

# 분자 구조 계산 1. 에너지 계산 방법

KAIST 화학과

이운섭

# 바닥상태 에너지 계산

- 계산 양자화학 개요
- Born-Oppenheimer 근사법(PES)과 독립입자 근사법 (오비탈)
- 전자 상태와 전자배치 – 다전자 계의 전자상태 파악
- Ab initio MO 방법 (sample calculations with 'webmo')
  - Hartree-Fock (SCF, basis set)
  - Post-HF methods
  - DFT method
- Resources
  - C. J. Cramer, 'Essentials of computational chemistry (Theory and models)' 2nd Ed., John Wiley & Sons LTD 2004
  - Prof. Cramer's (Univ. of Minnesota) lecture note
  - Prof. Schlegel's (Wayne State Univ.) lecture note
  - WebMO user's guide ([www.webmo.net](http://www.webmo.net)) KAIST site: [hartree.kaist.ac.kr](http://hartree.kaist.ac.kr)
  - Exploring chemistry with electronic structure method ([expchem3.com](http://expchem3.com))
-

20C: 이론화학 별거 없지만 계산화학 할게 있을거요

## Quantum Mechanics of Many-Electron Systems (Dirac '29)

“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 that are much too complicated to be soluble. **It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to explanation of the main features of complex atomic systems without too much computation.**”



1902 – 1984  
U.K. Physicist  
Nobel Prize(1933)

# Quantum Mechanics: Solving Schrödinger Equation (SE)

$$\hat{H}\Psi(\vec{r}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t)$$

$$H\Psi = E\Psi$$

- Solving SE yields energies and wave functions of the system – any property can be obtained (most of chemistry can be discussed)
- SE is defined once positions of atomic nuclei and number of electrons are given (any molecules can be handled)
- Exact solutions are usually impossible, but reasonable(?) **approximate solutions of SE** are possible for atoms, molecules, and crystals
  - *Ab initio* quantum chemistry for molecules
  - First-principle electronic structure for solids

# Computational Quantum Chemistry

$$H\Psi = E\Psi$$

- Approximate solution of Schrödinger Equation for molecules. (exact only for H atom)
- Test projects for computational science up to 60 years ago, theoretical research topics before then.
- Available only through computer centers (Rich men's pet project) and then workstations – 40 years ago (1975 CDC7600, \$50M, 36.4MHz, 65kword)
- Presently becoming a best tool for poor chemists (H/W \$1k, 3.5GHz, 16GB)
  - available everywhere at various levels to almost anyone willing to use
  - part of molecular modeling and simulations
  - Many chemical imaginations can be tested by
- Aim to find more accurate and/or efficient methods for larger systems (computationally demanding as system grows)
- Importance recognized by 2013 and 1998 chemistry Nobel prizes

Power of CQC grew by  $\sim 10^{17}$  (H/W 12 + S/W 5) in 40yrs! Next 10yrs?

In QM the basic Hamiltonian is known for systems of nuclei and electrons – SE can be written for any system

$$H\Psi = E\Psi$$

$$\hat{H} = \frac{-\hbar^2}{8\pi^2} \sum_A^{nuclei} \frac{1}{M_A} \nabla_A^2 - \frac{\hbar^2}{8\pi^2 m_e} \sum_a^{electrons} \nabla_a^2 - e^2 \sum_A^{nuclei} \sum_a^{electrons} \frac{Z_A}{r_{Aa}}$$

nuclear kinetic    electron kinetic    nuclear/electron potential

$$+ e^2 \sum_A^{nuclei} \sum_{B>A}^{nuclei} \frac{Z_A Z_B}{R_{AB}} \quad + e^2 \sum_a^{electrons} \sum_{a>b}^{electrons} \frac{1}{r_{ab}}$$

nuclear/nuclear potential    electron/electron potential

**h** : Plancks constant

**Z** : atomic number

**e** : electron charge

**r<sub>Aa</sub>** : distance separating nucleus A and electron a

**m<sub>e</sub>** : electron mass

**R<sub>AB</sub>** : distance separating nuclei A and B

**M** : nuclear mass

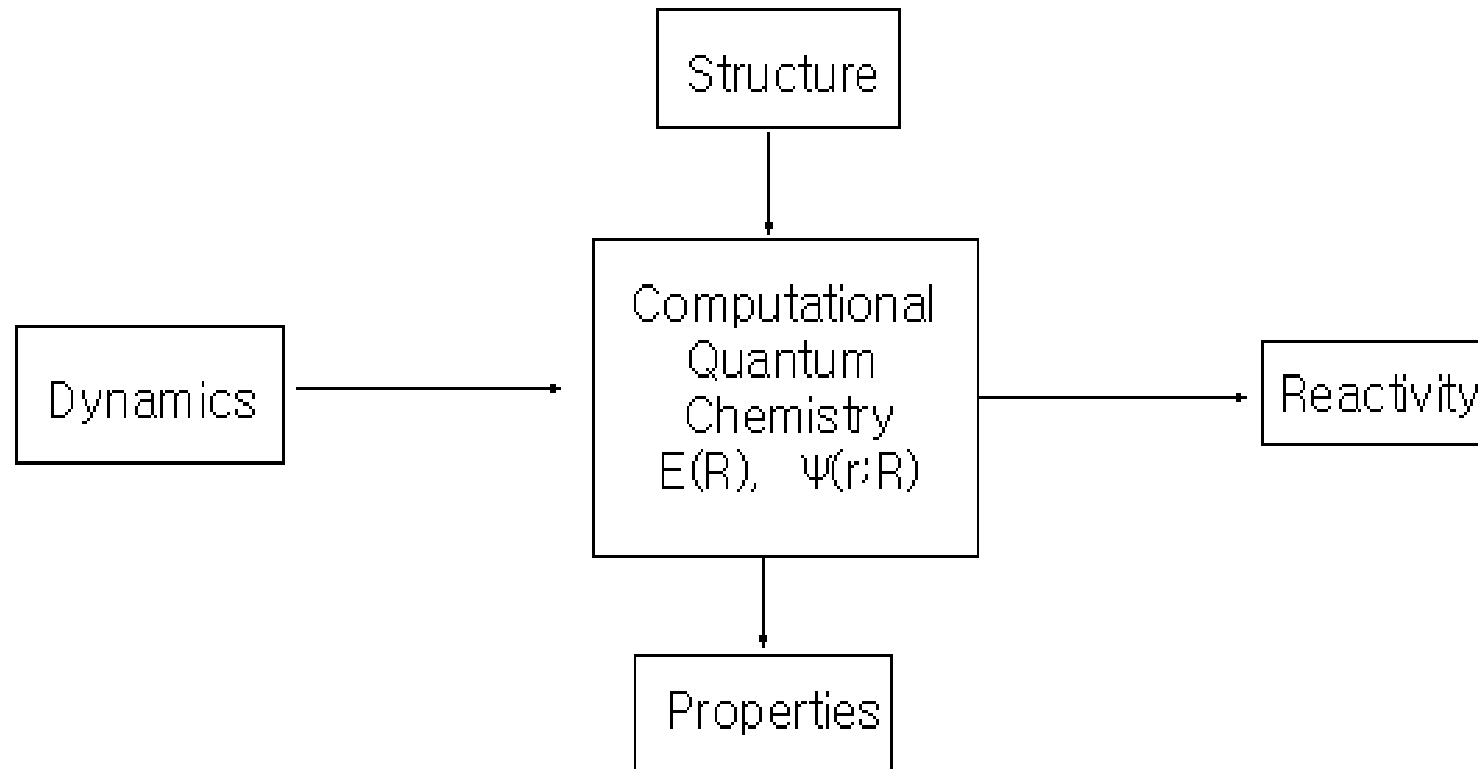
**r<sub>ab</sub>** : distance separating electrons a and b

- Only electrostatic force is treated in electronic structure methods
- In atomic units, most constants become 1

# Approximations almost always implicit in quantum chemical method – size of error acceptable?

- Born-Oppenheimer Approximation (leads to electronic structure and potential energy surface)
- Independent particle assumption (MO) as a starting point – best solution is HF limit – error is electron correlation energy ( $\sim 1\text{eV}$  per electron pair)
- This makes ‘right answer for the right reason’ very difficult.
- Effect of relativity and higher order interactions missing from the non-relativistic Hamiltonian

양자화학 계산은 분자의 모든 특성을 이해하는데 활용 가능  
(정확도가 충분하면 분석도구로 이용 – 작은 분자에 대한 현재 수준)





# Computational Quantum Chemistry: approximate solutions of Schrödinger Eq. for molecules (better accuracy and efficiency are goals)

Major factors affecting quality of *ab initio* MO (and DFT?) calculations

Basis set (Orbital) (LCAO-MO, AO~GTO)

Electron Correlation (Wavefunction) – 전자 상관성 에너지

Relativity and additional terms in Hamiltonian

- Importance of relativity, especially for heavy elements, well recognized
- RECP routinely utilized

ab initio MO methods  
refers to purely mathematical  
approximation of

$$H\Psi = E\Psi$$

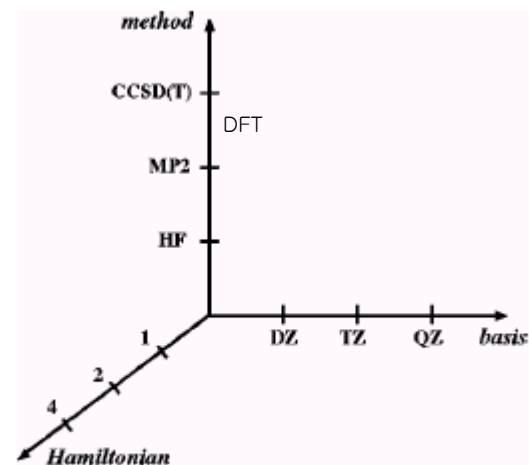


FIG. 1. 3D model chart.

Spin-orbit(SO) calculations are recent additions to many programs

Chemical accuracy required is about 1 kcal/mol ( $1.59 \times 10^{-3}$  a.u. or 0.04 eV): then most Quantum Chemical methods could be could be meaningless in chemistry, BUT

- Chemistry and properties of a molecule are usually determined by the difference (or derivatives), and not the total energy.
- We may expect a large **cancellation of errors** for systems of interest.
- Exploitation these error cancellations are necessary for any practical method – ( force-field and semi-empirical methods strongly rely on this)
- Unfortunately three axes of accuracy have different size(or level) dependence – in need of improvement all the time for Quantum Chemical method even in terms of accuracy
- Better method and theory for larger system is always in demand. Especially good multi-scale method
- Beyond HF calculations with non-rel H, errors easily identifiable are relativistic effect (scalar and spin-orbit) and electron correlation in addition to basis set deficiency. (Three principal axes)

# Fixed-Nuclei approximation and Potential Energy Surface (PES)

First approximation: separation of electronic and nuclear motions  $\rightarrow$  Born-Oppenheimer approximation or fixed-nuclei approximation

$$\Psi_M = \Psi_N(\vec{R})\Psi_e(\vec{r};\vec{R}) \quad (7-2)$$

where  $\Psi_e$  is an eigenfunction of  $\hat{H}_e$  (electronic Hamiltonian)

$$\hat{H}_e = \sum_{i=1}^n \left[ -\frac{\nabla_i^2}{2} - \sum_{A=1}^N \frac{Z_A}{r_{Ai}} \right] + \sum_{i>j}^n \frac{1}{r_{ij}}$$

$$\hat{H}_e \Psi_e = E_e \Psi_e$$

$\Psi_e$  is a function of electronic coordinates only, but parametrically depends on nuclear arrangements.

# SE of nuclear Hamiltonian

$$\left( \sum_{A=1}^N -\frac{\nabla_A^2}{2M_A} + \widehat{H}_e + \widehat{V}_{NN} \right) \Psi_N \Psi_e = E \Psi_N \Psi_e$$

$$\sum_{A=1}^N -\frac{\nabla_A^2}{2M_A} (\Psi_N \Psi_e) + \widehat{U}(\vec{R}) (\Psi_N \Psi_e) = E \Psi_N \Psi_e$$

$$\left[ \sum_{A=1}^N -\frac{\nabla_A^2}{2M_A} + U(\vec{R}) \right] \Psi_N = E \Psi_N \quad (7-13)$$

Now E contains all energies due to nuclear motions, too.

-  $U(\vec{R})$  defines PES: potential energy curve(one variable), potential energy surface( two variables), or potential energy hypersurface(three or more variables) for a given electronic state.

-The minimum on PES usually corresponds to stable species.

-PES if known in its entirety provide all chemical properties(stability and reactivity)

-Other properties can be derived from wave functions or as response to external perturbations.

Potential energy hypersurface (PES) is a plot of potential energy (electronic E + nuclear repulsion) as a function of nuclear arrangement (many E levels)

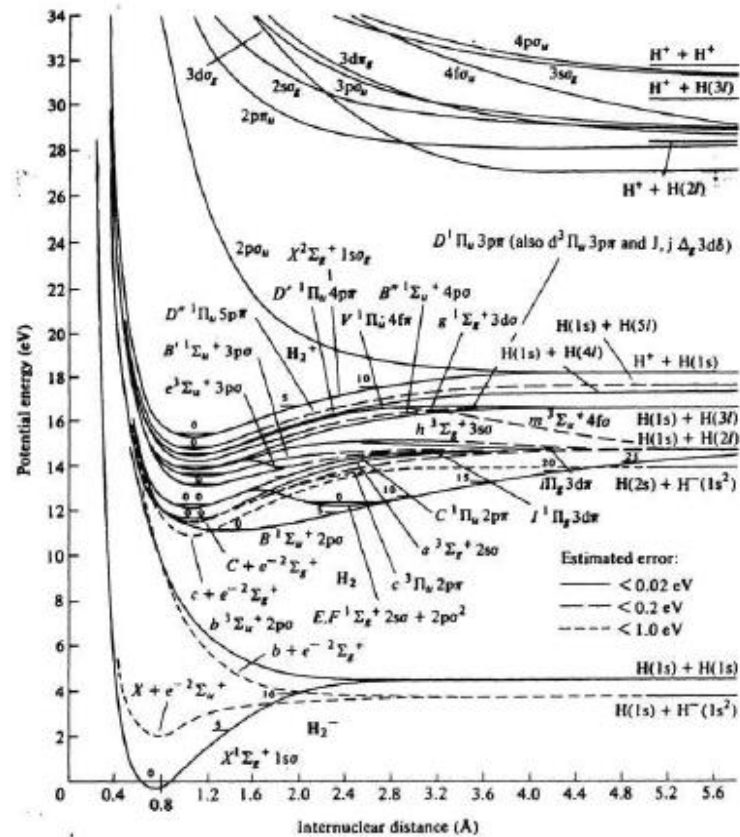
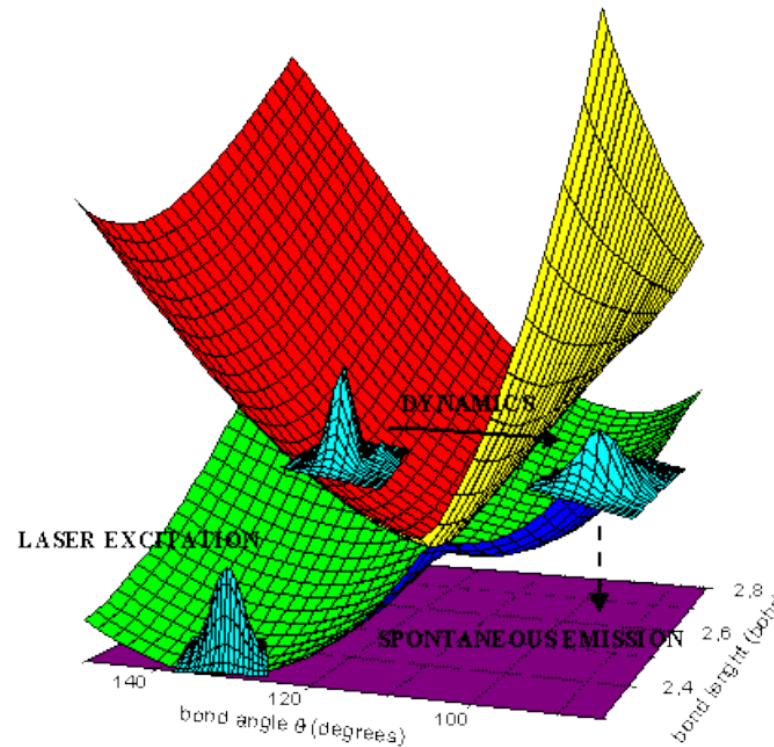


그림13-1 H<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub><sup>+</sup> 포텐셜 에너지 곡선.

Difficult to get the whole curve from the experiment!  
Relevant theoretical background to calculate the PEC covered,  
difficulty in details and the accuracy

### Conical Intersection Example (NO<sub>2</sub>)

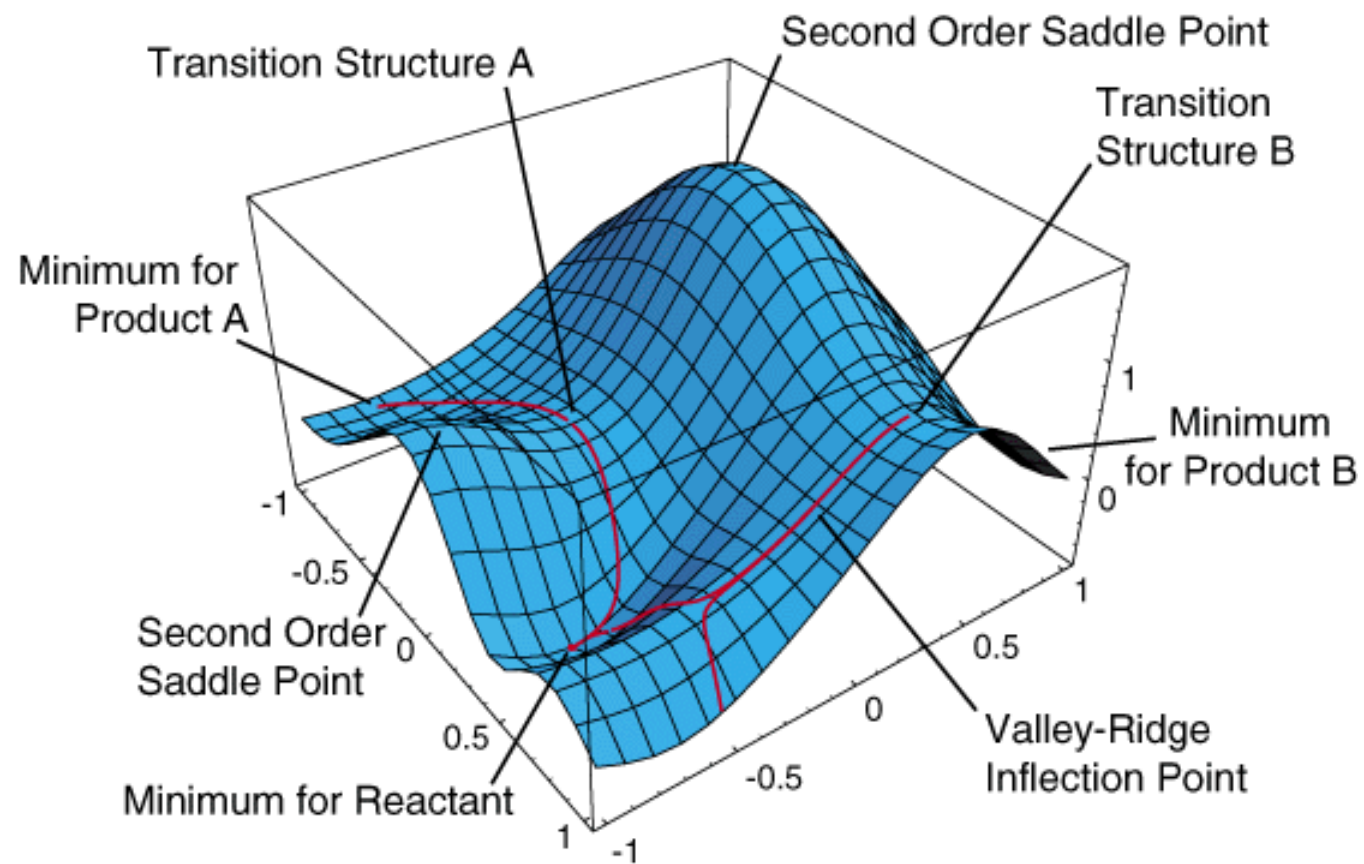


Note that 3 atoms leaves one final degree of freedom, so the CI is not a point, but a "seam" (that has a minimum)

Professor Carlo Petrongolo



## Features of Potential Energy Surfaces



Usually only critical points are considered to interpret stability and reactivity of molecules

# Ab Initio method and qualitative analysis of electronic structure starts with HF wavefunction (Independent Electron Approximation)

- Assuming that each electron moves independently in the mean field of all other electrons and nuclei (effective H)

$$\begin{aligned} H_{elec} &\approx \sum_{i=1}^n H_i^{eff} \\ \Psi_{elec} &\approx \prod_{i=1}^n \psi(r_i) \end{aligned} \quad \longrightarrow \quad H_i^{eff} \psi_i = \epsilon_i \psi_i$$

- Many electron H is approximated by the sum of one-electron effective H
- Many electron wavefunction is a product of one-electron wavefunctions (called **orbitals**)
- The energy of the orbital is the orbital energy (HMO is an example)

## 8. Electronic Structure of Many electron System

Atoms and molecules with two or more electrons require approximations for the solution of SE.

