1. **One can NEVER blindly trust a computational result**
   - **Is there an experimental result you can compare with?**
   - **Is there literature justifying the use of your computational model?**
   - **Do your computations seem in line with your chemical intuition?**

1. **One can NEVER blindly trust a computational result**
   - **Is there an experimental result you can compare with?**
   - **Is there literature justifying the use of your computational model?**
   - **Do your computations seem in line with your chemical intuition?**

1. **One can NEVER blindly trust a computational result**
   - **Is there an experimental result you can compare with?**
   - **Is there literature justifying the use of your computational model?**
   - **Do your computations seem in line with your chemical intuition?**

1. **One can NEVER blindly trust a computational result**
   - **Is there an experimental result you can compare with?**
   - **Is there literature justifying the use of your computational model?**
   - **Do your computations seem in line with your chemical intuition?**

2. Know your question before you start the computations

- **What do you want to know?**
- **How much time are you willing to spend?**
- **Will the computations bring you anything useful?**
- **Is your computation feasible?**

2. **Know your question before you start the computations**
   - **What do you want to know?**
   - **How much time are you willing to spend?**
   - **Will the computations bring you anything useful?**
   - **Is your computation feasible?**

2. **Know your question before you start the computations**
    - **What do you want to know?**
    - **How much time are you willing to spend?**
    - **Will the computations bring you anything useful?**
    - **Is your computation feasible?**

2. **Know your question before you start the computations**
    - **What do you want to know?**
    - **How much time are you willing to spend?**
    - **Will the computations bring you anything useful?**
    - **Is your computation feasible?**

2. **Know your question before you start the computations**
   - **What do you want to know?**
   - **How much time are you willing to spend?**
   - **Will the computations bring you anything useful?**
   - **Is your computation feasible?**

3. Computations can and will give fallacious results if a proper model isn't employed.

- "There are a growing number of computational chemists, as well as experimentalists, throughout the world who use standard codes without a deep understanding of their underlying theory. A disappointingly large number of papers are appearing that use inappropriate methods and make conclusions that are totally unfounded. So, there is a need to develop better ways to broadly educate users of computational chemistry codes."

- **Survey in 2009 by International Academy of Quantum Molecular Science**

- **See C&EN from 2011**

- **https://cen.acs.org/articles/89/i33/Black-Box-Chemistry.html**

What Is WebMO?

- **WebMO is an interface, not a computational engine!**
  - **You DON'T perform any but the simplest calculations with WebMO.**
  - **You DO use WebMO to perform calculations with other pieces of software.**
- **WebMO is NOT intended for research. There are built-in limitations to the size and time requirements of jobs.**
- **WebMO IS intended for pedagogical purposes.**
  - **Illustrate and elucidate concepts learned in lecture/lab.**

Computational Hierarchy

1. Molecular Mechanics

- Molecules are Balls and Springs
- No integral evaluations, fast and easy mathematical operations, limited memory consumption.
- Can be applied to very large systems.
- Empirical nature sometimes makes geometries even more accurate than QM calculations.
- ZERO INFORMATION ON ELECTRONIC STRUCTURE!!!

2. *Ab Initio*/DFT

- No empirical parameters
  - Sidenote ... theoreticians argue that DFT can be considered semi-empirical, you mustn't worry about that...
- If the correct method/basis set is used, can be extremely accurate.
- For *ab initio* methods, can systematically converge to exact solution.
- EXPENSIVE. LIMITED TO SMALL(ISH) SYSTEMS

3. Semi-Empirical Methods

- Expense is in-between MM and QM methods.
- Electronic structure is determined, although in a highly approximate manner.
- Able to calculate excited state properties.
- IMPORTANT ELECTRONIC INFORMATION CAN BE OMITTED OR LOST!!!

4. Hybrid QM/MM

- NOT COVERED HERE, BUT VERY IMPORTANT IN MODERN RESEARCH
- NOBEL PRIZE 2013

What is Chemistry?

Chemistry is knowing the energy of a molecular system as a function of the nuclear coordinates.

What are Chemical Properties?

Chemical properties are knowing how the energy changes upon adding a perturbation to the system.

What the programs do

Nearly all quantum chemistry techniques begin by finding an approximate solution to the Time-Independent Schrödinger Equation using the non-relativistic Born-Oppenheimer Hamiltonian.

