Introduction to Computational Chemistry

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What is what? Who is who?

Reference:

Essentials of Computational Chemistry, Theories and Models

By

Christopher J. Cramer

Theory

- A theory is one or more rules that are postulated to govern the behavior of physical systems
- These rules are quantitative in nature and expressed in the form of a mathematical equation
- The quantitative nature of scientific theories allows them to be tested by experiment
- Are you familiar with BIG THEORIES?

How far a Theory Goes?

- If a sufficiently large number of interesting systems falls within the range of the theory, practical reasons tend to motivate its continued use.
- Which examples do you know for the above mentioned statement?

Rule

- Occasionally, a theory has proven so robust over time, even if only within a limited range of applicability, that it is called a ***law***
- Which one is a law?

  Coulomb Law

  Huckel Rule
- Which ***laws*** you know?

Model

- A model, on the other hand, typically involves the deliberate introduction of simplifying approximations into a more general theory so as to extend its practical utility.
- Another feature sometimes characteristic of a *quantitative* model is that it incorporates certain constants that are empirically determined
- How many models in chemistry you know?
- What is the ***golden rule*** for successful application of a model?

Computation

- Computation is the use of digital technology to solve the mathematical equations defining a particular theory or model
- In general three groups of people can be listed as “Computational Chemists”. Usually they collaborate together and their disciplines overlap to a great extent
- Do you know who they are?

Who Are You?

- ***Theorists*** tend to have as their greatest goal the development of new theories and/or models that have improved performance or generality over existing ones

- Researchers involved in ***molecular modeling*** tend to focus on target systems having particular chemical relevance (e.g., for economic reasons) and to be willing to sacrifice a certain amount of theoretical rigor in favor of getting the right answer in an efficient manner.

- ***Computational chemists*** may devote themselves not to chemical aspects of the problem, *per se*, but to computer-related aspects, e.g., writing improved algorithms for solving particularly difficult equations, or developing new ways to encode or visualize data, either as input to or output from a model

Our Sacred Temple; Quantum Mechanics

- The ultimate goal of a computational chemist is to extract all information about his/her model system purely from high-level quantum mechanic computations
- Among several version of quantum mechanics, wave equation introduced by Erwin Schrödinger is the preferred version among chemists.

Schrödinger Equation

- Time dependent non-relativistic Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[\frac{-\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r},t)\right]\Psi(\mathbf{r},t)$$

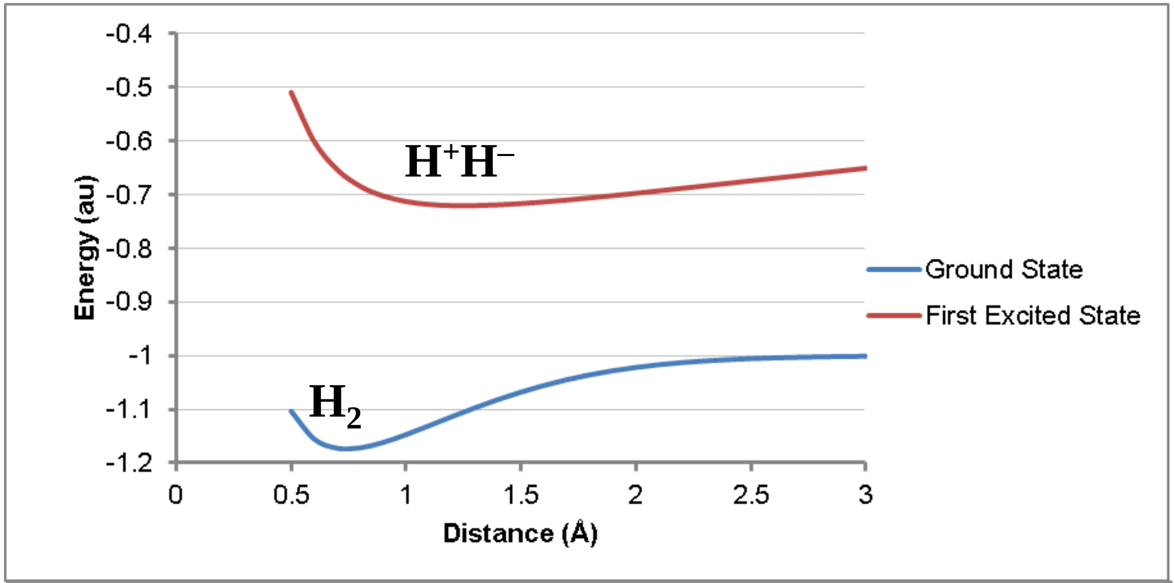
- Time independent non-relativistic Schrödinger equation

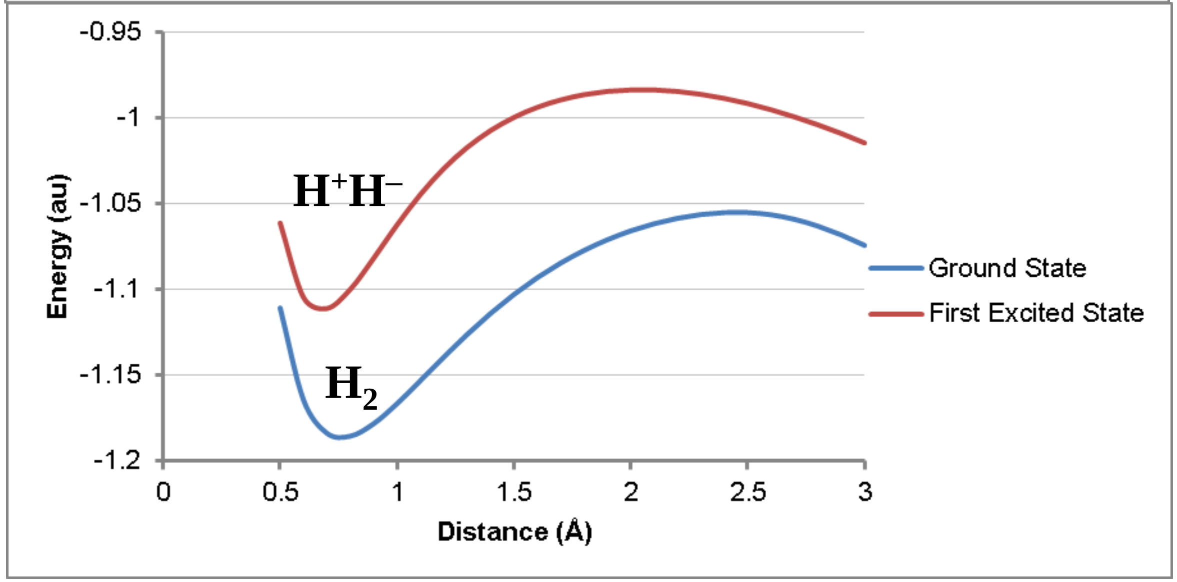
$$E\Psi(\mathbf{r}) = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r})$$

What a Computational Chemist Can Do?

