

# General Introduction to Electronic Structure Theory

C. David Sherrill

*School of Chemistry and Biochemistry  
Georgia Institute of Technology*

# Origins of Mathematical Modeling in Chemistry

- ◆ Plato (ca. 428-347 BC): The world around us is made of imperfect shadows of the perfect forms constituting the ultimate reality
- ◆ “We may even judge the degree of perfection to which a science has arrived by the facility with which it may be submitted to calculation.”  
A. Quetelet, 1828

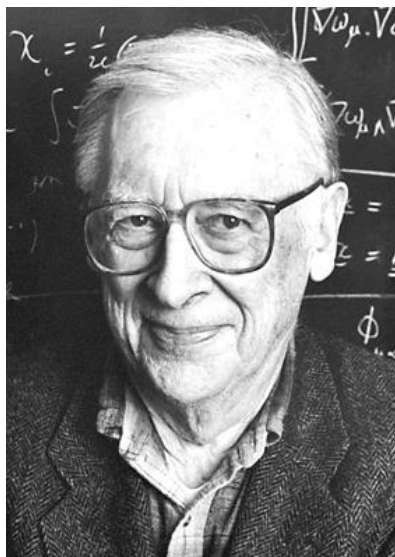
# Robert S. Mulliken

## 1966 Nobel Prize in Chemistry



“...the era of computing chemists, when hundreds if not thousands of chemists will go to the computing machine instead of the laboratory...is already at hand. There is only one obstacle, namely, that someone must pay for the computing time.”

# John Pople and Walter Kohn 1998 Nobel Prize in Chemistry



“for his development of computational methods in quantum chemistry”



“for his development of the density-functional theory”

# 2013 Nobel Prize in Chemistry



Martin Karplus



Michael Levitt



Arieh Warshel

“for the development of multiscale models for complex chemical systems”

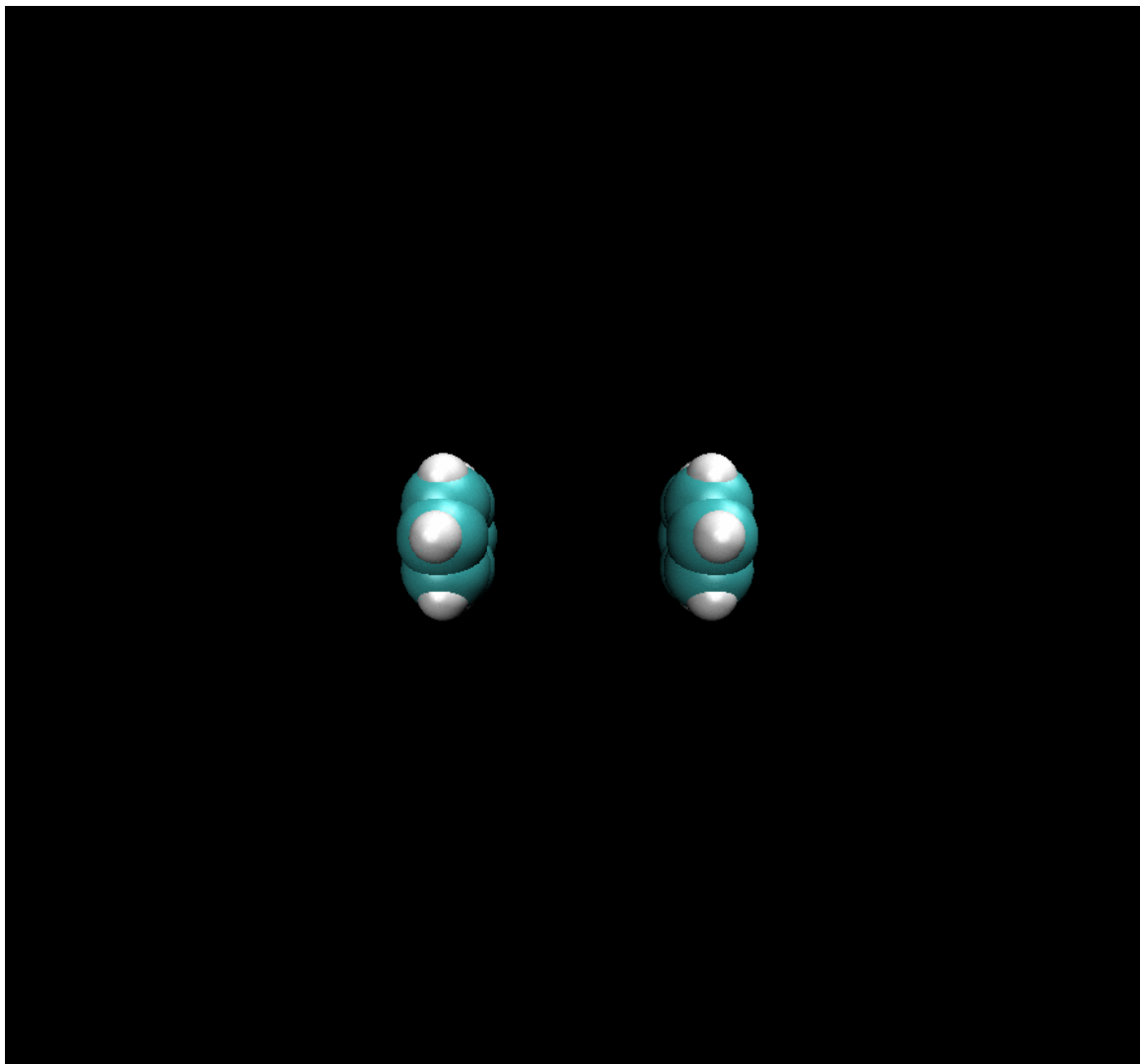
# Branches of Theoretical Chemistry

- ◆ Electronic Structure Theory / Quantum Chemistry: Solve for motions of electrons in molecules; provides static properties of individual molecules and potential energy surfaces
- ◆ Dynamics: Solve for motions of molecules on a (quantum or classical) potential energy surface; provides reaction rates
- ◆ Statistical Mechanics: Solve for bulk properties from properties of individual molecules

