Computational Chemistry using Gaussian: an Introduction

Adhitya Gandaryus Saputro

Computational chemistry using Gaussian

Gaussian Features at a Glance

1. **Model Chemistries: MM, semiempiric, HF, MP2,DFT, CC,based..**
2. **Geometry Optimizations ,Transition state, Reaction Modeling**
3. **Vibrational Analysis**
4. **Self-Consistent Reaction Field Solvation Models**
5. Molecular Properties: population analysis, electrostatic potential, electronic density, etc.
6. ONIOM Calculations (QM/MM)
7. Excited States

.

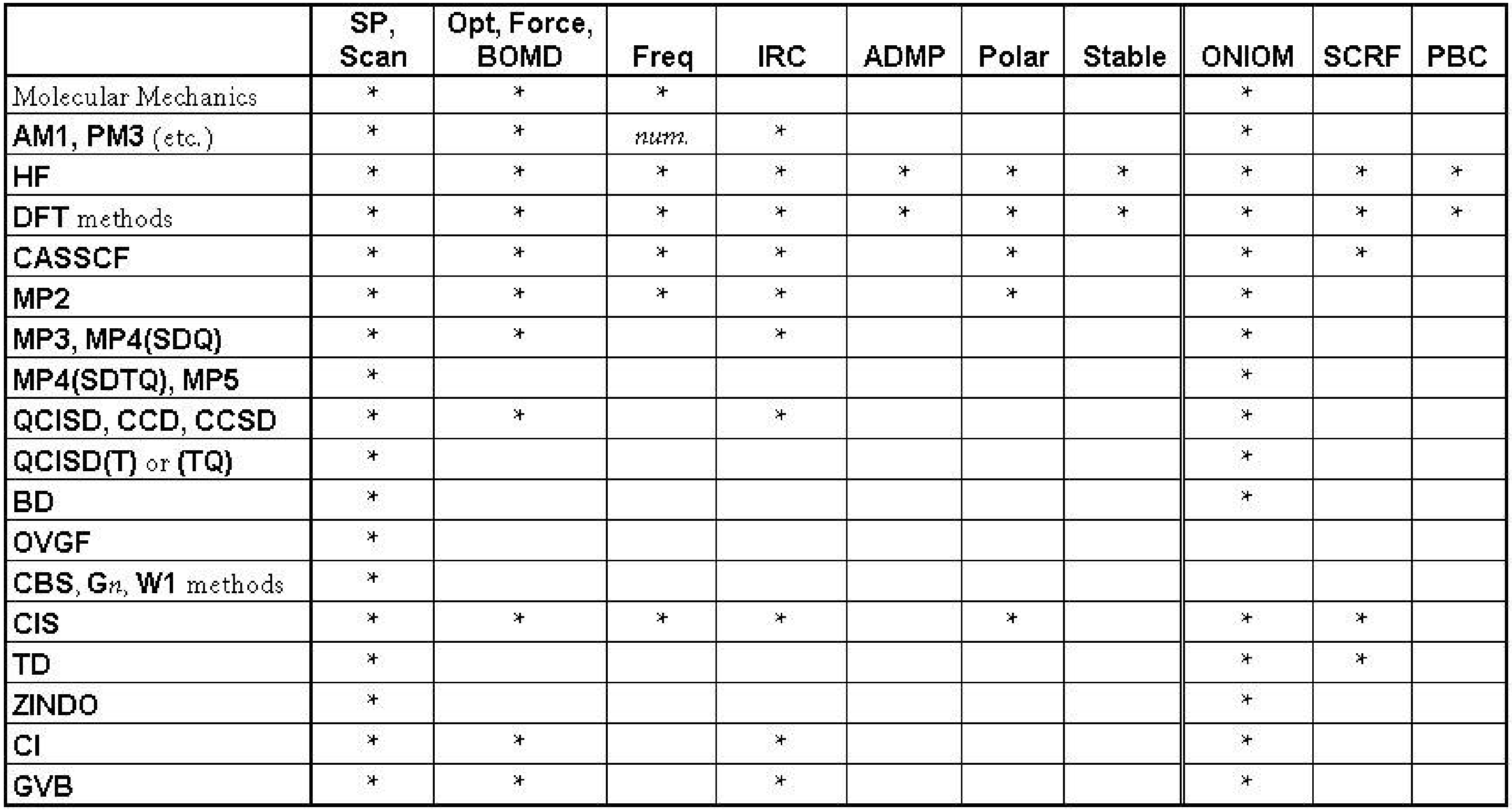
.

.

Different Levels of *Ab Initio* Calculations

1. Hartree-Fock (HF)
   - The simplest *ab initio* calculation
   - **No electron correlation**
2. The Møller-Plesset Perturbation Theory (MP-n)
3. **Density Functional Theory (DFT)**
4. Configuration Interaction (CIS,CISD, FCI)
5. Coupled cluster (CCSD,CCSD(T),..)

Methods availabilities in GAUSSIAN



	SP, Scan	Opt, Force, BOMD	Freq	IRC	ADMP	Polar	Stable	ONIOM	SCRF	PBC
Molecular Mechanics	*	*	*					*		
AM1, PM3 (etc.)	*	*	*num.*	*				*		
HF	*	*	*	*	*	*	*	*	*	*
DFT methods	*	*	*	*	*	*	*	*	*	*
CASSCF	*	*	*	*		*		*	*	
MP2	*	*	*	*		*		*		
MP3, MP4(SDQ)	*	*		*				*		
MP4(SDTQ), MP5	*							*		
QCISD, CCD, CCSD	*	*		*				*		
QCISD(T) or **(TQ)**	*							*		
BD	*							*		
OVGF	*									
CBS, G*n*, W1 methods	*									
CIS	*	*	*	*		*		*	*	
TD	*							*	*	
ZINDO	*							*		
CI	*	*		*				*		
GVB	*	*		*				*		

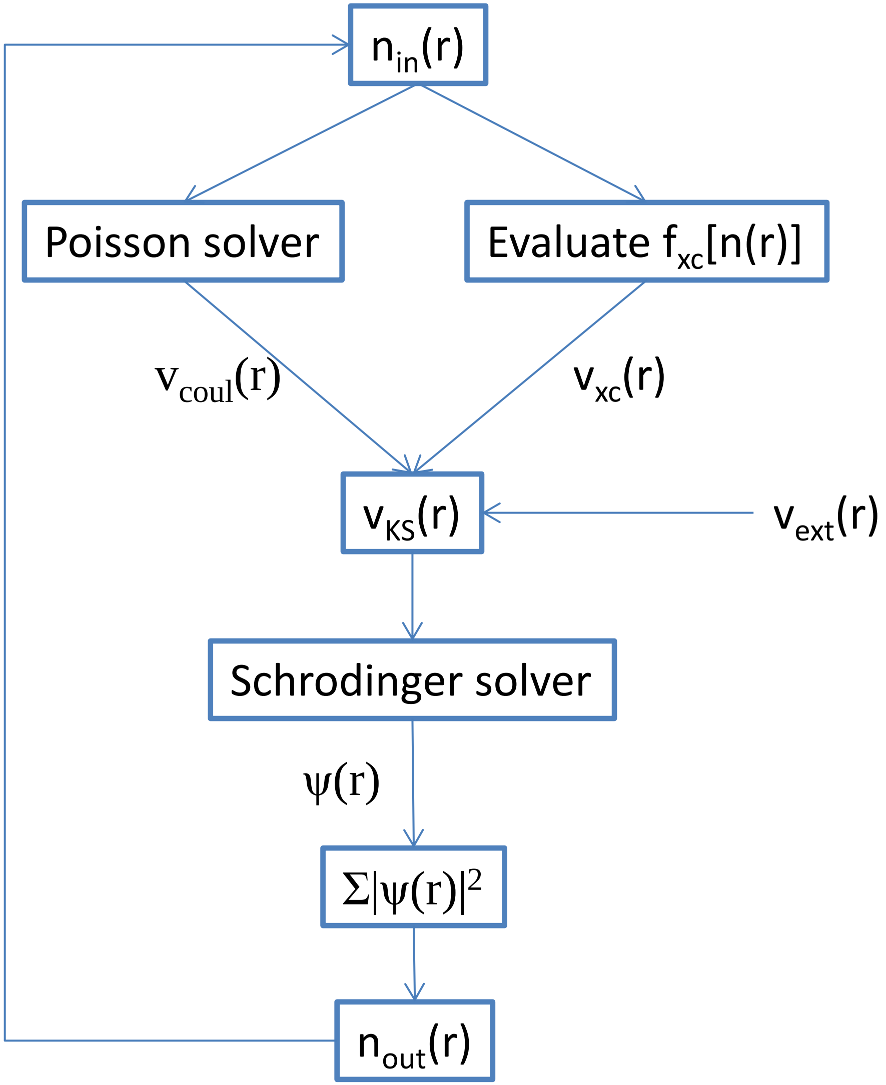
DFT: Solving Kohn-Sham Equation

SCF procedure: solving single electron Schrodinger-like equations for the molecular orbitals

$$\left(-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r})\right)\psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r})$$

$$V_{\rm KS}(\mathbf{r}) = V_{\rm ext}(\mathbf{r}) + V_{\rm Coul}(\mathbf{r}) + V_{\rm xc}(\mathbf{r})$$

$$= V_{\rm ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + \frac{\delta E_{\rm xc}}{\delta n}$$



$n_{in}(r)$

Poisson solver

Evaluate $f_{xc}[n(r)]$

$v_{coul}(r)$

$v_{xc}(r)$

$v_{KS}(r)$

$v_{ext}(r)$

Schrodinger solver

$\psi(r)$

$\Sigma|\psi(r)|^2$

$n_{out}(r)$

Basis Function

molecular (spatial) orbital

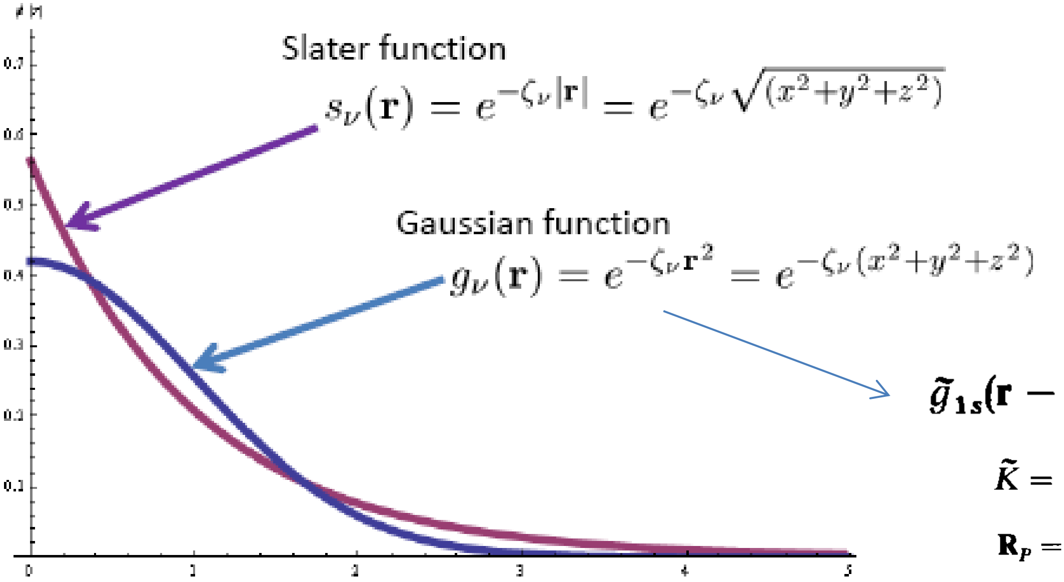
$$\psi_i(\mathbf{r}) = \sum_{\alpha=1}^{N_{BF}} G_\alpha(\mathbf{r})\, C_{\alpha i}$$

basis function

Slater functions are very suitable for expanding AOs, because they have correct shape:

