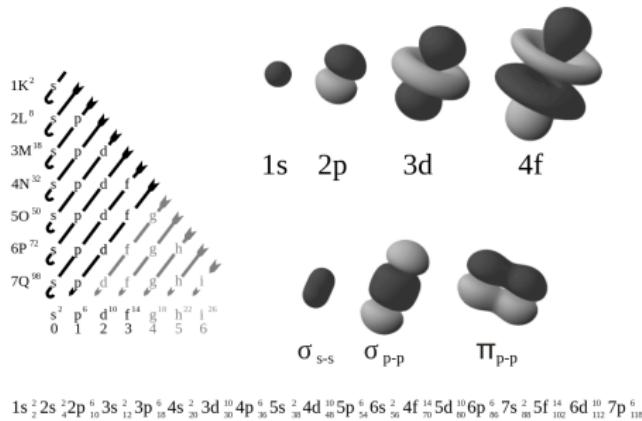
- Hohenberg and Kohn Theorems
- Kohn Sham DFT
- Geometry Optimization and Reaction Pathways

3 Applications

- Coking on Ni Surfaces
- Product Selectivity
- Challenges

Chemical Reactions - Schrödinger Equation

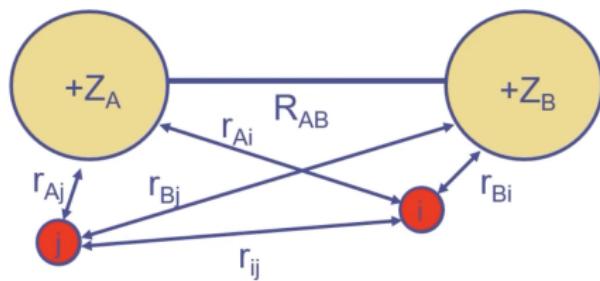
Chemical reactions involve bond breakage, electron transfer, and much more. However, Electrons are quantum objects. They exhibit wave-like and particle-like properties. Therefore we have no choice other than quantum mechanics if we hope to describe them.



$$\hat{\mathbf{H}}\psi = E\psi \quad (1)$$

$$\psi = \psi(x_1, y_1, z_1, \omega_1, \dots, x_N, y_N, z_N, \omega_N) \quad (2)$$

The Molecular Hamiltonian



$$\hat{\mathbf{H}} = - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_i \frac{1}{2} \nabla_i^2 - \sum_A \sum_i \frac{Z_A}{r_{i,A}}$$
$$+ \sum_i \sum_{j > i} \frac{1}{r_{i,j}} + \sum_A \sum_{B > A} \frac{Z_A Z_B}{r_{A,B}} \quad (3)$$

The Born Oppenheimer Approximation



Max Born
1882 - 1970

J. Robert Oppenheimer
1904 - 1967

The mass of a proton is roughly 2000 times larger than an electron.

$$M_{\text{Nuclei}} \gg M_{\text{Electron}} \quad (4)$$

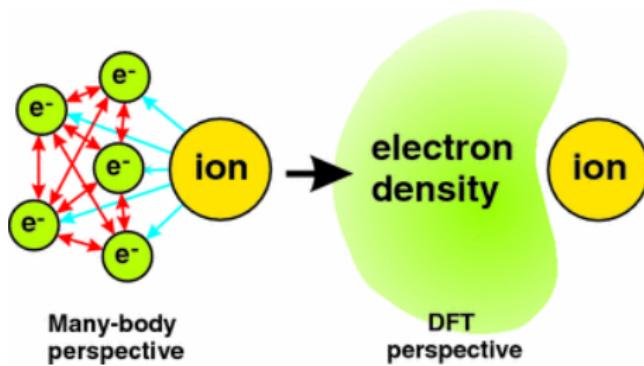
Therefore, the electrons will equilibrate so much faster than the nuclei, we might as well solve them independently. We can just treat the nuclei as frozen in time from the perspective of an electron.

What does DFT aim to solve?

$$\hat{H}_{\text{Elec.}}(\mathbf{r}; \mathbf{R}) = - \sum_i^{\text{Elec.}} \frac{1}{2} \nabla_i^2 - \sum_A^{\text{Nucl.}} \sum_i^{\text{Elec.}} \frac{Z_A}{r_{i,A}} + \sum_i^{\text{Elec.}} \sum_{j>i}^{\text{Elec.}} \frac{1}{r_{i,j}} \quad (5)$$

$$\hat{H}_{\text{Elec.}}(\mathbf{r}; \mathbf{R}) \psi_{\text{Elec.}}(\mathbf{r}; \mathbf{R}) = E_{\text{Elec.}}(\mathbf{R}) \psi_{\text{Elec.}}(\mathbf{r}; \mathbf{R}) \quad (6)$$

DFT is a specific electronic structure solution method. The key assumption for DFT is dealing with the electron density rather than the wave function!



