

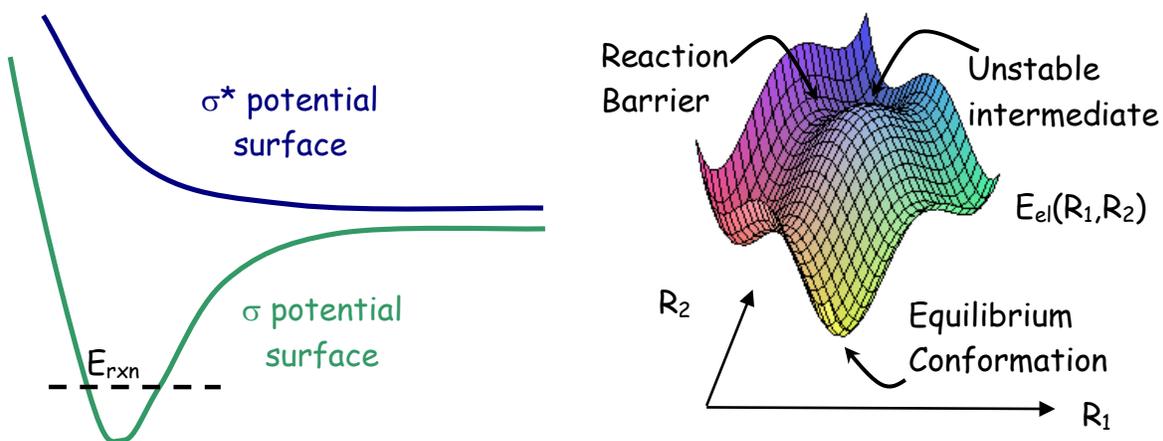
Born Oppenheimer Approximation:

$$\hat{H}_{el}(\mathbf{R})\Psi_{el}(\mathbf{r};\mathbf{R}) = E_{el}(\mathbf{R})\Psi_{el}(\mathbf{r};\mathbf{R})$$

For a molecule with N electrons and M nuclei:

$$\hat{H}_{el}$$

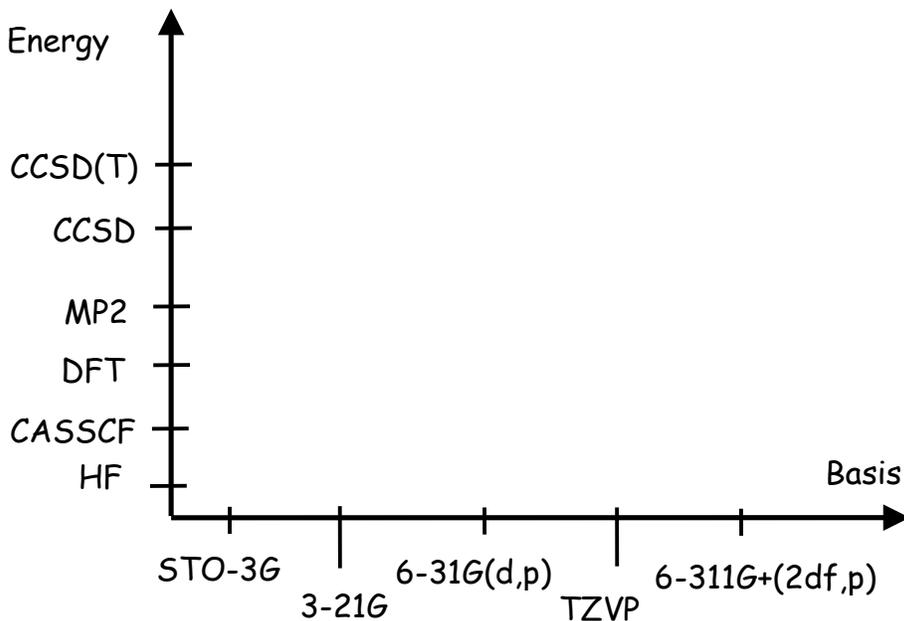
What is $E_{el}(\mathbf{R})$?



Electronic Structure Problem: How can we accurately solve for E_{el} and Ψ_{el} for an arbitrary molecule?