THIS GIVES US A WAVEFUNCTION AND AN ENERGY

$$\hat{H} = \sum_i^{N_{el}} -\frac{\nabla^2}{2} - \sum_i^{N_{el}} \sum_A^{N_{nuc}} \frac{Z_A}{r_{iA}} + \sum_{i,j>i}^{N_{el}} \frac{1}{r_{ij}}$$

The wavefunction is represented as a single Slater Determinant

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix}$$

ϕ_i **are the molecular orbitals**

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$

The energy is evaluated by introducing an effective one-electron operator ... the Fock Operator

$$J_{ji} \phi_i(1) = \langle \phi_j(2) | r_{12}^{-1} | \phi_j(2) \phi_i(1) \rangle$$

$$\widehat{F}_i = -\frac{\nabla_i^2}{2} - \sum_A^{N_{nuc}} \frac{Z_A}{r_{iA}} + \sum_j J_{ji} - K_{ji}$$

$$K_{ji} \phi_i(1) = \langle \phi_j(2) | r_{12}^{-1} | \phi_i(2) \phi_j(1) \rangle$$

The molecular orbitals are usually expressed as a linear combination of atom-centered "basis functions". The set of basis functions is called the "Basis Set"

$$\phi_i = \sum_{\alpha}^{M} c_{i\alpha} \chi_{\alpha}$$

For the sake of mathematical simplicity, the basis functions are usually expressed as linear combinations of gaussian "primitives"

$$\chi_{\alpha} = \sum_{i}^{N} \psi_i$$

$$\psi_{\zeta,a,b,c} = N x^a y^b z^c e^{-\zeta r^2}$$ **Cartesian Basis Sets**

$$\psi_{\zeta,n,l,m} = N r^{2n-2-l} Y_{l,m}(\theta,\phi) e^{-\zeta r^2}$$ **Spherical Basis Sets**

Minimal Basis Sets (*STO-3G*, *MINI*)

A minimal basis set is the smallest possible basis set for a given molecule. Below are some examples:

1) H$_2$: Each hydrogen has a single 1s BF. $\quad 1s_1^1 1s_2^1$

2) CH$_4$: Each hydrogen has a single 1s BF, the carbon has a 1s BF, a 2s BF, a 2$_{px}$ BF, a 2$_{py}$ BF, and a 2$_{pz}$ BF. $\quad 1s_1^2 2s_1^1 2p_1^3 1s_2^1 1s_3^1 1s_4^1 1s_5^1$

3) SO$_4$$^{2-}$: Each oxygen has a 1s BF, a 2s BF, a 2px BF, a 2py BF, a 2pz BF; the sulfur has a 1s BF, a 2s BF, a 3s BF, a 2px BF, a 2py BF, a 2pz BF, a 3px BF, a 3py BF, and a 3py BF, and a 3pz BF.

$$1s_1^2 2s_1^2 2p_1^6 3s_1^2 3p_1^4 1s_2^2 2s_2^2 2p_2^4 1s_3^2 2s_3^2 2p_3^4 1s_4^2 2s_4^2 2p_4^4 1s_5^2 2s_5^2 2p_5^4$$

Minimal basis sets, while fast, are rarely used for "real" computations because of their limited accuracy.

We tend to use basis sets that improve upon minimal sets through the use of **polarization** functions, **diffuse** functions, and **split valence** treatments.

Basis Set Options

Here are some contraction patterns for common basis sets

	hydrogen	1st row	2nd row
Minimal	{3}	{33/3}	{333/33}
6-31G*	{31}	{631/31/1}	{6631/631/1}
6-31G**	{31/1}	{631/31/1}	{6631/631/1}
6-311+G(2d,p)	{311/1}	{63111/3111/11}	{6311111/421111/11}
cc-pVDZ	{31/1}	{881/31/1}	{11,11,11,1/771/1}
cc-pVTZ	{311/11/1}	{8811/311/11/1}	{13,13,13,1,1/7711/11/1}
def2-SVP	{31/1}	{511/31/1}	{5311/511/1}
def2-TZVP	{311/1}	{62111/411/11/1}	{73211/51111/21/1}
def2-QZVP	{4111/111/11/1}	{8211111/5111/111/11/1}	{10,31111111/821111/1111/11/1}