# Quantum vs Classical Methods

| Quantum  | Classical  |
|--|--|
| More accurate (typically)  | Less accurate (typically)                                |
| Equations more complicated   | Equations less complicated                               |
| Computationally very expensive (can't typically do dynamics with it)                               | Computationally less expensive (can do dynamics with it) |
| Can describe motions of electrons: necessary for UV/vis spectra, electron transfer reactions, etc. | Can't easily describe motions of electrons               |
| Involves no empirical parameters ("ab initio" method) or only a few                                | Involves many empirical parameters                       |

# Molecular Dynamics Example



See <http://vergil.chemistry.gatech.edu/grafx/bz2-md.gif>



# Uses of Electronic Structure Theory

- ◆ Equilibrium geometries (microwave spectra)
- ◆ Vibrational frequencies (IR spectra)
- ◆ Excited states (UV/VIS spectra)
- ◆ NMR spectra
- ◆ CD spectra
- ◆ Dipole moment, polarizability, etc.
- ◆ Barrier heights and reaction paths
- ◆ With transition state theory or dynamics studies, can estimate reaction rates
- ◆ With statistical mechanics, can estimate thermodynamics properties

# The One Equation for a QM Description of a Molecule: $H\Psi = E\Psi$

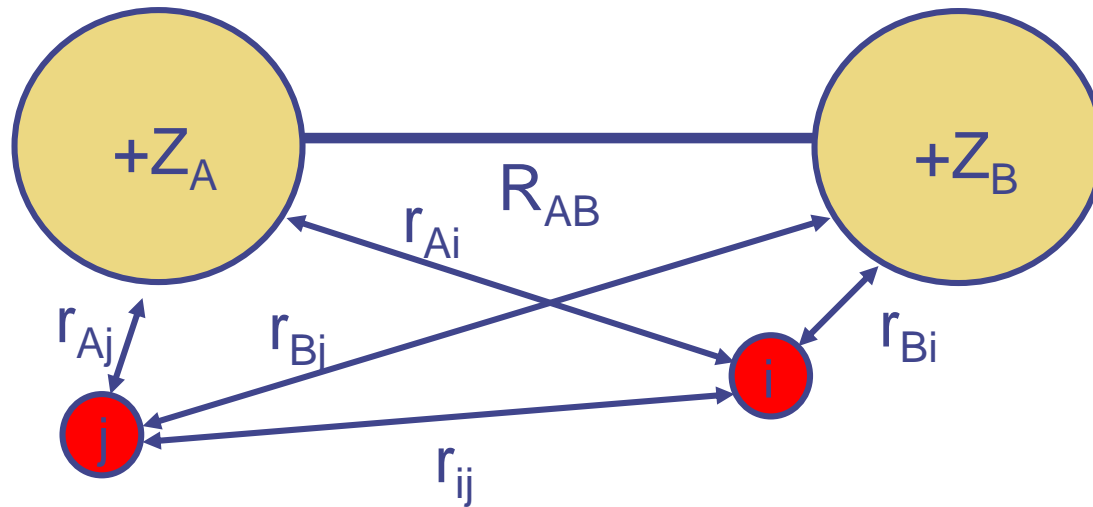
“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble” ---P.A.M. Dirac, *Proc. Roy. Soc. (London)* **123**, 714 (1929)

# The Schrödinger Equation for Molecules

$$\hat{H}\Psi = E\Psi$$

$$\Psi = \Psi(x_1, y_1, z_1, \omega_1, x_2, y_2, z_2, \omega_2, \dots)$$

# The Molecular Hamiltonian



$$\hat{H} = - \sum_A^{\text{nuc}} \frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2m} \sum_i^{\text{elec}} \nabla_i^2 - \sum_A^{\text{nuc}} \sum_i^{\text{elec}} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B}^{\text{nuc}} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} + \sum_{i>j}^{\text{elec}} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

Nuclear  
kinetic E

Electronic  
kinetic E

Electron/nuc  
attraction

Nuc/nuc  
repulsion

Elec/elec  
repulsion

# Simplified Notation

◆ In atomic units, the Hamiltonian goes from

$$\hat{H} = - \sum_A^{\text{nuc}} \frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2m} \sum_i^{\text{elec}} \nabla_i^2 - \sum_A^{\text{nuc}} \sum_i^{\text{elec}} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B}^{\text{nuc}} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} + \sum_{i>j}^{\text{elec}} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

to

$$\hat{H} = - \sum_A^{\text{nuc}} \frac{1}{2M_A} \nabla_A^2 - \frac{1}{2} \sum_i^{\text{elec}} \nabla_i^2 - \sum_A^{\text{nuc}} \sum_i^{\text{elec}} \frac{Z_A}{r_{Ai}} + \sum_{A>B}^{\text{nuc}} \frac{Z_A Z_B}{R_{AB}} + \sum_{i>j}^{\text{elec}} \frac{1}{r_{ij}}$$

◆ Shorthand:

$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R}) + V_{NN}(\mathbf{R}) + V_{ee}(\mathbf{r})$$

# Born-Oppenheimer Approximation

- ◆ Nuclei are much more massive than electrons ( $\sim 2,000:1$  or more)
- ◆ Electron motions much faster than nuclear motions
- ◆ To a first approximation, assume electrons move “instantly” compared to nuclei. Equivalently, nuclei frozen compared to electrons



Max Born



J. Robert Oppenheimer

# Born-Oppenheimer Mathematics

$$\hat{H} = \cancel{\hat{T}_N(\mathbf{R})} + \hat{T}_e(\mathbf{r}) + V_{eN}(\mathbf{r}; \mathbf{R}) + V_{NN}(\mathbf{R}) + V_{ee}(\mathbf{r})$$

- Solve for the motions of the electrons by (temporarily) freezing the nuclei at some positions given by vector  $\mathbf{R}$
- Nuclear coordinates  $\mathbf{R}$  become fixed parameters;  $V_{eN}$  now depends only parametrically on  $\mathbf{R}$  [denote this  $V_{eN}(\mathbf{r}; \mathbf{R})$ ]. We ignore  $T_N(\mathbf{R})$  for now because electronic wavefunction should depend only weakly on  $\mathbf{R}$
- This results in the *electronic* Hamiltonian and the *electronic* Schrödinger equation, which we solve for the *electronic* energy and the *electronic* wavefunction

$$\hat{H}_{el} = \hat{T}_e(\mathbf{r}) + V_{eN}(\mathbf{r}; \mathbf{R}) + V_{NN}(\mathbf{R}) + V_{ee}(\mathbf{r})$$

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

# The Nuclear Repulsion Energy

$$V_{NN}(\mathbf{R})$$

- With respect to electronic motions, this is a *constant*
- What happens when we add a constant to the Hamiltonian?
- The eigenfunctions stay the same. The eigenvalues are shifted by the value of the constant

$$\hat{H}\Psi_i = E_i\Psi_i$$

$$(\hat{H} + c)\Psi_i = \hat{H}\Psi_i + c\Psi_i$$

$$= E\Psi_i + c\Psi_i$$

$$= (E + c)\Psi_i$$



# The Nuclear Repulsion Energy

$$V_{NN}(\mathbf{R})$$

- Sensitive to molecular geometry ... good diagnostic to ensure two geometries are identical (should be able to compare to 1E-6 or better so long as the same angstrom to Bohr conversion factor used, etc.)
- Doesn't involve electrons, so a bit strange to include in the electronic Schrödinger equation, but it's traditional to do so

# Born-Oppenheimer Mathematics

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

Electronic Schrödinger equation

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_k \underbrace{\Psi_k(\mathbf{r}; \mathbf{R})}_{\text{electronic}} \underbrace{\chi_k(\mathbf{R})}_{\text{nuclear}}$$

Insert this expansion into the full Schrödinger equation, and  
After a few steps...

zero for real wavefunctions

$$\left[ \hat{T}_N(\mathbf{R}) + \cancel{\hat{T}'_{kk}(\mathbf{R})} + T''_{kk}(\mathbf{R}) + E_{el}(\mathbf{R}) - E \right] \chi_k(\mathbf{R}) =$$
$$- \sum_{\cancel{k' \neq k}} \left[ \cancel{\hat{T}'_{kk'}(\mathbf{R})} + \cancel{T''_{kk'}(\mathbf{R})} \right] \chi_{k'}(\mathbf{R})$$

usually very small

# Born-Oppenheimer Mathematics

Rearrange the last result to obtain

$$\left[ \hat{T}_N(\mathbf{R}) + T''_{kk}(\mathbf{R}) + E_{el}(\mathbf{R}) \right] \chi_k(\mathbf{R}) = E \chi_k(\mathbf{R})$$

Kinetic

Potential

- ◆ This is a Schrödinger equation for the nuclei!
- ◆ The term  $T''_{kk}(\mathbf{R})$  is small and usually neglected
- ◆ The electronic energy  $E_{el}(\mathbf{R})$  plays the role of the potential felt by the nuclei!

# Born-Oppenheimer Corrections

$$\left[ \hat{T}_N(\mathbf{R}) + T''_{kk}(\mathbf{R}) + E_{el}(\mathbf{R}) \right] \chi_k(\mathbf{R}) = E \chi_k(\mathbf{R})$$



DBOC = Diagonal Born-Oppenheimer Correction  
(also called “adiabatic correction”)

$$\begin{aligned} T''_{kk}(\mathbf{R}) &= \sum_A^{\text{nuc}} -\frac{1}{2M_A} \langle \Psi(\mathbf{r}; \mathbf{R}) | \nabla_A^2 | \Psi(\mathbf{r}; \mathbf{R}) \rangle \\ &= \sum_A^{\text{nuc}} \frac{1}{2M_A} \left\langle \frac{\partial \Psi(\mathbf{r}; \mathbf{R})}{\partial R_A} \middle| \frac{\partial \Psi(\mathbf{r}; \mathbf{R})}{\partial R_A} \right\rangle \end{aligned}$$

DBOC correction to barrier to  
linearity in H<sub>2</sub>O (cm<sup>-1</sup>)

---

|              | bent | linear | $\Delta E$ |
|--------------|------|--------|------------|
| CISD/cc-pVTZ | 612  | 597    | -15        |

E. F. Valeev and C. D. Sherrill, *J. Chem. Phys.*  
**118**, 3921 (2003)

# Born-Oppenheimer Corrections

Adiabatic corrections to bond length and harmonic vibrational frequencies of some diatomic molecules