- Schrödinger equation provides us information about “Energy” of a system. All molecular properties that are related to energy are within the realm of computational chemistry.
- **Which properties of matter are related to the energy?**

Potential Energy (Hyper)-Surface



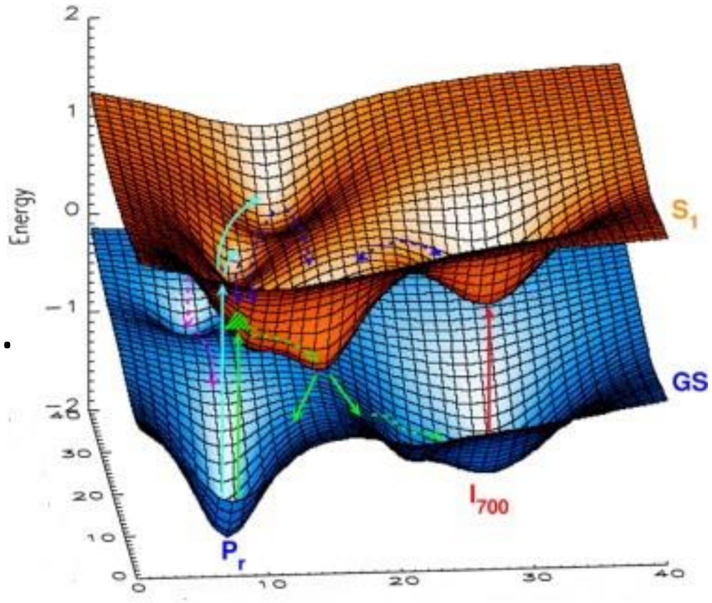


Potential Energy (Hyper)-Surface

PES is a hyper-surface defined by the potential energy of a group of atoms in a particular electronic state over all possible atomic arrangements.

Every atom in space has 3 degrees of freedom, corresponding to three dimensions.

An N-atomic molecule has 3N–6 (3N–5 for linear systems) internal degrees of freedom beside 3 degrees of rotational as well as 3 degrees of translational freedom. PES of a molecule denotes variation of energy by changing the degrees of freedom of that molecule.



Stationary Points on a PES

- An Stationary Point is a point at which

$$\frac{\partial E}{\partial x} = 0$$

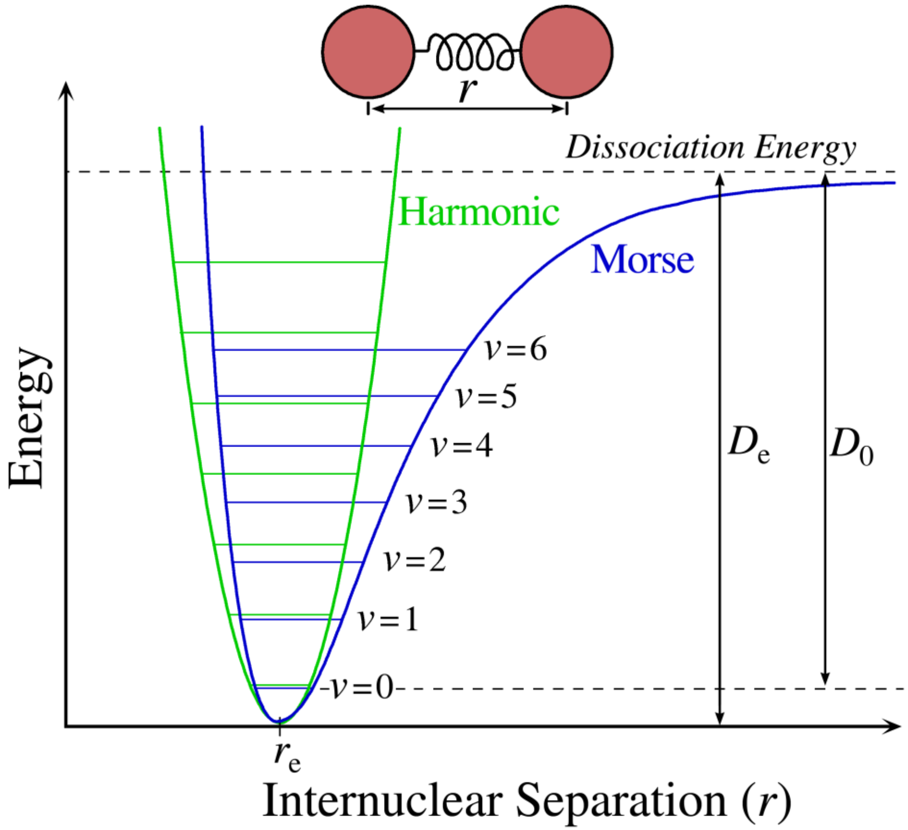
- If for all degrees of freedom $\frac{\partial^2 E}{\partial x^2} > 0$ then the stationary point is a ***Local*** **Minimum**
- If on a PES we find the most stable local minimum then we can call it the ***Global*** **Minimum**
- If for n degrees of freedom in a stationary point $\frac{\partial^2 E}{\partial x^2} < 0$ then the stationary point is an **nth order saddle point**

PES for Diatomics

- Morse Potential:

$$V(r) = D_e\left(1 - e^{-a(r-r_e)}\right)^2$$

- D_e is the depth of potential well
- a controls the width of potential
- r is the interatomic separation
- And r_e is the equilibrium distance

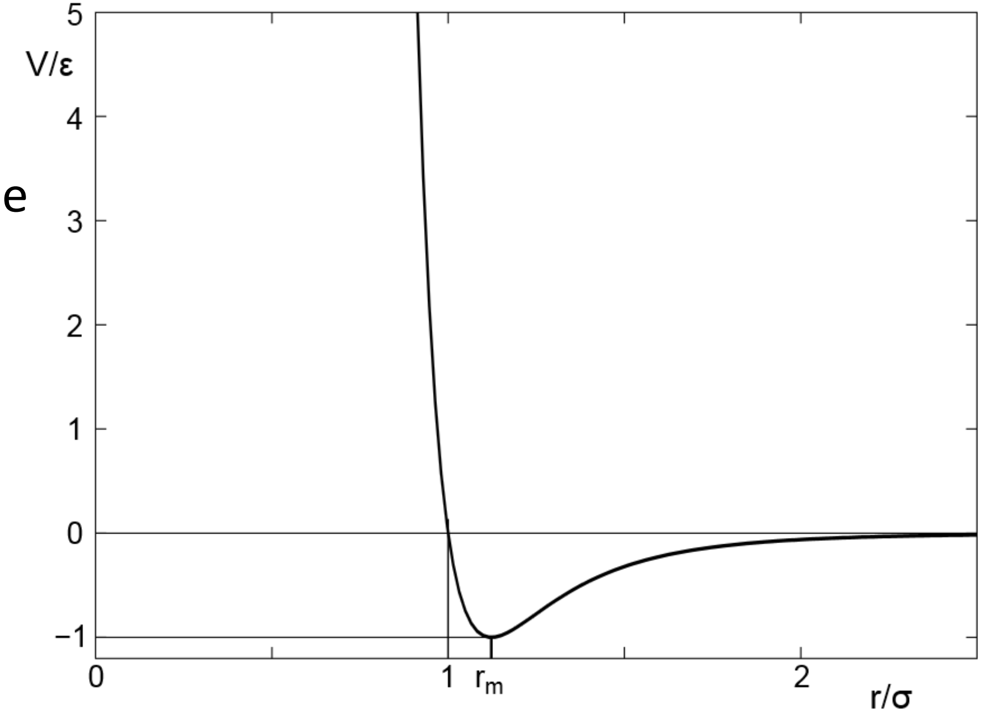


PES for Diatomics

- Lenard-Jones Potential:

$$V_{LJ} = 4\varepsilon[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}]$$