Basis Set Options: Polarization

	hydrogen	1st row	2nd row
Minimal	{3}	{33/3}	{333/33}
6-31G*	{31}	{631/31/1}	{6631/631/1}
6-31G**	{31/1}	{631/31/1}	{6631/631/1}
6-311+G(2d,p)	{311/1}	{63111/3111/11}	{6311111/421111/11}
cc-pVDZ	{31/1}	{881/31/1}	{11,11,11,1/771/1}
cc-pVTZ	{311/11/1}	{8811/311/11/1}	{13,13,13,1,1/7711/11/1}
def2-SVP	{31/1}	{511/31/1}	{5311/511/1}
def2-TZVP	{311/1}	{62111/411/11/1}	{73211/51111/21/1}
def2-QZVP	{4111/111/11/1}	{8211111/5111/111/11/1}	{10,31111111/821111/1111/11/1}

Basis Set Options: Split-Valence

	hydrogen	1st row	2nd row
Minimal	{3}	{33/3}	{333/33}
6-31G*	{31}	{631/31/1}	{6631/631/1}
6-31G**	{31/1}	{631/31/1}	{6631/631/1}
6-311+G(2d,p)	{311/1}	{63111/3111/11}	{6311111/421111/11}
cc-pVDZ	{31/1}	{881/31/1}	{11,11,11,1/771/1}
cc-pVTZ	{311/11/1}	{8811/311/11/1}	{13,13,13,1,1/7711/11/1}
def2-SVP	{31/1}	{511/31/1}	{5311/511/1}
def2-TZVP	{311/1}	{62111/411/11/1}	{73211/51111/21/1}
def2-QZVP	{4111/111/11/1}	{8211111/5111/111/11/1}	{10,31111111/821111/1111/11/1}

Basis Set Options: Diffuse Functions

	hydrogen	1st row	2nd row
Minimal	{3}	{33/3}	{333/33}
6-31G*	{31}	{631/31/1}	{6631/631/1}
6-31G**	{31/1}	{631/31/1}	{6631/631/1}
6-311+G(2d,p)	{311/1}	{63111/3111/11}	{6311111/4211111/11}
cc-pVDZ	{31/1}	{881/31/1}	{11,11,11,1/771/1}
cc-pVTZ	{311/11/1}	{8811/311/11/1}	{13,13,13,1,1/7711/11/1}
def2-SVP	{31/1}	{511/31/1}	{5311/511/1}
def2-TZVP	{311/1}	{62111/411/11/1}	{73211/51111/21/1}
def2-QZVP	{4111/111/11/1}	{8211111/5111/111/11/1}	{10,31111111/821111/1111/11/1}

Hartree-Fock Theory

$$\widehat{F}_i = -\frac{\nabla_i^2}{2} - \sum_A^{N_{nuc}} \frac{Z_A}{r_{iA}} + \sum_j J_{ji} - K_{ji}$$

$$J_{ji}\,\phi_i(1) = \langle \phi_j(2) | r_{12}^{-1} | \phi_j(2)\,\phi_i(1) \rangle$$

$$K_{ji}\,\phi_i(1) = \langle \phi_j(2) | r_{12}^{-1} | \phi_i(2)\,\phi_j(1) \rangle$$

$$\widehat{F}_i \big| \phi_i \big\rangle = \widehat{F}_i \Big| \sum_\alpha^M c_{i\alpha} \chi_\alpha \Big\rangle = \epsilon_i \Big| \sum_\alpha^M c_{i\alpha} \chi_\alpha \Big\rangle$$

$$FC = SC\,\epsilon$$

Roothaan-Hall Equations

$$E = \sum_i^{N_{el}} \sum_{\alpha\beta}^M c_{\alpha i} c_{i\beta} \langle \chi_\alpha | -\frac{\nabla^2}{2} - \sum_A^{N_{nuc}} \frac{Z_A}{r_{iA}} | \chi_\beta \rangle + \frac{1}{2} \sum_{ij}^{N_{el}} \sum_{\alpha\beta\gamma\delta}^M c_{\alpha i} c_{\gamma j} c_{\beta i} c_{\delta j} \left(\langle \chi_\alpha \chi_\gamma | \frac{1}{r_{12}} | \chi_\beta \chi_\delta \rangle - \langle \chi_\alpha \chi_\gamma | \frac{1}{r_{12}} | \chi_\delta \chi_\beta \rangle \right) + V_{nn}$$