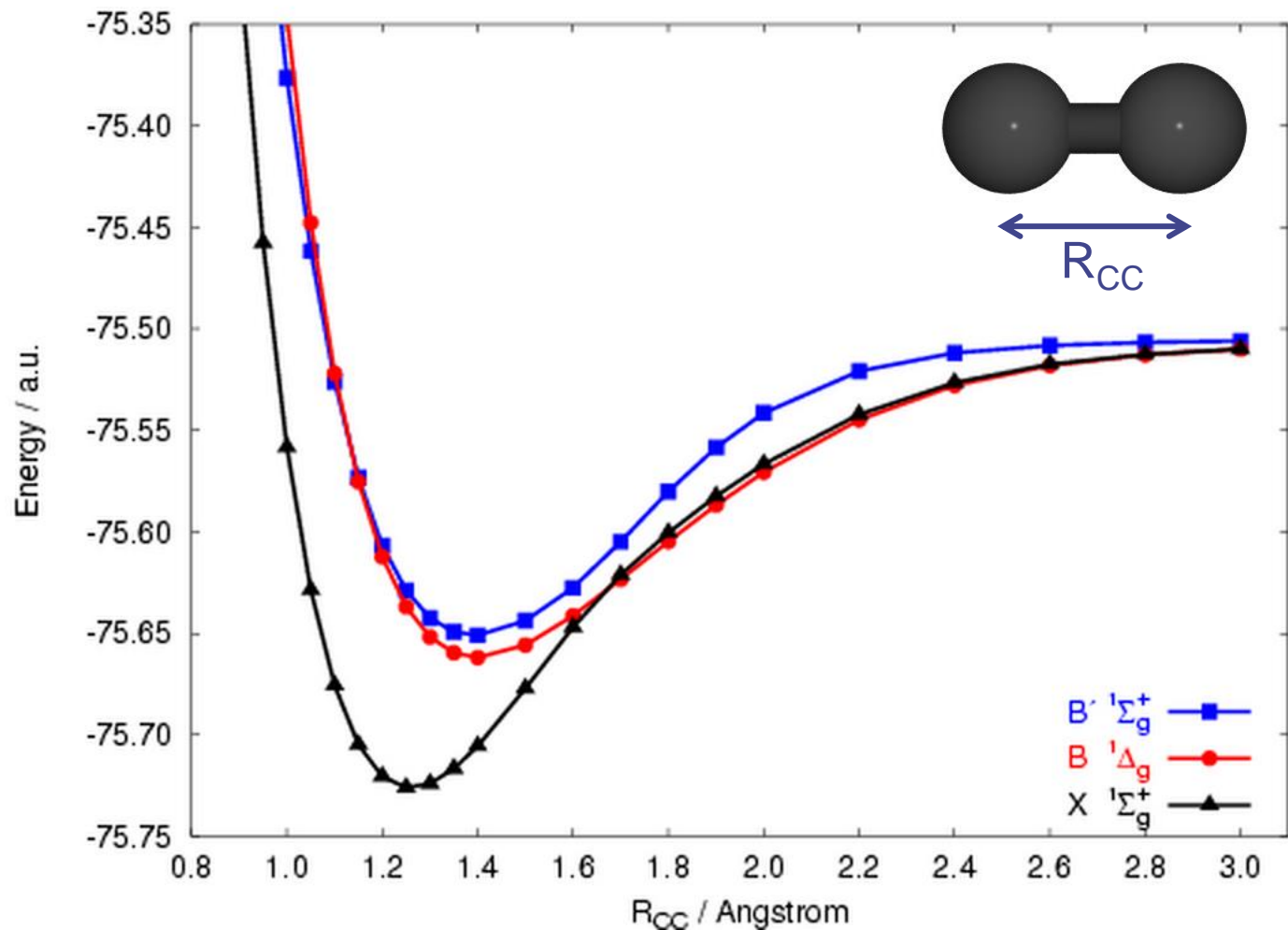
|                                       | BH      | CH <sup>+</sup> | NH      |
|---------------------------------------|---------|-----------------|---------|
| $\Delta r_e$ (Å)                      | 0.00066 | 0.00063         | 0.00027 |
| $\Delta \omega_e$ (cm <sup>-1</sup> ) | -2.25   | -2.81           | -1.38   |