- ε is the depth of potential well
- σ is the finite distance at which the inter-particle potential is zero
- r is the interatomic separation

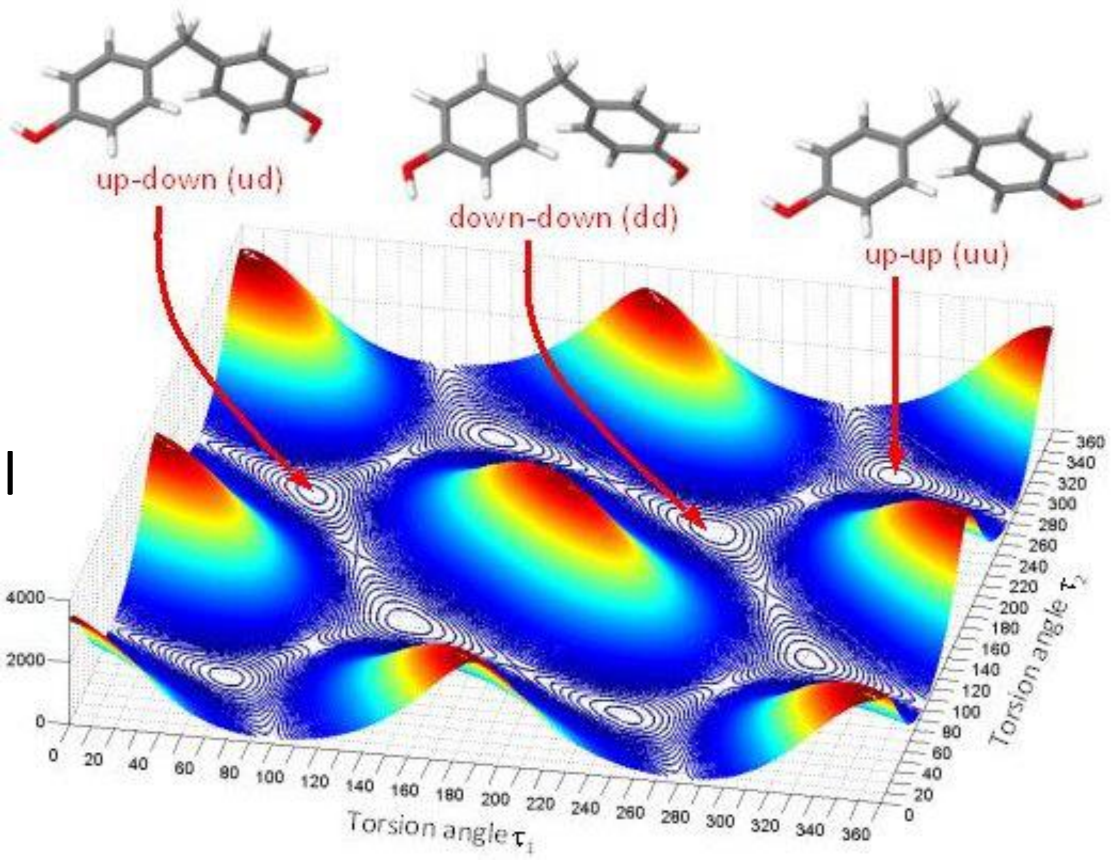


PES for Polyatomics

- On a 2-dimensional surface, only a 2D PES can be projected.
- For a reaction we conventionally

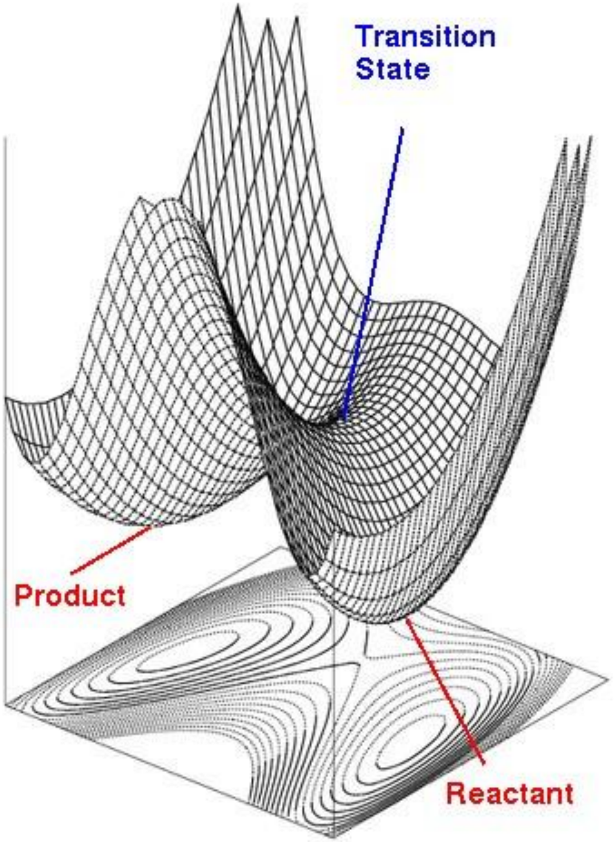
depict reaction coordinates which is the minimum energy path of the reaction.

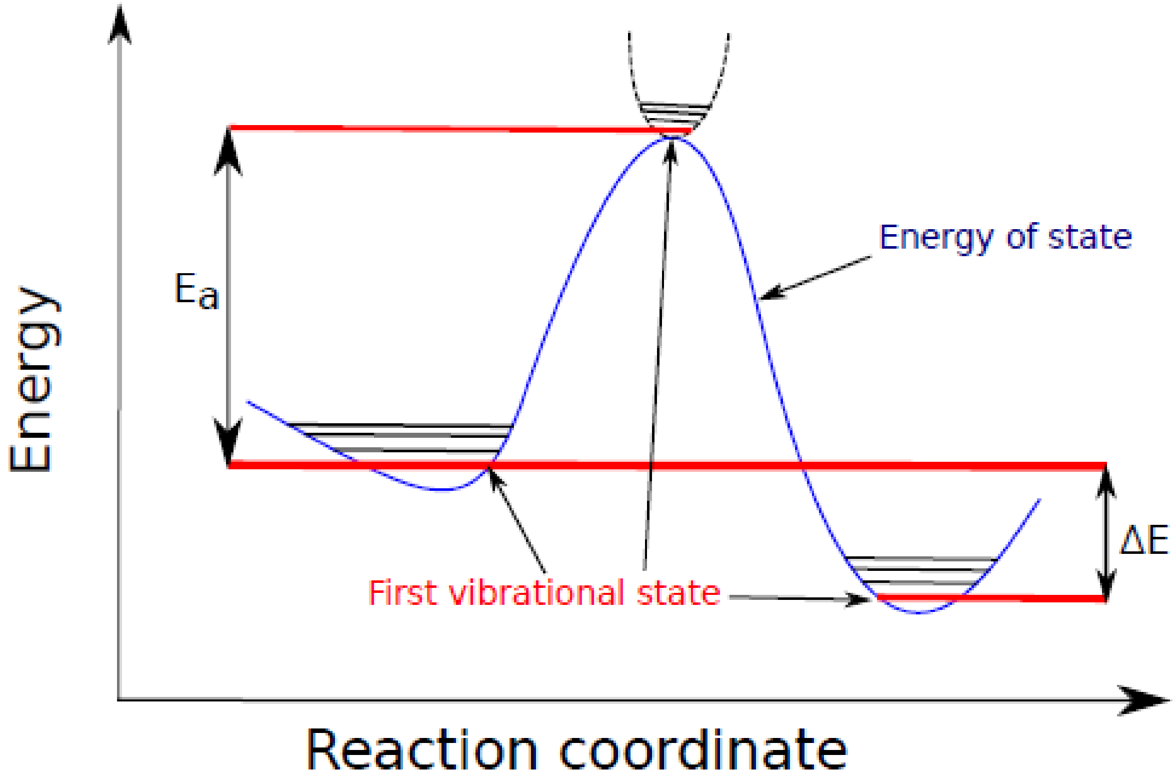
This may involve rearrangement of several degrees of freedom though.



