Q-Chem Workshop

UC Berkeley, July 22, 2005

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Q-Chem, Inc., Pittsburgh, PA

1. Introduction

Objectives of the Workshop

By the end of this workshop it is hoped that you will be able to do the following:

- Be able to use WebMO to build molecule and to run a range of quantum chemistry calculations.
- Be able to interpret the output obtained from running Q–Chem.
- Have an overview of the capabilities of the Q–Chem package.
- Know about some of the features that are unique to Q–Chem.
- Appreciate the limitations of the software.

Outline

The focus of this workshop will be on introducing Q–CHEM and running common job types. The outline is:

9:10	Introduction to Q–CHEM, running single point calculations
10:20	Geometry optimisations, frequency calculations, transition state searches
11:20	Excited-state methods

Further Information

- Q–CHEM's website is: `http://www.q-chem.com`
- Support Questions can be e-mailed to: `support@q-chem.com, or yihan@q-chem.com`
- The Q-Chem 2.1 Manual is available at: `http://www.q-chem.com/tech/guides/qchem.2.1.pdf`
- This workshop and its materials are available at: `http://www.q-chem.com/ yihan/workshop/`

Background of Q–CHEM Inc.

- Board:
  Peter M. W. Gill, Martin Head-Gordon, Anna I. Krylov
  Jing Kong, John A. Pople*, Henry F. Schaefer, III
- Scientific contributions from many academic groups worldwide:
  - Australia: Australian Nation U
  - Germany: U Tubingen, Hamburg U Tech
  - USA: UC Berkeley, USC, U Buffalo, Rutgers U, U Arkansas
- Business and technical personnels at Pittsburgh, Pennsylvania:
  - Chief Scientist: Jing Kong
  - Technical: Shawn Brown, Laszlo Fusti-Molnar, Emil Proynov, Yihan Shao
  - Administrative: Zita-Ann Berry
  - Sales: Jaime Martell
- Q–CHEM 3.0 is scheduled to be released this summer.

Strengths and Capabilities of Q–CHEM

- A wide range of ground-state methods
  - Mean-field Theories:
    Hartree-Fock (HF) and Density Functional Theory (DFT)
    - Each electron has its own molecular orbital (MO)
    - Each electron is subjected to mean field of other electrons
    - Solved self-consistently
  - Perturbative Methods:
    MP2, Resolution-of-Identity MP2 (RIMP2)
  - Highly-Correlation Methods:
    CCSD, CCSD(T), CCSD(2), OD, OD(2), PP, IP
- Extensive range of excited state methods:
  - CIS, XCIS, EOM–CCSD
  - TDDFT
  - SF–TDDFT, SF–CIS(D), SF–OD, SF–CCSD

Strengths and Capabilities of Q–CHEM

- Highly efficient codes
- Parallel Implementations
- Fully integrated ECP package for heavy elements
- Properties package allows the calculation of:
  - Optimized structures
  - Transition structures
  - Vibrational frequencies
  - Reaction pathways
  - Solvent effects
  - NMR chemical shifts
  - Electrostatic potentials

Afternoon Seminars

- 2:00-2:45pm
  - Prof. Peter M. W. Gill, Australian National University
  - Everything you’ve ever wanted to know about 2-electrons
- 2:45-3:30pm
  - Dr. King Kong, Q-Chem Inc
  - MrXC: A new numerical method to speed up DFT calculations
- 3:30-3:45pm
  - Coffee break
- 3:45-4:30pm
  - Prof. Anna I. Krylov, Univeristy of Southern California
- 4:30-5:15pm
  - Prof. Henry F. Schaefer III, Univeristy of Georgia at Athens
  - Lesions in DNA subunits: foundational studies of structure and energetics

2. Single-Point Calculations

WebMO input – Importing Cartesian Coordinates

- WebMO login http://glab.cchem.berkeley.edu/glab/webmo.html
- Click on "Creat New Job" to start a new job
- In the "Build Molecule" screen, click on "Import Molecule"
- In the "Import Molecule" screen, select "XYZ Format"
- In the same screen, enter atomic coordinates in the "2) Enter Text" box, for example,