- Near the nucleus
- Far from nucleus (decay like e^{-ar})

Gaussian functions are preferred in practice → easy to calculate molecular integrals



Slater function

$$s_\nu(\mathbf{r}) = e^{-\zeta_\nu|\mathbf{r}|} = e^{-\zeta_\nu\sqrt{(x^2+y^2+z^2)}}$$

Gaussian function

$$g_\nu(\mathbf{r}) = e^{-\zeta_\nu \mathbf{r}^2} = e^{-\zeta_\nu(x^2+y^2+z^2)}$$

$$\tilde{g}_{1s}(\mathbf{r}-\mathbf{R}_A)\tilde{g}_{1s}(\mathbf{r}-\mathbf{R}_B) = \tilde{K}\tilde{g}_{1s}(\mathbf{r}-\mathbf{R}_P)$$

$$\tilde{K} = \exp[-\alpha\beta/(\alpha+\beta)|\mathbf{R}_A-\mathbf{R}_B|^2]$$

$$\mathbf{R}_P = (\alpha\mathbf{R}_A+\beta\mathbf{R}_B)/(\alpha+\beta)$$

$$p = \alpha+\beta$$

Source: http://www.soton.ac.uk/~compchem/other/DFT_Lectures/

Contracted Gaussian Basis Sets (CGs)

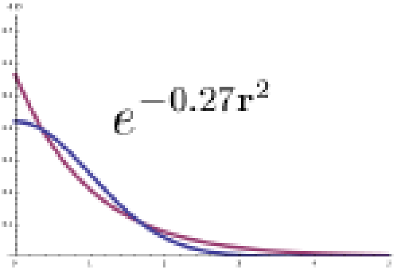
Fixed linear combinations of primitive Gaussian function

$$G_\alpha(\mathbf{r}) = \sum_{\nu=1}^{N_\alpha} c_\nu \, g_\nu(\mathbf{r})$$

Simplest basis sets: STO-nG approximate STO orbitals by n-CGs

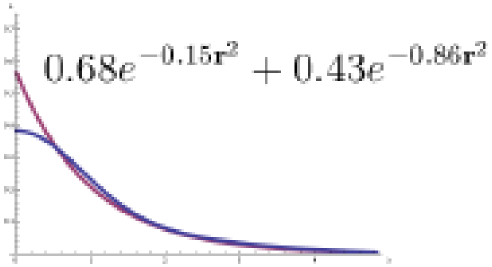
1s orbital of H atom

STO-1G



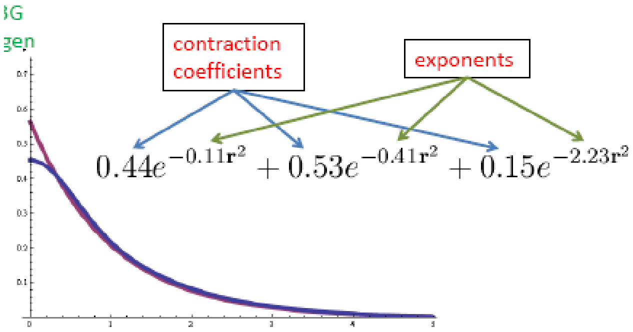
$e^{-0.27\mathbf{r}^2}$

STO-2G



$0.68e^{-0.15\mathbf{r}^2} + 0.43e^{-0.86\mathbf{r}^2}$

STO-3G

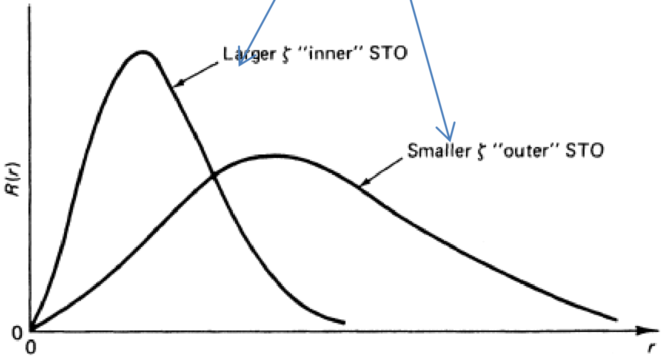


$0.44e^{-0.11\mathbf{r}^2} + 0.53e^{-0.41\mathbf{r}^2} + 0.15e^{-2.23\mathbf{r}^2}$

Bonding with neighboring atoms

Split valence basis sets
Ex: 6-31G

For core electrons



Polarized basis sets
Ex: 6-31G**

Add *p* character into *1s* orbital of H → s-p linear combination
Add *d* character into *p* orbitals → allow to change shape

diffuse basis sets
Ex: 6-31+G*

basis set augmented with a set of diffuse s- and p-type gaussian functions on each heavy atom, to permit representation of diffuse electronic distribution, as in anions. Hydrogen bond

```
3-21g
3-21++g
3-21gs
3-21++gs
3-21gsp
3-21gs_polarization
4-22gsp
4-31g
6-311g
6-311++g2d_2p
6-311g2df_2pd
6-311++g3df_3pd
6-311gs
6-311+gs
6-311gs_polarization
6-311gss
6-311++gss
6-311gss_polarization
6-31g
6-31++g
6-31g3df_3pd
6-31g-blaudeau
6-31gs
6-31+gs
6-31++gs
6-31gs-blaudeau
6-31gs_polarization
6-31gss
6-31++gss
6-31gss_polarization
ahlrichs_coulomb_fitting
ahlrichs_polarization
ahlrichs_pvdz
ahlrichs_tzv
ahlrichs_vdz
ahlrichs_vtz
aug-cc-pcv5z
aug-cc-pcvdz
aug-cc-pcvqz
aug-cc-pcvtz
aug-cc-pv5+dz
aug-cc-pv5+dz_diffuse
aug-cc-pv5z
aug-cc-pv5z_diffuse
aug-cc-pv6+dz
aug-cc-pv6+dz_diffuse
aug-cc-pv6z
aug-cc-pv6z_diffuse
aug-cc-pvd+dz
aug-cc-pvd+dz_diffuse
aug-cc-pvdz
aug-cc-pvdz_diffuse
aug-cc-pvq+dz
aug-cc-pvq+dz_diffuse
aug-cc-pvqz
aug-cc-pvqz_diffuse
aug-cc-pvt+dz
aug-cc-pvt+dz_diffuse
aug-cc-pvtz
aug-cc-pvtz_diffuse
bauschlicher_ano
binning-curtiss_1d_polarization
binning-curtiss_df_polarization
binning_curtiss_sv
binning_curtiss_svp
binning_curtiss_vtz
binning_curtiss_vtzp
blaudeau_polarization
cc-pcv5z
cc-pcv6z
cc-pcvdz
cc-pcvqz
cc-pcvtz
cc-pv5+dz
cc-pv5z
cc-pv5z_dk
cc-pv5zfi_sf_fw
cc-pv5zfi_sf_lc
cc-pv5zfi_sf_sc
cc-pv5zpt_sf_fw
cc-pv5zpt_sf_lc
cc-pv5zpt_sf_sc
cc-pv6+dz
cc-pv6z
cc-pvd+dz
cc-pvdz
cc-pvdz_dk
cc-pvdzfi_sf_fw
cc-pvdzfi_sf_lc
cc-pvdzfi_sf_sc
cc-pvdz-fit2-1
cc-pvdzpt_sf_fw
cc-pvdzpt_sf_lc
cc-pvdzpt_sf_sc
cc-pvdzseg-opt
cc-pvq+dz
cc-pvqz
cc-pvqz_dk
cc-pvqzfi_sf_fw
cc-pvqzfi_sf_lc
cc-pvqzfi_sf_sc
cc-pvqzpt_sf_fw
cc-pvqzpt_sf_lc
cc-pvqzpt_sf_sc
cc-pvqzseg-opt
cc-pvt+dz
cc-pvtz
cc-pvtz_dk
cc-pvtzfi_sf_fw
cc-pvtzfi_sf_lc
cc-pvtzfi_sf_sc
cc-pvtz-fit2-1
cc-pvtzpt_sf_fw
cc-pvtzpt_sf_lc
cc-pvtzpt_sf_sc
cc-pvtzseg-opt
chipman_dzp_+_diffuse
core_val._functions_cc-pcv5z
core_val._functions_cc-pcv6z
core_val._functions_cc-pcvdz
core_val._functions_cc-pcvqz
core_val._functions_cc-pcvtz
crenbl_ecp
crenbs_ecp
d-aug-cc-pv5z
d-aug-cc-pv5z_diffuse
d-aug-cc-pv6z
d-aug-cc-pv6z_diffuse
d-aug-cc-pvdz
d-aug-cc-pvdz_diffuse
d-aug-cc-pvqz
d-aug-cc-pvqz_diffuse
d-aug-cc-pvtz
d-aug-cc-pvtz_diffuse
demon_coulomb_fitting
dgauss_a1_dft_coulomb_fitting
dgauss_a1_dft_exchange_fitting
dgauss_a2_dft_coulomb_fitting
dgauss_a2_dft_exchange_fitting
dhms_polarization
dunning-hay_diffuse
dunning-hay_double_rydberg
dunning-hay_rydberg
dz_+_double_rydberg_dunning-hay
dz_dunning
dzp_+_diffuse_dunning
dzp_dunning
dzp_+_rydberg_dunning
dz_+_rydberg_dunning
dzvp2_dft_orbital
dzvp_dft_orbital
feller_misc._cvdz
feller_misc._cvqz
feller_misc._cvtz
gamess_pvtz
gamess_vtz
glendening_polarization
hay-wadt_mb_n+1_ecp
hay-wadt_vdz_n+1_ecp
hondo7_polarization
huzinaga_polarization
lanl2dzdp_ecp
lanl2dzdp_ecp_polarization
lanl2dz_ecp
mclean_chandler_vtz
midi!
midi_huzinaga
mini_huzinaga
mini_scaled
nasa_ames_ano
nasa_ames_cc-pcv5z
nasa_ames_cc-pcvqz
nasa_ames_cc-pcvtz
nasa_ames_cc-pv5z
nasa_ames_cc-pvqz
nasa_ames_cc-pvtz
partridge_uncontr._1
partridge_uncontr._2
partridge_uncontr._3
pople_2d_2p_polarization
pople_2df_2pd_polarization
pople_3df_3pd_polarization
pople-style_diffuse
pv6z
qmmm_zhang_3-21g_ecp
qmmm_zhang_6-31gs_ecp
sadlej_pvtz
sbkjc_vdz_ecp
sdb-aug-cc-pvqz
sdb-aug-cc-pvqz_diffuse
sdb-aug-cc-pvtz
sdb-aug-cc-pvtz_diffuse
sdb-cc-pvqz
sdb-cc-pvtz
sto-2g
sto-3g
sto-3gs
sto-3gs_polarization
sto-6g
stuttgart_rlc_ecp
stuttgart_rsc_1997_ecp
stuttgart_rsc_ano_ecp
stuttgart_rsc_segmented_ecp
sv_+_double_rydberg_dunning-hay
sv_dunning-hay
svp_+_diffuse_dunning-hay
svp_+_diffuse_+_rydberg
svp_dunning-hay
svp_+_rydberg_dunning-hay
sv_+_rydberg_dunning-hay
tz_dunning
tzvp_dft_orbital
wachters+f
wtbs
```