Possible Outputs From DFT

- Equilibrium Geometries (Microwave Spectra)
- Vibrational Frequencies (IR Spectra)
- Excited States (UV/VIS Spectra)
- NMR Spectra
- CD Spectra
- Polarizability
- Barrier Heights
- Reaction Paths
- Estimations of Reaction Rate by Including Dynamics on PE Surface
- With Statistical Mechanics, Thermodynamics of A Reaction
- Too Many to Name!!

Hoenberg and Kohn Theorems



Pierre Hoenberg
1934 - 2017



Walter Kohn
1923 - 2016

Hoenberg and Kohn Theorems

Theorem (The First Hoenberg and Kohn Theorem)

The ground state properties of a many body electron system depend only on the electronic density $\rho(x, y, z)$.

Theorem (The Second Hoenberg and Kohn Theorem)

The correct ground state energy for a system is the one that minimized the total energy through the functional $E[\rho(x, y, z)]$.

Kohn Sham DFT



Lu Jeu Sham
1938 - Present



Walter Kohn
1923 - 2016

Electron Density and Hartree Fock Orbital Approximation

We can steal ideas from Hartree Fock theory. For an N electron system the Slater determinant looks like:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix} \sim |ij\dots k\rangle \quad (7)$$

Where $|ij\dots k\rangle$ is a commonly used shorthand. With our wave function, we can write down the spacial electron density.

$$\rho(x, y, z) = N \sum_{i=1}^N |\phi_i(x, y, z)|^2 \quad (8)$$

$$\text{Such that } \phi_i(x, y, z) = \sum_{\mu=1}^K C_{\mu,i} \tilde{\phi}_{\mu}(x, y, z) \quad (9)$$

The Energy Functional

The energy functional is given by:

$$E_{eN}[\rho] = - \sum_A^{\text{Nucl.}} \int \frac{Z_A \rho(\mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|} d\mathbf{r} \quad (10)$$

$$T_S[\rho] = -\frac{1}{2} \sum_{i=1}^N \langle \phi_i(\mathbf{r}) | \nabla^2 | \phi_i(\mathbf{r}) \rangle \quad (11)$$

$$J[\rho] = \int \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (12)$$

$$\implies E_{\text{Elec.}}[\rho] = T_S[\rho] + E_{eN}[\rho] + J[\rho] + E_{xc}[\rho] \quad (13)$$

The exact exchange correlation functional is unknown. Choosing the correct functional for your application is the crux of any DFT analysis. Dirac showed that the functional for a uniform electron gas is:

$$E_{xc}[\rho] = \int c_x \rho(\mathbf{r})^{\frac{4}{3}} + E_c(\rho) d\mathbf{r} \quad (14)$$

The Resulting Optimization Procedure

$$\frac{\delta E_{\text{Elec.}}[\rho]}{\delta \rho} = 0 \quad (15)$$

After doing a lot of quantum mechanics and some variational calculus one can show:

$$\left(-\frac{1}{2}\nabla^2 - \sum_A^{\text{Nucl.}} \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (16)$$

This looks like N time independent Schrodinger equations for a set of non-interacting electron orbitals in an effective potential. The key point is that we can now solve a fictitious non-interacting system but we can attain the same ground state energy as an interacting one!

What is a PES?