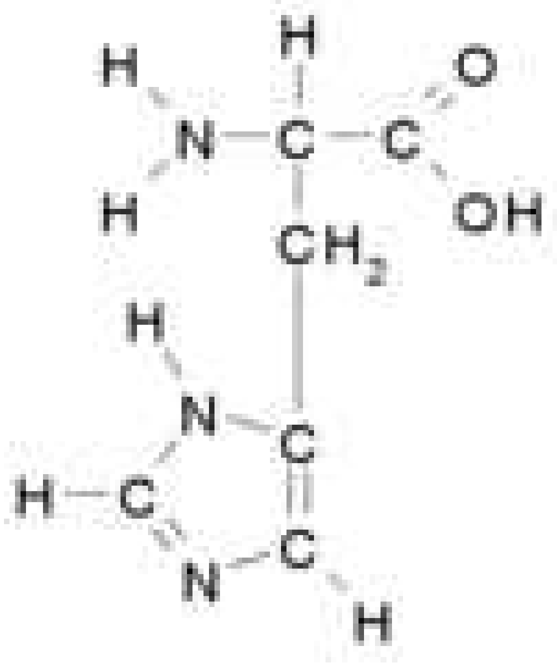
```
 O  1.319091  0.007854 -0.001645
 H  1.757412 -0.432462 -0.733540
 H  1.755727 -0.343047  0.778039
```

- Click on "Import Molecule" or "Close" button, to go back to the "Build Molecule" screen

WebMO input – Build a Molecule with WebMO Editor

- In the "Build Molecule" screen, click on "Open Editor"
- Click on the "Build" Button (which looks like a water molecule) to start building a molecule
- Click anywhere in the Editor, will get a new atom
- To add a different element, click on the "Perodic Table" button right under the "Build" button
- To add a new (single) bond to an existing atom, click on that atom, drag and then release
- To form a multiple bond, click on one end atom, drag and release when reaching the other end atom
- To undo a change, Click "Edit", Select "Undo"
- To add hydrogens, Click "Clean-Up", Select "Add Hydrogens"
- To optimize the molecule with molecular mechanics (before starting quantum calculations), Click "Clean-Up', Select "Geometry-Mechanics"
- To clear everything, Click "File", Select "New"

WebMO input – Build Histidine



Running Q-Chem with WebMO

- Click on "Choose Engine"
- On "Choose Computational Engine" screen, Select "QChem" and "Extended" queue, Click "Job Options"
- On "Configure QChem Job Options" screen,
  - Enter a job name
  - Select a Calculation Type
  - Select a Theoretical Method
  - Select a Basis Set
- Click "Submit Job"

Understanding Z-matrix

1. Introduction

2. Single-Point Calculations
- WebMO Input
- WebMO Run
- Q-Chem output
- Exercies 1 – Carbon Monoxide
- Exercies 2 – Cyclohexane
- Exercies 3 – Cytosine
- Exercise 4 – Water Dimer
- BSSE Correction

3. Geometry Optimization, Frequency Calculation, and Transition State Search

4. Excited States

5. Solution to the Exercies

The following two are equivalent descriptions of a water molecule:

```
O  1.319091  0.007854 -0.001645
H  1.757412 -0.432462 -0.733540
H  1.755727 -0.343047  0.778039
```

Cartesian input

```
O
H1  O  ROH1
H2  O  ROH2  H1  HOH

ROH1  =  0.9600384
ROH2  =  0.9600467
HOH   =  104.11393
```