Basis sets limit

- Basis set is an approximation to solve the KS equation
- The MOs obtained are solutions of the KS equation only within the “function space” of the basis set used
- A complete basis set can represent exactly any MOs
- However, complete basis sets are not practical for calculations (due to the size of the basis sets)

Exchange correlation potential

Molecular Mechanics

Ground State Semi-Empirical

Hatree-Fock

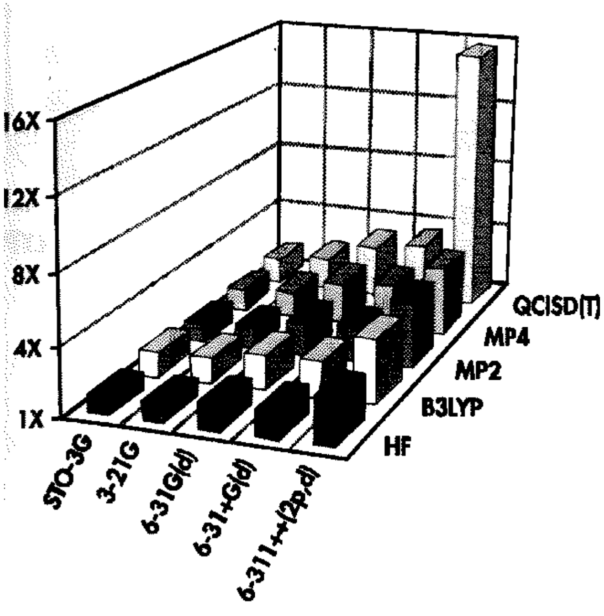
Density Functional Theory

EXCHANGE FUNCTIONALS: Slater, Xa, Becke 88, Perdew-Wang 91, Barone-modified PW91, Gill 96, OPTX, TPSS, BRx, PKZB, wPBEh, PBEh

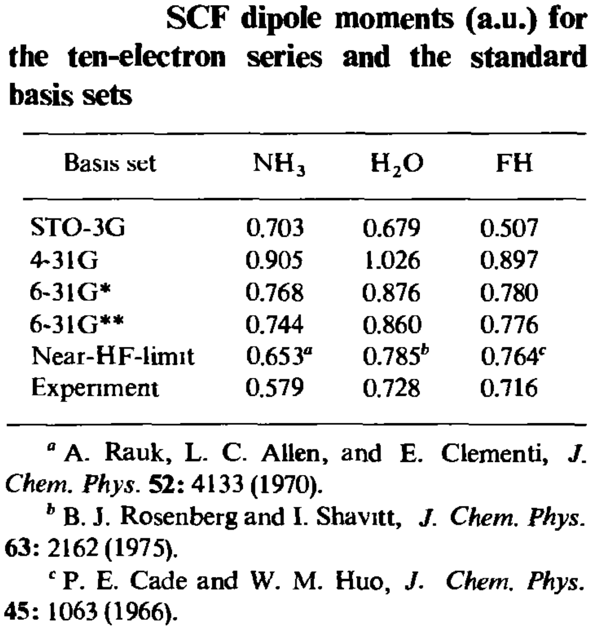
CORRELATION FUNCTIONALS: VWN, VWN5, LYP, Perdew 81, Perdew 86, Perdew-Wang 91, PBE, B95, TPSS, KCIS, BRC, PKZB

OTHER PURE FUNCTIONALS: VSXC, HCTH functional family

HYBRID METHODS: B3LYP, B3P86, P3PW91, B1 and variations, B98, B97-1, B97-2,PBE1PBE, HSEh1PBE and variations, O3LYP, TPSSh, BMK, M05 & M06 and variations, X3LYP; user-configurable hybrid methods



Choosing methods and basis sets



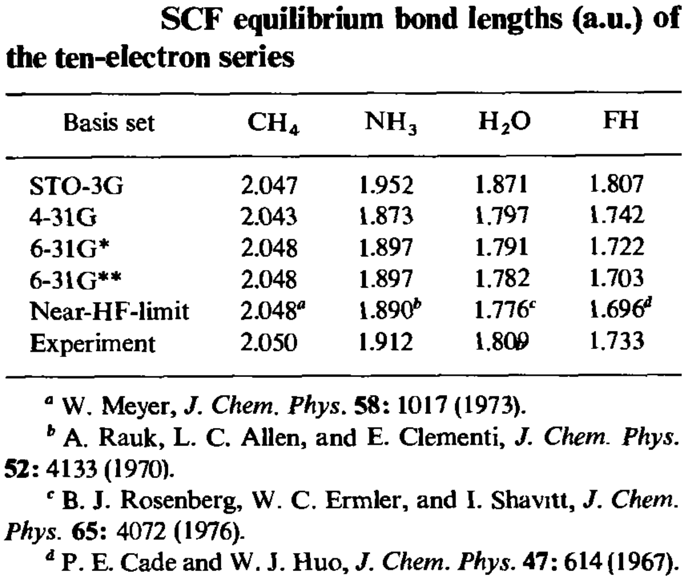
SCF dipole moments (a.u.) for the ten-electron series and the standard basis sets

Basis set	NH_3	H_2O	FH
STO-3G	0.703	0.679	0.507
4-31G	0.905	1.026	0.897
6-31G*	0.768	0.876	0.780
6-31G**	0.744	0.860	0.776
Near-HF-limit	0.653[a]	0.785[b]	0.764[c]
Experiment	0.579	0.728	0.716

[a] A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.* **52:** 4133 (1970).

[b] B. J. Rosenberg and I. Shavitt, *J. Chem. Phys.* **63:** 2162 (1975).

[c] P. E. Cade and W. M. Huo, *J. Chem. Phys.* **45:** 1063 (1966).



SCF equilibrium bond lengths (a.u.) of the ten-electron series

Basis set	CH_4	NH_3	H_2O	FH
STO-3G	2.047	1.952	1.871	1.807
4-31G	2.043	1.873	1.797	1.742
6-31G*	2.048	1.897	1.791	1.722
6-31G**	2.048	1.897	1.782	1.703
Near-HF-limit	2.048[a]	1.890[b]	1.776[c]	1.696[d]
Experiment	2.050	1.912	1.809	1.733

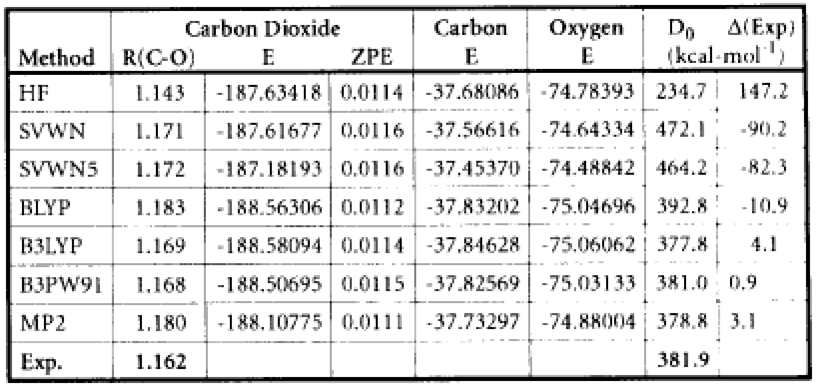
[a] W. Meyer, *J. Chem. Phys.* **58:** 1017 (1973).

[b] A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.* **52:** 4133 (1970).

[c] B. J. Rosenberg, W. C. Ermler, and I. Shavitt, *J. Chem. Phys.* **65:** 4072 (1976).

[d] P. E. Cade and W. J. Huo, *J. Chem. Phys.* **47:** 614 (1967).

CO_2

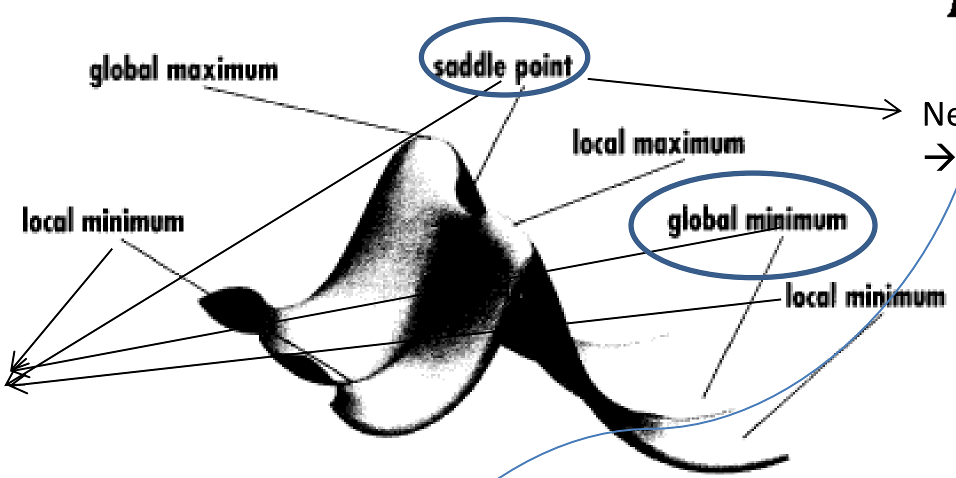


Method	Carbon Dioxide			Carbon	Oxygen	D_0	Δ(Exp)
	R(C-O)	E	ZPE	E	E	(kcal·mol^{-1})	
HF	1.143	-187.63418	0.0114	-37.68086	-74.78393	234.7	147.2
SVWN	1.171	-187.61677	0.0116	-37.56616	-74.64334	472.1	-90.2
SVWN5	1.172	-187.18193	0.0116	-37.45370	-74.48842	464.2	-82.3
BLYP	1.183	-188.56306	0.0112	-37.83202	-75.04696	392.8	-10.9
B3LYP	1.169	-188.58094	0.0114	-37.84628	-75.06062	377.8	4.1
B3PW91	1.168	-188.50695	0.0115	-37.82569	-75.03133	381.0	0.9
MP2	1.180	-188.10775	0.0111	-37.73297	-74.88004	378.8	3.1
Exp.	1.162					381.9	

Potential energy surface

Keyword: **OPT, QST2, FREQ**

$$H_{ij} = \frac{\partial E(\mathbf{X})}{\partial X_i\, \partial X_j}$$



Negative force constant
→ imaginary frequency

$$f_i = \frac{\partial E(\mathbf{X})}{\partial X_i} = 0$$

$$S_T = R\left(\ln(q_t q_e q_r q_v e) + T\left(\frac{\partial \ln q}{\partial T}\right)_V\right)$$

$$S_v = R\sum_K\left(\frac{\Theta_{v,K}/T}{e^{\Theta_{v,K}/T} - 1} - \ln(1 - e^{-\Theta_{v,K}/T})\right)$$