$$E_{\text{Elec}}(\mathbf{R}) = \text{Potential Energy Surface} = \text{PES}$$

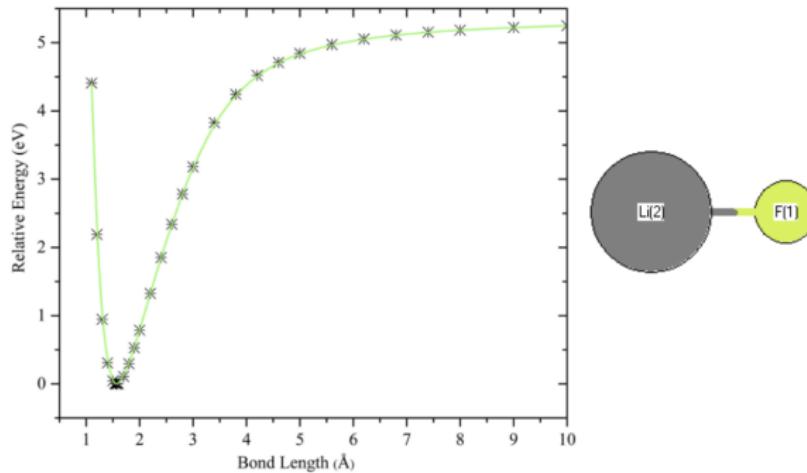
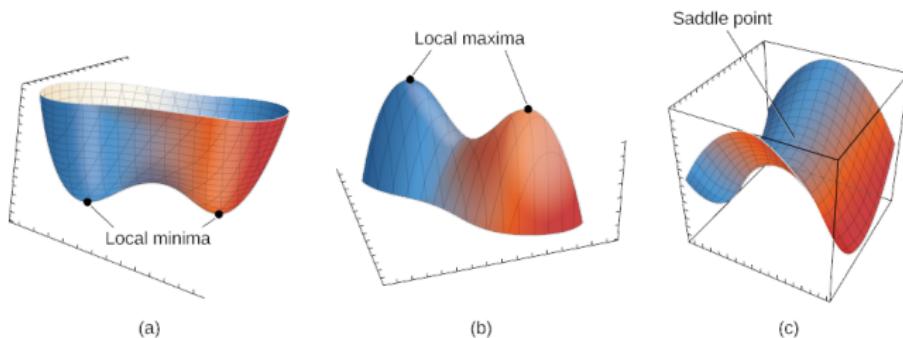


Figure: Relative energy dissociation curves of LiF obtained with the embedding-with-external-orbital-orthogonality DFT-in-DFT (green) and KS-DFT calculations (black). The green curve completely obscures the KS-DFT curve - Accurate Dissociation of Chemical Bonds Using DFT-in-DFT Embedding Theory with External Orbital Orthogonality by Tamukong et. al.

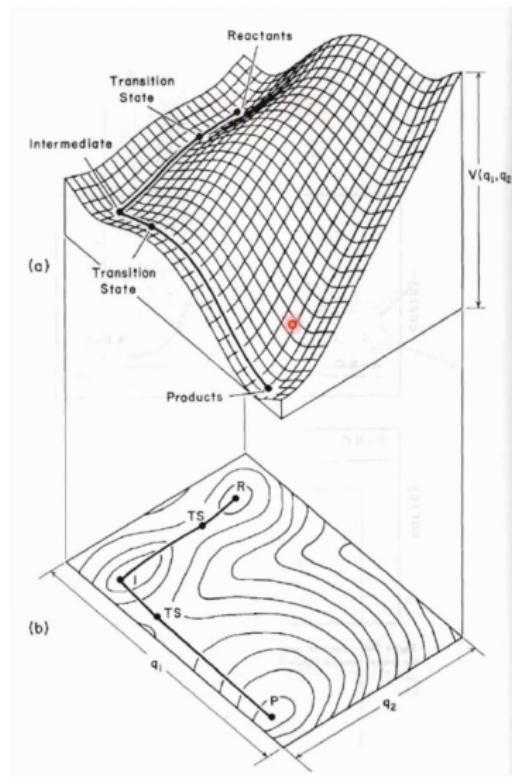
Geometry Optimization and Reaction Pathways

$$\left(\frac{dE_{\text{Elec.}}(\mathbf{R})}{d\mathbf{R}} \right) = \mathbf{0} \implies \mathbf{R} = \text{Stationary Point} \quad (17)$$



Reactions tend to take the path of least resistance. This implies they are most likely to take the minimum energy path. The minimum energy path always goes from a minimum, to a saddle point, then back to a minimum.