Reaction Coordinates

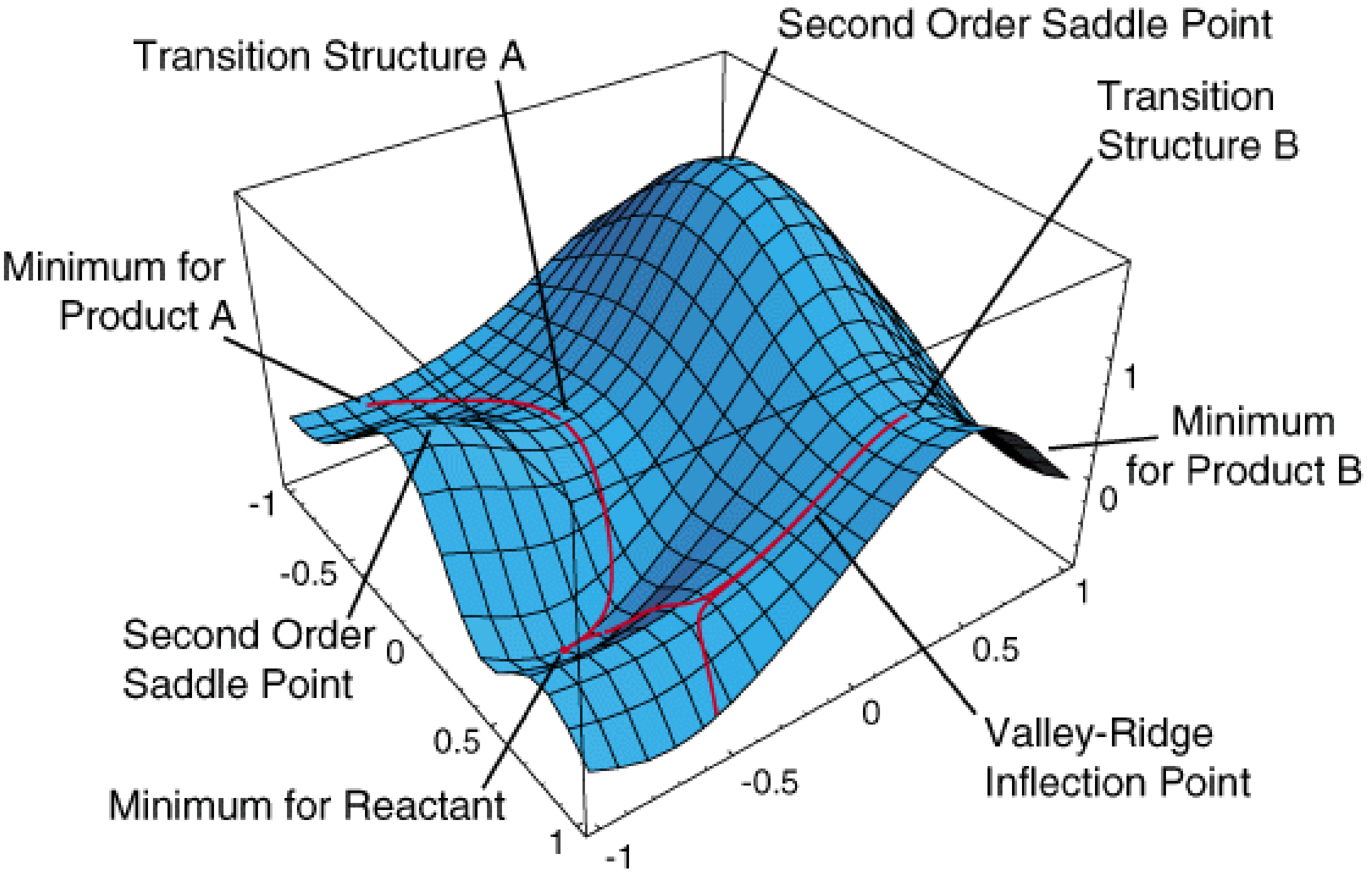
- A reaction coordinates can be roughly presented as the following.





How a Software Optimized a Molecule?

- Software is STUPID! Watch out!



Digging Schrödinger Equation

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References:

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Frank Jensen
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Schrödinger Equation

- The wave function or state function (Ψ) describes *state* of a system in quantum mechanics.
- For a one particle, one dimensional system, Ψ is a function of time and coordinate, $\Psi = \Psi(x,t)$
- Newton's second **law** tells us the future of a classical system but for a quantum system we need Schrödinger Equation

$$-\frac{\hbar}{i}\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t)$$

Time-Independent Schrödinger Equation

- If Potential energy does not change by time then $V = V(x)$ and then

$$-\frac{\hbar}{i}\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t) \quad (1)$$

Furthermore $\Psi(x,t)$ can be written as product of two functions: $\Psi(x,t) = \psi(x)f(t)$

Now, considering partial derivations one can write

- $\frac{\partial\Psi(x,t)}{\partial t} = \frac{df(t)}{dt}\psi(x)$, $\qquad \frac{\partial^2\Psi(x,t)}{\partial x^2} = \frac{\partial^2\psi(x)}{\partial x^2}f(t)$ (2)

Time-Independent Schrödinger Equation

- By substituting 2 in 1 we have

$$-\frac{\hbar}{i}\frac{df(t)}{dt}\psi(x) = -\frac{\hbar^2}{2m}f(t)\frac{d^2\psi(x)}{dx^2} + V(x)f(t)\psi(x) \quad (3)$$

$$-\frac{\hbar}{i}\frac{1}{f(t)}\frac{df(t)}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) \quad (4)$$

Now we have two equal functions while the left hand side of equation is a function of time and the right hand side is a function of *x*. This is only possible if both sides are equal to a constant, called ***E***.