Gibbs free energy

$$G = E^{DFT} + E_{ZPE} + E_T + k_bT - TS_T$$

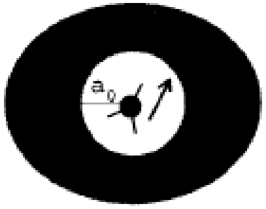
Calculate reaction energy

Solvation models

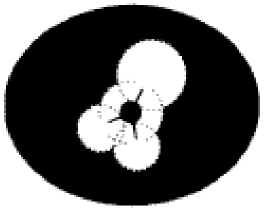
1. Super-molecule (large QM calculation)
2. Molecular Mechanics (difficult to treat bond breaking)
3. **Continuum models (Onsager, PCM,..)**

   Explicit consideration of solvent molecules is **neglected**

   Solvent effects are described in terms of macroscopic properties of the chosen solvent (e, $<R_{solvent}>$)
4. Hybrid/mixed (i.e. ONIOM/PCM, QM/MM)



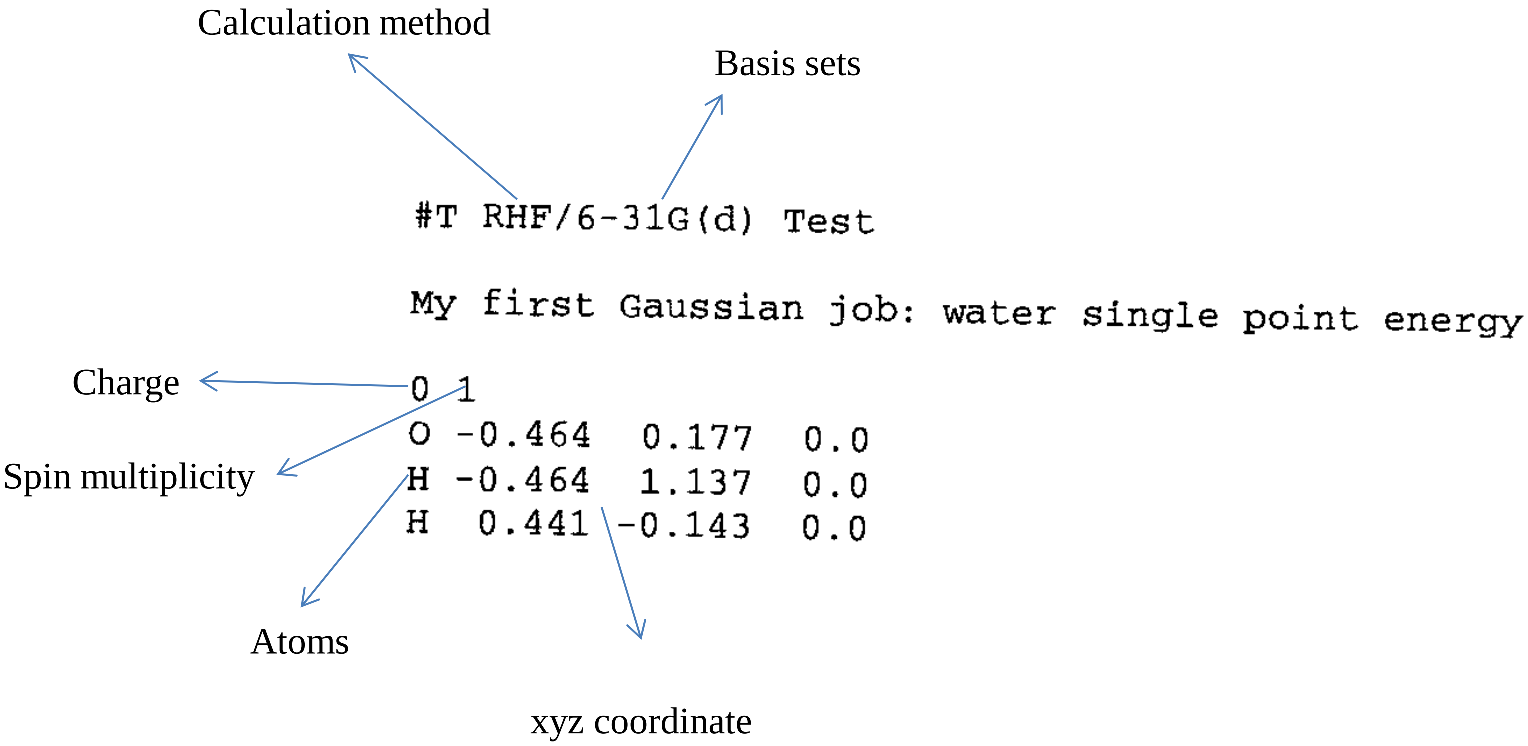
Onsager (Dipole & Sphere) Model
SCRF=Dipole



Tomasi's PCM Model
SCRF=PCM

Simple example: SCF calculation

Very simple and user friendly



Calculation method

Basis sets

```
#T RHF/6-31G(d) Test

My first Gaussian job: water single point energy

0 1
O -0.464  0.177  0.0
H -0.464  1.137  0.0
H  0.441 -0.143  0.0
```

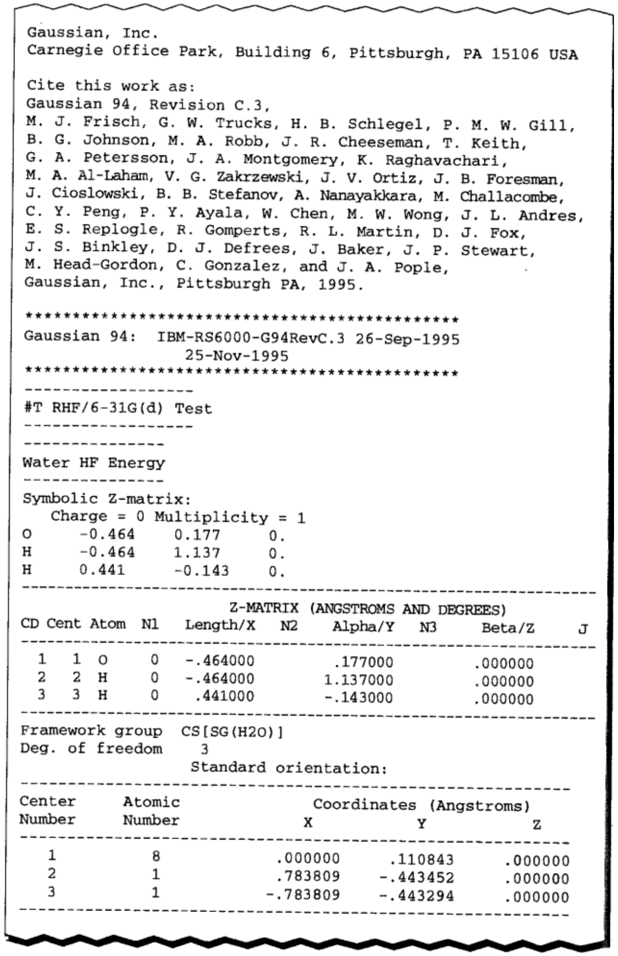
Charge

Spin multiplicity

Atoms

xyz coordinate

output



This is the official citation for the *Gaussian 94* program, which should be included in its entirety in all papers presenting results obtained by running *Gaussian 94* and *Gaussian 94W.*

This is the version of *Gaussian 94* that is running, in this case, Revision C.3. Include this information in any questions or problem reports you send to Gaussian, Inc.

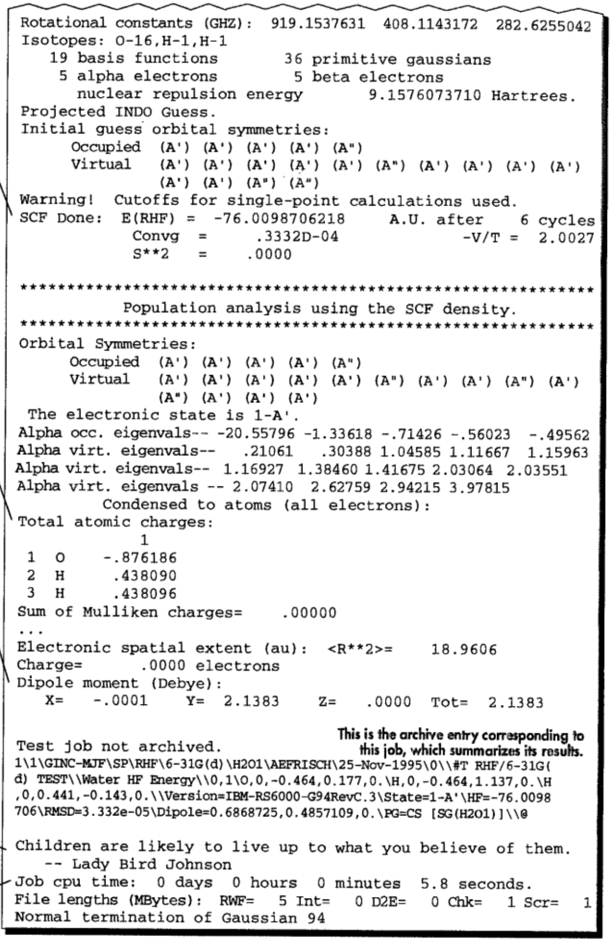
The route section, title section, and molecule specification from the input file are displayed next.

The standard orientation is the coordinate system used internally by the program as it performs the calculation, chosen to optimize performance. The origin is placed at the molecule's center of nuclear charge. Here, the oxygen atom sits on the Y-axis above the origin, and the two hydrogen atoms are placed below it in the XY plane.

```
Gaussian, Inc.
Carnegie Office Park, Building 6, Pittsburgh, PA 15106 USA

Cite this work as:
Gaussian 94, Revision C.3,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill,
B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith,
G. A. Petersson, J. A. Montgomery, K. Raghavachari,
M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman,
J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe,
C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres,
E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox,
J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart,
M. Head-Gordon, C. Gonzalez, and J. A. Pople,
Gaussian, Inc., Pittsburgh PA, 1995.

**********************************************
Gaussian 94:  IBM-RS6000-G94RevC.3 26-Sep-1995
                 25-Nov-1995
**********************************************
------------------
#T RHF/6-31G(d) Test
------------------
---------------
Water HF Energy
---------------
Symbolic Z-matrix:
   Charge = 0 Multiplicity = 1
O      -0.464    0.177     0.
H      -0.464    1.137     0.
H      0.441     -0.143    0.
-------------------------------------------------------------
                     Z-MATRIX (ANGSTROMS AND DEGREES)
CD Cent Atom  N1    Length/X   N2     Alpha/Y    N3      Beta/Z      J
-------------------------------------------------------------
  1   1  O     0    -.464000          .177000           .000000
  2   2  H     0    -.464000         1.137000           .000000
  3   3  H     0     .441000         -.143000           .000000
-------------------------------------------------------------
Framework group  CS[SG(H2O)]
Deg. of freedom    3
                  Standard orientation:
----------------------------------------------------------
Center      Atomic              Coordinates (Angstroms)
Number      Number                X            Y            Z
----------------------------------------------------------
   1           8              .000000      .110843      .000000
   2           1              .783809     -.443452      .000000
   3           1             -.783809     -.443294      .000000
----------------------------------------------------------
```



This line indicates the predicted energy computed by our single point calculation. It also indicates the values of the convergence criteria in the SCF computation. Appendix A discusses the iterative nature of SCF methods in more detail.