B. Temelso, E. F. Valeev and C. D. Sherrill, *J. Phys. Chem. A* **108**, 3068-3075 (2004)

# Potential Energy Surfaces

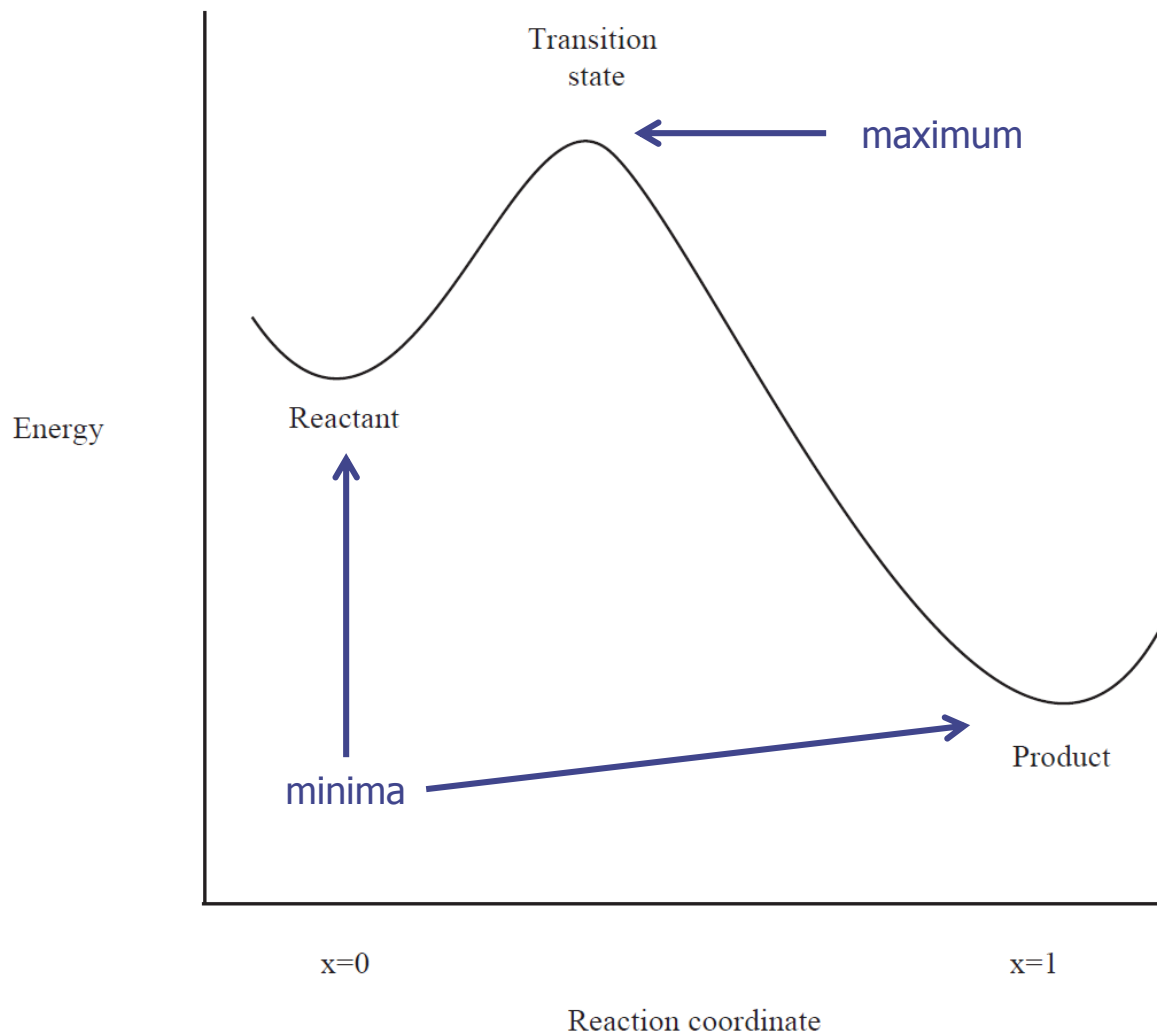
- The electronic energy,  $E_{el}(\mathbf{R})$ , is the potential that the nuclei feel. This depends on the nuclear coordinates  $\mathbf{R}$ , and is called the *potential energy surface (PES)*
- The electronic energy for an individual molecule shouldn't change if we translate or rotate the molecule --- it only depends on the internal degrees of freedom
- Each molecule has three translational degrees of freedom, and usually three rotational degrees of freedom (2 for linear molecules)
- For  $N$  atoms, there are  $3N-6$  of internal (vibrational) coordinates ( $3N-5$  for a linear molecule)
- The potential energy surface is a function of  $3N-6$  coordinates

