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Marshall University
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Division of Science and Research
WV Higher Education Policy Commission

WVU HPC Summer Institute
June 20, 2014

Outline

- Accessing WebMO on Marshall's HPC cluster
- Overview of WebMO capabilities
- Building molecules
- Submitting jobs
- Optimizing a geometry
- Electronic properties
- Visualizing orbitals, densities, and electrostatic potential
- IR spectrum and animating the vibrational modes
- UV-Vis spectrum
- Geometry scan, transition state, and reaction pathway
- Future topics
- Exercises

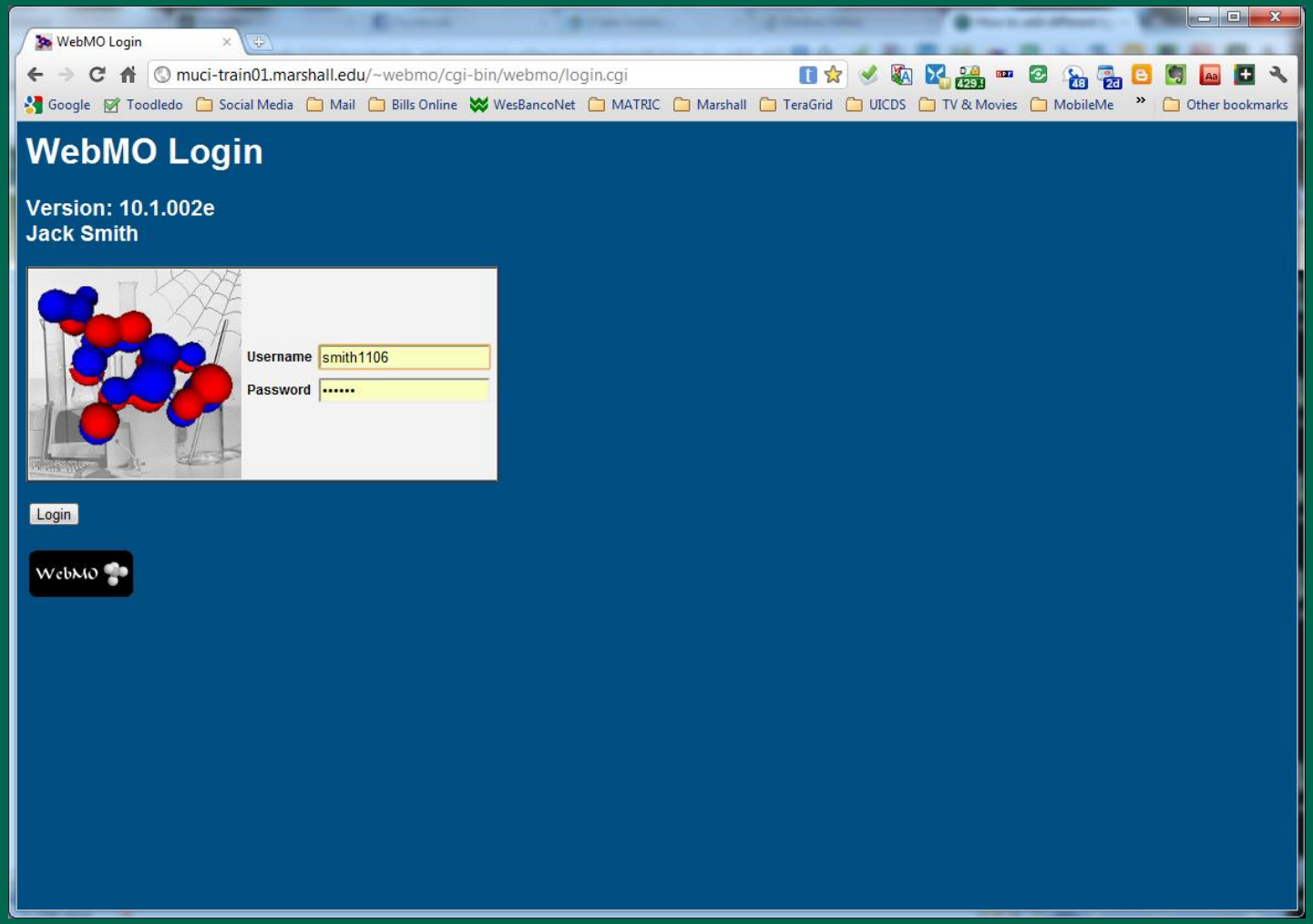
Accessing WebMO

- Non-Marshall people will first need to apply for MU ID
  - Contact Ed Aractingi at aractingi1@marshall.edu for form
- Apply for account on HPC cluster
  - Use form at: http://bit.ly/eDHJEU
  - Select 'Jack Smith' as sponsor
  - Check 'yes' for access to WebMO on form
- Already have an HPC cluster account, but no WebMO access?
  - Contact Jack Smith at smith1106@marshall.edu for WebMO access
- Log in to WebMO with web browser
  - http://biggreen.marshall.edu/~webmo/cgi-bin/webmo/login.cgi