A Mulliken population analysis follows the SCF energy results. This analysis partitions the charge on the molecule by atom.

The section labelled `Total atomic charges` indicates the estimated total charge on each atom in the molecule. Here, the oxygen atom has a negative charge balancing the slight positive charge on each of the hydrogen atoms.

This section gives the dipole moment for this molecule, in the standard orientation. This dipole moment has only a negative Y component, and its magnitude is 1.69 debye. By convention, the dipole moment "points" in the direction of positive charge. Referring back to the standard orientation for this molecule, we note that the oxygen atom is situated on the positive Y-axis. This indicates that the dipole moment points away from the oxygen atom, toward the positively-charged portion of the molecule.

This is the archive entry corresponding to this job, which summarizes its results.

Successful *Gaussian* jobs end with a quotation chosen at random from a collection stored internally.

CPU time and other resource usage information is presented at the conclusion of the job.

```
Rotational constants (GHZ):  919.1537631  408.1143172  282.6255042
Isotopes: O-16,H-1,H-1
   19 basis functions        36 primitive gaussians
    5 alpha electrons         5 beta electrons
      nuclear repulsion energy       9.1576073710 Hartrees.
Projected INDO Guess.
Initial guess orbital symmetries:
     Occupied  (A') (A') (A') (A') (A")
     Virtual   (A') (A') (A') (A') (A') (A") (A') (A') (A') (A')
               (A') (A') (A") (A")
Warning!  Cutoffs for single-point calculations used.
SCF Done:  E(RHF) =  -76.0098706218     A.U. after    6 cycles
           Convg  =      .3332D-04              -V/T =  2.0027
           S**2   =     .0000

**********************************************************
           Population analysis using the SCF density.
**********************************************************
Orbital Symmetries:
     Occupied  (A') (A') (A') (A') (A")
     Virtual   (A') (A') (A') (A') (A') (A") (A') (A') (A") (A')
               (A") (A') (A') (A')
 The electronic state is 1-A'.
Alpha occ. eigenvals-- -20.55796 -1.33618 -.71426 -.56023  -.49562
Alpha virt. eigenvals--   .21061   .30388 1.04585 1.11667  1.15963
Alpha virt. eigenvals-- 1.16927  1.38460 1.41675 2.03064  2.03551
Alpha virt. eigenvals -- 2.07410  2.62759 2.94215 3.97815
          Condensed to atoms (all electrons):
Total atomic charges:
             1
 1  O    -.876186
 2  H     .438090
 3  H     .438096
Sum of Mulliken charges=    .00000
...
Electronic spatial extent (au):  <R**2>=    18.9606
Charge=      .0000 electrons
Dipole moment (Debye):
   X=   -.0001    Y=  2.1383    Z=    .0000  Tot=  2.1383

Test job not archived.
1\1\GINC-MJF\SP\RHF\6-31G(d)\H2O1\AEFRISCH\25-Nov-1995\0\\#T RHF/6-31G(
d) TEST\\Water HF Energy\\0,1\O,0,-0.464,0.177,0.\H,0,-0.464,1.137,0.\H
,0,0.441,-0.143,0.\\Version=IBM-RS6000-G94RevC.3\State=1-A'\HF=-76.0098
706\RMSD=3.332e-05\Dipole=0.6868725,0.4857109,0.\PG=CS [SG(H2O1)]\\@

Children are likely to live up to what you believe of them.
   -- Lady Bird Johnson
Job cpu time:  0 days  0 hours  0 minutes  5.8 seconds.
File lengths (MBytes):  RWF=   5 Int=   0 D2E=   0 Chk=   1 Scr=   1
Normal termination of Gaussian 94
```

References:

1. www.gaussian.org
2. Forseman, J. B., and E. Frisch. "Exploring Chemistry with Electronic Structure Methods, Gaussian." *Inc., Pittsburgh* (1996)
3. Donald A. McQuarrie and John D. Simon. “Physical Chemistry: A Molecular Approach” (1997)
4. Attila Szabo and Neil S. Ostlund. “Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory” Dover (1996)

Case Study I:

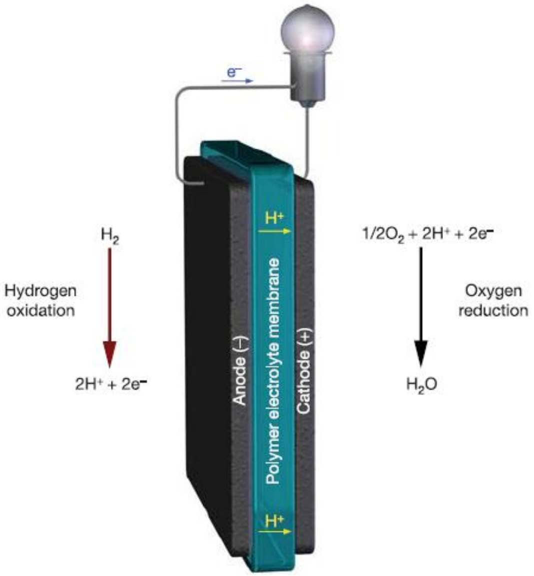
Theoretical Study of Biosynthetic reaction from Dopachrome to 5,6-Dihydroxyindole on Eumelanogenesis

(Will be distributed in the classroom)

Case Study II:

Oxygen Reduction Reaction on Co-(6)Ppy Cluster

Introduction



PEFC commercialization problems: Pt

☐ Co-Ppy-C [1] : high ORR activity , good stability
☐ Work well on other types of fuel cells (DBFC, DHFC) [2-3]

Detail ORR mechanism is **not clear**.
Interactions between the catalyst and O_2/H_2O_2 molecules are unknown.

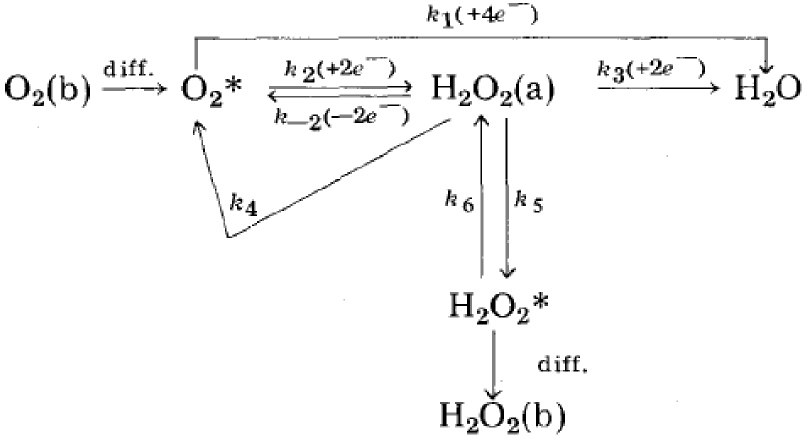
H_2O_2 formation is important information

If the two-electron reduction to H_2O_2 predominates : The produced H_2O_2 can not stay at the electrode → **diffuse into the environment** ; Degrades the performance of fuel cell (i.e., potential damage to the proton exchange membranes [5-6])

[1] R. Bashyam and P. Zelenay, *Nature* **443** (2006), pp. 63–66
[2] H.Y. Qin, Z.X. Liu, W.X. Yin, J.K. Zhu and Z.P. Li, *J. Power Sources* **185** (2008),pp. 909-912
[3] K. Asazawa, K. Yamada, H. Tanaka, A. Oka, M. Taniguchi and T. Kobayashi, *Angew. Chem. Int. Ed.* **46** (2007), pp. 8024–8027
[4] K. Lee, L. Zhang, H. Lui, R. Hui, Z. Shi, J. Zhang: Electrochimica Acta **54** (2009) 4704–4711
[5] M. Aoki, H. Uchida and M. Watanabe, *Electrochem. Commun.* **8** (2006), p. 1509.
[6] J.L. Qiao, M. Saito, K. Hayamizu and T. Okada, *J. Electrochem. Soc.* **153** (2006), p. A967.

Objective

General scheme of oxygen reduction [1]



A. **Without** H_2O_2 formation

possible reaction pathways

(1) $O_{2\ ads} \rightarrow \mathbf{2O_{ads}}$ **(with O_2 dissociation)**

$2O_{ads} + 4e^- + 4H^+ \rightarrow 2H_2O$

or

(2) $O_2 + 2e^- + 2H^+ \rightarrow \mathbf{O_{ads} + H_2O}$

$O_{ads} + 2e^- + 2H^+ \rightarrow H_2O$

or

(3) $O_{2ads} + 2e^- + 2H^+ \rightarrow \mathbf{2OH_{ads}}$

$2OH_{ads} + 2e^- + 2H^+ \rightarrow 2H_2O$

B. **With** H_2O_2 formation

(4) $O_{2ads} + 2e^- + 2H^+ \rightarrow \mathbf{H_2O_2}$

$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$

Goal:

1) Fundamental understanding of the interactions between Co-Ppy and O_2/H_2O_2 molecules (adsorption & dissociation)

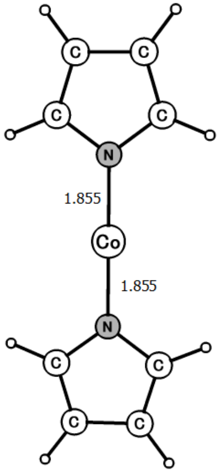
2) Comparison of the potential energy for reaction (1), (2), **(3)**, and (4)