$$E = \sum_{\alpha\beta}^M D_{\alpha\beta} \langle \chi_\alpha | -\frac{\nabla^2}{2} - \sum_A^{N_{nuc}} \frac{Z_A}{r_{iA}} | \chi_\beta \rangle + \frac{1}{2} \sum_{\alpha\beta\gamma\delta}^M D_{\alpha\beta} D_{\gamma\delta} \left(\langle \chi_\alpha \chi_\gamma | \frac{1}{r_{12}} | \chi_\beta \chi_\delta \rangle - \langle \chi_\alpha \chi_\gamma | \frac{1}{r_{12}} | \chi_\delta \chi_\beta \rangle \right) + V_{nn}$$

$$D_{\alpha\beta} = \sum_i^{N_{el}} c_{\alpha i} c_{i\beta}$$

The HF Algorithm

DFT is able to improve upon Hartree-Fock results with minimal excess cost.

- **Based on a completely different theoretical framework that won't be discussed here.**

- **The working equations are as follows:**

$$K_{\mu\nu} = \langle \chi_\mu | -\frac{\nabla^2}{2} - \sum_A^{N_{nuc}} \frac{Z_A}{r_{1A}} + \sum_{\alpha\beta}^M D_{\alpha\beta} \langle \chi_\mu \chi_\alpha | \frac{1}{r_{12}} | \chi_\nu \chi_\beta \rangle + V_{xc} | \chi_\nu \rangle \qquad KC = SC\epsilon$$
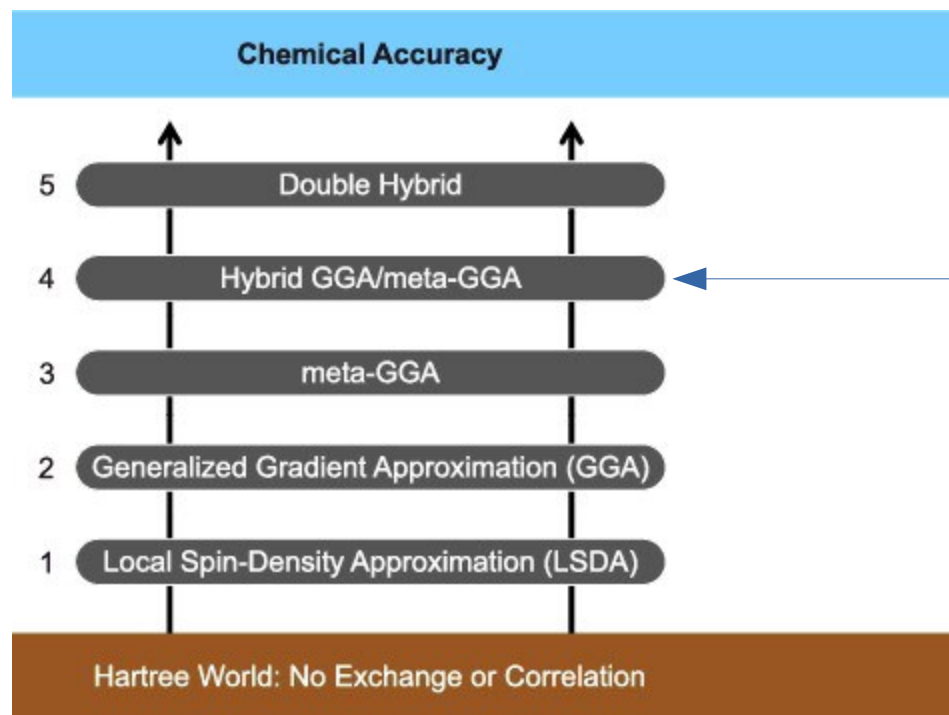
$$\langle \chi_\mu | V_{xc} | \chi_\nu \rangle = \int \chi_\mu(r) V_{xc} \chi_\nu(r) dr = \sum_k^G V_{xc} \big[\rho(r_k), \nabla \rho(r_k) \big] \chi_\mu(r) \chi_\nu(r) \Delta v_k$$
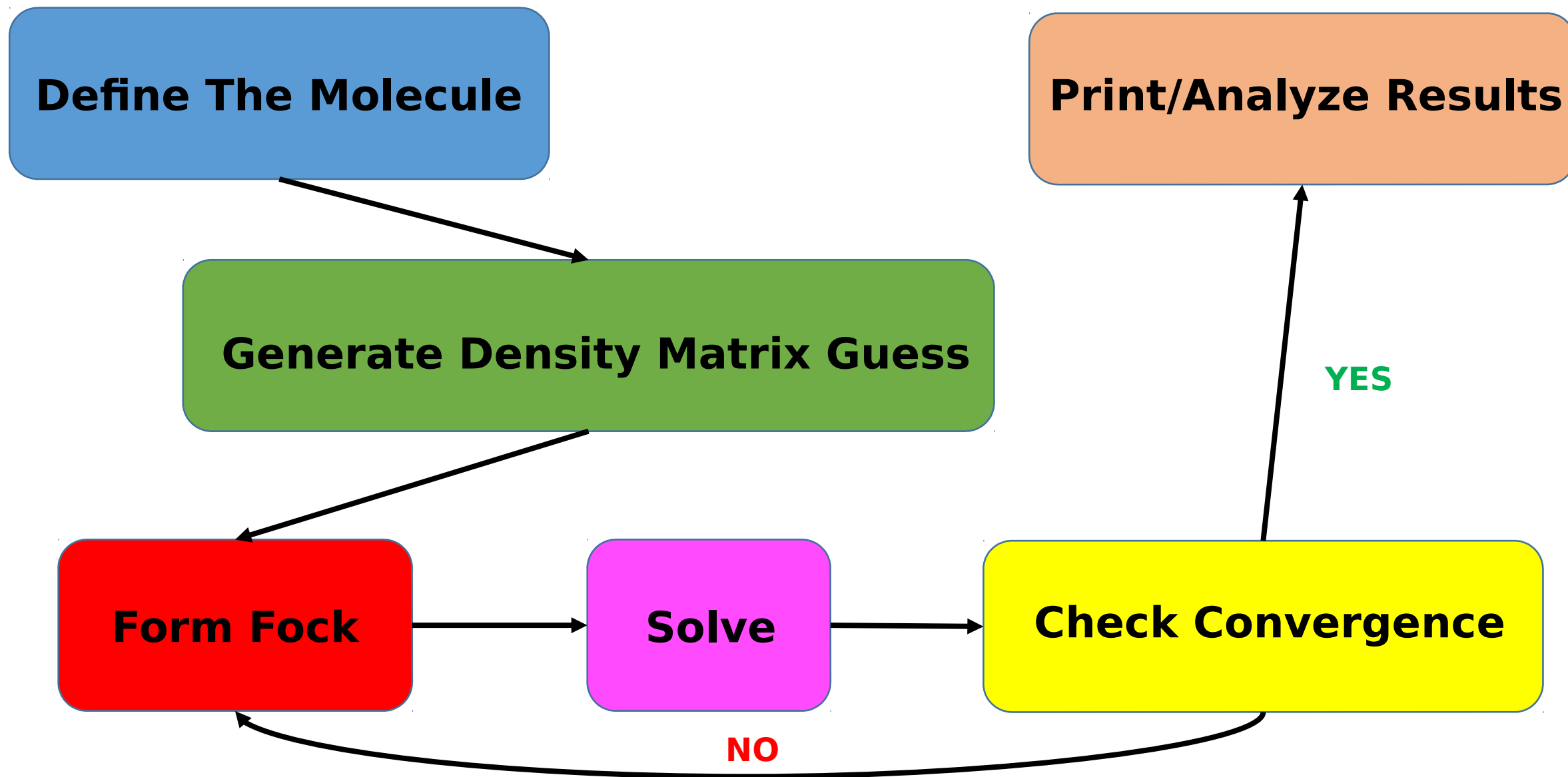
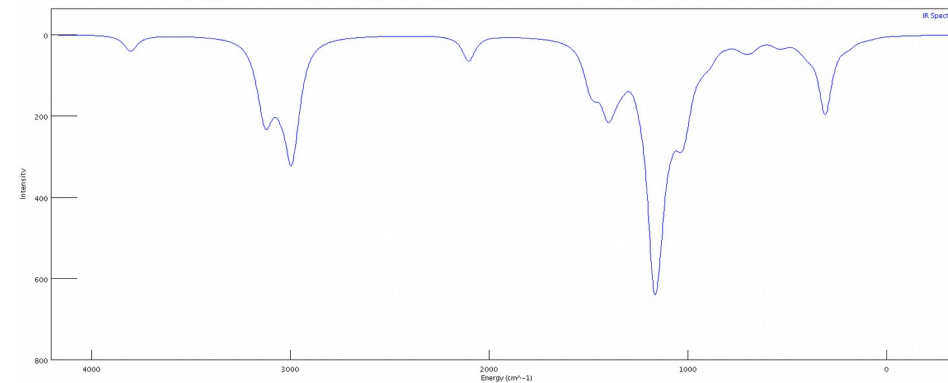**Different DFT methods differ in their treatment of V$_{xc}$**
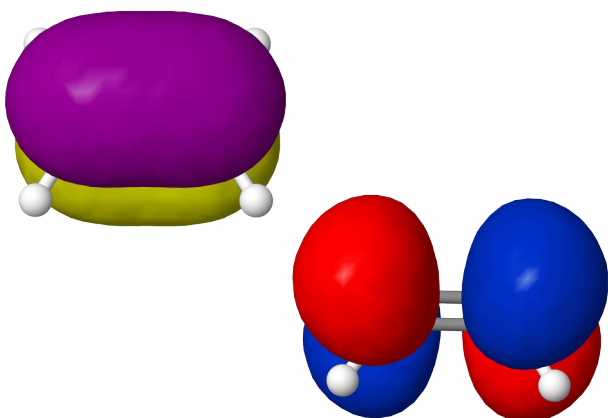
PBE0
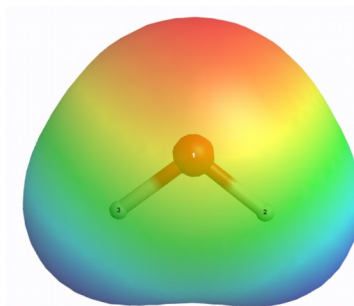
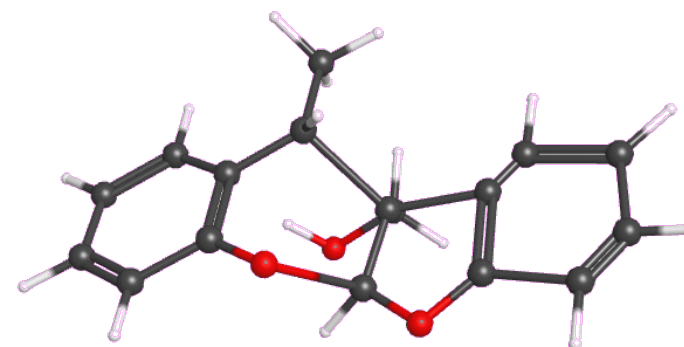**B3LYP**