  - Use your regular MU login credentials
  - Browser needs recent Java plug-in for 3D editor
- WebMO now available as an app for iPad ($4.99)
  - Still needs access to WebMO account on cluster

Accessing WebMO
* ***as workshop student only*** *

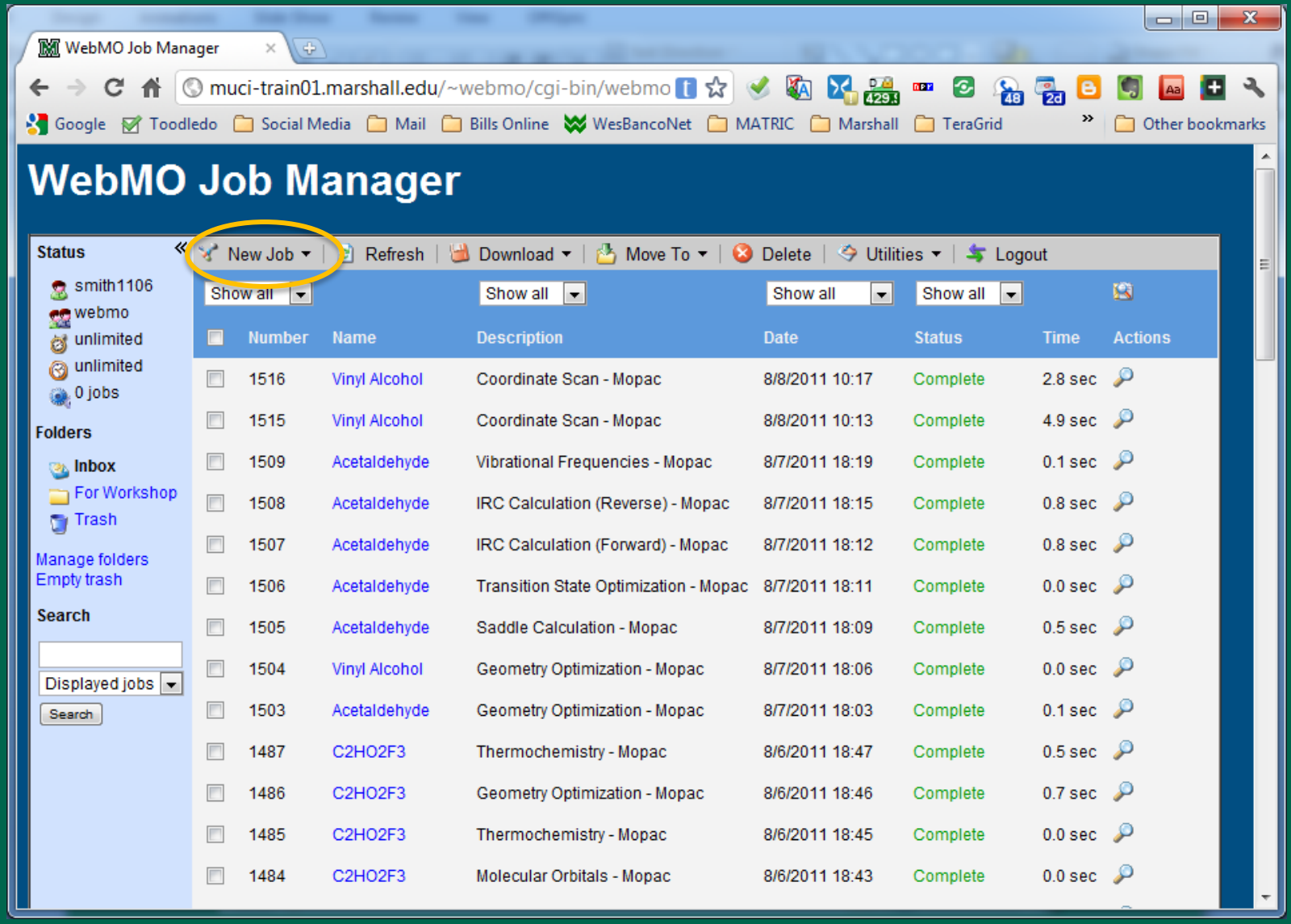
- Log in to WebMO with web browser
  - http://biggreen.marshall.edu/~webmo/cgi-bin/webmo/login.cgi
  - Use username provided by instructor (e.g., *student01*)
  - Password will also be provided by instructor
  - Accounts will expire at the end of the HPC Summer Institute
  - Browser needs recent Java plug-in for 3D editor