[1] Wroblowa H, Pan Y C and Razumney G 1976 J. Electroanal. Chem. 69 195–201

Co-(6)Ppy : Cluster Model

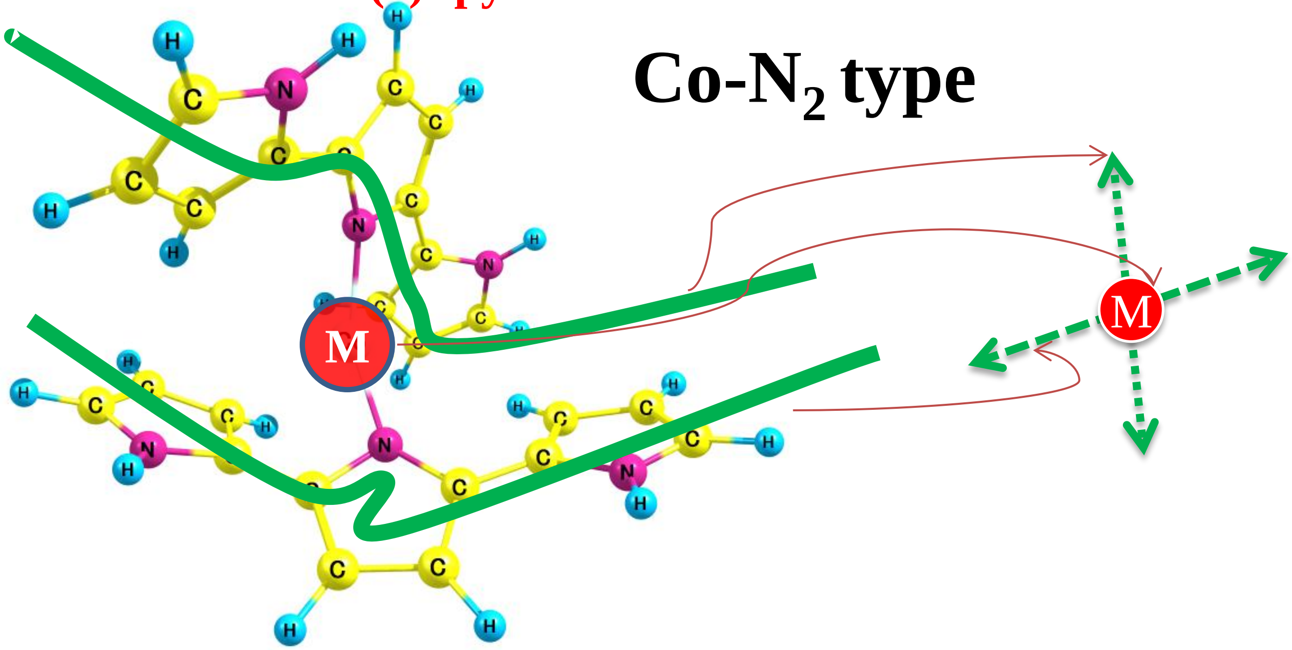
1. DFT calculation using **Gaussian 03**
2. Hybrid exchange correlation functional and (6-31G(d,p)/LANL2DZ) → 6-311+G(d,p) basis sets were used
3. Polypyrrole→ oligopyrrole (cluster model)
4. Unsupported Co-(6)Ppy cluster in the vacuum state

Co-(2)Ppy

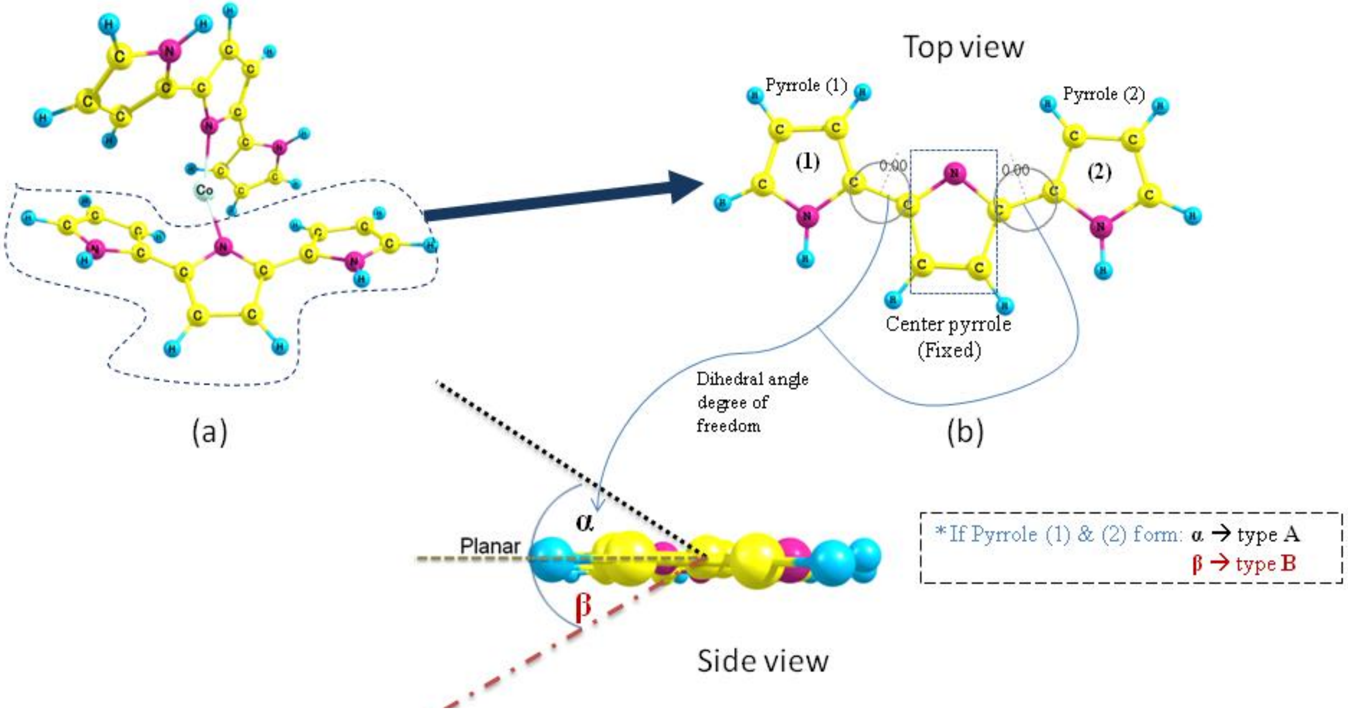


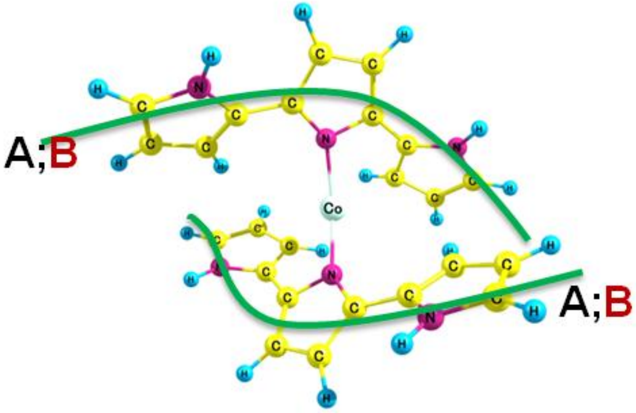
Co-(6)Ppy

Co-N_2 type



Cluster Models

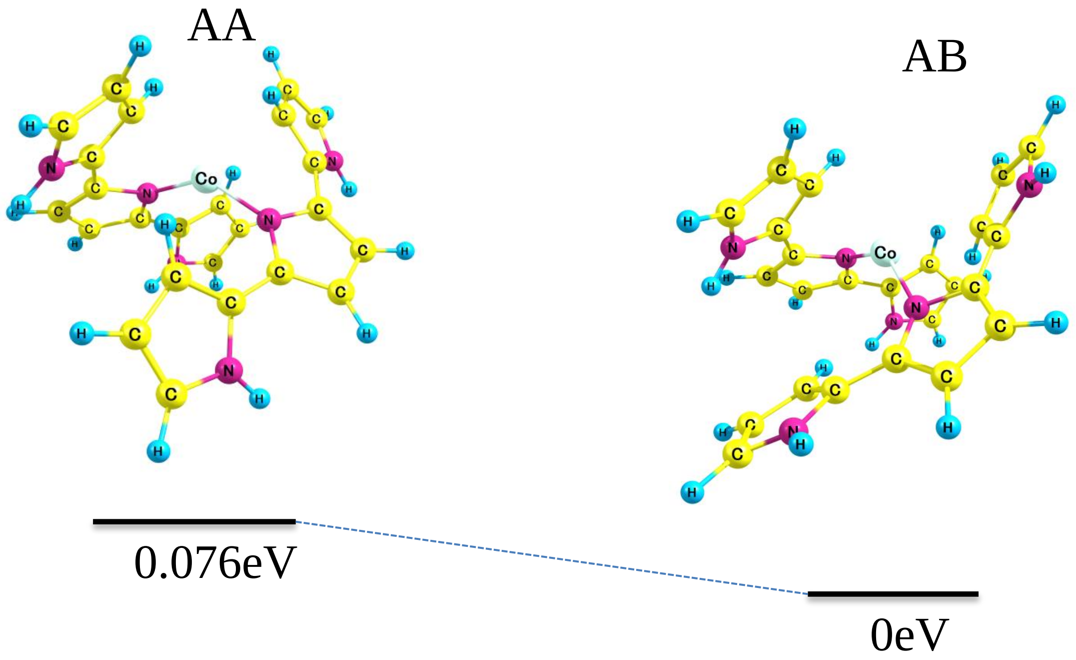


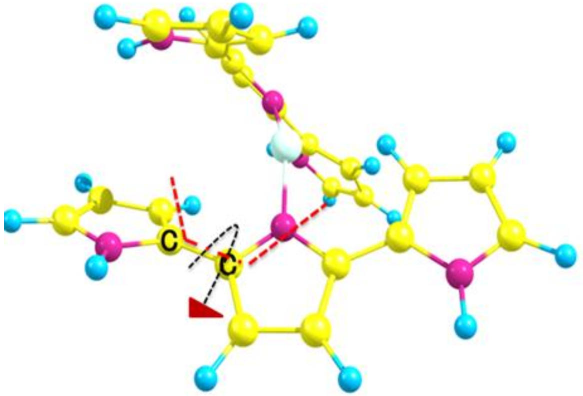


(d)

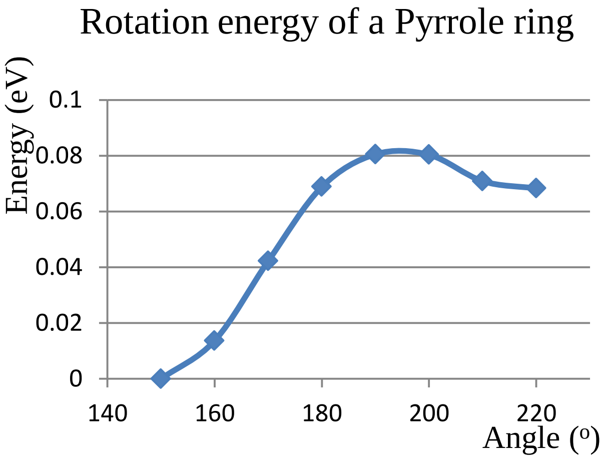
3 possible configurations
AA,AB,BB →AA,AB

Optimized Structure of Co-(6)Ppy





(a)



Easy to rotate !