We have seen elementary procedures for the two-electron systems. It can be generalized for more electron systems.

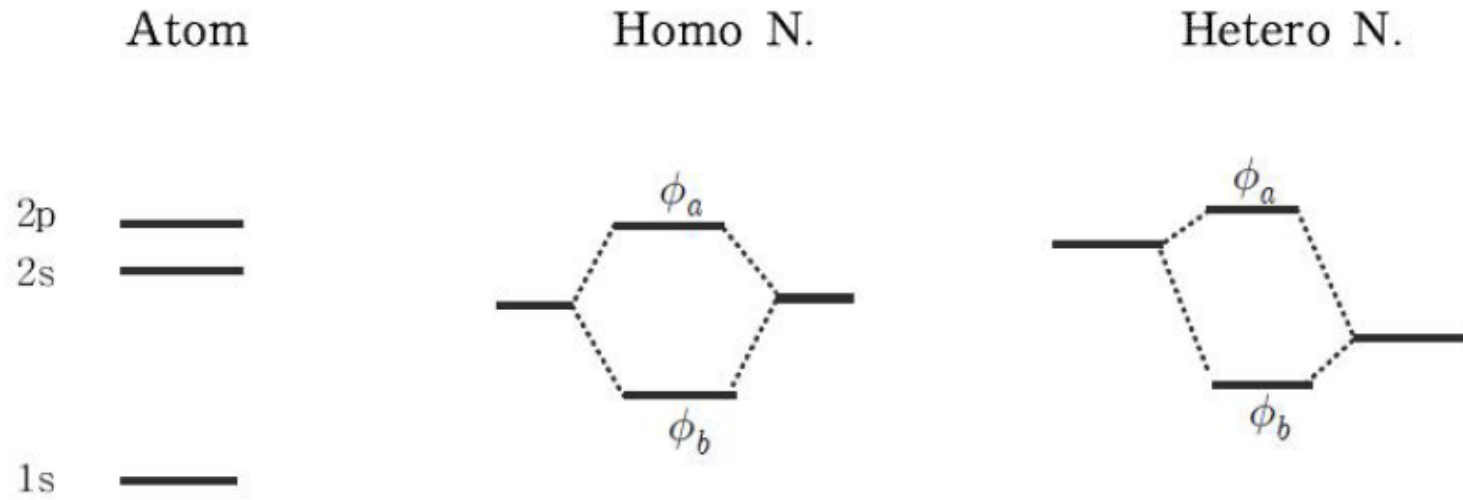
The starting point of the approximation for atoms and molecules is 'independent particle approximation (product of orbitals as wave functions)'.

- Independent particle approximation requires orbitals(one-electron wave functions) and electron configurations(basis of many electron wave function)



## Electronic Structure Determination

- 1) Generate Orbitals
- 2) Determine symmetry and energy of orbitals
- 3) Assign two electrons to each orbital starting from the most stable (lowest energy) one. For an excited state, hole(s) can be introduced. - Result is an electron configuration  
 $1s^2 2s^2 2p^2$
- 4) Generate all micro-states for the derived electron configuration. There are many micro-states for the open-shell configuration.
- 5) Determine symmetry of the wave function pertinent to the obtained configuration (atomic and molecular term symbol).
- 6) Estimate of energy order for derived terms
- 7) Actual calculation of wave function and energy for the term (or state) of interest



### 8.1 Orbitals and Energy Level

Orbitals are not physical observable. Once the system becomes more complex than the H atom, orbitals are not uniquely defined any more.

(Orbitals for many electron systems are generated usually for the conveniently defined effective-one-electron Hamiltonian. Sometimes these effective Hamiltonians are defined only in concept)

Symmetry of atoms and molecules can be a guideline to classify orbitals.

- Atom: spherical symmetry, Angular momentum
- Molecule: Point group symmetry, Irreducible representation

Atomic Orbitals(AO) : s, p, d, f

Hybrid Orbitals(HO) : sp, sp<sup>2</sup>, sp<sup>3</sup> .....

Molecular Orbitals(MO) :  $\sigma$ ,  $\pi$ , a, b, t<sub>2g</sub>

Symmetry adapted Orbitals(SAO) :  $\sigma_g$  1s,  $\sigma_u$  2p,

- Energy of AO is given by aufbau (build-up) principle (experiment and calculation)
- Energy of HO follows those of comprising AO's
- Energy of MO mainly follows those of constitute AO's and modified by the interaction of AO's.

## 8.2 Electron Configuration and Term Symbol

Electron configuration : Occupation number on all orbitals

e.g.  $1s^2 2s^2 2p^2$ ,  $1a^2 2a^1 1b^1$

- may contain many (micro) states or (micro-electron-configuration) electron micro-configuration?)

- many term symbols for a given configuration possible

Term symbol contains letters or numbers describing spin multiplicity and the irreducible representation of the given energy level.

Atom:  $^{2S+1}L_J$  ;  $S=0, 1/2, 1, \dots$   $L=S, P, D, F, \dots$   $J=L+S=0, 1/2, 1, \dots$

Linear molecule:  $^{2S+1}\Lambda_{\Omega}$  ;  $\Lambda = \Sigma, \Pi, \Delta, \Phi, \Gamma, \dots$   $\Omega = \Lambda + S$

Polyatomic molecule:  $^{2S+1}R$  ; R refers to irreducible representation(Irrep)

- Vector sum of angular momentum

- Direct product of representation matrices for point group symmetry

Note: **Closed-shell always results in  $S=0$  and totally symmetric Irrep.**( $L=0$  for atoms)

Many organic molecules have closed-shell ground state.

Hund's rule: most stable term has largest spin multiplicity and angular momentum (or largest degeneracy). Many exceptions to this rule.

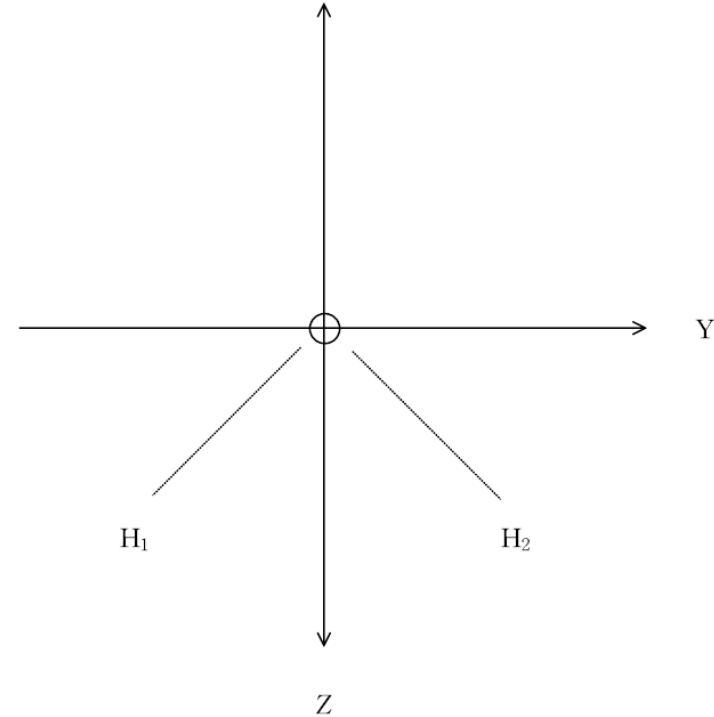
Theoretical calculations of electronic structure can make use of all the symmetry analysis.  
- Sometimes calculations are done for the states for which symmetry is not fully satisfied. (approximate symmetry) e.g.  $S_z=0$  state for an open shell molecule

Calculations and interpretation of experimental result indicate that true wave function of atoms and molecules usually contains many electron configurations and not one. (origin of dynamic and static electron correlation energy)

# HOH molecule as an example

- Linear or bent
- VSEPR predicts bent
- Coordinate defined on the right
- Walsh rule also predicts bent

그림 14-2 H<sub>2</sub>O 분자의 좌표



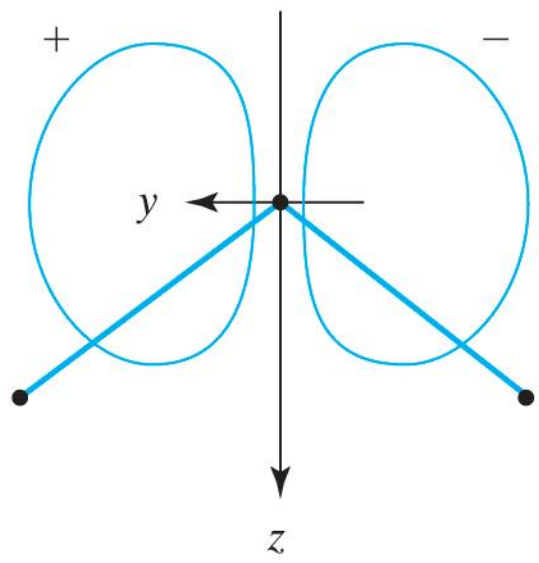
# SAO of HOH (basis functions: occ. AO of H and O)

표 14-2  $C_{2v}$  Character Table

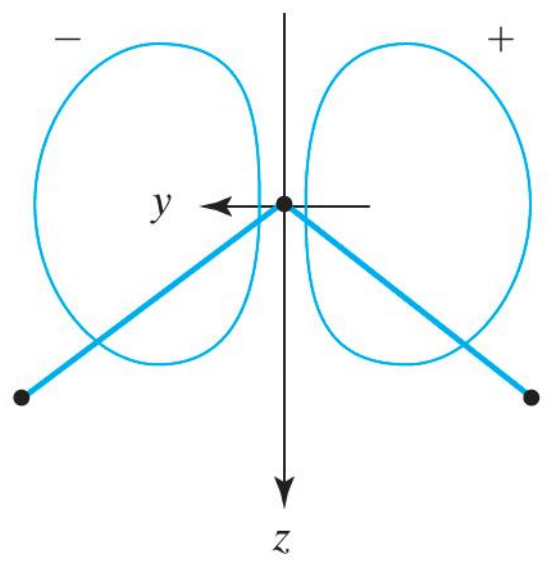
	E	$\hat{C}_2(z)$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v(yz)$		
A <sub>1</sub>	1	1	1	1	$z, 1s_0$	$x^2, y^2, z^2$
A <sub>2</sub>	1	1	-1	-1	$R_z$	$xy$
B <sub>1</sub>	1	-1	1	-1	$x$	$xz$
B <sub>2</sub>	1	-1	-1	1	$y$	$yz$

표 14-3 H<sub>2</sub>O 분자의 SAO

		$C_{2v}$	$D_{\infty h}$
X <sub>1</sub>	O <sub>1s</sub>	$a_1$	$\sigma_g$
X <sub>2</sub>	O <sub>2s</sub>	$a_1$	$\sigma_g$
X <sub>3</sub>	O <sub>2pz</sub>	$a_1$	$\pi$
X <sub>4</sub>	O <sub>2py</sub>	$b_2$	$\sigma_u$
X <sub>5</sub>	O <sub>2px</sub>	$b_1$	$\pi$
X <sub>6</sub>	H <sub>1</sub> 1s + H <sub>2</sub> 1s	$a_1$	$\sigma_g$
X <sub>7</sub>	H <sub>1</sub> 1s - H <sub>2</sub> 1s	$b_2$	$\sigma_u$

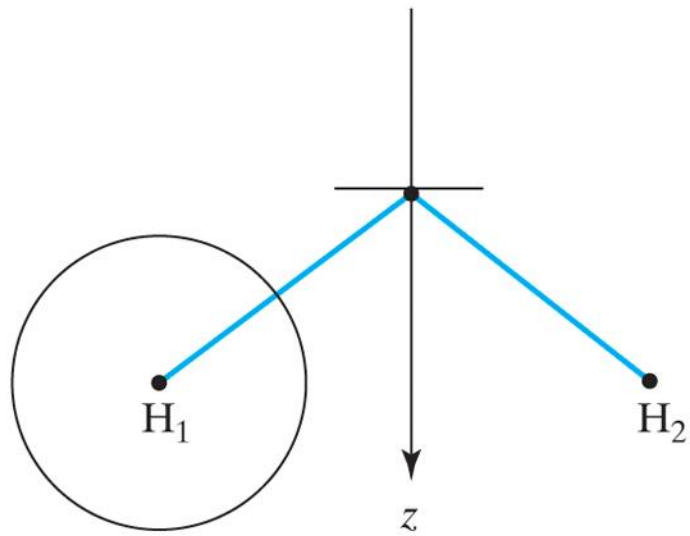


$$\xrightarrow{\hat{C}_2(z)}$$

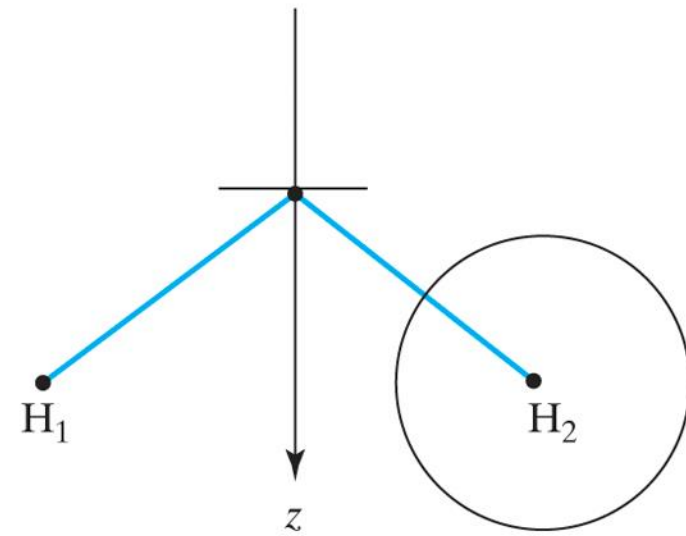


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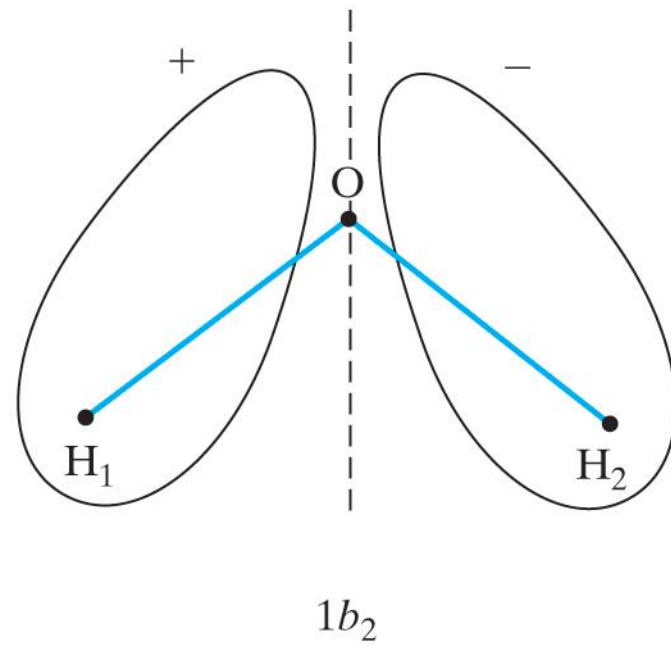
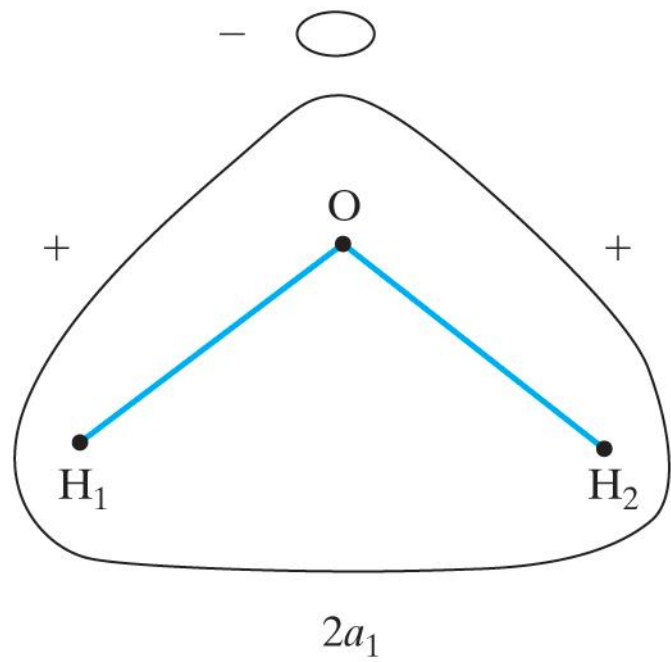




$$\xrightarrow{\hat{C}_2(z)}$$



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# Orbital interactions:

AO to SAO same as 2 equivalent  
SAOs to MO similar to non-equivalent

그림 14-3 Linear combination of two equivalent orbitals

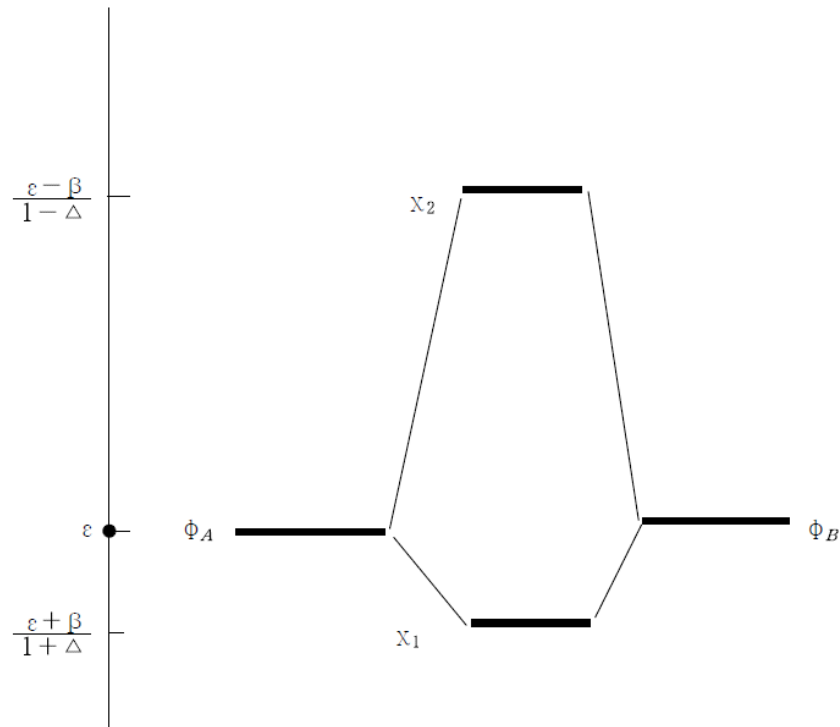


그림 14-4 Linear combination of non-equivalent orbitals

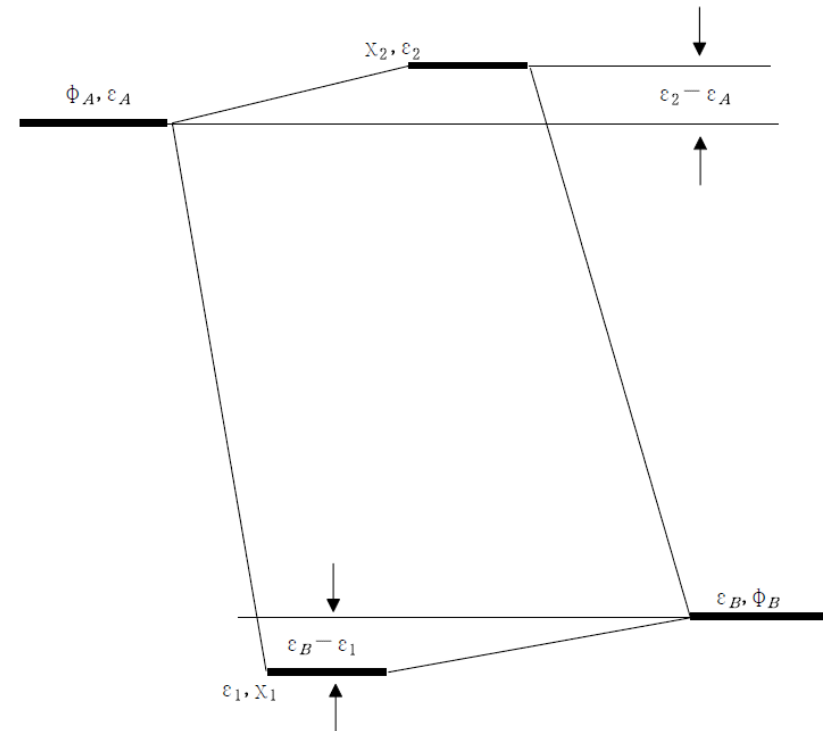
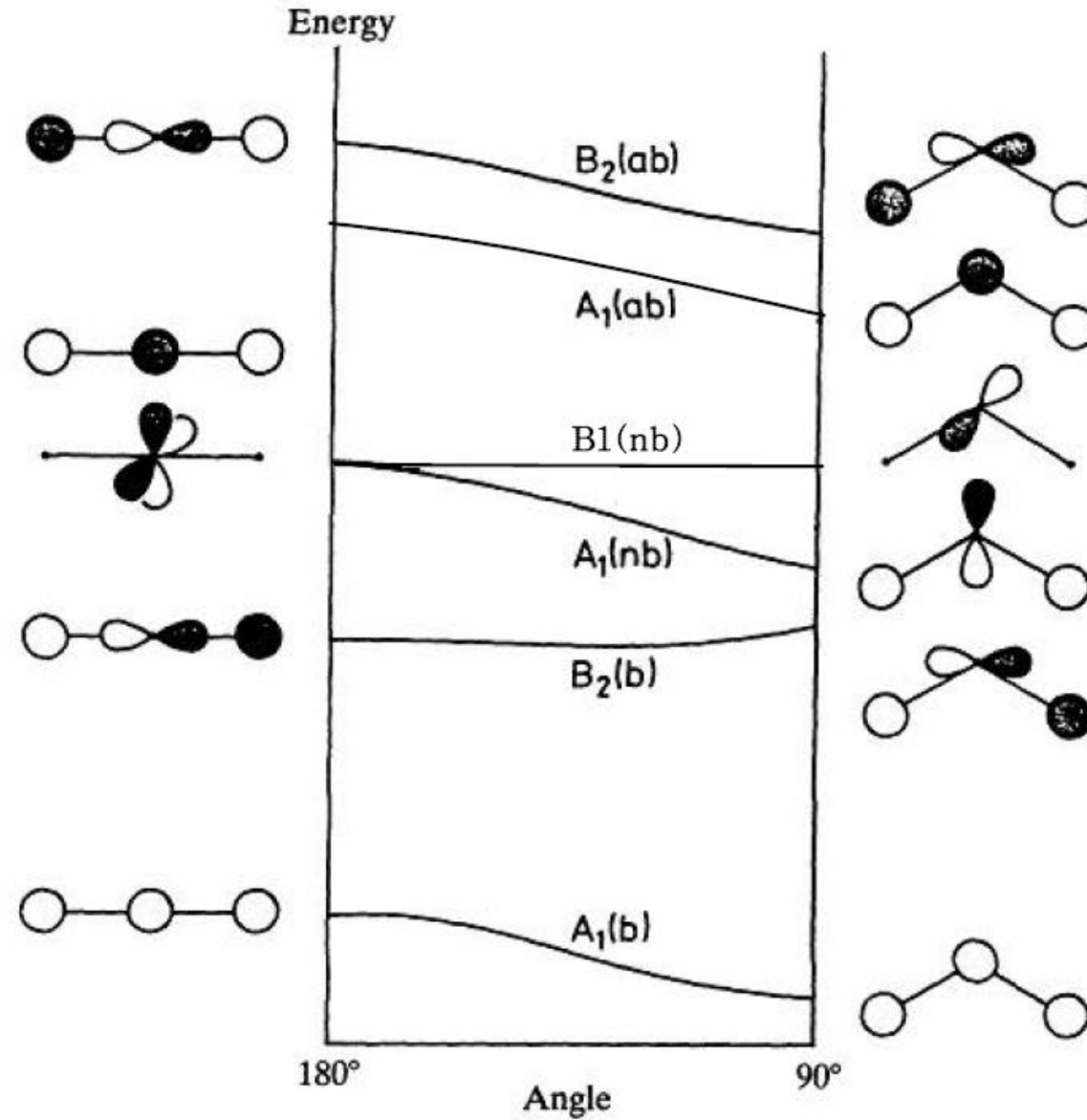
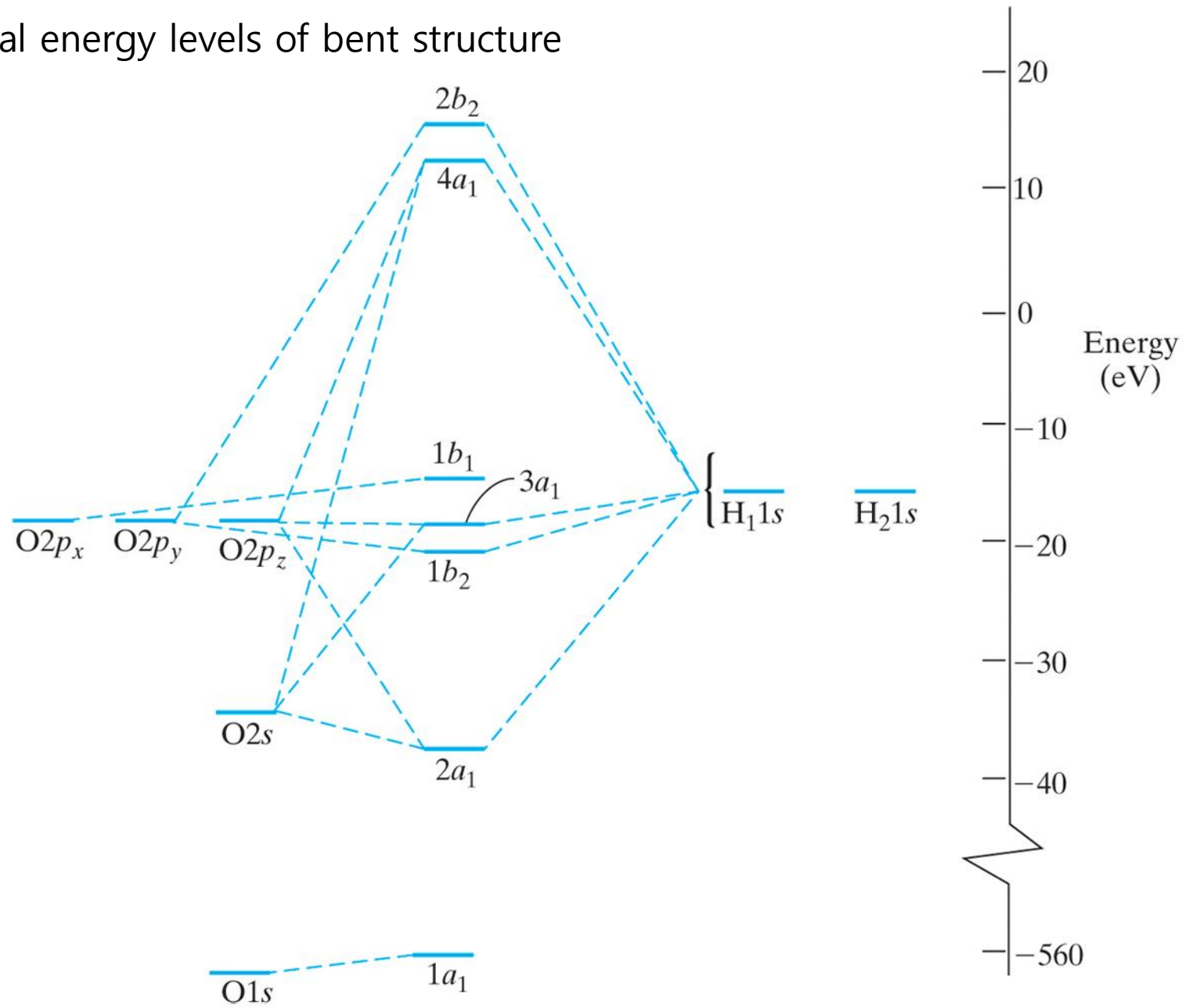


그림 14-5 H<sub>2</sub>O or AH<sub>2</sub> molecules. Energy of valence orbitals.



# Refined orbital energy levels of bent structure



상호작용의 정도와 결합성( $b$ ,  $nb$ ,  $ab$ )을 고려하면  $C_{2v}$  구조에서는 MO 에너지 순서가 그림14-5의 우측처럼

$$1a_1(nb) < 2a_1(b) < 1b_2(b) < 3a_1(nb) < 1b_1(nb) < 3a_1(ab) < 2b_2(ab)$$

가 예측된다. 선형 분자에서는

$$1\sigma_g(nb) < 2\sigma_g(b) < 1\sigma_u(b) < 1\pi_g(nb) < 3\sigma_g(ab) < 2\sigma_u(ab)$$

OHO bent structure preferred in all analyses.

# 양자화학 계산방법

## 8.3 ab initio Methods and Semi-empirical Methods

In electronic structure calculations there are two essentially different approaches, ab initio and semi-empirical.

Only mathematical approximation: ab initio

Empirical parameters: semi-empirical

Density functional theory (DFT) method is not based upon wave functions. Popular versions make use of orbitals determined by the 'first principle' method.

## QUANTITIES AVAILABLE FROM MO CALCULATIONS

- Molecular energies and structures
- Energies and structures of transition states
- Bond and reaction energies
- Molecular orbitals
- Multipole moments
- Atomic charges and electrostatic potentials
- Vibrational frequencies
- IR and Raman spectra
- UV/VIS spectra
- NMR properties
- Polarizabilities and hyperpolarizabilities
- Thermochemical properties
- Reaction pathways **and more**



# 양자화학 계산 체험 – webmo.net

The screenshot shows the webmo.net website interface. At the top, there is a navigation bar with the WebMO logo and links for Home, About, Features, Support, and Get WebMO. A banner below the navigation bar states "WebMO 21.0 is now available!". The main content area features the heading "WebMO" and a section titled "What is WebMO?". Below this, a paragraph states "WebMO is a web-based interface to computational chemistry packages." followed by a bulleted list of features:

- WebMO allows students and non-specialists to run state-of-the-art computational chemistry programs from the web-browser on their computer
- Intuitive for novices: point-and-click molecular editor, pre-defined job types, reasonable default values
- Flexible for experts: advanced job options, full access to input and output files

To the right of the text is a plot titled "Coordinate Scans". The y-axis is labeled "Energy" and ranges from -200 to -50. The x-axis is labeled "Coordinate" and ranges from 1.00 to 3.00. The plot shows a blue line with circular markers representing the energy profile. The energy starts at approximately -50 at coordinate 1.00, drops sharply to a minimum of about -190 at coordinate 1.45, then rises to a local maximum of about -160 at coordinate 2.00, and finally levels off around -175 for coordinates greater than 2.50. The plot is titled "Coordinates Scan" in the legend.

Below the plot, there is a section titled "Install WebMO Once; Run from Anywhere". At the bottom of the screenshot, the Windows taskbar is visible, showing the search bar and various application icons. The system tray on the right indicates the date and time as "오전 10:46 2022-02-01".

Various quantum chemical calculations can be readily performed by packages – can be used directly or through user interface program like 'webmo'

The screenshot displays the WebMO web interface. At the top, there is a navigation bar with the WebMO logo and links for Home, About, Features, Support, and Get WebMO. A 'Demo' button is also present. Below the navigation bar, there is a section titled 'Choose Computational Engine'. This section contains a table with columns for 'Engine' and 'Description'. The 'Gaussian' engine is selected. To the right of the table, there is explanatory text about supported engines and configuration options. Below the table, there is a 'Select Server' dropdown menu set to 'buchner.chem.hope.edu'. At the bottom of the interface, there is a 'Job Options' section. The browser's address bar shows 'webmo.net/about/screenshots.html'. The Windows taskbar at the bottom indicates the system time as 10:48 on 2022-02-01.

Build - C (click = add atom, drag = add bond, click & drag = add atom & bond, letter = change atom)

### Choose Computational Engine

Status	Engine	Description
smith	<input type="radio"/> Gamess	Ab initio and semi-empirical calculations
webmo	<input checked="" type="radio"/> Gaussian	Ab initio and semi-empirical calculations
unlimited	<input type="radio"/> Molpro	Ab initio calculations
unlimited	<input type="radio"/> Mopac	Semi-empirical calculations
0 jobs	<input type="radio"/> NWChem	Ab initio calculations
	<input type="radio"/> ORCA	Ab initio calculations
	<input type="radio"/> PS14	Ab initio calculations
	<input type="radio"/> Quantum Espresso	Periodic plane wave DFT
	<input type="radio"/> QChem	Ab initio calculations
	<input type="radio"/> Tinker	Molecular mechanics calculations

Select Server: buchner.chem.hope.edu

WebMO supports a wide variety of free and commercial computational engines, including Gamess, Gaussian, MolPro, Mopac, NWChem, Orca, PQS, PSI, Q-Chem, TeraChem, Tinker, Quantum Espresso, and VASP.

These computational engines can be enabled, disabled, and configured from the web-based WebMO administration interface.

### Job Options

**Hartree-Fock (HF) wavefunction satisfies antisymmetry. – electrons are fermions**

$$\Psi(\dots, r_i, \dots, r_j, \dots) = -\Psi(\dots, r_j, \dots, r_i, \dots)$$

- Slater determinant is the way to achieve antisymmetry from the product functions. (row for electrons, column for spin-orbitals)

$$\Psi = \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \dots & \psi_n(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \dots & \psi_n(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{r}_n) & \psi_2(\mathbf{r}_n) & \dots & \psi_n(\mathbf{r}_n) \end{vmatrix}$$

$$\Psi = \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \dots & \psi_n(\mathbf{r}_n) \end{vmatrix}$$

Normalization factor (1/n!) omitted.

# Constructing a 1-Electron Wave Function

The units of the wave function are such that its square is electron per volume. As electrons are quantum particles with non-point distributions, sometimes we say “density” or “probability density” instead of electron per volume (especially when there is more than one electron, since they are indistinguishable as quantum particles)

For instance, a valid wave function in cartesian coordinates for one electron might be:

$$\phi(x, y, z; Z) = \underbrace{\frac{\sqrt{2}Z^{5/2}}{81\sqrt{\pi}}}_{\text{normalization factor}} \underbrace{\left(6 - Z\sqrt{x^2 + y^2 + z^2}\right)}_{\text{radial phase factor}} \underbrace{y}_{\text{cartesian directionality (if any)}} \underbrace{e^{-Z\sqrt{x^2 + y^2 + z^2}/3}}_{\text{ensures square integrability}}$$

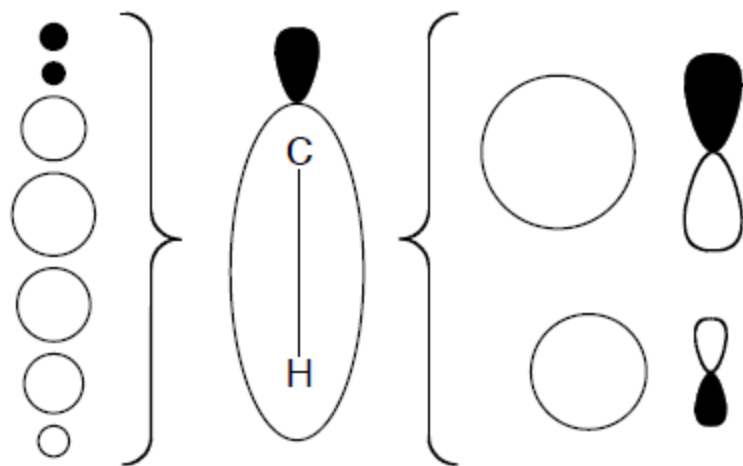


# Constructing a 1-Electron Wave Function

To permit additional flexibility, we may take our wave function to be a linear combination of some set of common “basis” functions, e.g., atomic orbitals (LCAO). Thus

$$\phi(\mathbf{r}) = \sum_{i=1}^N a_i \varphi(\mathbf{r})$$

For example, consider the wave function for an electron in a C–H bond. It could be represented by *s* and *p* functions on the atomic positions, or *s* functions along the bond axis, or any other fashion convenient.