Accessing WebMO
Login



http://biggreen.marshall.edu/~webmo/cgi-bin/webmo/login.cgi

Accessing WebMO
Job Manager



WebMO Capabilities

- Supports many computational engines
  - **GAUSSIAN**, **GAMESS**, **MOPAC**, **Tinker**, **NWChem**, Quantum Espresso, VASP, MolPro, PQS, PSI, QChem
- GUI is completely browser-based (+Java 3D)
- Built-in 3D molecular editor
- Batch (PBS, SGE, built-in) job submission and management
- Visualization of results
- Tabulation of results
- Upload/download files from/to desktop
- See WebMO website for more info:

  http://www.webmo.net

WebMO Capabilities
Calculation Types

- Single-point energy calculation
- Geometry optimization
- Electronic properties
  - Molecular orbitals, partial charges, dipole moment
- Geometry scan
  - Conformational analysis, reaction coordinates
- IR spectrum (vibrational analysis)
- UV-Vis spectrum (excitations)
- NMR spectrum (chemical shifts, shielding)
- Thermochemistry and “model chemistries”

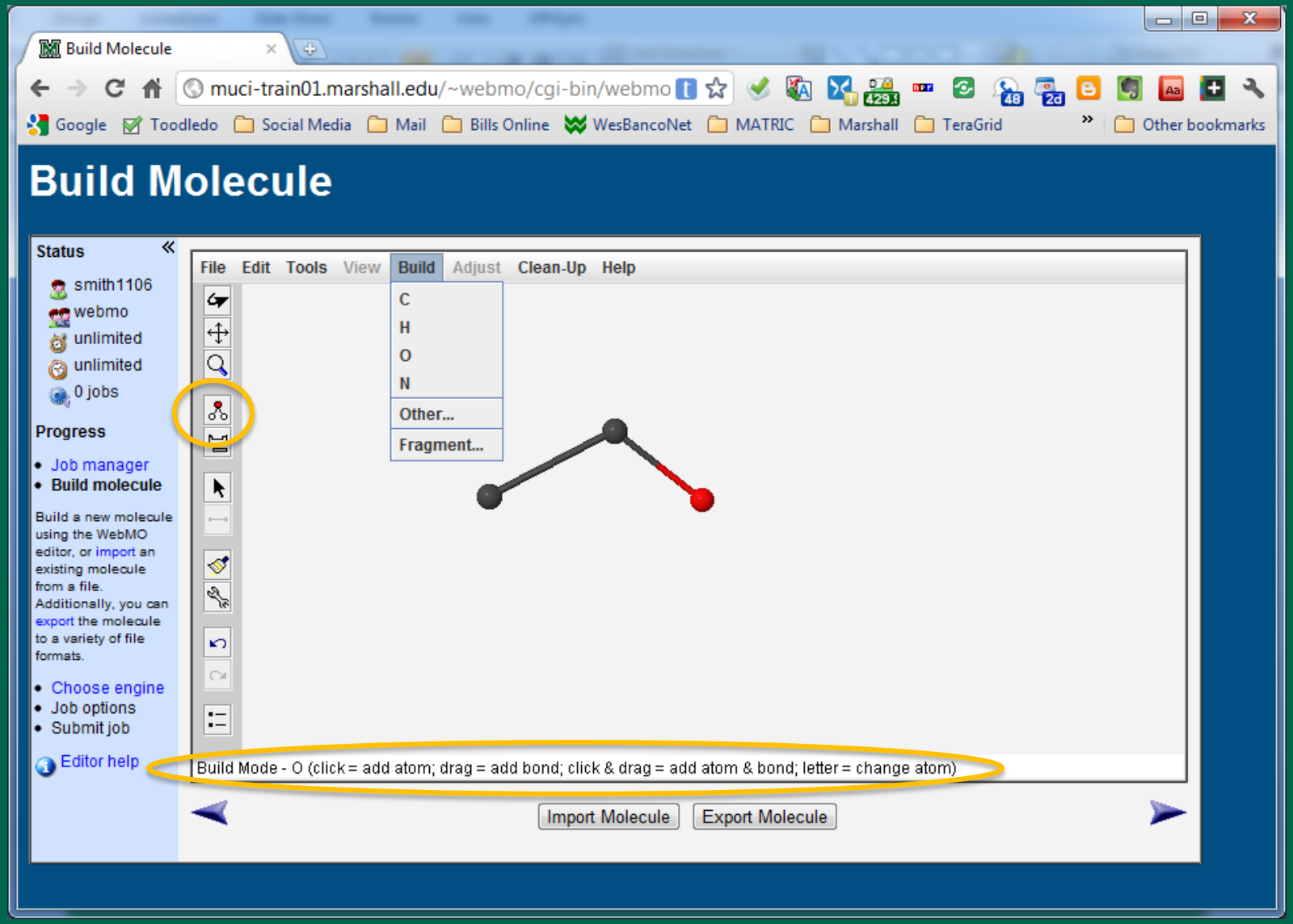
WebMO Capabilities
Levels of Theory

- Molecular Mechanics — **Tinker**
  - No electrons! No breaking or forming bonds!
  - Forcefields: MM3,…
- Semi-empirical (Quantum Mechanical) — **MOPAC**
  - HF with parameterized integrals
  - Fit to Heats of Formation
- Density Functional Theory — **GAMESS**, NWChem, *GAUSSIAN*, :
  - No wavefunction!
  - Approximate exchange-correlation: B3LYP,…
- *Ab initio* (Wave Function)
  - HF – no electron correlation!
  - Correlation: CI, MP, MBPT, CC,…