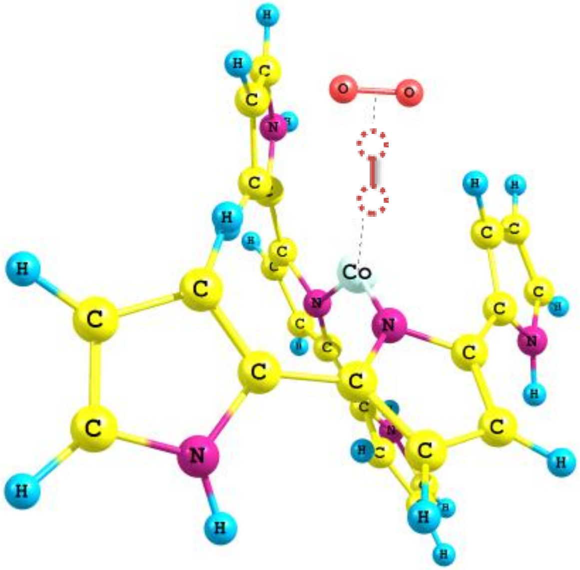
O_2 Adsorption on Co-(6)Ppy Clusters :

$$O_2 \rightarrow O_{2(ads)}$$

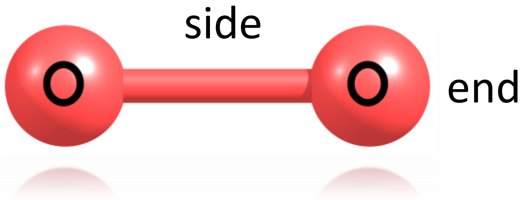
H.K. Dipojono, A.G. Saputro, R. Belkada, H. Nakanishi, H. Kasai, M. David, and E.S. Dy, *J. Phys. Soc. Jpn.* **78** 094710 (2009)

Adsorption of O_2 on Co-(6)Ppy

Initial geometry



Co-6Pyrrole : AA;AB

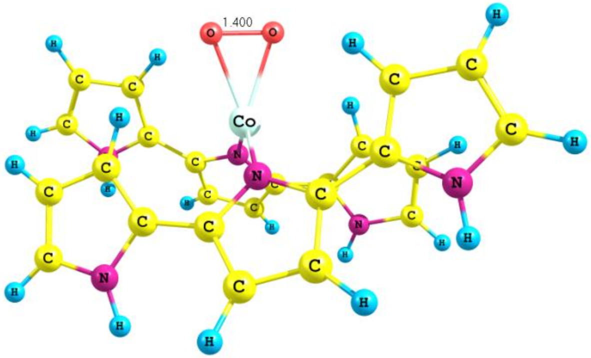


O_2 Adsorption on The Clusters

O-O elongation :
10.6%

AA1

O-O: 1.334 Å



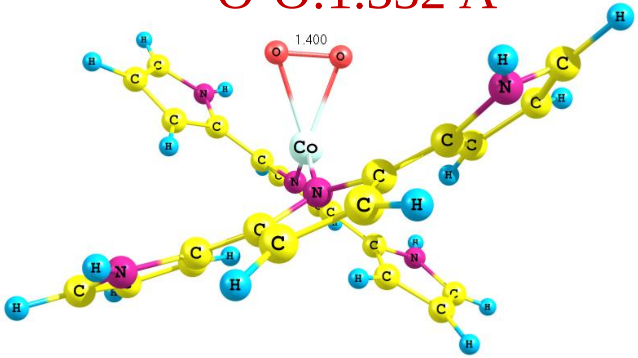
0 eV

E_{ads} = 0.48 eV

O-O elongation :
10.4%

AA2

O-O:1.332 Å



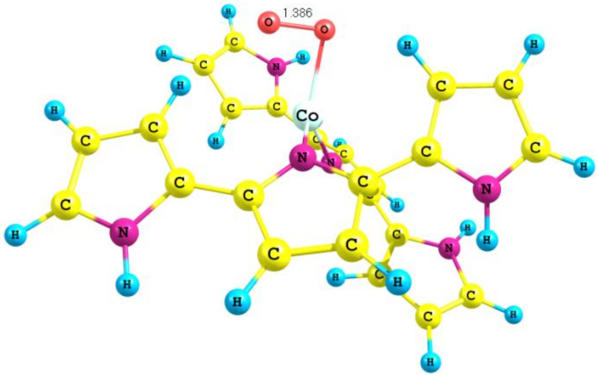
0.10 eV

E_{ads} = 0.37 eV

O-O elongation :
9.5%

AB

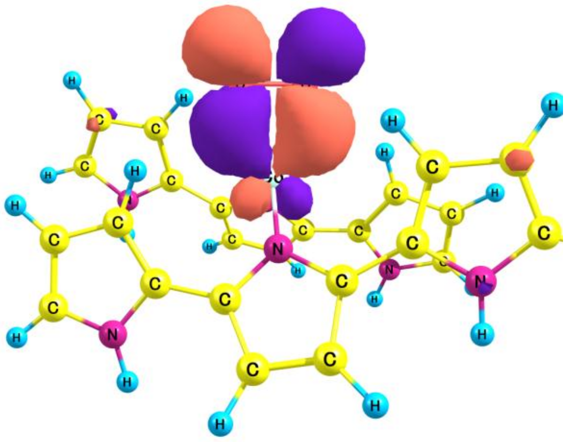
O-O: 1.321 Å



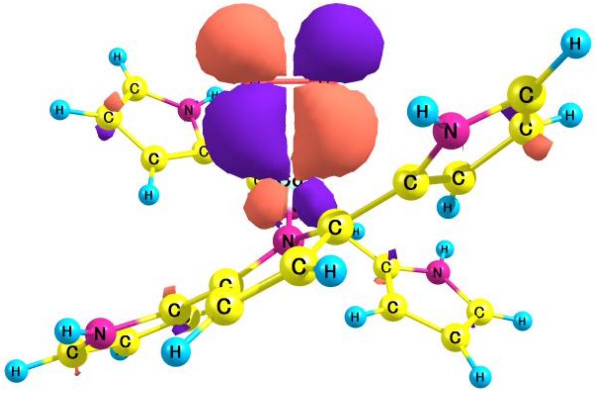
0.15 eV

E_{ads} = 0.25 eV

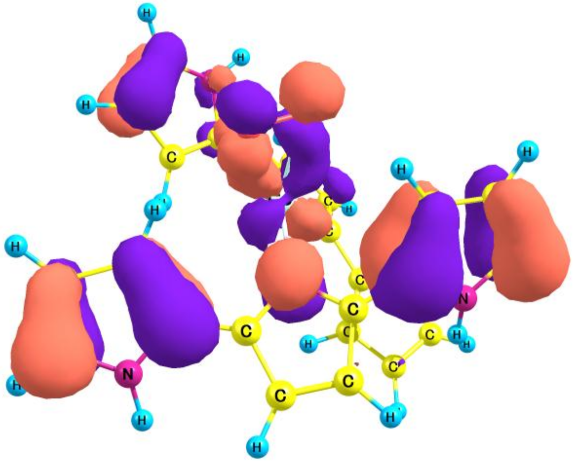
Adsorption mechanism



HOMO-4 (-6.65 eV)



HOMO-4 (-6.38 eV)



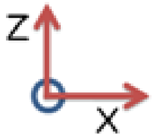
HOMO-4 (-6.29eV)

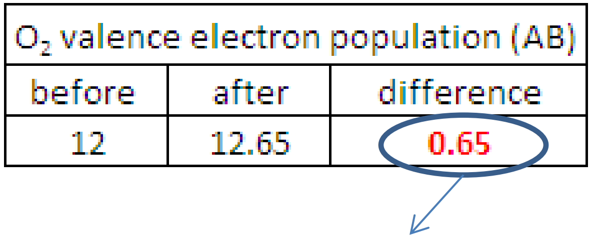
π*

d_{xz}

+ Color: 🟥

- Color: 🟪





O$_2$ valence electron population (AB)		
before	after	difference
12	12.65	0.65

O-O elongation

O_2 Dissociation

$O_{2\,ads} \rightarrow \mathbf{2O_{ads}}$ *(with O_2 dissociation)*

$2O_{ads} + 4e^- + 4H^+ \rightarrow 2H_2O$

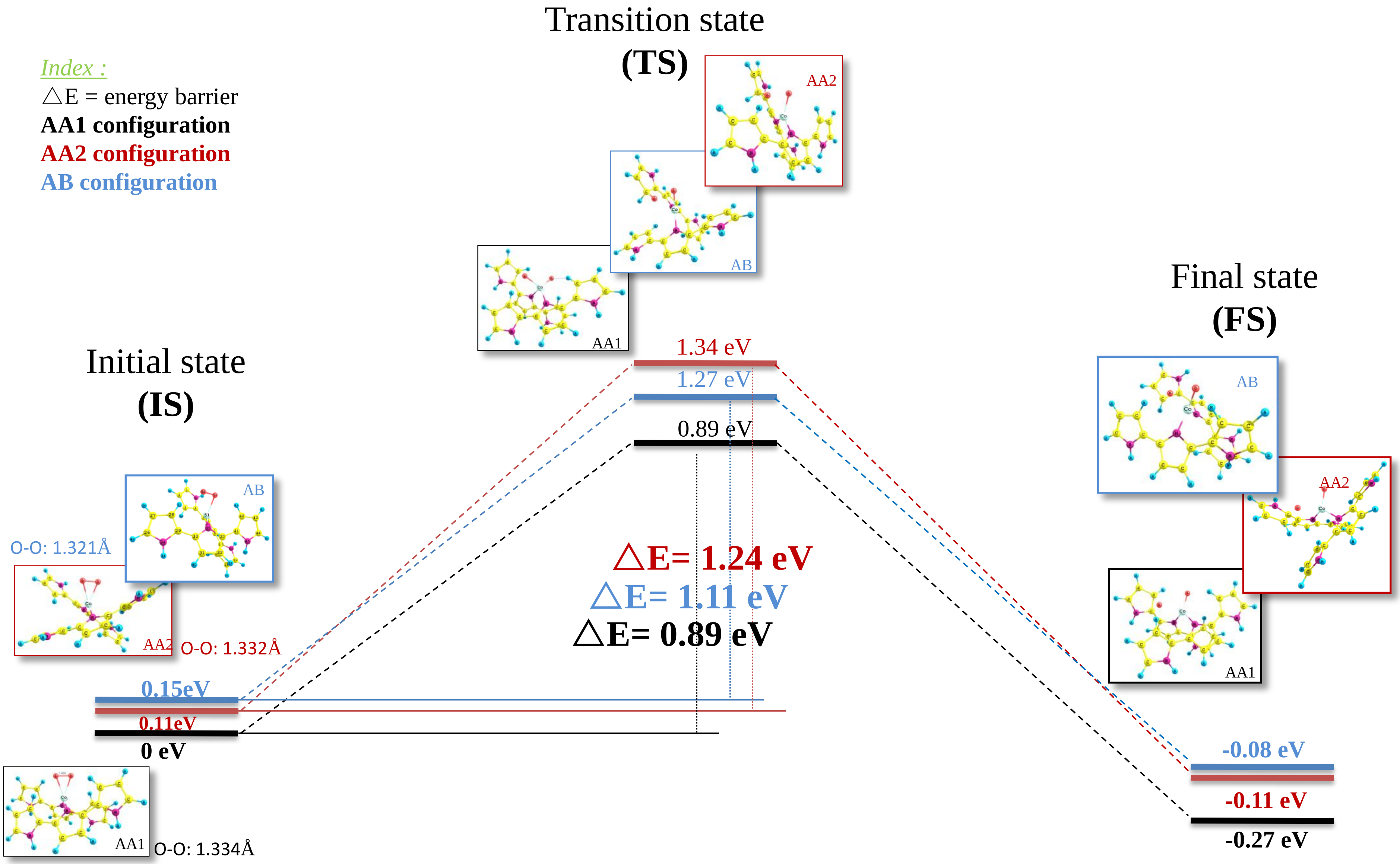
Index :

△E = energy barrier

AA1 configuration

AA2 configuration

AB configuration



H.K. Dipojono, A.G. Saputro, S.M. Aspera, H. Kasai, Jpn. J. Appl. Phys. **50** (2011) 055702

Comparison : O_2 dissociation energy

Co- (6)Ppy (O_2 adsorption state: side-on)
Co-6Pyrrole : **0.89 eV ~ 1.24 eV**

Metal-Porphyrin (O_2 adsorption state: end-on)
1.65 eV - 3.13 eV [1]

Pt (111)
Dissociation from precursion state **0.9 eV** [2] **~1.7 eV** [3]
Dissociative adsorption **0.3 -1.5 eV** [4]

The ORR mechanism in Co-(6)Ppy system will prefer direct reduction process (without initial O_2 dissociation).