Z–matrix input

Exercise 1 – Carbon Monoxide

- Using the following geometry for CO

C	0.000000	0.000000	-0.643261
O	0.000000	0.000000	0.482445

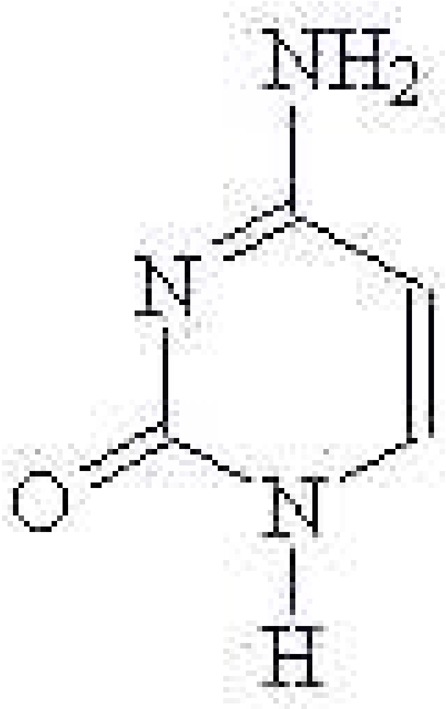
  which was optimized at CCSD//cc–pvDZ level. This geometry can be found in www.q-chem.com/ yihan/workshop/co.dat
- Compute B3LYP energies with STO–3G, 6–31G(d), 6–311+G(d,p), cc-pVDZ, cc-pVTZ basis sets. Tabulate the energies together with the number of basis functions, total job time, and dipole moment. Observe how the energy and job time change with the size of basis set.
- Compute Hartree-Fock, B3LYP, MP2, CCSD, CCSD(T) energies with cc-pVTZ basis set. Observe how the energy and job time change with the level of electron correlation.

Exercise 2 – Cyclohexane

- Build the chair and boat configurations of cyclohexane
  - Use "WebMO Editor"
  - Click "Build", Select "Fragment"
  - For "Category", Select "Rings"
  - For "Fragment", Select the desired configuration
- Compute the B3LYP//6-31G(d) energies and compare

Exercise 3 – Cytosine

- Build this molecule with "WebMO Editor"



- use "Geometry – Mechanics" to optimize its geometry
- computes its B3LYP//6-31G(d) energy

Exercise 4 – Water Dimer

- Using the following geometry of water dimer,

O	1.373315	0.001353	0.093692
H	1.828382	0.752625	-0.293835
H	1.825082	-0.761472	-0.274675
O	-1.527171	-0.001703	-0.118814
H	-0.568223	-0.000323	-0.012029
H	-1.854385	0.011969	0.781514

  which was optimized at MP2//6–311+G(d,p) level. This geometry can be found in www.q-chem.com/ yihan/workshop/dimer.dat
- Compute the MP2//6–311+G(d,p) energy of the dimer.
- Compute the MP2//6–311+G(d,p) energies of two water monomers (using the geometry above).
- Compute the dimer binding energy (1 hartree=627.51 KCal/mol).

Correction of Basis Set Superposition Error

- Use all basis functions for monomer calculations

```
$molecule
0 1
 O  1.373315  0.001353  0.093692
 H  1.828382  0.752625 -0.293835
 H  1.825082 -0.761472 -0.274675
Gh -1.527171 -0.001703 -0.118814
GH -0.568223 -0.000323 -0.012029
GH -1.854385  0.011969  0.781514
$end
$rem
JOBTYPE SP
EXCHANGE HF
CORRELATION MP2
BASIS MIXED
PURECART 111
UNRESTRICTED FALSE
$end
```

Correction of Basis Set Superposition Error

```
$basis
O 1
6-311+G(d,p)
***
H 2
6-311+G(d,p)
***
H 3
6-311+G(d,p)
***
O 4
6-311+G(d,p)
***
H 5
6-311+G(d,p)
***
H 6
6-311+G(d,p)
***
$end
```

Basis Set Superposition Error

- energy of water dimer: -152.597 166 h
- energy of the first monomer
    - -76.293 712 h (before BSSE correction)
    - -76.295 704 h (after BSSE correction)
- energy of the first monomer
    - -76.293 689 h (before BSSE correction)
    - -76.294 313 h (after BSSE correction)
- dimer binding energy
    - 9.766 mh = 6.030 Kcal/mol (before BSSE correction)
    - 7.149 mh = 4.486 Kcal/mol (after BSSE correction)

1. Introduction

2. Single-Point Calculations

3. Geometry Optimization, Frequency Calculation, and Transition State Search
- Critical Points
- Frequency
- WebMO calculations
- Example – Diels-Alder
- Exercise 5 – Acetone and Acetic Acid
- Exercise 6 – HCN isomerization