Most modern approximations follow the MO outline:

- 1) Choose an Atomic Orbital Basis
- 2) Build the Relevant Matrices
- 3) Solve the Eigenvalue Problem
- 4) Occupy the orbitals based on a stick diagram
- 5) Compute the energy



Step 1: Choosing an AO basis

For H_2^+ : $\psi = c_1 1s_A + c_2 1s_B$

Basis Set: A pre-defined set of AO basis functions for each atom (or at least most atoms) in the periodic table

<u>Type</u>	H,He	Li-Ne	Na-Ar	<u>Names</u>
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Concept 1: Single, Double, Triple ... Zeta

Concept 2: Polarization Functions

Concept 3: Diffuse FunctionsAside: Transition Metals

Note: Valence is ambiguous for most transition metals (4s4p3d? 4s3d?) and so the number of functions in DZ/TZ/QZ basis sets will vary slightly.

	K-Ca	Sc-Zn	Ga-Kr
3-21G	5s4p	5s4p2d	5s4p1d
6-31G(d,p)	5s4p1d	5s4p2d1f	N/A
6-311G(d,p)	8s7p2d	N/A	8s7p3d
TZV	6s3p	6s3p2d	6s5p2d

For 2nd and 3rd transition series, core electrons are moving at relativistic velocities → freeze core and replace with an effective core potential (ECP). An ECP thus requires a specification of which electrons are frozen and the *valence* AOs. Examples:

	Y-Cd	Hf-Hg
LANL2DZ	[Argon]/3s3p2d	N/A
SDD	[Argon]/8s7p6d	[Kr4d ¹⁰ 4f ¹⁴]/8s7p6d

Complete Basis Set (CBS) limit: the result that would (hypothetically) be obtained with an infinite number of AOs.

Methods for Computing the Energy

Hartree Fock

$$E_{IPM} = \sum_{\mu=1}^N E_{\mu} + \sum_{\mu < \nu}^N \tilde{J}_{\mu\nu} - \tilde{K}_{\mu\nu}$$

$$E_{\mu} = \int \psi_{\mu}(1) \hat{H}_0 \psi_{\mu}(1) d\tau$$

$$\tilde{J}_{\mu\nu} \equiv \iint \psi_{\mu}^*(1) \psi_{\nu}^*(2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{\mu}(1) \psi_{\nu}(2) d\mathbf{r}_1 d\mathbf{r}_2 d\sigma_1 d\sigma_2$$

$$\tilde{K}_{\mu\nu} \equiv \iint \psi_{\mu}^*(1) \psi_{\nu}^*(2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{\mu}(2) \psi_{\nu}(1) d\mathbf{r}_1 d\mathbf{r}_2 d\sigma_1 d\sigma_2$$

Perturbation Theory

$$\hat{H} = \hat{H}_{HF} + (\hat{H} - \hat{H}_{HF}) \equiv \hat{H}^{(0)} + \hat{H}^{(1)}$$

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots$$

Accuracy and Feasibility

Property	HF	MP2		

What is the largest molecule I do this for?

Memory (RAM) Required

CPU Time Required

Resource	HF	MP2	
Storage			
CPU Time			
Maximum Feasible N			
Maximum Feasible Atoms			

Density Functional Theory

For a Slater Determinant, electron density is:

$$\rho(\mathbf{r}) = \sum_{\mu=1}^N |\psi_{\mu}(\mathbf{r})|^2$$

Theorem: There exists a functional $E_v[\rho]$ such that, given the ground state density, ρ_0 , $E_v[\rho_0]=E_0$ where E_0 is the **exact ground state energy**. Further, for any density, ρ' , that is not the ground state density, $E_v[\rho']>E_0$.