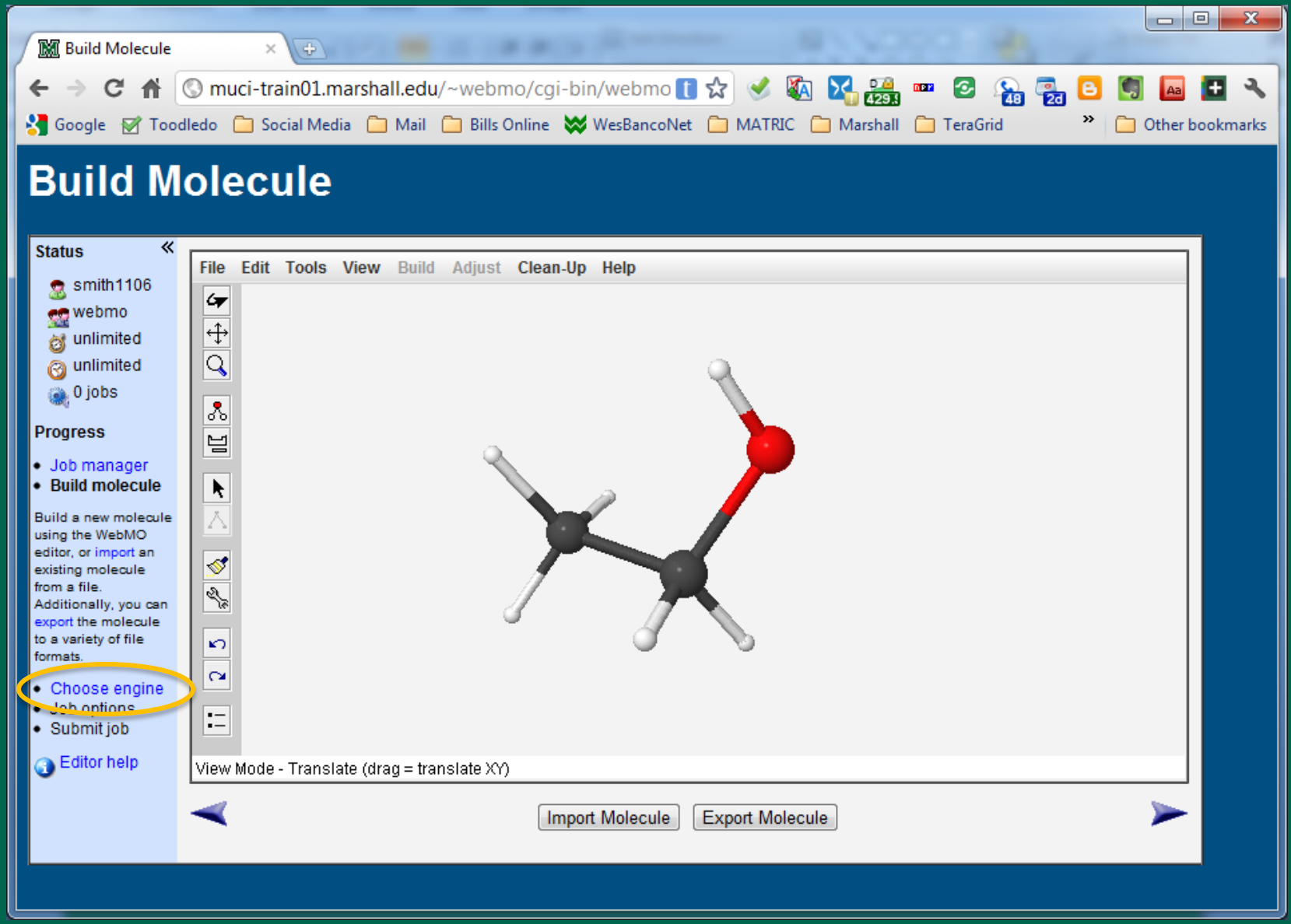
Building Molecules

- Use build tool to click and drag atoms and bonds
- Use build menu (or periodic table) to change element or add a pre-defined fragment
- Use right-click context menu to change element hybridization/charge or bond order
- Use cleanup tool/menu to add Hydrogens, assign hybridizations, and clean up geometry
- Use rotate, translation and zoom tools to manipulate view
- Use adjust tool and shift-click to select atoms, bonds, angles or dihedrals and modify their values
- Check status line for current tool/view mode and available mouse/keyboard options