With basis set expansion, Fock equation in HF method can be written in matrix form

## Fock Operator (effective Hamiltonian of HF method)

$$F_{\mu\nu} = \langle u | -\frac{\nabla^2}{2} | v \rangle - \sum_k \langle u | \frac{Z_k}{r} | v \rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[ \langle \mu\nu | \lambda\sigma \rangle - \frac{1}{2} \langle \mu\lambda | \nu\sigma \rangle \right]$$

Density Matrix  $P_{\lambda\sigma} = 2 \sum_i^{\text{occupied MOs}} a_{\lambda i} a_{\sigma i}$

Treat electrons as average field

2 electron integral

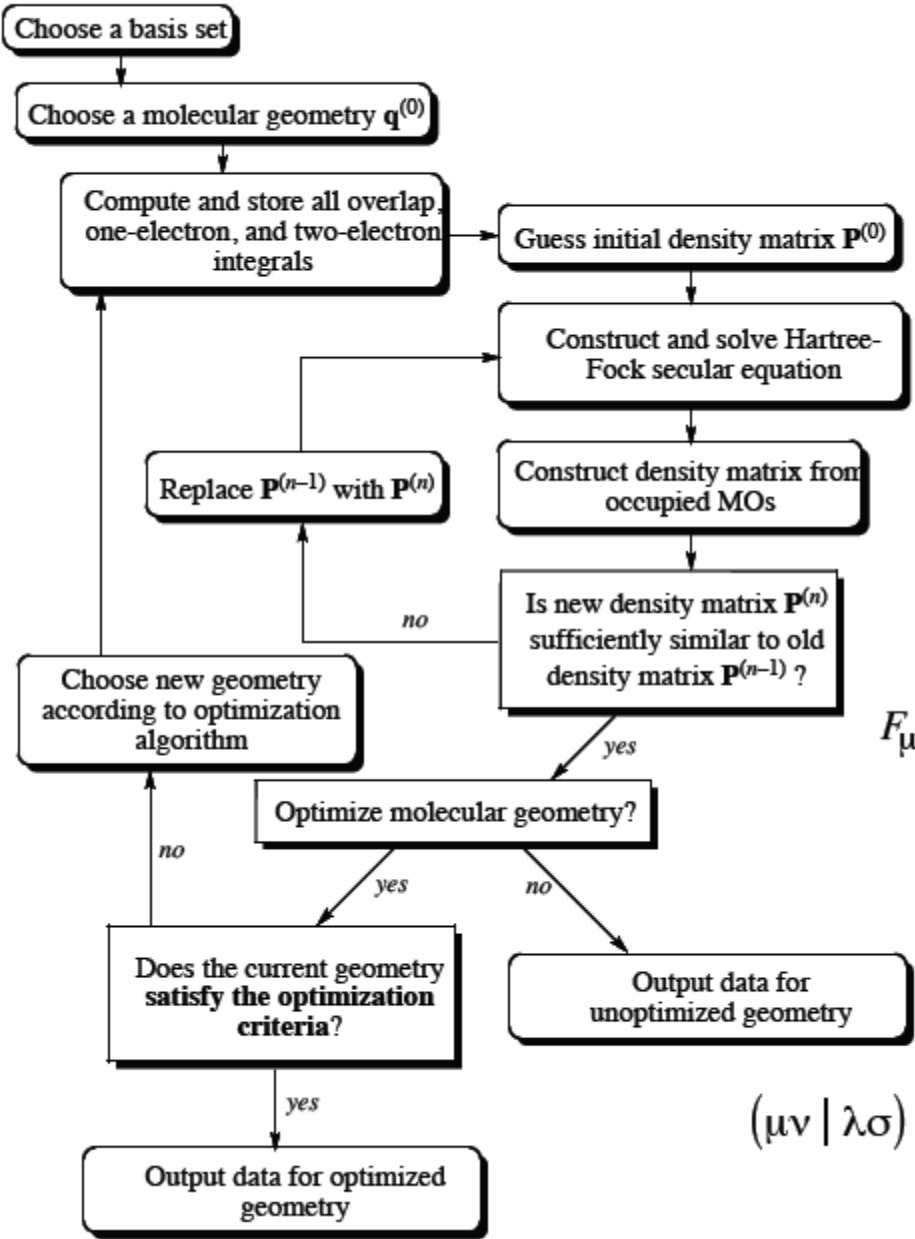
- 2 electron integrals scale as  $N^4$

Expansion coefficients and thus the density matrix is required to define Fock operator  
 - Iterative method is usually required to obtain HF orbitals and energies

## Roothaan-Hall Equations (same as HFR)

- basis set expansion leads to a matrix form of the Fock equations
$$\mathbf{F} \mathbf{C}_i = \varepsilon_i \mathbf{S} \mathbf{C}_i$$
- $\mathbf{F}$  – Fock matrix
- $\mathbf{C}_i$  – column vector of the molecular orbital coefficients
- $\varepsilon_i$  – orbital energy
- $\mathbf{S}$  – overlap matrix

# The Hartree-Fock procedure



$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \dots & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \dots & F_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ F_{M1} - ES_{M1} & F_{M2} - ES_{M2} & \dots & F_{MN} - ES_{MN} \end{vmatrix} = 0$$

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right]$$

$$P_{\lambda\sigma} = 2 \sum_i^{\text{occupied}} a_{\lambda i} a_{\sigma i}$$

$$(\mu\nu | \lambda\sigma) = \iint \phi_\mu(1)\phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda(2)\phi_\sigma(2) d\mathbf{r}(1)d\mathbf{r}(2)$$

One MO per root E



# Total E of molecule in HF!

- Not equal to sum of orbital binding energy of occupied electrons.

- HF energy

$$E_{HF} = \sum_{i=1}^{n/2} \epsilon_i + \sum_{i=1}^{n/2} H_{ii} = \sum_{i=1}^{n/2} \epsilon_i + \frac{1}{2} \sum_{r=1}^b \sum_{s=1}^b P_{rs} H_{rs}^{core}$$

- Reported HF energy for molecules also contains **nuclear repulsion contributions** – called potential E of a molecule (or E on PES)
- Same applies to some semiempirical MO methods.

# HF results at the given geometry

- Electron configuration (lowest state of each symmetry)
  - Charge
  - Multiplicity
  - RHF or UHF (restricted or unrestricted orbitals)
- Basis set (set of mathematical functions)
  - LCAO defines orbitals (AO's are basis functions)
  - Wavefunction approximated by Slater determinant of spinorbitals

## What functions to use?

- Slater Type Orbitals (STO)

$$\phi_{1s} = \left(\frac{\zeta}{\pi}\right)^{1/2} e^{-\zeta \cdot r}$$

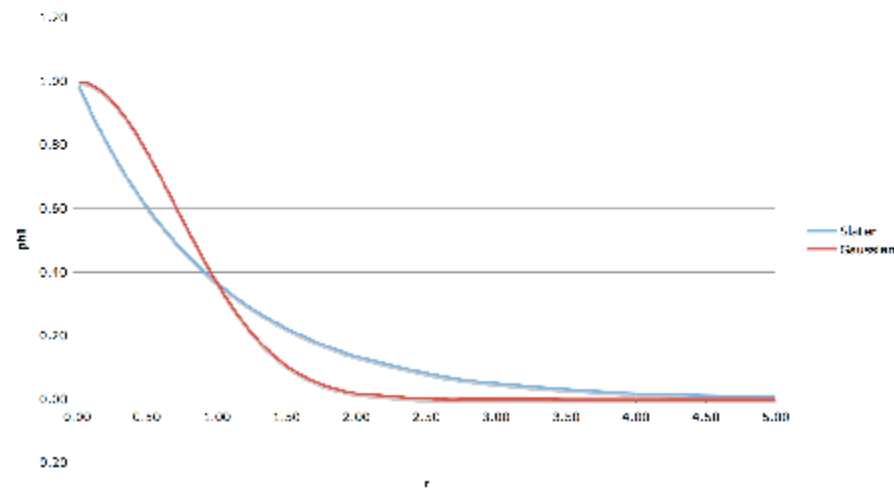
- Can't do 2 electron integrals analytically

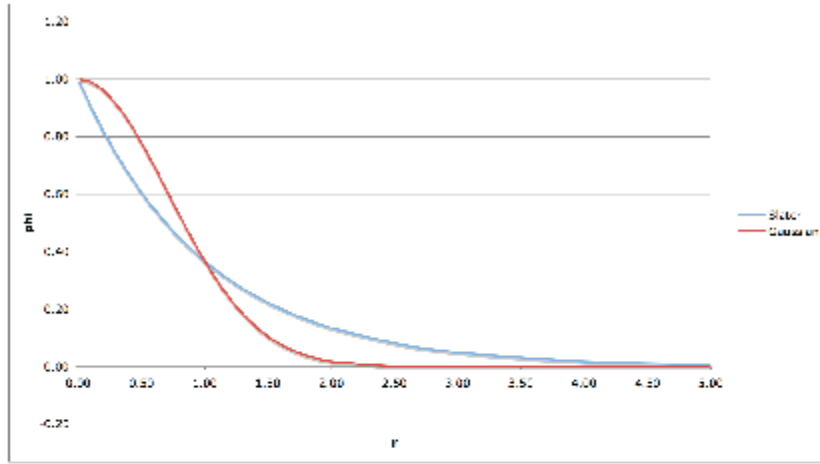
$$\iint \phi_{\mu}(1) \phi_{\nu}(1) \frac{1}{r_{12}} \phi_{\lambda}(2) \phi_{\sigma}(2) dr_1 dr_2$$

- 1950s

- Replace with something similar that is analytical: a gaussian function

$$\phi_{1s} = \left(\frac{\zeta}{\pi}\right)^{1/2} e^{-\zeta \cdot r} \quad \text{VS.} \quad \phi_{"1s"} = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha r^2}$$

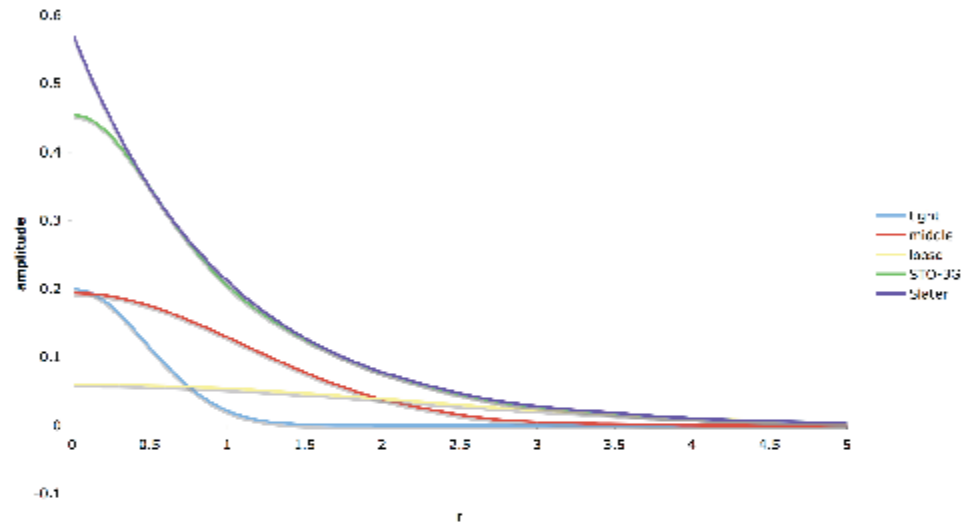




- Wow, not the best
- How about more than just one gaussian?

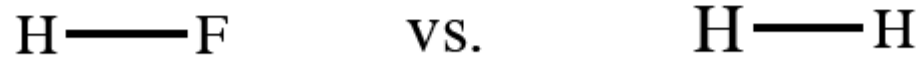
$$\phi_{1s^n} = \sum_i^N a_i \left( \frac{2\alpha_i}{\pi} \right)^{3/4} e^{-\alpha_i r^2}$$

# Contracted Basis Set

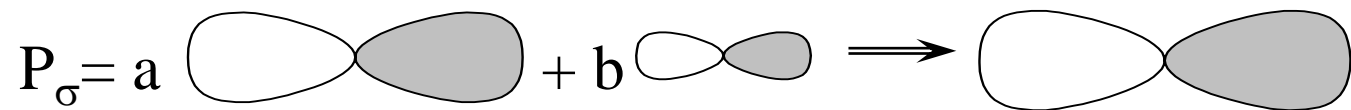


- STO-#G - minimal basis
- Pople - optimized  $a$  and  $\alpha$  values

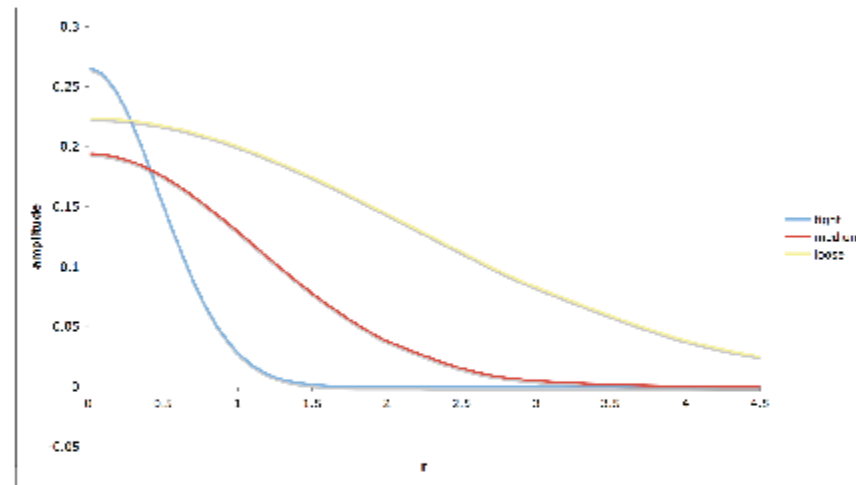
$$\phi_{1s} = \sum_i^N a_i \left( \frac{2\alpha_i}{\pi} \right)^{3/4} e^{-\alpha_i r^2}$$



- What            about very different bonding situations?
  - Have more than one 1s orbital
- Multiple- $\zeta$ (zeta) basis set
  - Multiple functions for the same atomic orbital



- Double- $\zeta$  – one loose, one tight
  - Adds flexibility



- Triple- $\zeta$  – one loose, one medium, one tight
- Only for valence



## Generating 21G from STO-3G

- Decontraction

- Allow  $a_i$  to vary

$$\phi_{1s_H}^{STO-3G} = \sum_i^3 a_i \left( \frac{2\alpha_i}{\pi} \right)^{3/4} e^{-\alpha_i r^2}$$

locked in STO-3G

primitive gaussians

- Pople - #-##G

- 3-21G

gaussian

valence: 2 tight, 1 loose

primitives in all core functions

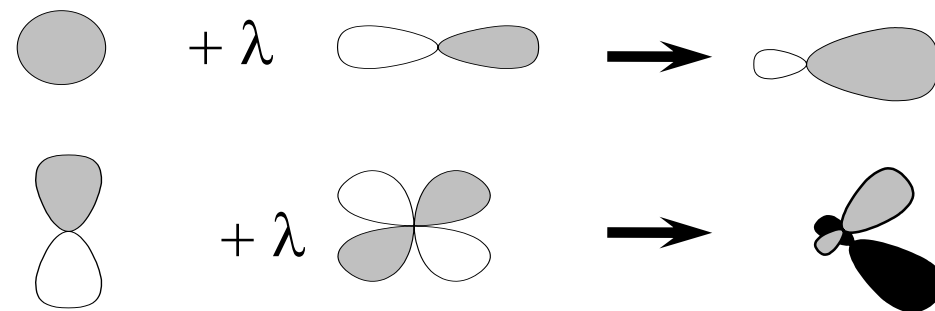
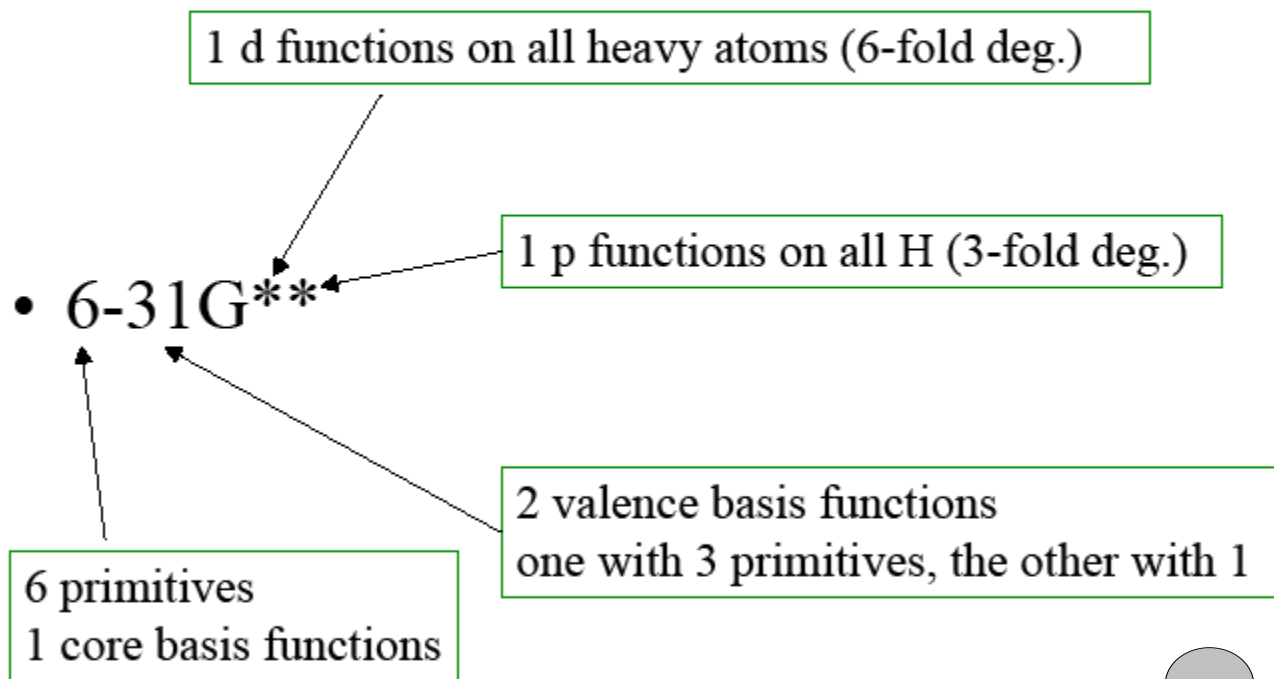
## Contraction basis set sample

**TABLE 15.1 The 3-21G Basis Set for the Oxygen Atom**

O	0			
S	3	1.00		
		322.03700000	0.05923940	
		48.43080000	0.35150000	
		10.42060000	0.70765800	
SP	2	1.00		
		7.40294000	-0.40445300	0.24458600
		1.57620000	1.22156000	0.85395500
SP	1	1.00		
		0.37368400	1.00000000	1.00000000

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# Polarization Functions



6 component d (Cartesian) vs 5 component d (Spherical)

# Additional basis

- More than two split valence
- Diffuse functions for (-) ionic character
- Effective core potentials (or pseudopotentials) and matching basis
- k-lmn..+...G(xdyf...,zp...)
  - e.g. 6-311++G(3d2f1g,3p2f)

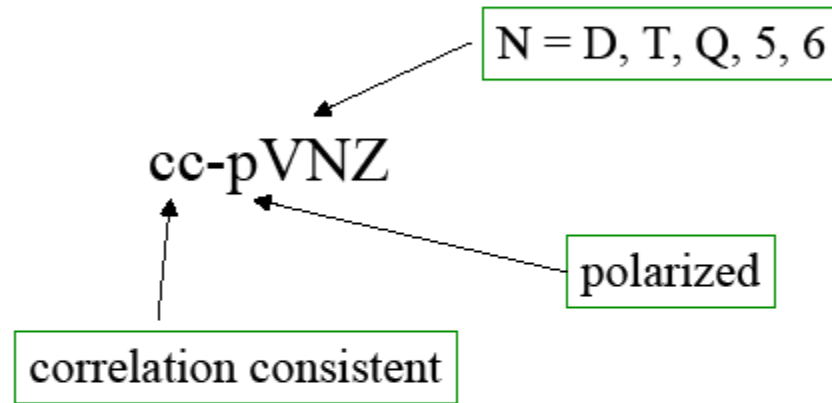
- For HF,  $\text{NH}_3$  is planar with infinite basis set of s and p basis functions!!!!