FEATURES

Partial Charge
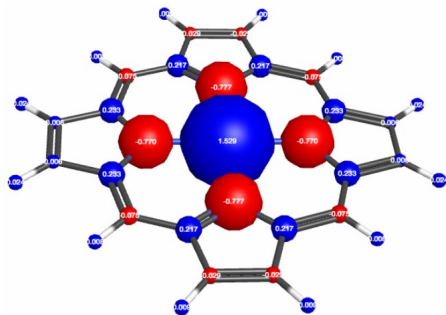
Symmetry
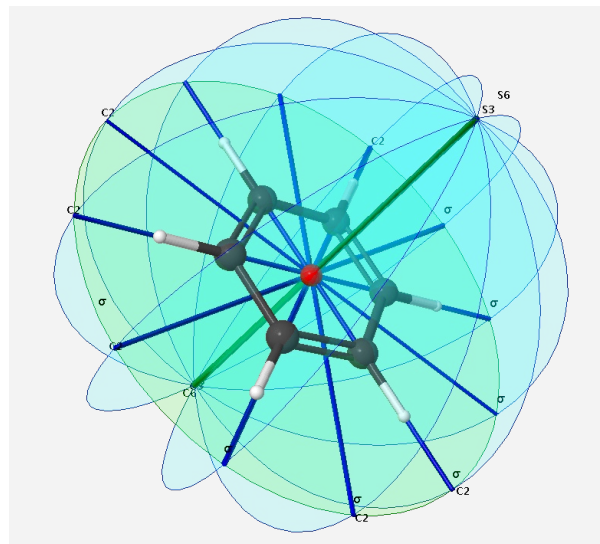
Spectra

MOs

ESP

Normal Modes

WebMO: Introduction and Logging In

Choice of Web Browser:

Works with all the popular web browsers:

BESTEST!

LOGIN:

https://bu-webmo.bu.edu