Time-Independent Schrödinger Equation

- The left hand side is not of our interest but the right hand side of equation 4 is the time independent Schrödinger Equation for a one particle, one dimensional system

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x)$$

$$\widehat{H}\psi(x)=E\psi(x)$$

Acceptable Wave Function

- A wave function ψ is called well behaved (or acceptable) if

1. Is *Continues* all over space
2. Its first derivative is *Continues* over space
3. Is *Single Valued*
4. Is *Quadratically Integrable, i.e.* $\int \psi\psi^{*} d\tau$ over space exist

Since we do not know what ψ is, any function that satisfies these conditions is a Suitable *First Guess* for ψ.

Molecular Hamiltonian

- The Hamiltonian operator of a molecule, neglecting relativistic effects and spin-orbit can be written as the following

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{\alpha}\frac{1}{m_\alpha}\nabla_\alpha^2 - \frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_\alpha \sum_{\beta>\alpha}\frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}} - \sum_\alpha \sum_i \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_i \sum_{j>i}\frac{e^2}{r_{ij}}$$

Born-Oppenheimer Approximation

- Concerning the fact that nuclei are way heavier than electrons one can imagine that nuclei almost remain still while electrons circle around the molecule. Therefore, nuclear kinetic energy can be separated from the *Electronic Hamiltonian*

$$\widehat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 +$$

$$-\sum_\alpha \sum_i \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{e^2}{r_{ij}} + \sum_\alpha \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}}$$

Atomic Units

- Atomic Units are units of nature
- Schrödinger Equation written in *au* looks much less complicated

Energy: 1 Hartree = $E_h = e^2/a_0 = 27.2114$ eV
$=4.35974417(75)\times10^{-18}$ J = 627.5095 kcal.mol^{-1}

Length: $a_0 = 5.2917721092(17)\times10^{-11}$ m = 0.52917721092 Å

Charge: $e = 1.602176565(35)\times10^{-19}$ C

Mass: $m_e = 9.10938291(40)\times10^{-31}$ kg $\neq$ 1 amu (Atomic Mass Unit)

Schrödinger Equation; A Differential Equation

Schrödinger Equation is a differential equation. This means that Schrödinger Equation has more than one acceptable eigenfunctions, ψ, for one particular problem, i.e. molecule. Each ψ is associated with a particular eigenvalue that is a particular *energy.* All these eigenfunctions for a one-particle system in three dimensions are *orthonormal*. *Orthonormal* means:

$$\int \psi_i \psi_j d\tau = \delta_{ij} \begin{cases} \delta_{ij} = 1 \; if \; i = j \\ \delta_{ij} = 0 \; if \; i \neq j \end{cases} \qquad (5)$$

δ_{ij} is called *Krönecker Delta*

Schrödinger Equation; A Differential Equation

- Regarding (5) one can propose a way for evaluation of **Energy** associated with a wave function. We knew $\widehat{H}\psi_i = E\psi_i$; multiplying this equation by ψ_j and integrating both sides gives:

$$\int \psi_i H \psi_j d\tau = \int \psi_i E \psi_j d\tau$$

Since E is a constant, we have:

$$\int \psi_i H \psi_j d\tau = E_i \delta_{ij}$$

Solving an Equation with Two Missing Variables!

- We have no clue about the nature of ψ
- We do not know the energy of the system
- Don’t panic! There is a solution:

The Variational Principle

The Variational Principle

- Let’s assume an arbitrary function, Φ, to be an eigenfunction of Schrödinger Equation. Φ should be a linear combination of some of infinite number of real eigenfunctions, ψ, that is:

$$\Phi = \sum_i c_i \psi_i \qquad (6)$$

Unfortunately yet we don’t know anything about ψ_i and of course C_i!

The Variational Principle

- Fortunately, *normality* of Φ imposes a constraint on the coefficients of (6).

$$\int \Phi^2 d\tau = 1 = \int \sum_i c_i \, \psi_i \sum_j c_j \, \psi_j d\tau =$$

$$\sum_{ij} c_i \, c_j \int \psi_i \psi_j d\tau = \sum_{ij} c_i \, c_j \delta_{ij} = \sum_i c_i^2$$

The Variational Principle

- For measuring the **Energy** associated with wave function Φ, one can write:

$$\int \Phi H \Phi d\tau = \int \left(\sum_i c_i \, \psi_i \right) H \left(\sum_j c_j \, \psi_j \right) d\tau =$$

$$\sum_{ij} c_i \, c_j \int \psi_i H \psi_j d\tau = \sum_{ij} c_i \, c_j E \delta_{ij} = \sum_i c_i^2 E$$

The Variational Principle

The Variational Principle states that there is a lower limit for the energy of a quantum system that is the energy obtained form its *exact wave function*. Therefore, energy obtained form any arbitrary wave function is always higher than that of exact wave function.

$$\frac{\int \Phi H \Phi d\tau}{\int \Phi^2 d\tau} \geq E_0$$

Here, E_0 is the energy of exact wave function. The Variational Principle enable us to start from any primary guess for wave function and try to minimize energy as much as possible close the energy of the *exact wave function*.

Definition of Terms:
Ab Inotio and **DFT** Methods

- The word **ab initio** means from the beginning. In a nutshell, **ab initio** methods are different approximations for solving the Schrödinger Equation. Ab initio methods are NOT parameterized based on experiments.
- Density Functional Theory or DFT is an old method for finding the energy of a molecular system based on Hohenberg-Kohn Theorem as the following:

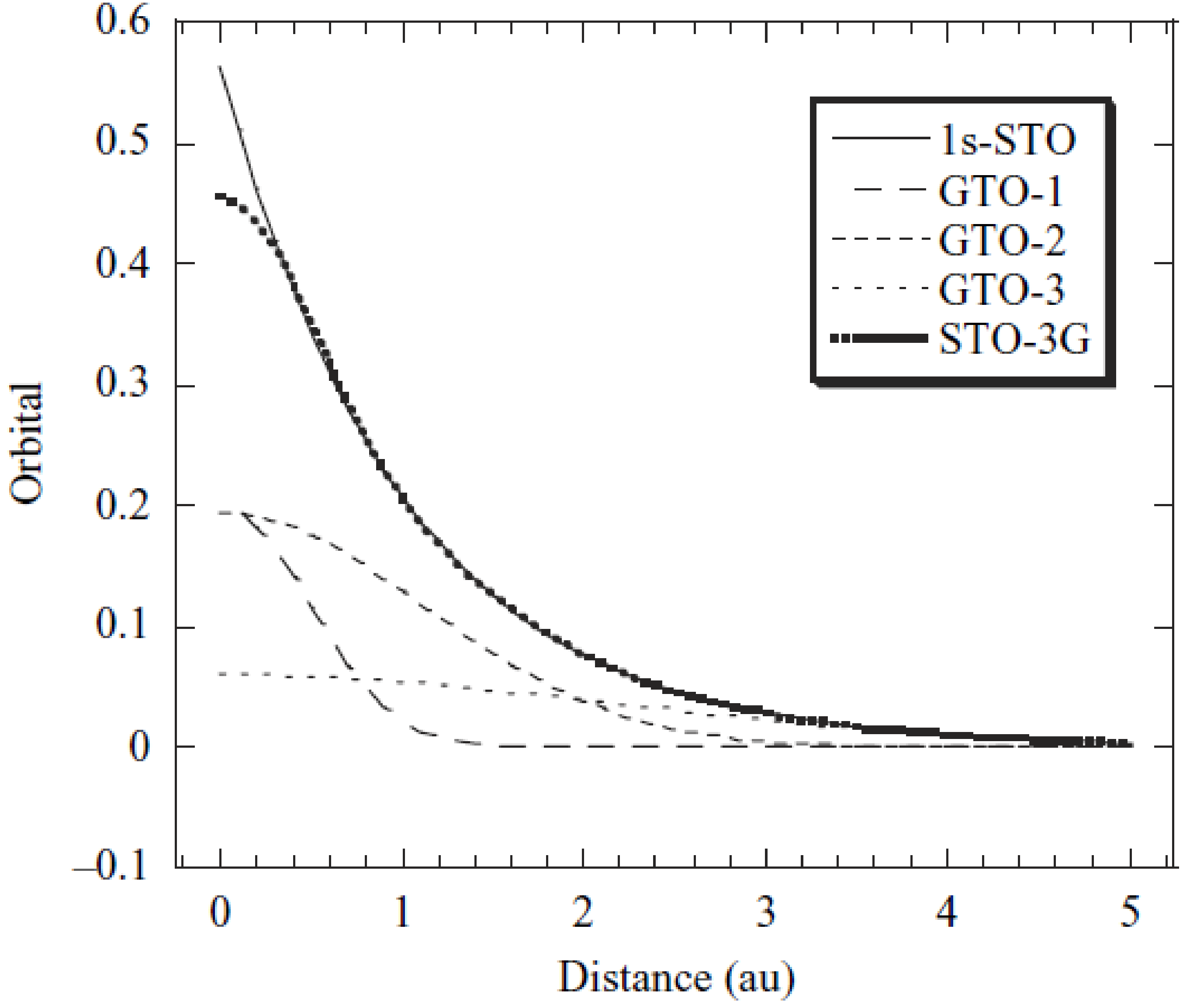
$$\boldsymbol{F[\rho(r)] = E_{elec}}$$

- Unfortunately, because the ideal functional is not known, DFT methods are parameterized to be as consist as possible with experiments.

Suitable Guess For Wave Function

- An approximation used widely in computational chemistry is application of a ***Basis set*** to simulate the exact wave function as much as possible.
- A basis set is a limited number of functions which are used to construct a first guess for the molecular wave function.
- Two types of basis sets are Slater and Gaussian basis sets.
- **Computational cost** for the fastest *ab initio* or DFT method increases by increasing the number of basis functions, **M**, by $\mathbf{M^4}$. So, an ideal basis set provides a **reasonable** solution to a problem with least number of basis functions.

STO and GTO


0.6
0.5
0.4
0.3
0.2
0.1
0
–0.1
Orbital
0
1
2
3
4
5
Distance (au)
1s-STO
GTO-1
GTO-2
GTO-3
STO-3G

STO and GTO; Mathematical Form

- An STO has the following form:

$$s(r) = N_s e^{-\zeta r}$$

- A GTO has the following form:

$$g(r) = N_g e^{-\zeta r^2}$$

$$g(r) = x^a y^b z^c N_g e^{-\zeta r^2}$$

N_s/N_g is the normalization constant and ζ is orbital exponent. $x^a y^b z^c$ is used for defining orbital type for example for a *p* orbital a = 1, b = c = 0.

Gaussian Basis Sets

- Every GTO is consisted of one or more Primitive GTOs

$$\chi(\mathrm{CGTO}) = \sum_{i}^{k} a_i \chi_i(\mathrm{PGTO})$$

- The degree of contraction is the number of PGTOs that enter a CGTO or Contracted GTO

Basis Sets

- Pople Type Basis Sets
  STO-nG→ n*1s*,n*2s*,n*2p*,… Minimal Basis set
  for second row elements
  STO-3G→ (*6s,3p*) → (*2s,1p*)
  k-nlmG→ k *core*, 2 (nl) or 3 (nlm) zeta, n *inner valence*, l *middle valence*, and m *outer valence*
  for second row elements
  6-311G→ (*11s,5p*) → (*4s,3p*)

Basis Sets

- Correlation Consistent Basis Sets
  s and p optimized at HF, polarization optimized at CISD

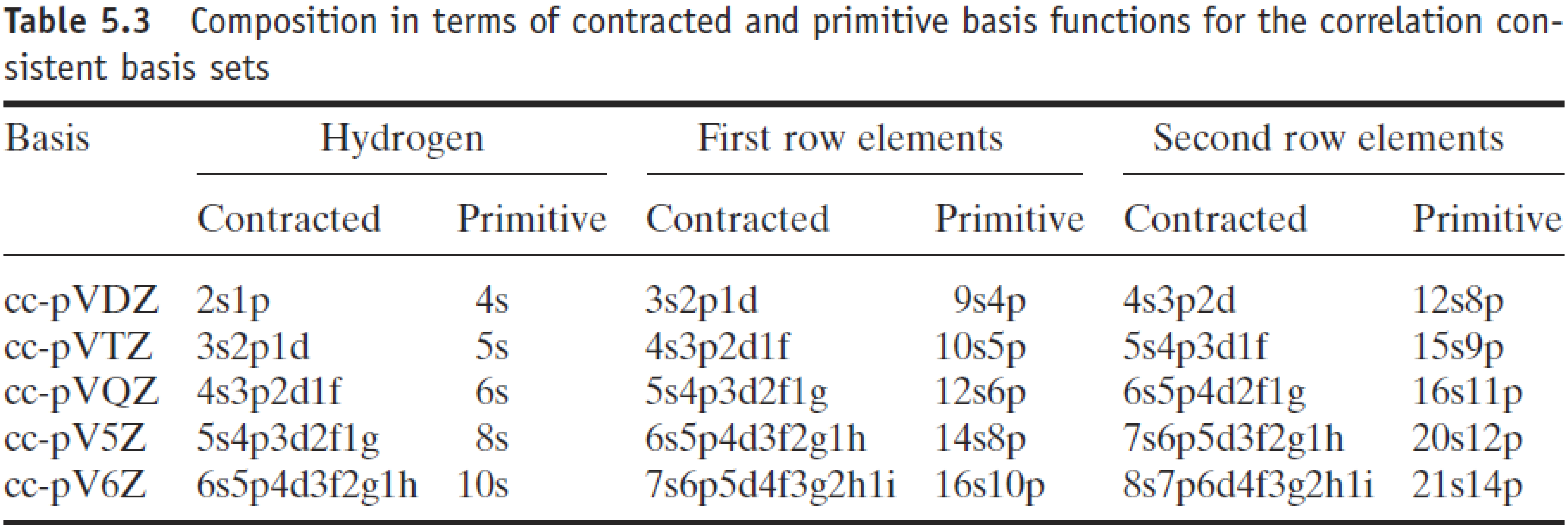


Table 5.3 Composition in terms of contracted and primitive basis functions for the correlation consistent basis sets