- Better way to write – 6-31G(3d2f, 2p)
- Keep balanced

Valence split	polarization
2	d, p
3	2df, 2pd
4	3d2fg, 3p2df

# Dunning basis set



Expansion is carried out systematically –  
quickly becomes very large

# Diffuse functions

- “loose” electrons
  - anions
  - excited states
  - Rydberg states
- Dunning - aug-cc-pVNZ
  - Augmented
- Pople
  - 6-31+G - heavy atoms/only with valence
  - 6-31++G - hydrogens
    - Not too useful

Inbox (51.694) - yilee@kaist.edu X Build Molecule x 받은 메일함 | Computational C x 신문@가게 x +

hrtree.kaist.ac.kr/webmo/cgi-bin/webmo/build\_molecule.cgi

### Build Molecule

Status yilee webmo unlimited unlimited 0 jobs

File Edit Tools Build Cleanup Calculate Lookup Help


Progress

- Job manager
- Build molecule

Build a new molecule using the VABMO editor or import an existing molecule from a file. Additionally, you can export the molecule to a variety of file formats.

- Choose engine
- Job options
- Submit job

Editor help



Build - H (click = add atom; drag = add bond; click & drag = add atom & bond; letter = change atom)

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hrtree.kaist.ac.kr/webmo/cgi-bin/webmo/build\_molecule.cgi

### Build Molecule

Status yilee webmo unlimited unlimited 0 jobs

File Edit Tools Build Cleanup Calculate Lookup Help

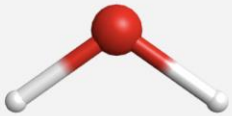
Progress

- Job manager
- Build molecule

Build a new molecule using the VABMO editor or import an existing molecule from a file. Additionally, you can export the molecule to a variety of file formats.

- Choose engine
- Job options
- Submit job

Editor help



Build - H (click = add atom; drag = add bond; click & drag = add atom & bond; letter = change atom)

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# Configure Gaussian Job Options

Status << Job Options | Advanced | Preview | Notes

yslee  
webmo  
unlimited  
unlimited  
0 jobs

Progress

- Job manager
- Build molecule
- Choose engine
- Job options

Configure options for the selected job and computational engine.

- Submit job

Help

Job Name:

Calculation:

Theory:

Basis Set:

Charge:

Multiplicity:

# Configure Gaussian Job Options

**Status** << Job Options Advanced Preview Notes

- yslee
- webmo
- unlimited
- unlimited
- 0 jobs

**Progress**

- Job manager
- Build molecule
- Choose engine
- Job options

Click Generate, edit input file if desired, and click Submit Job to submit edited file.

- Submit job
- Help

```
#N HF/6-31G(d) SP Geom=Connectivity
H2O
0 1
0
H 1 B1
H 1 B2 2 A1
B1 1.050000000
B2 1.050000000
A1 109.4712206
1 2 1 3 1
2 1 1
3 1 1
```

Generate

# Calculated Quantities

Collapse all

## Overview

Quantity	Value
Route	#N HF/6-31G(d) SP Geom=Connectivity
Stoichiometry	H <sub>2</sub> O
Symmetry	C2V
Basis	6-31G(d)
RHF Energy	-75.9914343657 Hartree
Dipole Moment	2.2006 Debye
Server	hartree.kaist.ac.kr (0)
CPU time	0.6 sec

## Rotational Constants

Constant	Frequency (GHz)	Frequency (cm <sup>-1</sup> )
a	768.2279737	25.62532689532
b	341.1259186	11.37873583864
c	236.2298226	7.87977870344

## Partial Charges

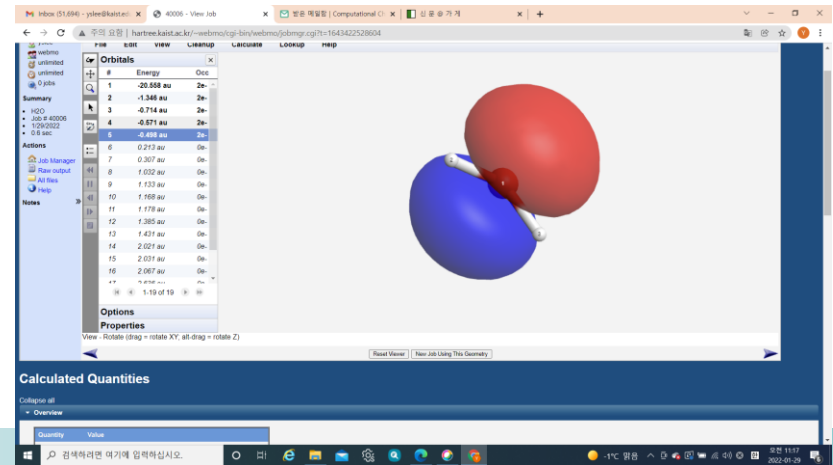
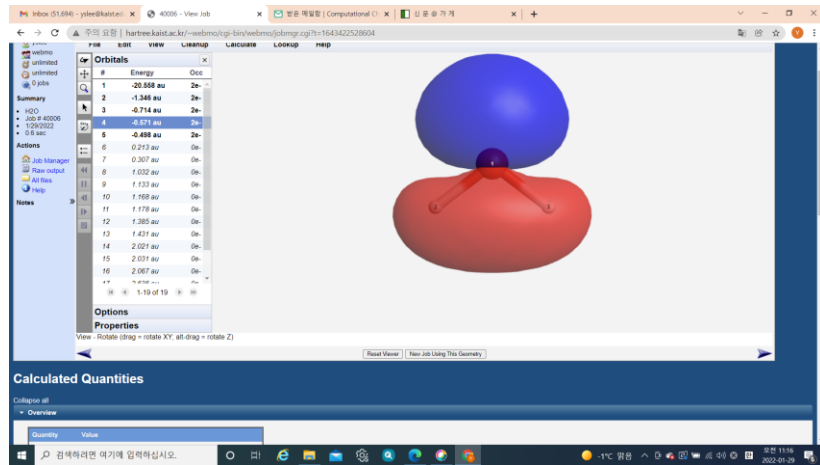
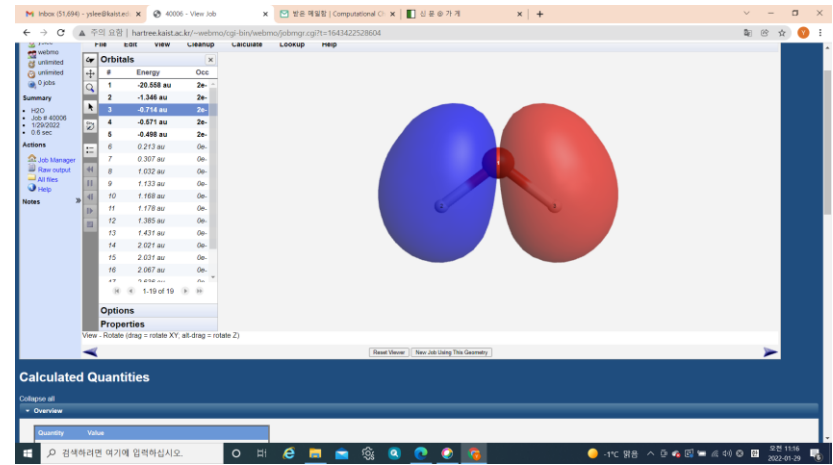
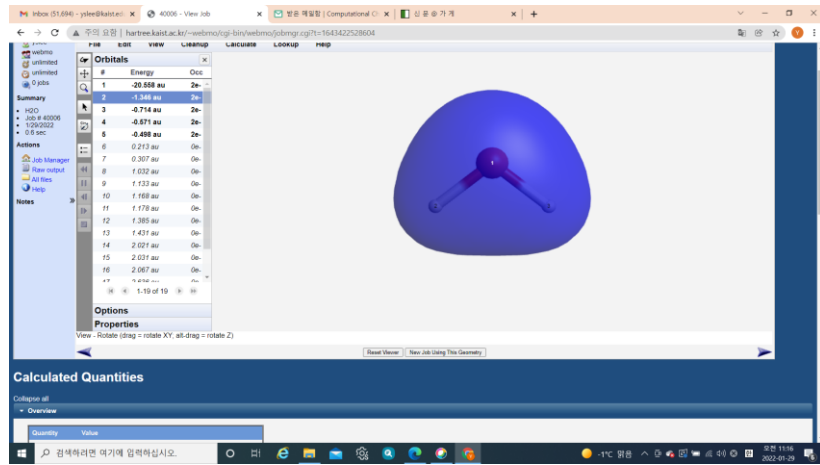
Atom	Symbol	Charge
1	O	-0.855136
2	H	0.427568
3	H	0.427568

## Quote

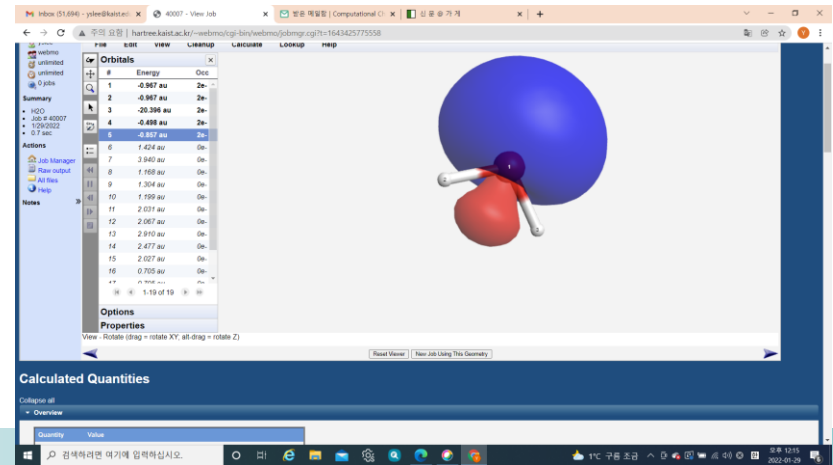
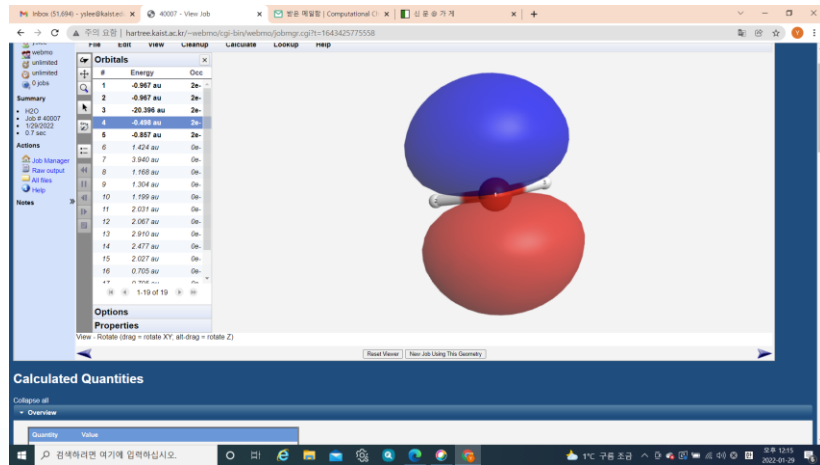
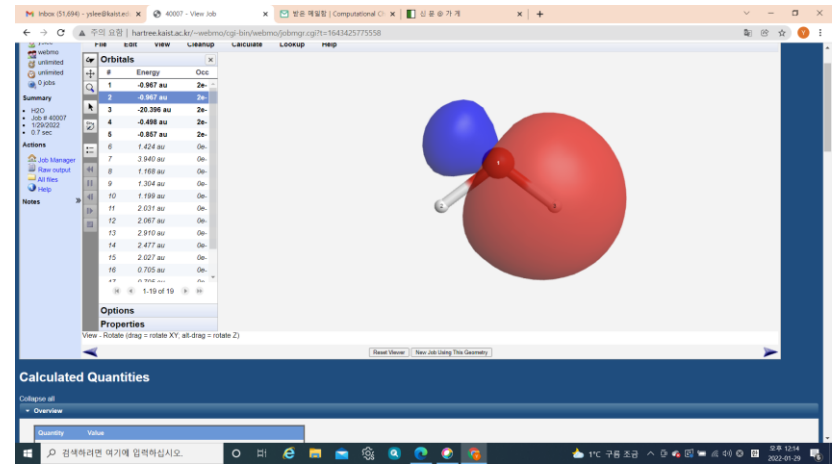
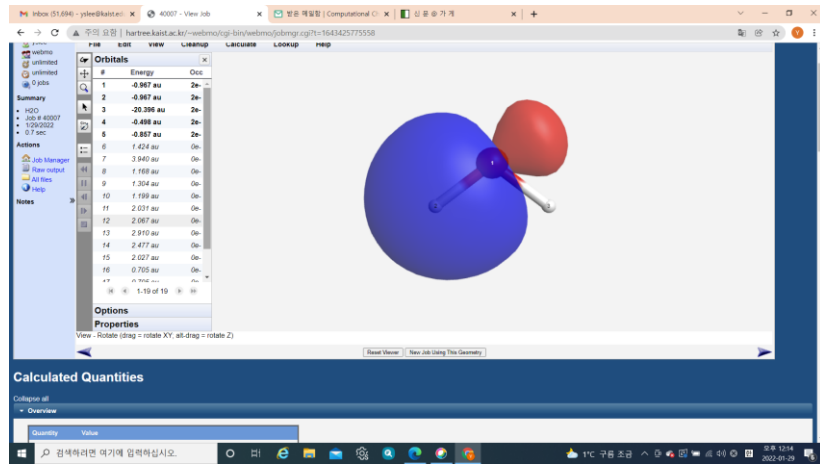
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3°C 맑음 오후 5:32  
2022-01-28

# Canonical HF orbitals of H<sub>2</sub>O



# Valence bond orbitals obtained from natural bond analysis HF orbitals – similar to hybrid atomic orbital ( $sp^2$ on O)



Dec. 5, 2003

# HF limit

- With the infinite number of basis functions, one gets HF-limit solutions
  - Finite basis set always contains basis set incompleteness error (minimize by balancing)
- One may utilize additivity and/or extrapolation to estimate HF-limit
- HF-limit wave functions are still crude approximation
  - Electron correlation energy ( $E_{\text{exact}} - E_{\text{HF}}$ )

# Effective core potentials (ECP)

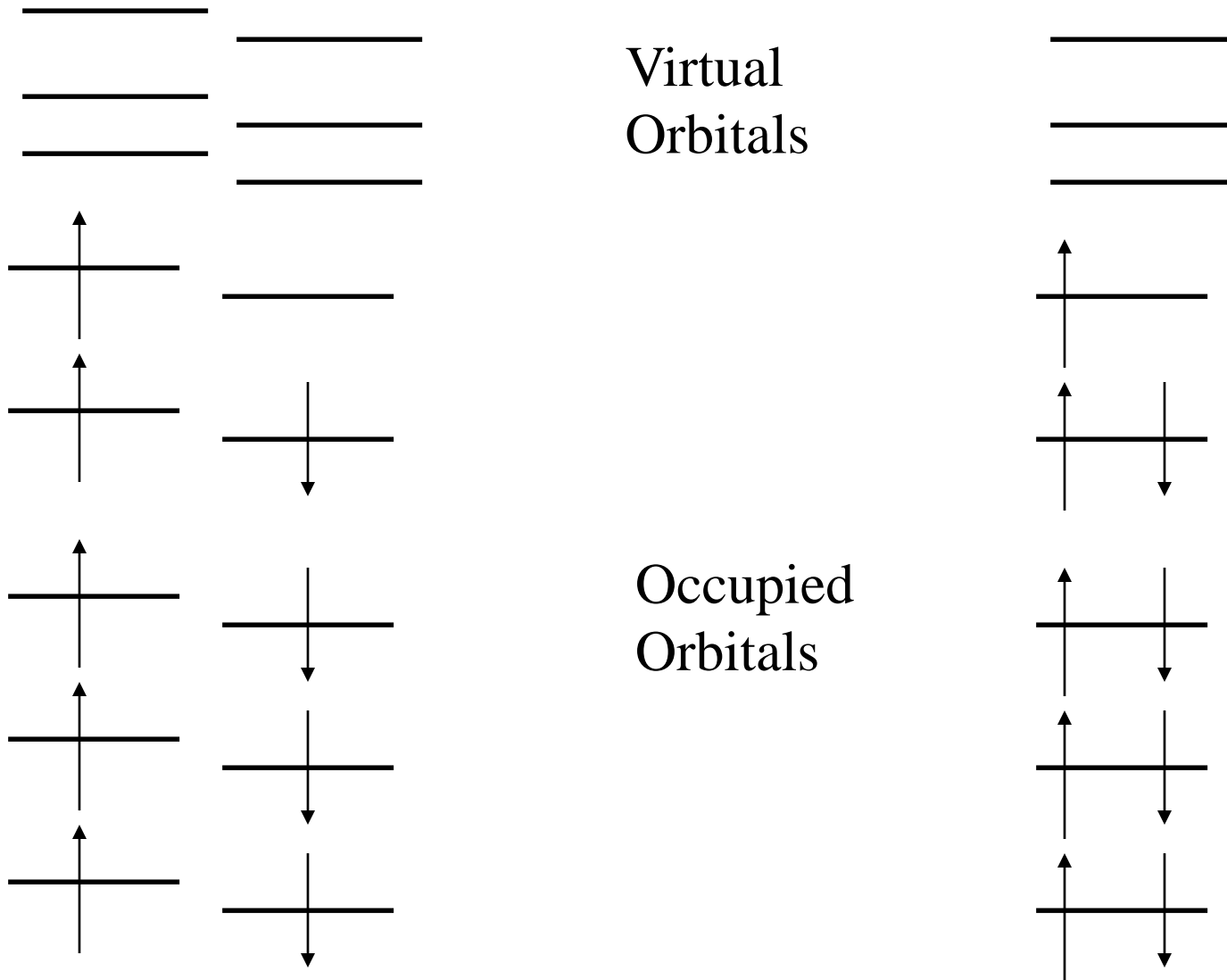
- ECP, pseudo potential, model potentials are different names
- Replace core electrons with effective potentials and omit core from calculation
  - Save computation (reduce number of basis functions and dimensions of F matrix)
- Useful for heavy atoms
  - Could include relativistic and other higher order contributions
- Many sets have been developed and available (ex. LANL, SD etc.)
- Frozen core approximation (usually no core orbitals in calculations)
- Transferability determines accuracy