4. Excited States

5. Solution to the Exercies

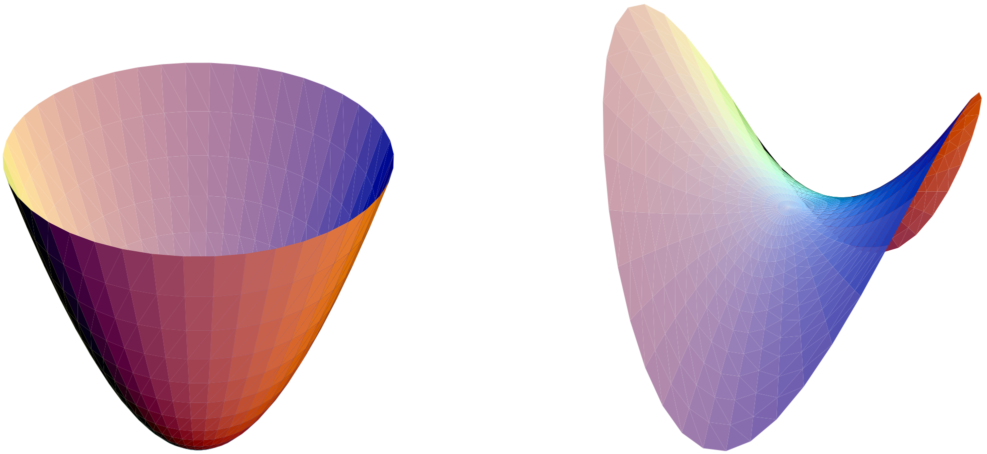
3. Geometry Optimization, Frequency Calculation, and Transition State Search

Critical points

Critical points on the molecular potential energy surface play an important role in chemistry. These points are characterized by a vanishing energy gradient:

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

- Local minima on the PES correspond to equilibrium geometries.
- Saddle points correspond to transition structures.



Energy Hessian

- The Taylor expansion for the energy function is

$$E(\mathbf{x}) \quad = \quad E(0) + \sum_i G_i x_i + \frac{1}{2} \sum_{jk} x_i H_{i,j} x_j + \ldots$$

- At a stationary point, the gradient term varnishes by definition,

$$G_i \quad = \quad \frac{\partial E}{\partial x_i} = 0$$

- The Hessian describe the curvature of the potential energy surface

$$H_{i,j} \quad = \quad \frac{\partial^2 E}{\partial x_i \partial x_j}$$

Vibrational Frequencies

- Define the mass-weighted Hessian

$$\bar{H}_{i,j} = \frac{H_{i,j}}{\sqrt{m_i m_j}}$$

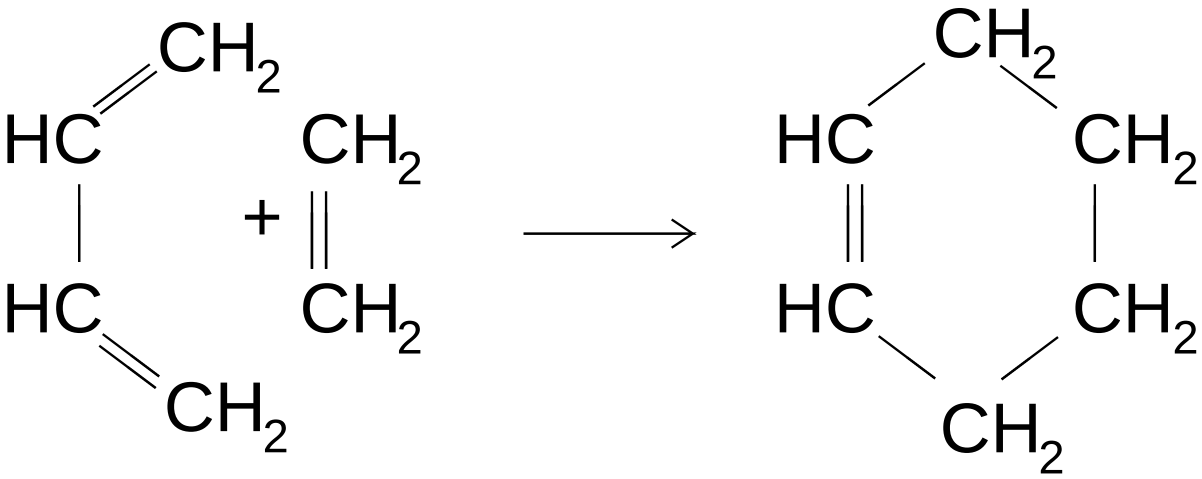
- Its eigenvalues correspond to vibrational frequencies, and eigenvectors normal modes