[1] M. Tsuda, E. S. Dy, and H. Kasai . J. Chem. Phys. 122, 244719 2005
[2] A. Eichler, J. Hafner, Phys. Rev. Lett. 79, 4481 (1997)
[3] S. Yotsuhashi, Y. Yamada, W.A. Di˜no, H. Nakanishi, H. Kasai, Phys. Rev. B 72, 033415 (2005)
[4] A. Eichler, F. Mittendorfer, and J. Hafner, Phys. Rev. B. 62, 4744 (2000)

O_2 reduction to H_2O/H_2O_2

Without H_2O_2 formation

(2) $O_2 + 2e^- + 2H^+ \rightarrow \mathbf{O_{ads} + H_2O}$

$O_{ads} + 2e^- + 2H^+ \rightarrow H_2O$

(3) $O_{2ads} + 2e^- + 2H^+ \rightarrow \mathbf{2OH_{ads}}$

$2OH_{ads} + 2e^- + 2H^+ \rightarrow 2H_2O$

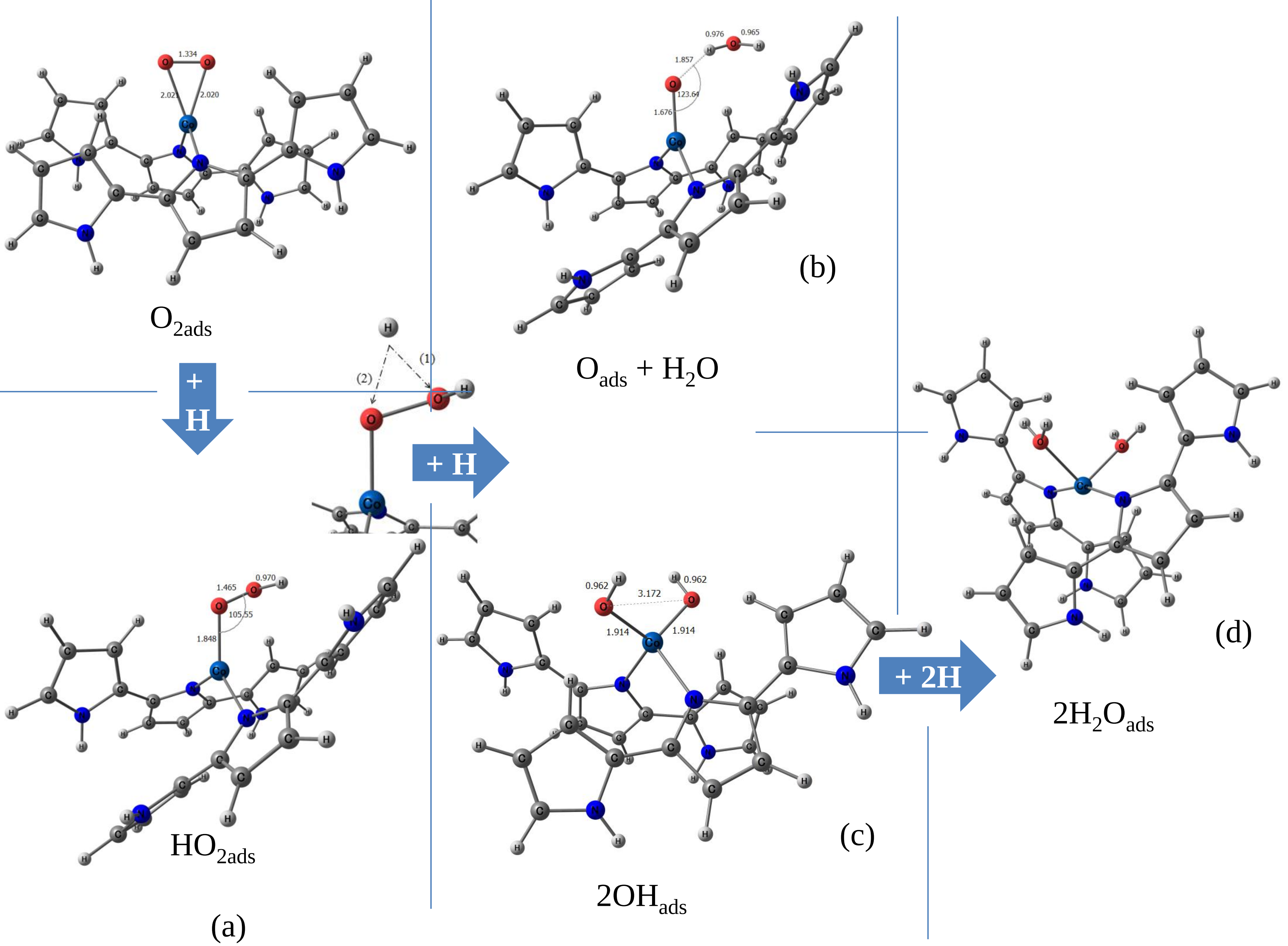
with H_2O_2 formation

(4) $O_{2ads} + 2e^- + 2H^+ \rightarrow \mathbf{H_2O_2}$

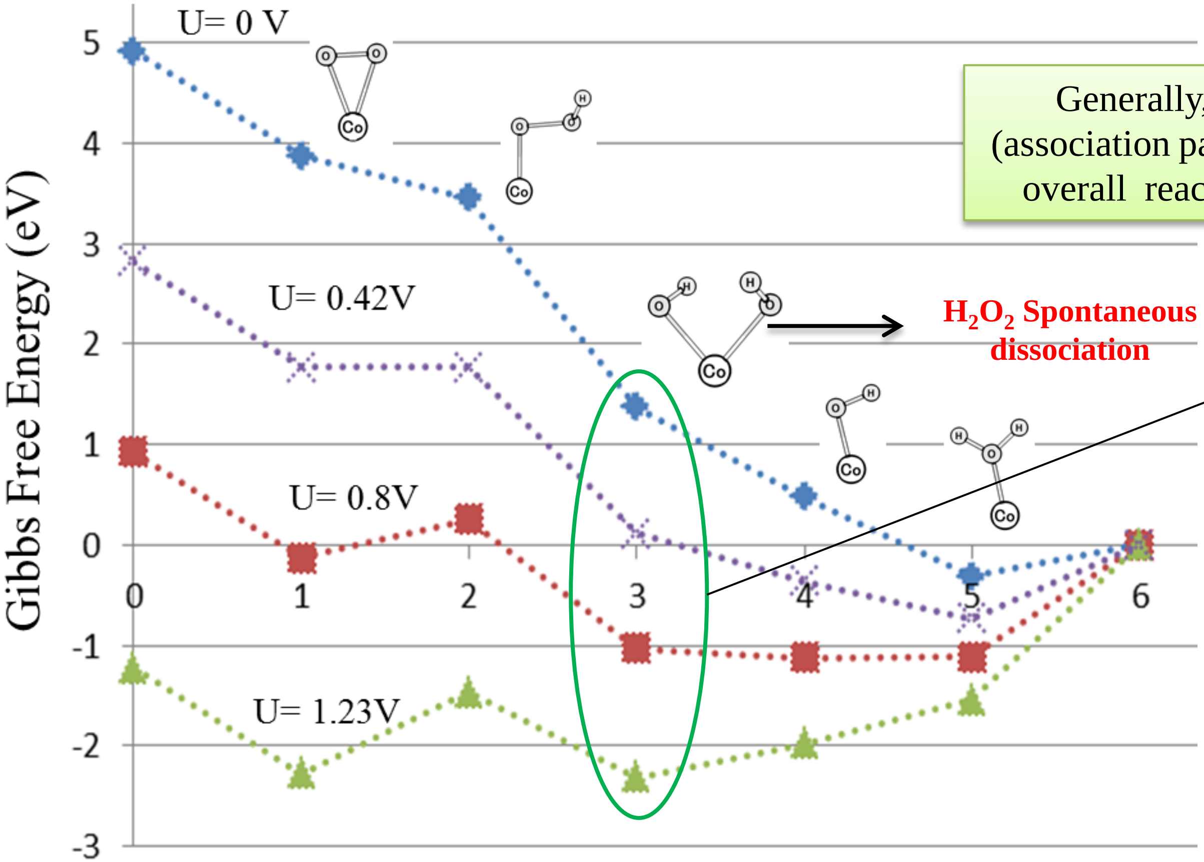
$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$

How ?

By adding 4H atoms **one by one** to the O_{2ads} on Co-(6)Ppy


1.334
2.021
2.020
O_{2ads}
+ H
H
(1)
(2)
0.976
0.965
1.857
123.64
1.676
(b)
$O_{ads} + H_2O$
+ H
1.465
0.970
105.55
1.848
HO_{2ads}
(a)
0.962
3.172
0.962
1.914
1.914
(c)
$2OH_{ads}$
+ 2H
(d)
$2H_2O_{ads}$

The Potential Energy Surface Profile for Water Formation Reaction [1] → $4e^{-}$ pathway , but…

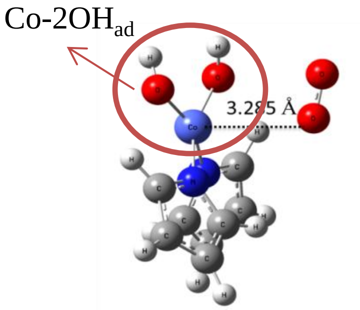


H_2O_2 Spontaneous dissociation

Generally, the direct O_2 reduction to water (association pathway) is very efficient, because the overall reaction is downhill at U= 0 – 0.42 V).

At Pt(111) (low coverage), the overall reaction is downhill at U= 0 – 0.78 V
→ Pt(111) still better

$E_{ad}(2OH)$ = 2.70 eV
→ could result in OH poisoning !!



$2OH_{ad}$ + O_2

O_2 weakly adsorbed on the Co-$2OH_{ad}$ site
→ E_{O2ad} ~ *0.001 eV.*
→OH poisoning[2]

1. A.G. Saputro, F. Rusydi, H. Kasai, and H.K. Dipojono: *J. Phys. Soc. Jpn.* **81** (2012) 034703.
2. A.G. Saputro and H. Kasai, *in preparation*, 2013.

Summary

1. We have studied various possible ORR mechanisms on the unsupported Co-(6)Ppy system in the vacuum state.
2. The O_2 adsorption and elongation are induced from the interaction between *d* orbitals of Co and antibonding orbital of O_2
3. O_2 reduction to water via O_2 dissociation is not favorable due to high dissociation energy
4. The direct O_2 reduction to water (without initial O_2 dissociation) is very efficient, because the overall reaction has downhill profile (U=0-0.42V)
5. While the H_2O_2 spontaneous dissociation is energetically more favorable than the direct O_2 dissociation in the general ORR mechanism, the resulted Co-2OH_{ad} site is subject to OH poisoning due to the high 2OH adsorption energies.