# Potential Energy Surface for C<sub>2</sub>



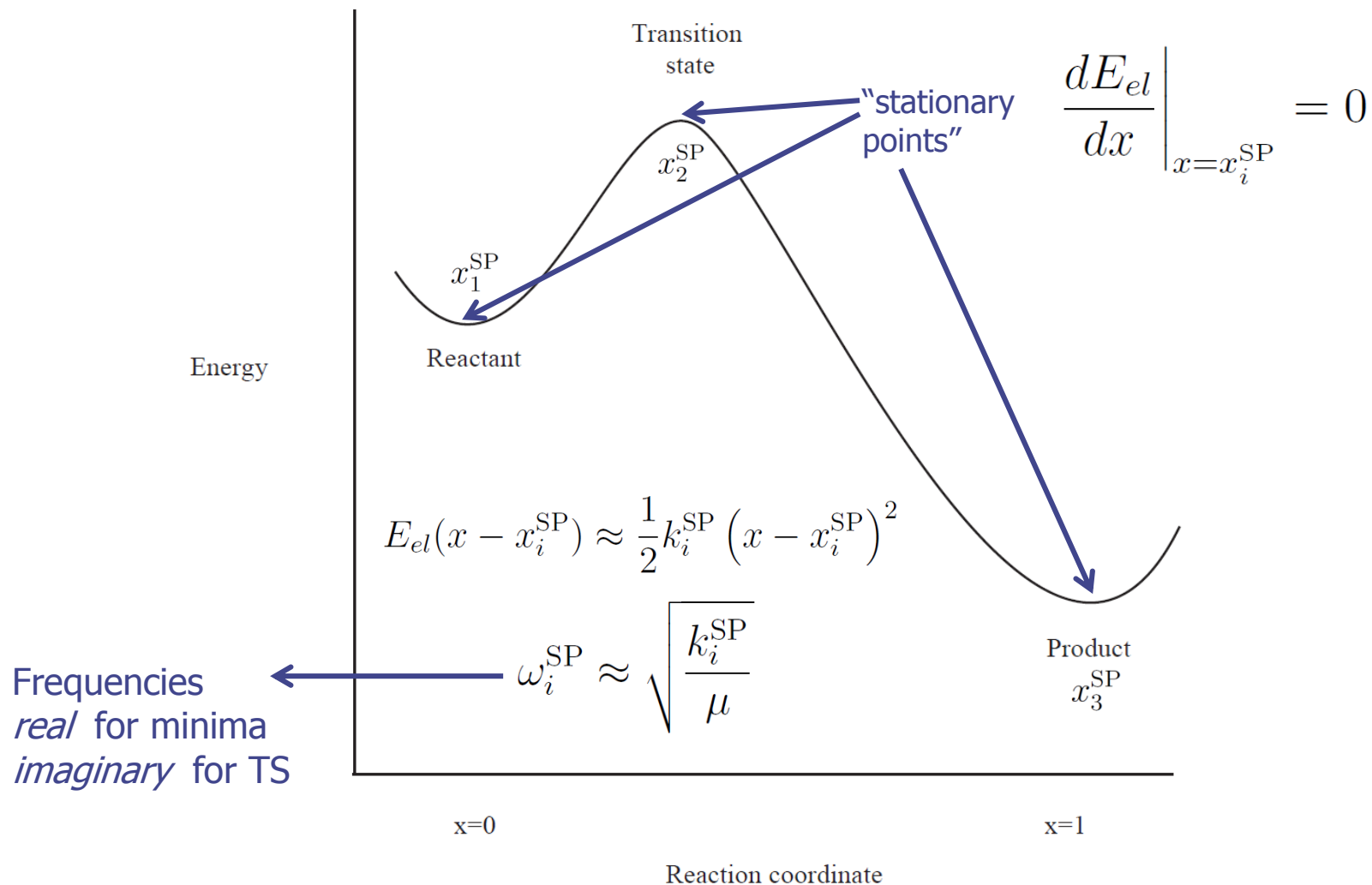
M. L. Abrams and C. D. Sherrill, *J. Chem. Phys.* **121**, 9211-9219 (2004)

# Potential Energy Surface Topology

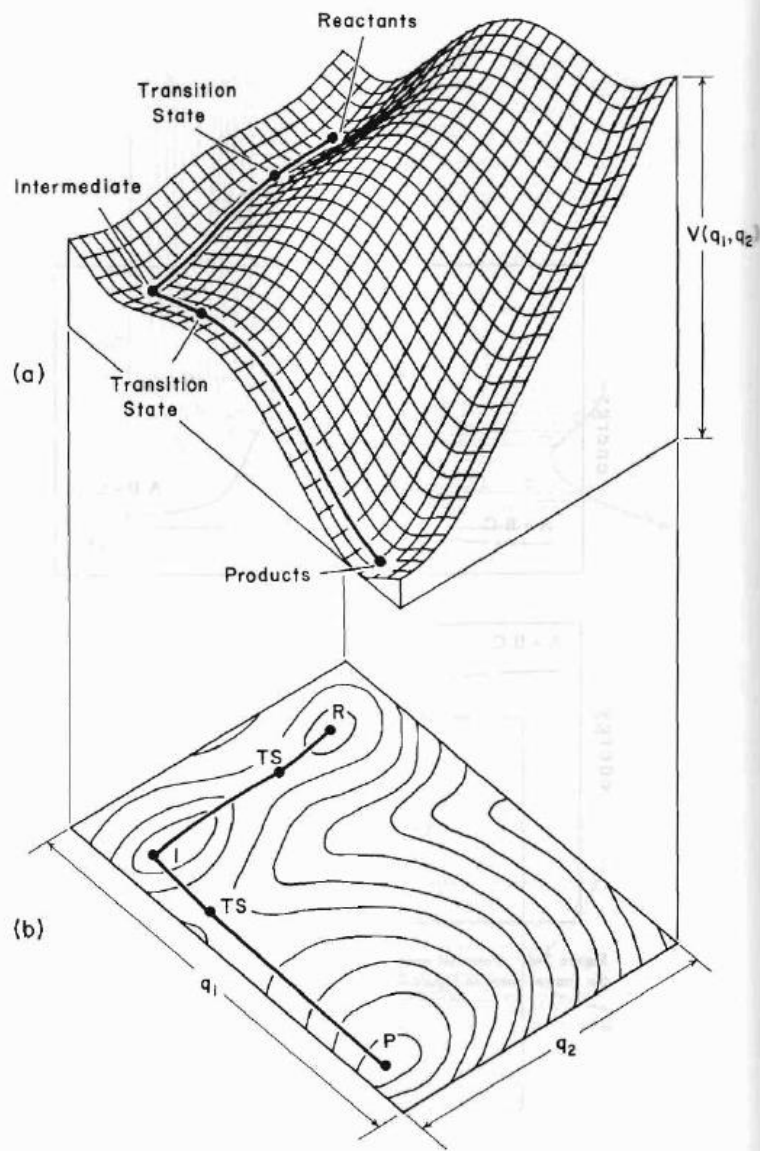




# Potential Energy Surface Topology



# Multi-Dimensional Example



- A multidimensional PES can support multiple minima and TS's
- Ideal reaction path is a "minimum energy path" following the valleys; can trace this out using Intrinsic Reaction Coordinate (IRC) analysis
- TS is a max in only one dimension; min in all other dimensions

# Types of Stationary Points

- **Minima:** minimum in all dimensions; all vibrational frequencies are real. Correspond to stable or quasi-stable species; i.e., reactants, products, and intermediates
- **Transition states:** minimum in all dimensions but one, maximum in the remaining dimension; exactly one imaginary vibrational frequency. Corresponds to a maximum (barrier) on the minimum energy path between reactants and products
- **Higher-order saddle point:** minimum in all dimensions but  $n$ , where  $n > 1$ , maximum in all other dimensions;  $n$  imaginary vibrational frequencies. No real chemical significance (higher-energy parts of PES)
- **Hessian Index:** the number of imaginary vibrational frequencies for a stationary point. Should be 0 for a minimum, 1 for a TS,  $> 1$  for a higher-order saddle point.