$$\omega_i^2 q_i = \sum_j \bar{H}_{i,j} q_j$$

WebMO calculations

- Job Types:
  - Geometry Optimization
  - Vibrational Frequencies
  - Optimize + Vib Freq
  - Transition State Optimization
- Useful things to know about geometry optimization/transition state optimization
  - Can optimize the geometry at a lower level of theory (HF//STO-3G, for example) before going to the target (higher) level of theory
  - If the geometry does not converge (after 50 geometry steps), can restart the job with the final (unconverged) geometry, or start from a totally different initial geometry

Transition state for Diels-Alder Reaction



Exercise 5 – Acetone and Acetic Acid

- Optimize the geometry of Acetone (CH3COCH3) with HF//6–311+G(d,p), and computes its vibrational frequency at the same level of theory. Find the frequency for CO double bond stretching.
- Repeat the same procedure for Acetic Acid (CH3COOH).

Exercise 6 – HCN Isomeriation

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- Frequency
- WebMO calculations
- Example – Diels-Alder
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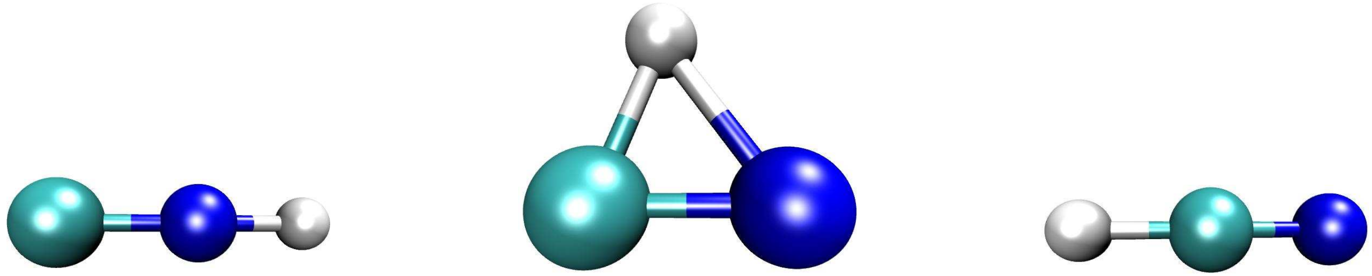
- Exercise 6 – HCN isomerization

4. Excited States
5. Solution to the Exercies



- Optimize the geometry of HCN and HNC with HF//6-311+G(d,p)
- Starting from the following geometry,

C	.608900	.098250	.000000
N	-.546443	.051269	.000000
H	.171697	-.948384	.000000

  search for the transition state with HF//6-311+G(d,p). These coordiates can be found at www.q–chem.com/ yihan/workshop/chn.dat
- Compute the vibrational frequencies at the transition state. Is there an imaginary frequency?
- What is the barrier height?

4. Excited States

Overview of Excited States

- Excited state wavefunctions exhibit a far wider range of behaviours and are therefore more difficult to model.
- Many excited states can lie close together, giving rise to multi–determinant character and resulting in a breakdown of the single–reference model.
- Larger basis sets are required to model both the valence and Rydberg states and thus avoid artifactual mixing.
- Diffuse functions should be included, especially when modelling Rydberg states.
- Because of this, a black–box approach is rarely recommended and each system should be treated on its own merits.