# Types of Hartree-Fock Wavefunctions

- Closed shell, RHF
  - spin restricted Hartree-Fock
  - $\alpha$  and  $\beta$  spin electrons share the same spatial orbitals
- Open shell, UHF
  - spin unrestricted Hartree-Fock
  - $\alpha$  and  $\beta$  spin electrons have different spatial orbitals
- Open shell, ROHF
  - spin restricted open shell Hartree-Fock
  - most  $\alpha$  and  $\beta$  spin electrons have the same spatial orbitals
  - singly occupied orbitals hold the remaining electrons

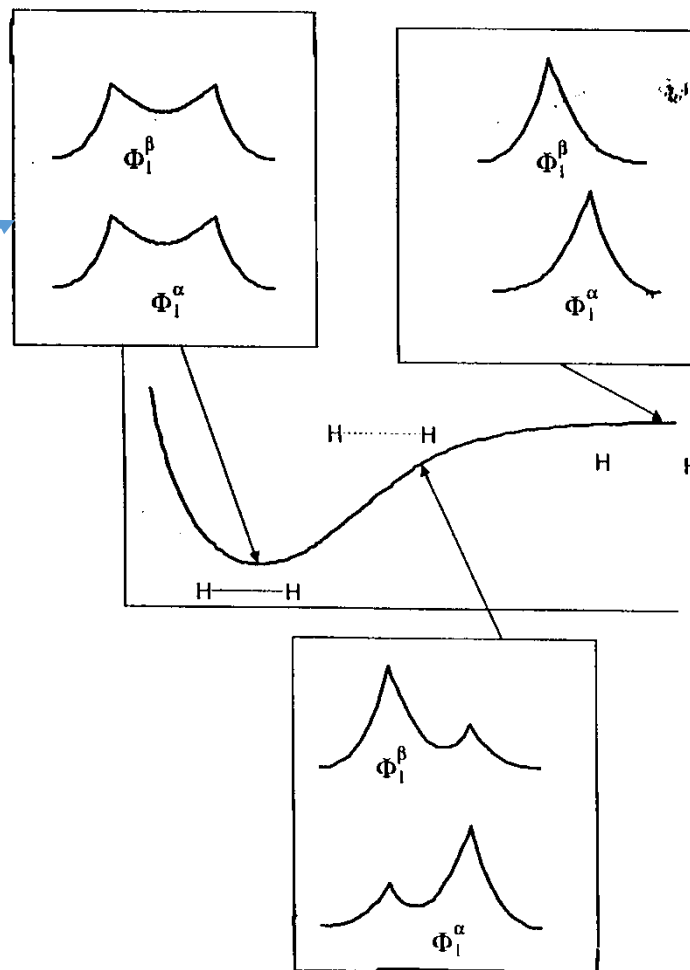


# UHF and ROHF open shell



# UHF orbitals for H<sub>2</sub>

RHF orbitals for all bond distances



# Practical points of HF methods

- SCF convergence
  - Good initial guess important (solution of similar systems if available may be best, otherwise default options)
  - Extrapolations and interpolations
- Symmetry can reduce computation
  - block diagonal F matrix
  - smaller number of unique integrals
  - Reduced dimensionality of PES, especially useful for transition state search

# Larger systems

- Direct method: recompute integrals when needed and do not store 2-e integrals
- Linear scale method
  - Only calculate integrals larger than the threshold
  - Calculate small integrals crudely or only approximately
- Efficient geometry optimization and/or Hessian evaluation

# Performance of ab initio HF theory

- Problem dependent – search literature
  - Good geometry
  - Poor energy difference when different bondings are involved
  - Rough estimates of ionization energies from Koopmans theorem useful
  - Charge distributions reasonable in many cases



# Electron Correlation

## How Important is It?

Recall the fundamental approximation of the Hartree-Fock method: interactions between opposite-spin electrons are treated in an *average* way, not an instantaneous way

$$f_i = -\frac{1}{2}\nabla_i^2 - \sum_k^{\text{nuclei}} \frac{Z_k}{r_{ik}} + V_i^{\text{HF}}\{j\}$$

Infinite basis set results



H

*One electron*

$$E_{\text{HF}} = -0.500\ 00 \text{ a.u.}$$

$$E_{\text{exact}} = -0.500\ 00 \text{ a.u.}$$



He

*Two electrons*

$$E_{\text{HF}} = -2.861\ 68 \text{ a.u.}$$

$$E_{\text{exact}} = -2.903\ 72 \text{ a.u.}$$

Error  $\sim 26 \text{ kcal mol}^{-1}$  !

# Electron Correlation Energy

## Post HF Methods ; Electron Correlation Methods.

### Definition

- $E_{\text{corr}} = E_{\text{non-rel,true}} - E_{\text{HF}}$  : Difference between the exact non-relativistic energy and the Hartree-Fock limit energy.
- Static correlation : near-degeneracy effects, internal correlation . Improper description of a state by a single determinant wave function. --> Demands multi-reference determinants. cf. MCSCF and CASSCF.
- Dynamic correlation : from the two-electron cusp. -- Improper description for short distance multi-electron coordinates. (about 20 kcal per e pair)
- Multi-particle basis expansion.  $\Psi = \sum_i C_i \Psi_i$  :  $\Psi_i$ =Slater Determinants.



# General Approaches

- include  $r_{12}$  in the wavefunction
  - suitable for very small systems
  - too many difficult integrals
  - Hylleras wavefunction for helium
- expand the wavefunction in a more convenient set of many electron functions
  - Hartree-Fock determinant and excited determinants
  - Large number of excited determinants, slow to converge
  - configuration interaction (CI)

# Goals for Correlated Methods

- well defined
  - applicable to all molecules with no ad-hoc choices
  - can be used to construct model chemistries
- efficient
  - not restricted to very small systems
- variational
  - upper limit to the exact energy
- size extensive
  - $E(A+B) = E(A) + E(B)$
  - needed for proper description of thermochemistry
- hierarchy of cost vs. accuracy
  - so that calculations can be systematically improved

## Correlated Methods. I. Configuration Interaction

A Hartree-Fock one-electron orbital is expressed as a linear combination of basis functions with expansion coefficients optimized according to a variational principle

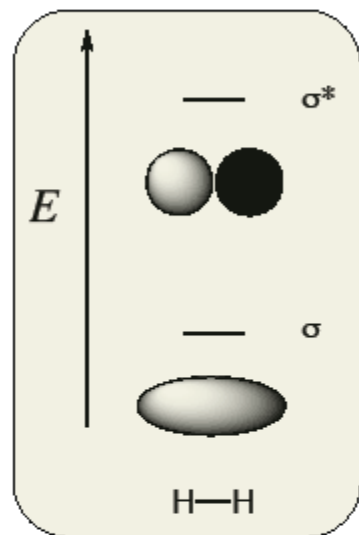
$$| \mathbf{F} - E\mathbf{S} | = 0 \quad \longrightarrow \quad \phi = \sum_{i=1}^N a_i \varphi_i$$

The HF many-electron wave function is the Slater determinant formed by occupation of lowest possible energy orbitals, *but, the HF orbitals are not "perfect" because of the HF approximation*

So, one way to improve things would be to treat the different Slater determinants that can be formed from *any occupation of HF orbitals to themselves* be a basis set to be used to create an improved many-electron wave function

$$| \mathbf{H} - E\mathbf{S} | = 0 \quad \longrightarrow \quad \Psi = a_0 \Psi_{\text{HF}} + \sum_i^{\text{occ.}} \sum_r^{\text{vir.}} a_i^r \Psi_i^r + \sum_{i < j}^{\text{occ.}} \sum_{r < s}^{\text{vir.}} a_{ij}^{rs} \Psi_{ij}^{rs} + \dots$$

## Configuration Interaction (CI) Example: Minimal Basis H<sub>2</sub>



$$\Psi_{\text{CI}} = a_0 \Psi_{\text{HF}} + \sum_i^{\text{occ. vir.}} \sum_r a_i^r \Psi_i^r + \sum_{i < j}^{\text{occ. vir.}} \sum_{r < s} a_{ij}^{rs} \Psi_{ij}^{rs} + \dots$$

$$= a_{1(0)} |\sigma^2\rangle + 0 + a_2 |\sigma^{*2}\rangle$$

$$|\mathbf{H} - E\mathbf{S}| = 0 \longrightarrow \begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

$$E^2 - (H_{11} + H_{22})E + (H_{11}H_{22} - H_{12}^2) = 0$$

$$E = \frac{(H_{11} + H_{22}) \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2}}{2}$$

Recall:

$$H_{ab} = \langle \Psi_a | H | \Psi_b \rangle, \quad \text{e.g., } H_{11} = E_{\text{HF}}, \quad H_{12} = K_{\sigma\sigma^*}$$

Lowest energy eigenvalue  
is lower than  $E_{\text{HF}}$  if  $H_{12}$  is  
positive (as it is)

# CI in a Nutshell

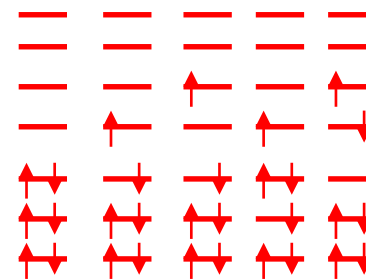
	$\Psi_{\text{HF}}$	$\Psi_i^a$	$\Psi_{ij}^{ab}$	$\Psi_{ijk}^{abc}$
$\Psi_{\text{HF}}$	$E_{\text{HF}}$	0	dense	0
$\Psi_i^a$	0	dense	sparse	very sparse
$\Psi_{ij}^{ab}$	d e n s e	sparse	sparse	extremely sparse
$\Psi_{ijk}^{abc}$	0	very sparse	extremely sparse	extremely sparse

The bigger the CI matrix, the more electron correlation can be captured.

The CI matrix can be made bigger either by increasing basis-set size (each block is then bigger) or by adding more highly excited configurations (more blocks).

CI calculations generally more sensitive to basis-set incompleteness than HF.

Most common compromise is to include only single and double excitations (CISD)—not size extensive.



0    singles    D

## CI (Configuration Interaction) Methods.

$$\Psi = \sum_i C_i \Psi_i \quad : \quad \Psi_i = \text{Slater Determinants.}$$

- From the reference configuration --> one-, two-, ... , electron excitation from occupied MO into virtual MO. --> Produce multi-particle basis,  $\Psi_i$
- Optimize  $C_i$ 's by the linear variation theory.
- Limits to single electron excitation --> CIS  
(Actually no correlation, but it gives excitation energy)
- Limits to single and double excitation --> SD-CI
- D-CI, SDT-CI, ....., Full-CI (FCI).
- QCISD and QCISD(T) for size extensivity.

## Correlated Methods. II. Many-body Perturbation Theory

Rayleigh-Schrödinger perturbation theory maps an inexact operator with known eigenfunctions to an exact operator with increasing orders of accuracy

$$\mathbf{A} = \mathbf{A}^{(0)} + \lambda \mathbf{V} \quad \mathbf{A}^{(0)} \Psi_0^{(0)} = a^{(0)} \Psi_0^{(0)}$$

$$a_0^{(1)} = \langle \Psi_0^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle$$

$$\Psi_0^{(1)} = \sum_j c_j \Psi_j^{(0)}$$

$$a_0^{(2)} = \sum_{j>0} \frac{|\langle \Psi_j^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle|^2}{a_0^{(0)} - a_j^{(0)}}$$

$$c_j = \frac{\langle \Psi_j^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle}{a_0^{(0)} - a_j^{(0)}}$$

$$a_0^{(3)} = \sum_{j>0, k>0} \frac{\langle \Psi_0^{(0)} | \mathbf{V} | \Psi_j^{(0)} \rangle [\langle \Psi_j^{(0)} | \mathbf{V} | \Psi_k^{(0)} \rangle - \delta_{jk} \langle \Psi_0^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle] \langle \Psi_k^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle}{(a_0^{(0)} - a_j^{(0)}) (a_0^{(0)} - a_k^{(0)})}$$

# Møller-Plesset (MP) Perturbation Theory

Møller and Plesset (MP) first suggested mapping from the zeroth-order Fock operator (a sum of one-electron mean-field operators) to the correct Hamiltonian (the “perturbation” is the entire electron repulsion energy, which is double counted in the sum of HF occupied eigenvalues)

$$H = F^{(0)} + \lambda \left[ \sum_i^{\text{occ.}} \sum_{j>i}^{\text{occ.}} \frac{1}{r_{ij}} - \sum_i^{\text{occ.}} \sum_j^{\text{occ.}} \left( J_{ij} - \frac{1}{2} K_{ij} \right) \right] \quad F^{(0)} \Psi_0^{(\text{HF})} = \sum_i^{\text{occ.}} \varepsilon_i \Psi_0^{(\text{HF})}$$

Similar for all other 0<sup>th</sup> states (SDs)

$$a_0^{(1)} = \langle \Psi_0^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle \quad \text{By construction,} \quad a^{(0)} + a^{(1)} = E_{\text{HF}}$$

$$a_0^{(2)} = \sum_i^{\text{occ.}} \sum_{j>i}^{\text{occ.}} \sum_a^{\text{vir.}} \sum_{b>a}^{\text{vir.}} \frac{[(ij|ab) - (ia|jb)]^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

*Eigenvalues already available;  
requires computation of electron-  
repulsion integrals over MOs;  
favorable scaling; size extensive;  
higher orders well defined but not  
necessarily convergent.*



## Correlated Methods. III. Many-body Perturbation Theory

- Rayleigh-Schrödinger perturbation theory maps an inexact operator with known eigenfunctions to an exact operator with increasing orders of accuracy
- Møller and Plesset (MP) first suggested mapping from the zeroth-order Fock operator to the correct Hamiltonian (the “perturbation” is the entire electron repulsion energy...)
- MP0 double-counts electron repulsion, MP1 = HF, MP2 captures a “good” amount of correlation energy at low cost, higher orders available (up to about MP6 in modern codes—becomes expensive rapidly)
- Multireference options available: CASPT2 and analogs
- No guarantee of convergent behavior—pathological cases occur with unpleasant frequency

Reset Viewer New Job Using This Geometry

## Calculated Quantities

Collapse all

### Overview

Quantity	Value
Job History	40004,40005,40006,40007,40008,40009
Route	#N CISD/6-31G(d) SP Geom=Connectivity
Stoichiometry	H <sub>2</sub> O
Symmetry	C2V
Basis	6-31G(d)
CI Energy	-76.197496199 Hartree
RHF Energy	-76.0107465156 Hartree
MP2 Energy	-76.195958412118 Hartree
Dipole Moment	2.1989 Debye
Server	hartree.kaist.ac.kr (15068)
CPU time	0.9 sec

### Rotational Constants

Constant	Frequency (GHz)	Frequency (cm <sup>-1</sup> )
a	858.6604887	28.64183089956
b	440.9403911	14.70818825936
c	291.3341300	9.71786054738

### Partial Charges

2017skku-comp....pptx

2202.00328v1-Rel....pdf

모두 표시

## Correlated Methods. Coupled-cluster and Quadratic CI Theories

- CC is rigorous and horribly complicated; QCI is a limited version of CC
- Simplest description is that CC and QCI extend CI with some extra terms that make CC and QCI size extensive and improve their ability to capture electron correlation energy
- A choice must still be made to truncate as a function of number of excited electrons allowed in formation of excited states
- Single-reference (i.e., post-HF) and multireference options available
- CCSD(T): The single-reference “gold standard”

## Correlated Methods. III. Coupled Cluster

CI adopts a linear ansatz to improve upon the HF reference

$$\Psi = a_0 \Psi_{\text{HF}} + \sum_i^{\text{occ.}} \sum_r^{\text{vir.}} a_i^r \Psi_i^r + \sum_{i < j}^{\text{occ.}} \sum_{r < s}^{\text{vir.}} a_{ij}^{rs} \Psi_{ij}^{rs} + \dots$$

Coupled cluster proceeds from the idea that accounting for the interaction of one electron with more than a single other electron is unlikely to be important. Thus, to the extent that “many-electron” interactions are important, it will be through simultaneous pair interactions, or so-called “disconnected clusters”

An exponential ansatz can accomplish this in an elegant way. If we define excitation operators, e.g., the double excitation operator as

$$\mathbf{T}_2 \Psi_{\text{HF}} = \sum_{i < j}^{\text{occ.}} \sum_{a < b}^{\text{vir.}} t_{ij}^{ab} \Psi_{ij}^{ab}$$

Then the full CI wave function for n electrons can be generated from the action of  $1 + \mathbf{T} = 1 + \mathbf{T}_1 + \mathbf{T}_2 + \dots + \mathbf{T}_n$  on the HF reference

## Correlated Methods. III. Coupled Cluster (cont.)

More importantly, if we consider the action of  $e^{\mathbf{T}}$  on the HF reference, restricting ourselves for the moment to just  $\mathbf{T} = \mathbf{T}_2$

$$\begin{aligned}\Psi_{\text{CCD}} &= e^{\mathbf{T}_2} \Psi_{\text{HF}} \\ &= \left( 1 + \mathbf{T}_2 + \frac{\mathbf{T}_2^2}{2!} + \frac{\mathbf{T}_2^3}{3!} + \dots \right) \Psi_{\text{HF}}\end{aligned}$$

Note that repeated applications of  $\mathbf{T}_2$  (which is what is implied in squared, cubed, etc. terms) generates the desired “disconnected clusters”

Like CID, an iterative solution to coupled equations can be undertaken

$$\langle \Psi_{\text{HF}} | \mathbf{H} | e^{\mathbf{T}_2} \Psi_{\text{HF}} \rangle = E_{\text{corr}} \left\langle \Psi_{\text{HF}} \left| \left( \Psi_{\text{HF}} + \sum_{A < B, I < J} t_{ab}^{ij} \Psi_{ab}^{ij} \right) \right. \right\rangle = E_{\text{corr}}$$

$$\langle \Psi_{ab}^{ij} | \mathbf{H} | e^{\mathbf{T}_2} \Psi_{\text{HF}} \rangle = \left\langle \Psi_{ab}^{ij} | \mathbf{H} \left| \left( 1 + \mathbf{T}_2 + \frac{1}{2} \mathbf{T}_2^2 \right) \Psi_{\text{HF}} \right. \right\rangle = t_{ab}^{ij} E_{\text{corr}}$$

## Correlated Methods. III. Coupled Cluster (cont.)

The math is somewhat tedious, but the CC equations can be shown to be size-extensive for any level of excitation

CCSD (single and double excitations) is convenient but addition of disconnected triples (CCSDT) is very expensive. A perturbative estimate of the effect of triple excitations defines the CCSD(T) method, sometimes called the “gold standard” of modern single-reference WFT

Reset Viewer | New Job Using This Geometry

# Calculated Quantities

Collapse all

## Overview

Quantity	Value
Job History	40004,40005,40006,40007,40008
Route	#N CCSD(T)/6-31G(d) SP Geom=Connectivity
Stoichiometry	H <sub>2</sub> O
Symmetry	C2V
Basis	6-31G(d)
CCSD Energy	-76.204970944 Hartree
Corr Energy	-76.200754656 Hartree
RHF Energy	-76.0107465156 Hartree
MP2 Energy	-76.195958412118 Hartree
CCSD(T) Energy	-76.206787548 Hartree
Dipole Moment	2.1989 Debye
Server	hartree.kaist.ac.kr (15008)
CPU time	1.2 sec

## Rotational Constants

Constant	Frequency (GHz)	Frequency (cm <sup>-1</sup> )
a	858.6604887	28.64183089956
b	440.9403911	14.70818825936
c	264.2241200	8.71788054720

## Post-HF levels: Price/Performance

HF < MP2 ~ MP3 ~ CCD < CISD

< MP4SDQ ~ QCISD ~ CCSD < MP4 < QCISD(T) ~ CCSD(T) < ...