# First Things First!

- ◆ Invoke the Born-Oppenheimer approximation
- ◆ Solve the Electronic Schrödinger Equation to get the potential energy surface,

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

- ◆ ... and then solve for the nuclear motion by quantum or classical means!
- ◆ *The Electronic Schrödinger Equation is the equation that Quantum Chemistry seeks to solve!*

# How do we solve the Electronic Schrödinger Equation?

- ◆ Hartree: Try a product of orbitals!
- ◆ Actually need to include a “spin coordinate”  $\omega$  in addition to spatial coordinates



Douglas Hartree

$$\Psi_{HP}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \cdots \phi_N(\mathbf{r}_N) \quad \mathbf{r} = \{x, y, z\}$$

$$\Psi_{HP}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \cdots \chi_N(\mathbf{x}_N) \quad \mathbf{x} = \{\mathbf{r}, \omega\}$$

# Problem with the Hartree Product

- ◆ Electrons are supposed to be mathematically indistinguishable
- ◆ Wavefunction is supposed to change sign upon interchange of two sets of electron coordinates

$$\Psi_{HP}(\mathbf{x}_1, \mathbf{x}_2) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)$$

$$\Psi_{HP}(\mathbf{x}_2, \mathbf{x}_1) = \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1)$$

$$\Psi_{HP}(\mathbf{x}_1, \mathbf{x}_2) \neq \Psi_{HP}(\mathbf{x}_2, \mathbf{x}_1)$$

# A Brute-Force Solution

- ◆ *Make* the wavefunction antisymmetric by construction

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1)]$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1)$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix}$$

# The Slater Determinant

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$



John Slater

Shorthand:  $|\chi_i \chi_j \cdots \chi_k\rangle$  or  $|ij \cdots k\rangle$

Enforces an antisymmetric wavefunction. Excellent!  
.... But....where do we get the orbitals from??



# The Variational Theorem

- ◆ The expectation value of the energy is always greater than or equal to the true energy

$$\begin{aligned} E_{el}(\mathbf{R}) &= \langle \Psi(\mathbf{r}; \mathbf{R}) | \hat{H}_{el} | \Psi(\mathbf{r}; \mathbf{R}) \rangle \\ &= \int_{-\infty}^{\infty} d\mathbf{r} \Psi^*(\mathbf{r}; \mathbf{R}) \hat{H}_{el} \Psi(\mathbf{r}; \mathbf{R}) \\ &\geq \mathcal{E}_0 \end{aligned}$$

- ◆ ...so, vary the orbitals until the energy is a minimum!

# Hartree-Fock Molecular Orbital Theory

- ◆ 1. Invoke the Born-Oppenheimer approximation
- ◆ 2. Express the electronic wavefunction as a single Slater Determinant
- ◆ 3. Solve for those orbitals which minimize the electronic energy (variational method)
- ◆ This winds up being mathematically equivalent to assuming *each electron interacts only with the average charge cloud of the other electrons*



Douglas Hartree



V. A. Fock

# Introduction of a Basis Set

$$\underset{\substack{\uparrow \\ \text{orbital}}}{\chi_i} = \sum_{\mu=1}^K C_{\mu i} \underset{\substack{\uparrow \\ \text{basis function}}}{\tilde{\chi}_\mu}$$

- ◆ The Hartree-Fock equations (and other equations in quantum chemistry) are easier to solve if we write each orbital as a linear combination of fixed basis functions
- ◆ In Hartree-Fock this is called the Linear Combination of Atomic Orbitals Molecular Orbital (LCAO-MO) theory
- ◆ The basis functions are usually plane waves (physicists) or atom-centered Gaussian functions (chemists)



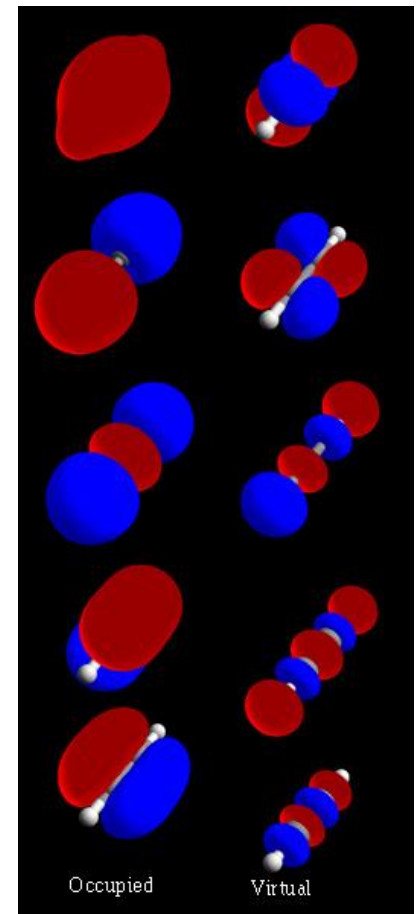
Clemens C. J. Roothan

# Semi-Empirical Methods

- ◆ Speeds up Hartree-Fock by replacing some of the two-electron integrals by empirical parameters
- ◆ Examples: MNDO, AM1, PM3
- ◆ Rotational barriers around partial double bonds too low, weakly bound complexes poorly predicted, parameters not always available (e.g., metals)