Basis	Hydrogen		First row elements		Second row elements	
	Contracted	Primitive	Contracted	Primitive	Contracted	Primitive
cc-pVDZ	2s1p	4s	3s2p1d	9s4p	4s3p2d	12s8p
cc-pVTZ	3s2p1d	5s	4s3p2d1f	10s5p	5s4p3d1f	15s9p
cc-pVQZ	4s3p2d1f	6s	5s4p3d2f1g	12s6p	6s5p4d2f1g	16s11p
cc-pV5Z	5s4p3d2f1g	8s	6s5p4d3f2g1h	14s8p	7s6p5d3f2g1h	20s12p
cc-pV6Z	6s5p4d3f2g1h	10s	7s6p5d4f3g2h1i	16s10p	8s7p6d4f3g2h1i	21s14p

How a Basis Set Looks Like?

```
6-311+G(3df,3pd)
C    0
S   6   1.00
   4563.2400000          0.00196665
    682.0240000          0.0152306
    154.9730000          0.0761269
     44.4553000          0.2608010
     13.0290000          0.6164620
      1.8277300          0.2210060
SP   3   1.00
     20.9642000          0.1146600          0.0402487
      4.8033100          0.9199990          0.2375940
      1.4593300         -0.00303068         0.8158540
SP   1   1.00
      0.4834560          1.0000000          1.0000000
SP   1   1.00
      0.1455850          1.0000000          1.0000000
SP   1   1.00
      0.0438000          1.0000000          1.0000000
D   1   1.00
      2.5040000          1.0000000
D   1   1.00
      0.6260000          1.0000000
D   1   1.00
      0.1565000          1.0000000
F   1   1.00
      0.8000000          1.0000000
```