A Reaction Pathway



Applications

A Real Potential Energy Surface

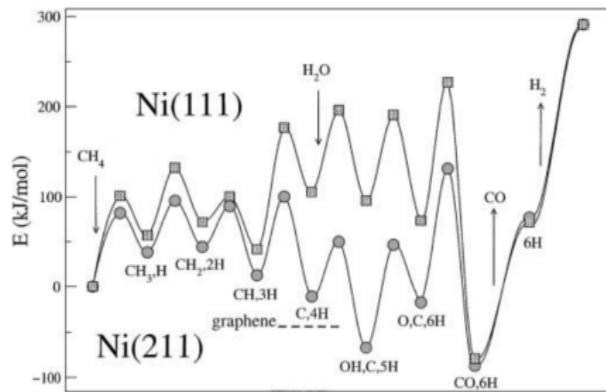
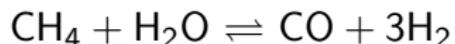
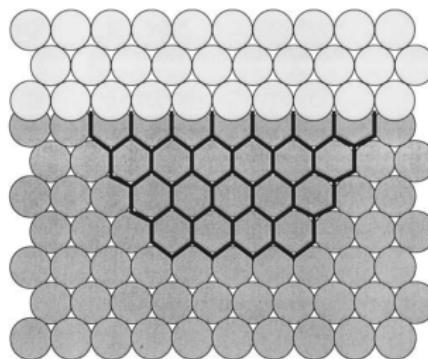


Figure: Energies for the species on Ni(211) and Ni(111). All energies are relative to CH₄ and H₂O in the gas phase and calculated using the results for the individual species. - Steam Reforming and Graphite Formation on Ni Catalysts by Bengaard et. al.

Coking

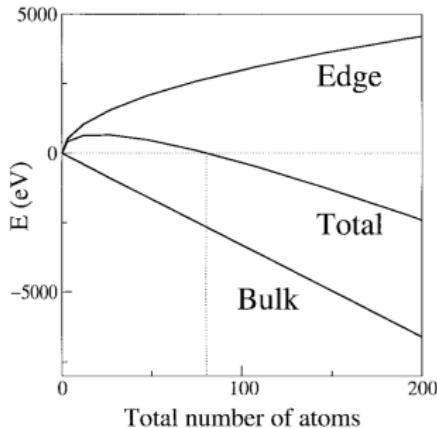
Relative Energies (kJ/mol) per Carbon Atom on the Two Surfaces,
and the Edge Energy for Graphene on Ni(111)

Ni(211) atomic C		Ni(111)		
1C : 2Ni edge atoms	1C : 1Ni edge atom	Atomic C	Monolayer graphene	Graphene edge energy
E (kJ/mol)	0	43	97	-33
				172



$$E_{\text{Carbon Cluster}} = N_{\text{Tot}} \times E_{\text{Graphene}} + N_{\text{Edge}} \times E_{\text{Edge}} \quad (18)$$

Coking Mechanism



- The carbon first attaches to a step site, as it has lower energy than the carbon on the Ni (111) surface.
- Once more atoms attach to the step, it starts to build up an edge. This has a large energy penalty.
- Rather than bind to the step site and catalyze the reaction, it becomes more favorable to continue build the graphite island.

How to Prevent Coking

$$N_{\text{Crit}} \approx 80 \text{ Atoms of Carbon} \iff 25 \text{ \AA Step Size} \quad (19)$$

If you can engineer your catalyst to have a step sizesmaller than the 25 angstroms, you can make it energetically unfavorable to cause large scale coking. Similarly, you can strategically place additives into the catalyst to block the step sites from nucleating. Its very easy to tests thousands of these additives without running a single experiment (\$\$\$!!).

Optimization For Selectivity

"We will take the selective hydrogenation of acetylene in the presence of an excess of ethylene as an example.... A selective catalyst should have an activation barrier for the hydrogenation of ethylene that is higher than its desorption energy to favor desorption of the product rather than its further hydrogenation ... (the) energies are comparable for Pd(111), the desorption barrier is smaller than the activation barrier for the PdAg(111) surface, making this surface more selective"

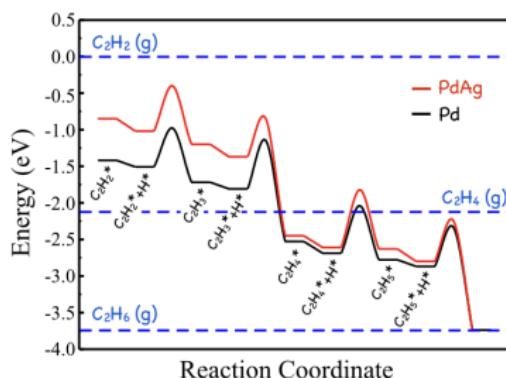


Fig. 8. Potential energy diagram obtained from DFT calculations for the hydrogenation of acetylene to ethane on close-packed surfaces of Pd (black) and PdAg (red) surfaces. Adapted from ref. 59.

Current Challenges for DFT in Catalysis

- Choosing the correct exchange correlation functional
- Developing an efficient catalyst optimization algorithm for rate, selectivity, cost effectiveness, etc.
- Actually having enough computational resources to compute these for large systems

Thanks!