Scaling behavior	Method(s)
$N^4$	HF
$N^5$	MP2
$N^6$	MP3, CISD, MP4SDQ, CCSD, QCISD
$N^7$	MP4, CCSD(T), QCISD(T)
$N^8$	MP5, CISDT, CCSDT
$N^9$	MP6
$N^{10}$	MP7, CISDTQ, CCSDTQ





- Density Functional Theory (DFT) is now probably the most popular quantum mechanical method for electronic structure calculations.
- *Ab initio MO* methods, HF and post-HF, are sometimes called wave function theory (WFT).

# Electron Correlation

- In the Hartree-Fock approximation, each electron sees the average density (aka mean field) of all of the other electrons
- Two electrons cannot be in the same place at the same time
- Electrons must move to avoid each other, i.e. their motion is correlated
- Types of electron correlation
  - Dynamical
  - Non-dynamical (or static)
- The difference between the exact energy and the Hartree-Fock energy is the correlation energy for a particular basis set.

# DFT Motivation

- The wave function itself is essentially uninterpretable.
- Reduce problem size: Wave functions for  $N$ -electron systems contain  $4N$  coordinates.
- Wave function based methods quickly become intractable for large systems, even with continued improvement in computing power, due to the coupled motion of the electrons.
- A desire to work with some physical observable rather than probability amplitude.

# Electronic Energy Components

- Total electronic energy can be partitioned

$$E = E_T + E_{NE} + E_J + E_X + E_C$$

$E_T$  = kinetic energy of the electrons

$E_{NE}$  = Coulomb attraction energy between electrons and nuclei

$E_J$  = Coulomb repulsion energy between electrons

$E_X$  = Exchange energy, a correction for the self-repulsions of electrons

$E_C$  = Correlation energy between the motions of electrons with different spins

- $E_T$ ,  $E_{NE}$ , &  $E_J$  are largest contributors to  $E$
- $E_X > E_C$  (magnitude)

To obtain electron density

## Kohn-Sham Self-consistent field

- **Trick:** Take a fictitious system of non-interacting electrons where ground-state density is the same density as the *real* system where the electrons interact.
- Real and fictitious system have the same positions and atomic numbers of the nuclei (same density)
- An easy Hamiltonian: a sum of one-electron operators.
- **Eigenfunctions:** Slater determinants of the individual one-electron eigenfunctions (cf. text, Section 4.5.1).
- **Eigenvalues:** sum of one-electron eigenvalues (cf. text, Section 4.5.1).

# Kohn-Sham Self-consistent field

- Divide energy functional into specific components

$$E[\rho(r)] = T_{ni}[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)] \\ + \Delta T[\rho(r)] + \Delta V_{ee}[\rho(r)] \quad (13)$$

- $T_{ni}$ : kinetic energy of non-interacting electrons
- $V_{ne}$ : nuclear-electron interaction
- $V_{ee}$ : classical electron-electron repulsion
- $\Delta T$ : correction to kinetic energy
- $\Delta V_{ee}$ : all non-classical corrections to el.-el. repulsion energy

## KS SCF II

- Express the density in an orbital basis set:

$$E[\rho(r)] = \sum_i^N \left( \langle \chi_i | -\frac{1}{2} \nabla_i^2 | \chi_i \rangle - \langle \chi_i | \sum_k^{\text{nuclei}} \frac{Z_k}{|r_i - r_k|} | \chi_i \rangle \right) \quad (14)$$
$$+ \sum_i^N \langle \chi_i | \frac{1}{2} \int \frac{\rho(r')}{|r_i - r'|} dr' | \chi_i \rangle + E_{xc}[\rho(r)]$$

- $N$ : number of electrons.
- Density for a Slater determinantal wf (exact for the non-interacting system)

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\chi_i(\mathbf{r})|^2 \quad (15)$$



# Simplest functional: LSDA

local spin-density approximation

*Kohn & Sham 1965, von Barth & Hedin 1972*

*Example: for a closed-shell system:*

$$\text{Energy} = T_{\text{KS}} + V_{\text{en}} + V_{\text{ee}} + \int d^3\vec{r} \rho(\vec{r}) \{ \epsilon_x[\rho(\vec{r})] + \epsilon_c[\rho(\vec{r})] \}$$

density

Exchange energy

of uniform electron gas  
neutralized by uniform  
positive background charge

$$= -0.73856 \rho^{1/3} \text{ (from Dirac } \alpha=2/3)$$

Correlation energy.

Fit to Monte Carlo  
calculations for  
uniform electron gas

# KS SCF V

- Use the first term on the r.h.s. of (14) to compute the kinetic energy of the non-interacting electrons.
- To determine the KS orbitals use the same approach as in MO theory:
- Express **KS orbitals within a set of basis functions**  $\{\phi\}$ , determine the individual orbital coefficients by solution of a secular equation entirely analogous to that employed in the HF theory.
- Replace the  $F_{\mu\nu}$  elements by the the  $K_{\mu\nu}$  elements

$$K_{\mu\nu} = \left\langle \phi_{\mu} \left| -\frac{1}{2} \nabla^2 - \sum_k^{\text{nuclei}} \frac{Z_k}{|r - r_k|} + \int \frac{\rho(r')}{|r - r'|} dr' + V_{xc} \right| \phi_{\nu} \right\rangle \quad (20)$$

# HF vs DFT I

## Similarities between HF and KS

- Common variational principle
- Kinetic energy and nuclear attraction component of matrix elements of  $\mathbf{K}$  are identical to those of  $\mathbf{F}$ .
- If the density in the *classical* interelectronic repulsion operator is expressed in the same basis functions used for the KS orbitals, then the same four-index electron-repulsion integrals will appear in  $\mathbf{K}$  as in  $\mathbf{F}$ .
- Density required for computation of the secular matrix elements.
- Density determined using the orbitals obtained from the solution of the secular equation:
- KS procedure is a SCF iterative procedure.
- Historically: modify existing codes for HF calculations to perform DFT calculations.

# HF vs DFT II

## Key differences between HF and KS

- DFT as derived so far contains no approximations: it is exact.
- But, we need to know  $E_{xc}$  as a function of  $\rho$ .
- HK: proved that a functional of  $\rho$  must exist.
- No guidance, though, as to what the functional should look like.
- Contrast between HF and DFT:
- HF **approximate** theory: solve the relevant equations **exactly**.
- DFT **exact** theory: solve the relevant equations **approximately** because the **form of the operator is unknown**.
- Exact DFT is variational. When approximations of  $E_{xc}$  are introduced, this is no longer true.
- Both exact and approximate DFT are size extensive.

HK (Hohenberg Korn)

DFT contains electron correlation energy while HF does not

## Exchange-correlation Energy

- $E_{xc}$ : difference between the classical and quantum mechanical el.-el. repulsion.
- It *also* includes the **difference in kinetic energy between the fictitious non-interacting system and the real system.**
- Most functionals do not attempt to compute the K.E. correction explicitly.
- Either they ignore the term, or construct a hole function analogous to that of eq. (5) that also incorporates the kinetic energy difference between the interacting and non-interacting systems, perhaps empirically.

# Exchange-correlation (xc) Functionals

- In many functionals, empirical parameters introduce some kinetic energy correction based on experiment.
- Common notations in the field follow
- Functional dependence of  $E_{xc}$  on  $\rho$  expressed as an **interaction between  $\rho$  and an energy density**, that is itself dependent on the electron density

$$E_{xc}[\rho(r)] = \int \rho(r) \varepsilon_{xc}[\rho(r)] dr \quad (21)$$

# xc Functionals II

- Energy density  $\varepsilon_{xc}$  is treated as a sum (separable or not) of individual exchange and correlation contributions.
- Slater (or Dirac, or empirical  $[\alpha]$ ) exchange energy density:

$$\varepsilon_x[\rho(r)] = -\frac{9\alpha}{8} \left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}(r) \quad (22)$$

- Electron density can also be expressed in terms of an effective radius such that exactly one electron would be contained within the sphere defined by that radius were it to have the same density throughout as its center

$$r_s(r) = \left(\frac{3}{4\pi\rho(r)}\right)^{1/3} \quad (23)$$

## xc Functionals III

- Spin not considered so far.
- Use individual functionals of the  $\alpha$  and  $\beta$  densities.
- Spin density at any position is expressed in terms of the normalized spin polarization:

$$\zeta(r) = \frac{\rho^\alpha(r) - \rho^\beta(r)}{\rho(r)} \quad (24)$$

- $\alpha$  spin density is one-half of the product of the total  $\rho$  and ( $\zeta + 1$ ) and the  $\beta$  spin density is the difference between the total rho and that value.



# Local Density Approximation

- **LDA**: any DFT where the value of  $\varepsilon_{xc}$ , at some position  $r$ , can be computed exclusively from the value of  $\rho$  at that position, i.e., the ‘local’ value of  $\rho$ .
- Functionals derived primarily from the uniform electron gas (uniform density at every position in space).
- L(S)DA implies that it is the UEG exchange and correlation functionals that are employed for molecular calculations.
- Can be extended to spin-polarized cases ( $z$  from eq. (24), “0” and “1” refer to “no-spin” and “all-same-spin” UEG).

$$\varepsilon_x[\rho(r), \zeta(r)] = \varepsilon_x^0[\rho(r)] + \left\{ \varepsilon_x^1[\rho(r)] - \varepsilon_x^0[\rho(r)] \right\} \left[ \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2}{2(2^{1/3} - 1)} \right] \quad (25)$$

# Local Density Correlation

- Correlation energy: no analytical derivation of this functional has proven possible.
- Quantum Monte Carlo: Ceperley and Alder (1980) computed the **total energy** for fully interacting uniform electron gases of various densities.
- **Subtract the analytical exchange** energy to determine the **correlation energy**.
- Vosko, Wilk and Nusair (1980): designed local functionals of the density fitting to these results.
- Spin-polarized functional analogous to (25), but with the unpolarized and fully polarized correlation energy densities.

# Local Density Correlation

- Different sets of empirical constants.
- VWN: several fitting schemes varying the functional forms.
- LSDA that employs a combination of Slater exchange and the VWN correlation energy expression: SVWN.
- Correlation energy functional is very complex.
- DFT methods are often semiempirical: they include empirically optimized constants and functional forms.
- Solution of  $E_{xc}$  integrals typically not possible analytically.
- Evaluation of integrals involving exchange and correlation energy densities in DFT is done numerically on a grid.
- Use of efficient quadrature schemes.
- In modern codes: default grid unless otherwise specified by the user.

# KS-SCF Procedure

- In HF theory: Number of Coulomb integrals requiring evaluation is  $N^4$ .
- In DFT it can be reduced to  $N^3$ ,  $N$  number of KS AO basis functions.
- After basis set and molecular geometry choice, the overlap integrals, kinetic-energy, and nuclear-attraction integrals are computed. Same in HF and DFT
- **HF**: construct a density matrix and then compute the two-electron integrals: Coulomb and exchange.
- **DFT**: construct a density matrix and also construct  $V_{xc}$
- Evaluate the remaining integrals in each KS matrix element.
- After this point KS and HF SCF are identical.

# KS-SCF Procedure II

- New orbitals are determined from solution of the secular equation.
- Density is determined from these orbitals and compared with density of the previous iteration.
- When SCF procedure is converged: compute the energy by using the final density plugged into eq (14).
- Cf. HF, where the energy is evaluated as the expectation value of the H operator acting on the HF Slater determinant.
- Geometry optimization? Determine whether the structure corresponds to a stationary point.
- Using the LSDA approximation means that:
- The exchange-correlation energy density at every position in space for the molecule is the same as that for the uniform electron gas having the same density as is found at that position.

## LSDA enjoyed early success in physics.

The local spin-density approximation “gives bond lengths and thus the geometries of molecules and solids typically with an astonishing accuracy of ~1%.”

– *W. Kohn (Nobel lecture, 1998)*

## But LSDA molecular *energies* have systematic errors.

In rest of lecture: Results are given for representative or large databases and reasonable basis sets; details in papers.

### Mean (unsigned) errors in kcal/mol

	<u>MAIN-GROUP</u>	
	bond energies	barrier heights
Hartree-Fock theory	31	9
Local spin-density approximation	16	18

## Next step: add gradient dependence.

Local spin-density approx.  $F^{\text{LSDA}} = F[\rho(\mathbf{r})]$

Gradient expansion  $F = F^{\text{LSDA}} \left[ 1 + \mu s^2 + \text{higher - order} \right]$

*known: Antoniewicz &  
Kleinman 1985*

$$s \equiv \text{constant} \times \frac{|\nabla\rho|}{\rho^{4/3}}$$

*Later slide: a second order method with this correct  $\mu$*



**SOGGA**

# Density Gradient Corrections

- In a molecule the electron density is not spatially uniform.
- LDA has serious limitations for energies, although it gives good geometries.
- Improve functionals by making them depend on the extent to which the density is locally changing, i.e. the gradient of the density.
- Functionals that depend on both the density and the gradient of the density: **gradient corrected or generalized gradient approximation (GGA) functionals**.
- Most GGA functionals are constructed with the correction being a term added to the LDA functional

$$\varepsilon_{x/c}^{GGA}[\rho(r)] = \varepsilon_{x/c}^{LSD}[\rho(r)] + \Delta\varepsilon_{x/c} \left[ \frac{|\nabla\rho(r)|}{\rho^{4/3}(r)} \right] \quad (28)$$

*verify that this term is dimensionless*

- x/c: same functional for either exchange or correlation.
- The dependence of the correction term is on the dimensionless reduced gradient.



# Density Gradient Corrections II

- Most popular **GGA exchange functional to date: Becke 1988 (B)**. (*23,000+ citations in March 2013*)
- Correct asymptotic behaviour at long range for the energy density and incorporates a single empirical parameter.
- Value of the parameter optimized by fitting to the exactly known exchange energies of six noble gas atoms (from He to Rn).
- Other exchange functionals similar to Becke: CAM(B), PW, FT98, mPW.
- Alternative GGA exchange functionals have been developed based on a rational function expansion of the reduced gradient. They contain no empirically optimized parameters: B86, P, PBE.
- **Correlation functionals: P86** (Perdew 1986); PW91 (Perdew Wang 92).
- **LYP correlation**: (Lee, Yang, Parr 1988) does not correct the LDA expression but computes the full correlation energy.
- It contains four empirical parameters fit to helium atom. It is a correlation functional that provides an exact cancellation of the self-interaction error in one-electron systems.

## Progress: GGAs

$$F^{\text{GE}} = F^{\text{LSDA}}(\rho) \left[ 1 + \mu s^2 + \text{higher - order} \right] \quad s \equiv \text{constant} \times \frac{|\nabla\rho|}{\rho^{4/3}}$$

correct  $\mu = 0.1235$  : “Gradient expansion”

$$F^{\text{GGA}} = F(\rho, s)$$

incorrect  $\mu$  : “Generalized gradient approximation”  $\equiv$  GGA

Examples: BLYP (1988)	$\mu = 0.2743$
PBE (1996)	$\mu = 0.2195$

## Generalized gradient approximation shows promise.

	Mean (unsigned) errors in kcal/mol	
	Bond energies	Barrier heights
Hartree-Fock theory	31	9
Local spin-density approximation	16	18
Correct thru 2nd order: SOGGA	7	13
GGA: BLYP (1988)	1.5	8
↙ ↘ Becke-Lee-Yang-Parr		

This aroused the attention of many quantum chemists.