# Beyond Hartree-Fock

- ◆ Hartree-Fock is only an approximation
- ◆ Sources of error: (1) assumption of a single Slater determinant / assumption each electron only sees the average of the other electrons; (2) use of a finite basis set
- ◆ Address error (2) by using a series of larger basis sets
- ◆ Address error (1) by using Density Functional Theory or post-Hartree-Fock methods / electron correlation methods
- ◆ The error in the Hartree-Fock energy is called the *correlation energy*
- ◆ Hartree-Fock struggles for bond-breaking, diradicals, transition metals with unfilled *d*- or *f*-shells, excited states



MOs for HCCH

# Accuracy of Hartree-Fock

| Property                | Accuracy                            |
|-------------------------|-------------------------------------|
| Bond lengths            | $\pm 0.02 \text{ \AA}$              |
| Bond angles             | $\pm 2^\circ$                       |
| Vibrational frequencies | $\pm 11\%$                          |
| Dipole moments          | $\pm 0.3 \text{ D}$                 |
| Dissociation energies   | $\pm 25\text{-}40 \text{ kcal/mol}$ |

# Density Functional Theory (DFT)

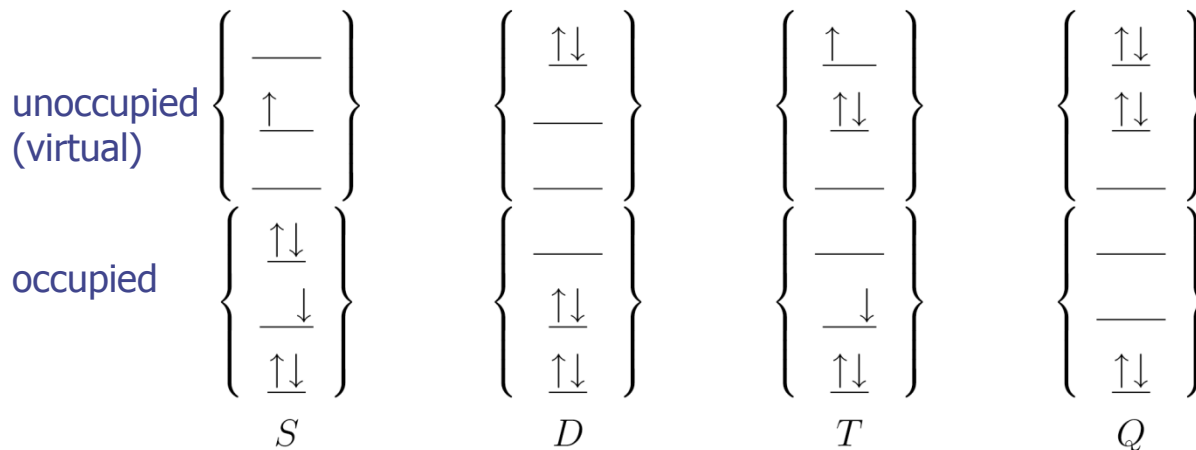
- ◆ Use the electron density as the fundamental quantity instead of complicated many-electron wavefunctions
- ◆ Variational: minimize the energy with respect to the density. Relationship of the energy to the density is the “functional”  $E[\rho]$
- ◆ The true functional is unknown, use various approximations
- ◆ Computational cost similar to Hartree-Fock if we use exact exchange; otherwise it's less expensive

# Wavefunction-Based Electron Correlation Methods

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum c_i^a|\Phi_i^a\rangle + \sum c_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \sum c_{ijk}^{abc}|\Phi_{ijk}^{abc}\rangle \dots$$

Reference                      Singles                      Doubles                      Triples                      ...

- ◆ Express the wavefunction as a linear combination of Slater determinants. The reference determinant is (usually) the Hartree-Fock determinant
- ◆ Typically generate the other determinants by substituting some number of occupied orbitals for (previously) unoccupied orbitals
- ◆ Most methods stop at single and double substitutions





# How Do We Get the Coefficients?

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum c_i^a|\Phi_i^a\rangle + \sum c_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \sum c_{ijk}^{abc}|\Phi_{ijk}^{abc}\rangle \dots$$

Reference                      Singles                      Doubles                      Triples                      ...

- ◆ Variationally: configuration interaction (CI). Including single and double substitutions gives CISD
- ◆ Perturbationally: Many-body perturbation theory (MBPT) = Møller-Plesset Perturbation theory (MPPT). Including double substitutions at first order gives the energy to second order and yields MP2
- ◆ Coupled-cluster theory (CC): sums certain terms through infinite order. Including singles and doubles gives CCSD. If we approximately include triples we get CCSD(T), the “gold standard” of quantum chemistry

# Computational Cost of Electronic Structure Methods

| Method               | Accuracy    | Max atoms* |
|----------------------|-------------|------------|
| Semiempirical        | Low         | ~4000      |
| Hartree-Fock         | Medium      | ~500       |
| (Standard) DFT       | Medium/High | ~500       |
| MP2                  | High        | ~100       |
| CISD                 | High        | ~30        |
| CCSD, CCSD(T)        | Very High   | ~30        |
| Multireference CI,CC | Ultra High  | ~10        |

\*larger systems are possible when using "local" approximations