Excited State Options Within Q–Chem

- Q–Chem has a variety of methodologies applicable to excited state calculations including:
  - Inexpensive uncorrelated single–excitation methods (CIS,XCIS).
  - Time–dependent density functional theory (TDDFT).
  - Spin–flip density functional theory (SF–TDDFT).
  - More expensive correlated wavefunction based treatments (EOM–CCSD, EOM–OD).
- Cheaper methods can often yield a qualitative picture of the system, but do not usually provide quantitatively correct results.
- The more expensive wavefunction based methods have the potential to yield results for excited states that are of chemical accuracy (< 0.1eV error), but this comes at a high price.
- Q–Chem does not have support for multi–determinant wavefunction based methods such as CASSCF, CASPT2 and MRCI.

Types of Excited State Calculations Available

- *Vertical absorption spectra*
  Calculations of electronic excitation energies provide insight into absorption spectra, and are available for CIS, RPA, XCIS CIS(D), EOM–CISD and EOM–OD.
- *Excited state optimisations*
  These provide understanding of the relaxation that occurs in the excited states. Analytic first derivatives are available for UCIS and RCIS, allowing for the efficient computation of excited state geometries. Geometries for CIS(D), CCSD and OD are obtainable via finite difference methods.
- *Excited state vibrational analyses*
  Given a structure corresponding to a minimum on the excited state potential energy surface, Q–CHEM can determine the force constants and hence the frequencies. Excited state vibrational analyses use efficient analytic second derivatives, and are only available for UCIS and RCIS.

Exercise 7: Carbon Monixide

- Build carbon monoxide with a C–O bond length of 1.1283 Angstom
- Set up an "Excited states" calculation, turn "Preview Input File" on
- After "Submit Job", Edit the input file, replace

  ```
  CC_NLOWSPIN [10]
  CC_NHIGHSPIN []
  ```

  by

  ```
  CIS_N_ROOTS 10
  ```

- Find the first five excitation energies. How do they compare with the experimental values:

$$V^3\Pi : 6.32eV, 6.32eV, \quad V^3\Sigma^+ : 8.51eV, \quad V^1\Pi : 8.51eV, 8.51eV$$

5. Solution to the Exercies

Exercise 1 – Carbon Monoxide

- CO, B3LYP energy computed with various basis
  - STO–3G, 10 bas, E=–111.763 545, D=-0.5007, CPU = 0.22 s
  - 6-31G(d), 30 bas, E=–112.308 966, D=-0.1007, CPU = 0.72 s
  - 6-311+G(d,p), 44 bas, E=–113.349627, D=-0.0789, CPU = 1.1s
  - cc-pVDZ, 28 bas, E=–113.321723, D=0.2102, CPU = 0.88 s
  - cc-pVTZ, 60 bas, E=–113.357469, D=0.1266, CPU = 3.88 s
  - a positive dipole moment means a positive charge on O
  - see JCP, 1993, 98, 3972 for experimental dipole values

- CO, energy with various theoretical methods with cc-pVTZ basis
  - Hartree-Fock, E=–112.780 639, CPU = 3.33 s
  - B3LYP, E=–113.357 469, CPU = 3.88 s
  - MP2, E=–113.160 106, CPU = 5.3 s
  - CCSD, E=–113.163 219, CPU = 31.91 s
  - CCSD(T), E==-113.180 394, CPU = 42.22 s

Exercises 2, 3, 4

- Exercise 2 – Cyclohexane
  - Boat, Energy = -235.866 718 h
  - Chair, Energy = -235.877 189 h

- Exercise 3 – Cytosine
  - Energy = -394.509 621 h

- Exercise 4 – Water dimer
  - See slide 22 for the energies
  - See JCP, 1990, 92, 1240 for theoretical values

Exercises 5, 6, 7

- Exercise 5 – Acetone and acetic acid
  - CH3COCH3, Energy = –192.017 098 h, CO stretch: 1984 cm-1
  - CH3COOH, Energy = –227.872 691 h, CO stretch: 2037 cm-1

- Exercise 6 – HCN isomerization
  - HCN, Energy = –92.901 464 h
  - HNC, Energy = –92.855 328 h
  - Transition State, Energy = –92.822 649 h
  - Barrier height: 0.032 679 h (20.5 Kcal/mol)

- Exercise 7 – CO excited states
  - The excitation energies are: 6.0444, 6.0444, 8.2655, 8.6087, 8.6087eV