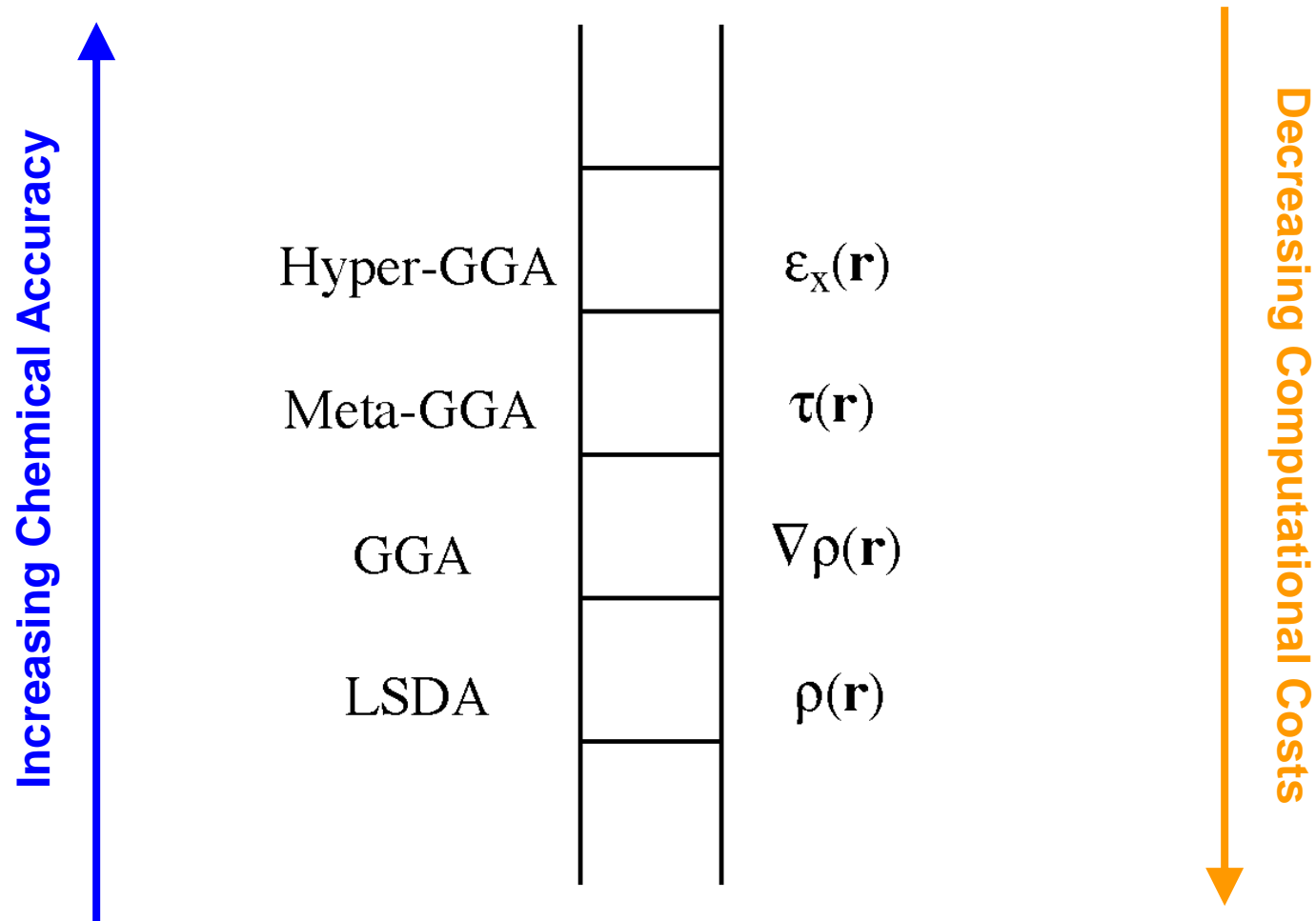
# Density Gradient Corrections III

- Taylor-function-expansion justification for the importance of the gradient.
- “Obvious” next step: include second derivative of the density, i.e. the Laplacian.
- Becke and Rousell proposed an exchange functional (BR).
- Proynov, Salahub, and co-workers examined the same idea for the correlation functional (Lap).
- Meta-GGA because they go beyond the gradient correction.
- Alternative Meta-GGA formalism, numerically more stable is to include in the exchange-correlation potential a dependence on the kinetic-energy density  $\tau$ :

$$\tau(r) = \sum_i^{\text{occ}} \frac{1}{2} |\nabla \psi_i(r)|^2 \quad (29)$$

- Functions  $\psi$  are the self-consistently determined KS orbitals.
- Some examples of MGGA functionals for exchange, correlation, or both, are B95, B98, ISM,  $\tau$ HCTH, and the Minnesota local functionals M06-L and M11-L.
- Cost of MGGA comparable to that for GGA. MGGA generally more accurate than GGA.

# Accuracy vs. Computational Cost



Hartree World

## Hybrid Functionals (B3LYP one of them)

# Adiabatic Connection Methods

- Posits controlling the amount of electron-electron interaction in a many-electron system.
- A switch that smoothly converts the non-interacting KS reference system to the real, interacting system.
- Thus, clearly the exchange-correlation energy can be computed as

$$E_{xc} = \int_0^1 \langle \Psi(\lambda) | V_{xc} | \Psi(\lambda) \rangle d\lambda \quad (30)$$

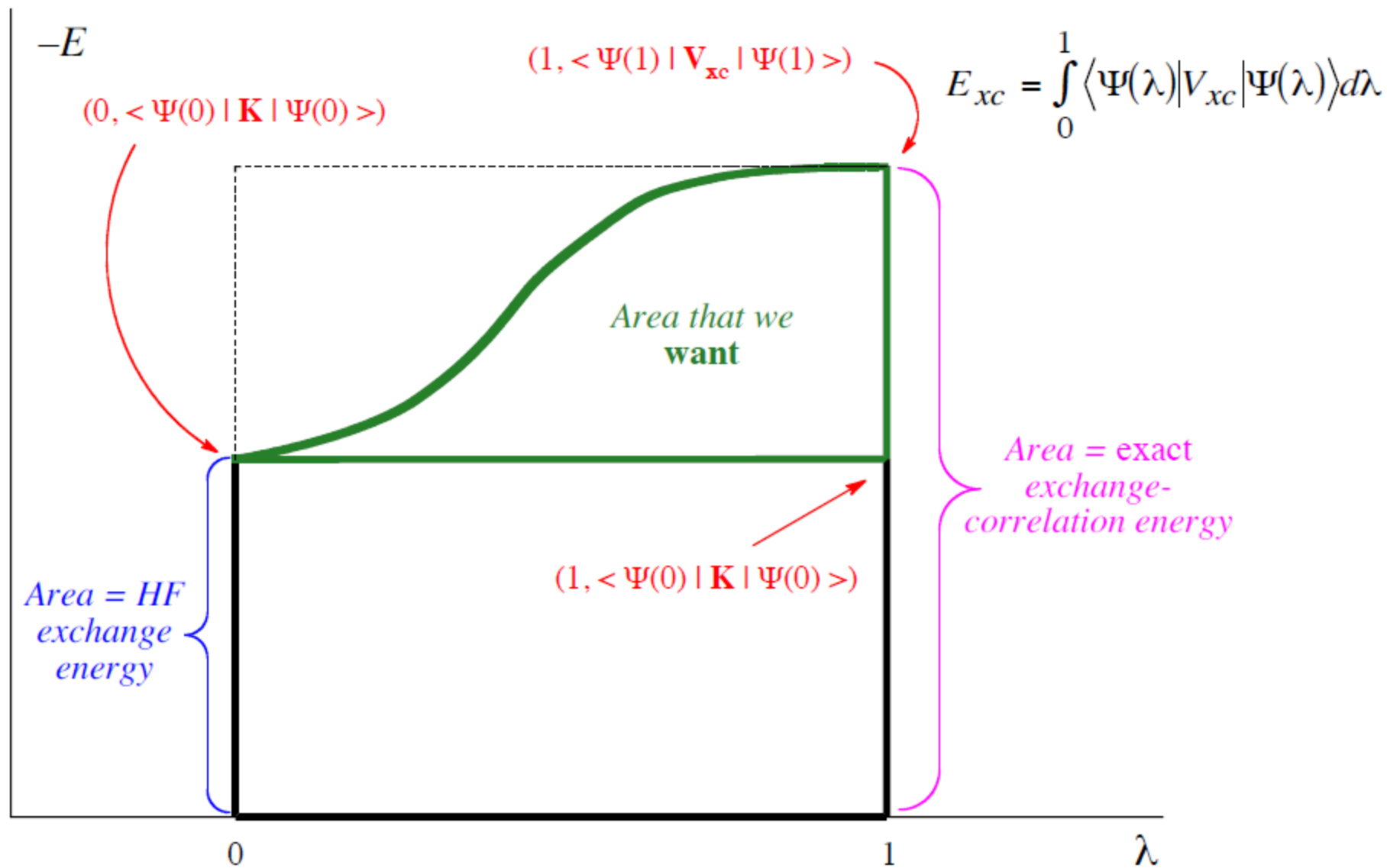
- Where lambda describes the extent of interelectronic interaction: 0 (none) to 1(exact).

# Adiabatic Connection Methods II

$$E_{xc} = \int_0^1 \langle \Psi(\lambda) | V_{xc} | \Psi(\lambda) \rangle d\lambda \quad (30)$$

- Non-interacting limit: only component of  $\mathbf{V}$  is exchange (from antisymmetry of the wf).
- Slater determinant of the KS orbitals *is* the exact wave function for the non-interacting Hamiltonian operator.
- Expectation value: exact exchange for the non-interacting system. Compute as in a HF calculation. Use KS orbitals.
- Area of the rectangle defined by integration in next slide is thus  $E_x^{\text{HF}}$

# Adiabatic Connection Methods III





# Adiabatic Connection IV

- Area that we want: fraction  $z$  of the area of the rectangle above, which itself has area

$$\langle \Psi(1) | V_{xc}(1) | \Psi(1) \rangle - E_x^{HF} \quad (31)$$

- We do not know  $z$ . Consider it as an empirical parameter to be optimized.
- Approximate the right endpoint with  $E_{xc}$  computed with some choice of DFT, so area of top rectangle is  $E_{xc}^{DFT}$
- Total area under the curve.

$$E_{xc} = E_x^{HF} + z(E_{xc}^{DFT} - E_x^{HF}) \quad (32)$$

# Adiabatic Connection V

$$E_{xc} = E_x^{HF} + z(E_{xc}^{DFT} - E_x^{HF}) \quad (32)$$

- In practice (32) is written using another variable  $a = 1-z$

$$E_{xc} = (1-a)E_{xc}^{DFT} + aE_x^{HF} \quad (33)$$

- Analysis forms the basis of the ‘adiabatic-connection method’ because it connects between the non-interacting and fully interacting states.

# Adiabatic Connection VI

- If expectation value of the curve is a line, then  $z = 0.5$ : This defines the “Half and Half” method (H&H).
- Using LDA exchange-correlation, Becke (1993) showed that the H&H method has an error of 6.4 kcal/mol for enthalpy of formation of the G1 test set.
- Estimate  $a$  in a better way: perhaps include additional parameters if warranted.
- Becke (1993) developed a 3-parameter functional (B3).

$$E_{xc}^{B3PW91} = (1 - a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^B + E_c^{LSDA} + cE_c^{PW91} \quad (34)$$

## Adiabatic Connection VII

$$E_{xc}^{B3PW91} = (1-a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^B + E_c^{LSDA} + cE_c^{PW91} \quad (34)$$

- Where a,b,c were optimized to 0.20, 0.72, 0.81.
- The name B3PW91: three-parameter scheme, GGA exchange, correlation functionals B and PW91.
- Model modified to use LYP instead of PW91 by Stephens et al. LYP is designed to compute the full correlation energy and not a correction to LSDA

# Adiabatic Connection VIII

- B3LYP model is defined as

$$E_{xc}^{B3LYP} = (1-a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^B + (1-c)E_c^{LSDA} + cE_c^{LYP} \quad (35)$$

- $a, b, c$  same values as in B3PW91.
- Of all the modern functionals B3LYP has proven the most popular to date, although its reign seems to be ending.
- Adiabatic Connection methods incorporate both HF and DFT: hybrid methods (including HF means  $N^4$  scaling).

## Mix GGA with Hartree-Fock exchange.

Kohn-Sham theory (1965) – equation for orbitals:

$$\left( T + V_{\text{ne}} + V_{\text{ee}} + \frac{\partial F_{\text{x}}}{\partial \rho} + \frac{\partial F_{\text{c}}}{\partial \rho} \right) \varphi_i = \varepsilon_i \varphi_i$$

Compare Hartree-Fock theory (1930):

$$\left( T + V_{\text{ne}} + V_{\text{ee}} + V_{\text{x}}^{\text{HF}} \right) \varphi_i = \varepsilon_i \varphi_i$$

Advantages: Attractive HF exchange cancels self-interaction in  $V_{\text{ee}}$

Hybrid DFT (Becke 1993):



$$\left( T + V_{\text{ne}} + V_{\text{ee}} + \frac{X}{100} V_{\text{x}}^{\text{HF}} + \left(1 - \frac{X}{100}\right) \frac{\partial F_{\text{x}}}{\partial \rho} + \frac{\partial F_{\text{c}}}{\partial \rho} \right) \varphi_i = \varepsilon_i \varphi_i$$

*(39,000+ citations in March 2013)*

## Hybrid DFT was a breakthrough.

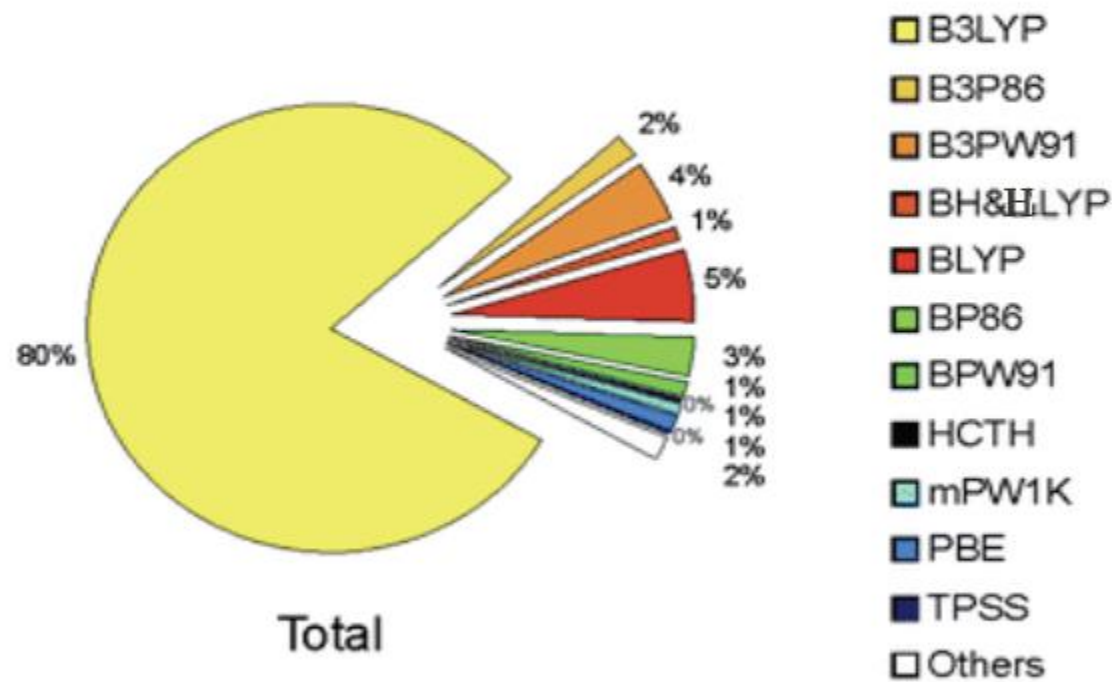
	Mean (unsigned) errors in kcal/mol	
	Bond energies	Barrier heights
Hartree-Fock theory	31	9
Local spin-density approximation	16	18
Correct thru 2nd order: SOGGA	7	13
GGA: BLYP (1988)	1.5	8
Hybrid: B3LYP (1993)	0.9	4

Becke-3 parameter-Lee-Yang-Parr

“chemical accuracy” for main-group bond energies, bond lengths, ...

This was the tipping point—making DFT the accepted everyday tool.

## B3LYP is enormously popular.



Sousa, Fernandes, Ramos, *JPC A* (2007)

PBE is most popular in band structure calculations



## DFT – summary and...

# DFT versus MO theory

- DFT optimizes an electron density while WFT theory optimizes a wave function.
- To determine a molecular property:
- In DFT: how does the property depend on the density?
- In MO theory: need to know the **quantum mechanical operator**.
- WF has a broader utility because there are more well-characterized operators than there are generic property functionals of the density.
- Example: total energy of interelectronic repulsion:
- **Even if we had the exact density, exact exchange-correlation energy functional not known: exact interelectronic repulsion cannot be computed.**
- With the exact wave function, evaluate the expectation value for the interelectronic repulsion operator

$$E_{ee} = \left\langle \Psi \left| \sum_{i < j} \frac{1}{r_{ij}} \right| \Psi \right\rangle \quad (36)$$

Reset Viewer | New Job Using This Geometry

# Calculated Quantities

Collapse all

Overview

Quantity	Value
Job History	40004,40005,40012,40013,40014
Route	#N B3LYP/6-31G(d) OPT FREQ Geom=Connectivity
Stoichiometry	H <sub>2</sub> O
Symmetry	C2V
Basis	6-31G(d)
RB3LYP Energy	-76.4089533398 Hartree
ZPE	0.021163 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-76.384955 Hartree
Enthalpy	-76.384011 Hartree
Free Energy	-76.405457 Hartree
C <sub>v</sub>	5.997 cal/mol-K
Entropy	45.137 cal/mol-K
Dipole Moment	2.0953 Debye
Server	hartree.kaist.ac.kr (17068)
CPU time	5.3 sec

Geometry Sequence Energies

2017skku-comp....pptx | 2202.00328v1-Rel....pdf

모두 표시

# DFT versus MO theory II

- There is a DFT wave function. How useful is it?
- Slater Determinant from the KS orbitals is the exact wave function for the fictional non-interacting system having the same density as the real system.
- Properties of the KS determinants: extremely low level of spin contamination, even for cases where HF behaves badly.
- It is by no means guaranteed that the expectation value for  $S^2$  over the KS determinant has any relationship at all to the corresponding expectation value over the exact wave function that corresponds to the KS density.
- Empirical observation suggests that DFT is more robust in dealing with open-shell systems where HF shows high spin contamination.
- In WFT methods, excited states can be generated as linear combinations of determinants derived from exciting one or more electrons from occupied to virtual orbitals.
- DFT applied to excited states requires invocation of time-dependent formalism.

# Computational Efficiency I

- Scaling of local DFT no worse than  $N^3$ .
- For programs that use approximately the same routines and algorithms to perform a HF and DFT calculation, the cost of DFT is ca. double that of HF (15 atoms), but scaling gives DFT the win very quickly thereafter.
- Improvement using basis functions which are not contracted Gaussians.
- A density can be represented using an auxiliary basis set or numerically.
- Slater-type functions can be used.

## Computational Efficiency II

- Plane waves as basis sets in periodic infinite systems.
- Large number of plane waves to represent the aperiodic densities that are possible within the unit cells, the necessary integrals are simple to solve.
- Used in dynamics and solid-state physics.
- Convergence with respect to basis set is typically much more rapid in DFT than in WFT methods.
- Linear scaling DFT available.
- Most of above optimal with *local* DFT functionals.

# Limitations of KS

- Most applications in DFT are run within the KS formalism.
- It permits the kinetic energy to be computed as the expectation value of the kinetic-energy operator over the KS single determinant.
- No need to determine the kinetic energy as a functional of the density.
- Some systems not well described by a single Slater determinant.
- Need to introduce non-dynamical correlation but not double count.

# Systematic Improvability

- WF theory: well defined path to the exact solution (Full CI with infinite basis).
- In DFT, how to do a better calculation?
- All current functionals are approximate for molecular systems.
- No obvious way to determine which functional may be optimal for a particular case.
- Basis set convergence can be explored.
- Compare behavior of different functionals.
- Compare with a highly correlated MO treatment.
- Compare with experiment.
- Experience shows that for a large variety of systems DFT is quite robust.

## More names of functionals following(list only partial)

- Still many new functionals are being developed
- Partial list of recent and not so recent developments
  - Range corrected
  - Dispersion
  - Double hybrid
  - Orbital dependent
  - Exact MPn, CC etc..
  - Machine-learning optimized and more
- Recommend benchmarking before extensive applications