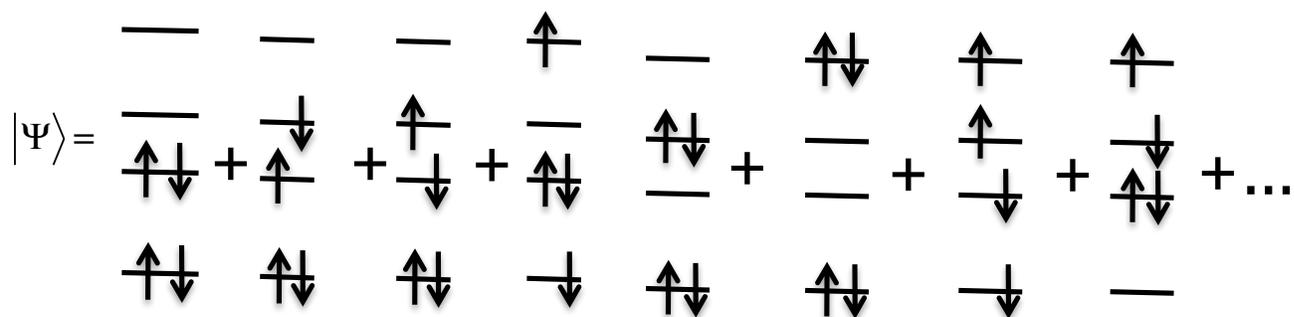
Wave Function Approximations

$$\Psi_{HF} \neq \Psi_{exact} \qquad E_{HF} \neq E_{exact}$$

$$E_{corr} = E_{exact} - E_{HF} .$$

Configuration Interaction (CI)

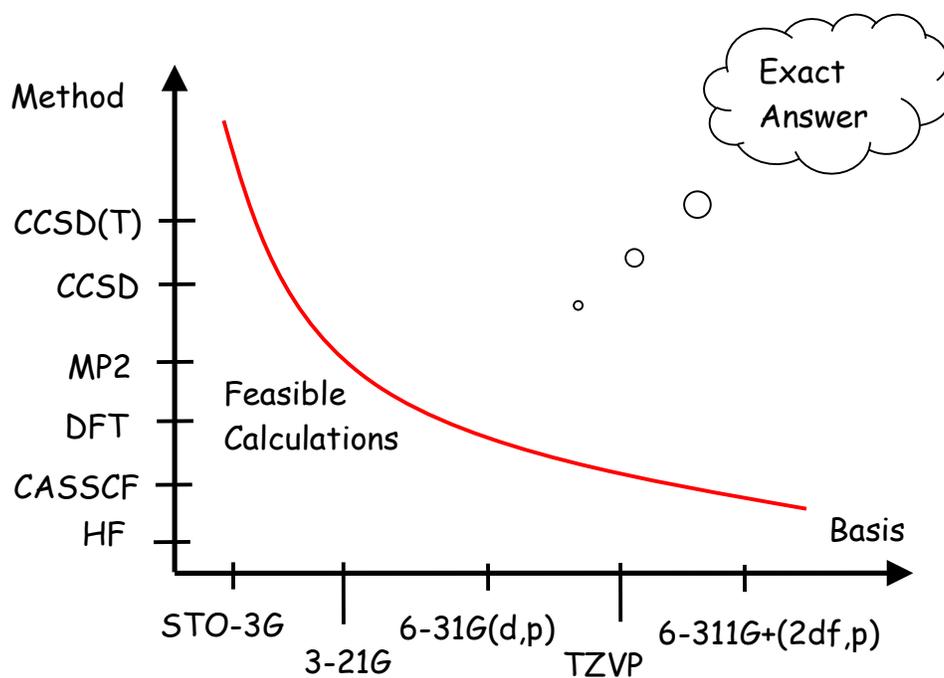
$$\Psi(1,2,3,\dots) = \sum_{p<q<r<\dots} C_{pqr\dots} \begin{vmatrix} \psi_p(1) & \psi_q(1) & \psi_r(1) & \dots \\ \psi_p(2) & \psi_q(2) & \psi_r(2) & \\ \psi_p(3) & \psi_q(3) & \psi_r(3) & \\ \vdots & & & \ddots \end{vmatrix}$$



Coupled Cluster (CC)

$$\begin{aligned} \Psi_{CISD} &= \Psi_{HF} + \hat{T}_S \Psi_{HF} + \hat{T}_D \Psi_{HF} = (1 + \hat{T}_S + \hat{T}_D) \Psi_{HF} \\ &\equiv (1 + \hat{T}) \Psi_{HF} \end{aligned}$$

$$\begin{aligned}\Psi_{CCSD} &= e^{\hat{T}} \Psi_{HF} \\ &= \Psi_{HF} + \hat{T} \Psi_{HF} + \frac{1}{2} \hat{T}^2 \Psi_{HF} + \dots\end{aligned}$$



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