Normalization & Contraction constants

```
Aug-cc-pV5Z
C    0
S   10   1.00
  96770.0000000          0.0000250
  14500.0000000          0.0001900
   3300.0000000          0.0010000
    935.8000000          0.0041830
    306.2000000          0.0148590
    111.3000000          0.0453010
     43.9000000          0.1165040
     18.4000000          0.2402490
      8.0540000          0.3587990
      3.6370000          0.2939410
S   10   1.00
  96770.0000000         -0.0000050
  14500.0000000         -0.0000410
   3300.0000000         -0.0002130
    935.8000000         -0.0008970
    306.2000000         -0.0031870
    111.3000000         -0.0099610
     43.9000000         -0.0263750
     18.4000000         -0.0600010
      8.0540000         -0.1068250
      3.6370000         -0.1441660
S   1   1.00
      1.6560000          1.0000000
S   1   1.00
      0.6333000          1.0000000
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Normalization & Contraction constants

Introduction to Ab Initio Methods

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Hatree Product Wave Function

Neglecting electron-electron repulsion one can write a molecular Hamiltonian in terms of one-electron Hamiltonians.

$$H = \sum_{i}^{N} h_i$$

$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{M} \frac{Z_k}{r_{ik}}$$

All eigenfunctions of one-electron Hamiltonian must satisfy the one-electron Schrödinger equation.

$$h_i \psi_i = \varepsilon_i \psi_i$$

If Hamiltonian is separable then many-electron eigenfunction should be a product of one-electron eigenfunctions:

$$\Psi_{HP} = \psi_1 \psi_2 \dots \psi_N$$

Hatree Product Wave Function

Then the energy of “Hartree Product” wave function is:

$$H\Psi_{HP} = H\psi_1\psi_2 \dots \psi_N = \sum_{i=1}^{N} h_i\psi_1\psi_2 \dots \psi_N =$$

$$(h_1\psi_1)\psi_2 \dots \psi_N + \psi_1(h_2\psi_2) \dots \psi_N + \psi_1\psi_2 \dots (h_N\psi_N\ )$$

$$= (\varepsilon_1\psi_1)\psi_2 \dots \psi_N + \psi_1(\varepsilon_2\psi_2) \dots \psi_N + \psi_1\psi_2 \dots (\varepsilon_N\psi_N\ )$$

$$= \sum_{i}^{N} \varepsilon_i\, \psi_1\psi_2 \dots \psi_N = (\sum_{i}^{N} \varepsilon_i)\Psi_{HP}$$

If one-electron wave functions are normal, then Hartree Product wave function is normal.

$$|\Psi_{HP}|^2 = |\psi_1|^2|\psi_2|^2 \dots |\psi_N|^2$$

Hatree Product Hamiltonian

In the one-electron Hatree Hamiltonian electron electron repulsion is considered as an average as the following:

$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{M}\frac{Z_k}{r_{ik}} + \sum_{i\neq j}\int\frac{\rho_j}{r_{ij}}dr$$

The last term measures interaction potential between all other electrons (except *i*) that occupy the same orbital. ρ_j represents the electron density of electron *j*. Second and third terms on the r.h.s. of the equation are essentially the same but electron is treated as a wave so its probability density is integrated over space but nucleus is treated as a point charge.

Hatree Product Hamiltonian

To calculate energy form Hartree Hamiltonian on should be aware that electron-electron repulsion for each pair of electrons is two times considered in the Hartree Hamiltonian. So, energy is:

$$E = \sum_{i} \varepsilon_i - \frac{1}{2} \sum_{i \neq j} \iint \frac{|\psi_i|^2 |\psi_j|^2}{r_{ij}} dr_i dr_j$$

Hartree approach has a major limitation!

It does not consider a major property of electrons; the electron

SPIN

Electron Spin

- Spin is a fundamental property of matter that is NOT conceivable for human being based on his/her daily experiences.
- We are living in a 3D world so all we need is 3 numbers, corresponding to 3 dimensions of space to describe any object around us.
- Spin is an additional index that is necessary for describing electrons in an atom or molecule.

Slater Determinants

A real wave function must include the effect of spin so must be ***antisymmetric*** that is the wave function must change sign if a pair of electrons are replaced between two one-electron orbitals. A mathematical trick to have such wave function is using a matrix. In a matrix changing any two rows (or columns) change the sign of the matrix.

$$ {}^{3}\Psi_{\mathrm{SD}} = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(1)\alpha(1) & \psi_b(1)\alpha(1) \\ \psi_a(2)\alpha(2) & \psi_b(2)\alpha(2) \end{vmatrix} $$

Slater Determinants

A Slater determinant can be abbreviated for spin-orbit spatial products, $\chi_N(N)$. Furthermore, in SD all electrons are permitted to be in all orbitals. This is a very important property that satisfies “indistinguishability” principle.

$$\Psi_{\mathrm{SD}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix}$$

Quantum Mechanical Exchange

Electron spin has a unique effect on the energy of a multi-electron system. Since electrons with same spin exclude each other, the energy of a molecular system decreases proportional to the degree of electron exclusion, i.e. electrons with same spin do not meet each other and do not repel each other!

This unique property can be calculated based on a Slater determinant.

Hartree-Fock Approach

- Hartree was the first man who used self-consistent field approach to reduce the energy of his wave function
- Fock for the first time used Hartree’s SCF method for minimizing the energy of a wave function based on Slater determinant.
- Roothaan years later introduced matrix algebra necessary for HF calculations using a “basis set” representation for Mos.

Electron Correlation

We saw that exchange decreases energy of a molecule by keeping electrons with the same spin away. Electron correlation is another phenomenon that decreases the energy of a molecule by keeping electrons with the different spin as far as possible. In fact, electron motions in a molecular system is always synchronized to some degrees to keep the energy as low as possible! Nevertheless, HF approach did not provide us a way to evaluate this energy.

Correlated Mthods

HF method is most accurate single-determinant approach. We cannot lower the energy of a molecule by a single determinant more that HF approach. But what if we use more than a single determinant to construct our wave function?

In fact wave function can be made based on linear combination of different wave functions as the following:

$$\Psi = c_0\Psi_{HF} + c_1\Psi_1 + c_2\Psi_2 + \cdots$$

Coefficients reflect the weight of every wave function.

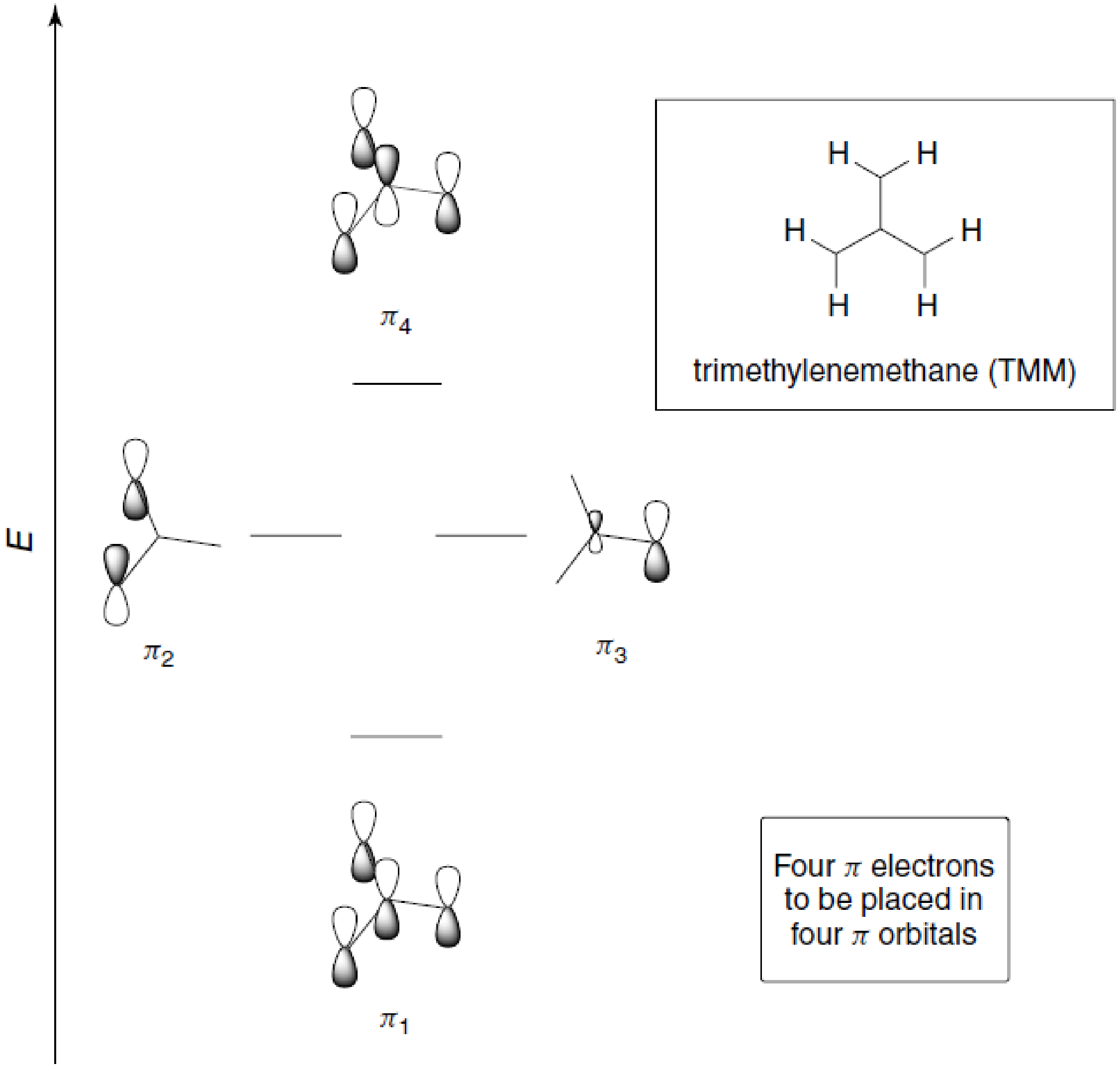
Dynamic *vs.* Static Correlation

Empirical studies suggest that weight of HF wave function is usually the most in final wave function. In such cases the electron correlation originates from so called *Dynamic Correlation*. Dynamic correlation is result of instantaneous electron-electron interactions.

However, in some cases several wave functions have exactly the same or very close weights in the final wave function. In such cases with “degenerate” or “near degenerate” energy levels we are dealing with a so-called “multi-reference” system. The correlation in such systems is of static correlation type. Although, there is no clear distinction between the mechanism of these two types of correlation, conventionally this distinction is made.

Static Correlation

An example
of systems with
static correlation



Four π electrons to be placed in four π orbitals

CASSCF and Full CI

- Complete Active Space-SCF is a method for considering static correlation to a great extent by considering a limited number of orbitals called “active space”.
- A CASSCF approach uses HF wave function and is denoted as CAS(m,n) were m and n are number of electrons and orbitals in the active space.
- Each single wave function that in CAS approach is used is called a “Configuration State Function” and number of all CSFs for a typical CAS(m,n) is as the following:

$$N = \frac{n!\,(n+1)!}{\left(\frac{m}{2}\right)!\left(\frac{m}{2}+1\right)!\left(n-\frac{m}{2}\right)!\left(n-\frac{m}{2}+1\right)!}$$

CASSCF and Full CI

- A CASSCF for all orbitals of a system is called Full CI.
- Full CI approach is the most accurate approach for solving non-Born-Oppenheimer non-relativistic time-independent Schrödinger equation!
- Unfortunately, full CI is so EXPENSIVE that only is doable for smallest molecules.
- This because the number of CSFs increase unbelievably by increasing the number of electrons and available orbitals that is the basis function.

More Correlated Methods

- CASSCF/Full CI are not the only correlated methods. There are several methods based on Perturbation theory. Here we do not talk about those approaches but to be familiar with them it is useful to know that their accuracy and unfortunately computational cost increases as the following:

  HF < MP2 ~ MP3 ~ CCD < CISD < MP4SDQ ~ QCISD ~ CCSD < MP4SDTQ (MP4) < QCISD(T) ~ CCSD(T)

- Number of basis functions with computational cost of HF has M^4 relationship; computational cost of CCSD(T) increases by M^7.

Density Functional Theory

- DFT is an alternative approach based on the Kohn-Sham theorem.

$$F[\rho(r)] = E$$

- Unfortunately, the exact functional is not known to us! Nevertheless, many functional are suggested. All these functionals are empirically corrected by comparison with high-level ab initio approaches or based on experimental data.

Density Functional Theory

- Although the exact functional is not known, efficiency of DFT attracted many researchers. Therefore, DFT approaches are in fact the most widely used approaches worldwide.
- There are four different types of functionals: LDA, GGA, Hybrid-GGA and meta-Hybrid-GGA.
- Some of popular functionals of each type are LSDA, BLYP, B3LYP and M062X.

(Hopefully) The End!