Building Molecules



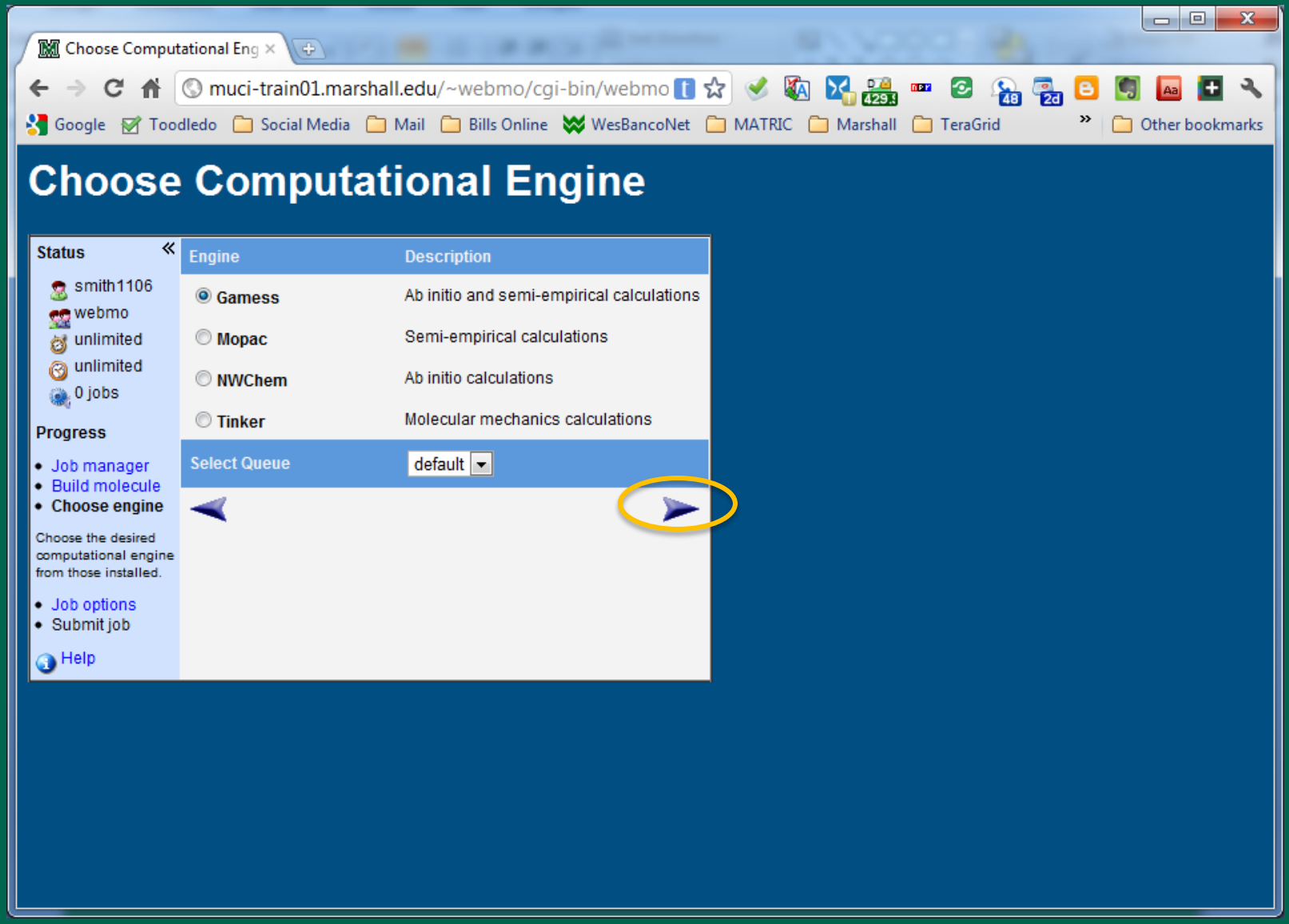
Building Molecules



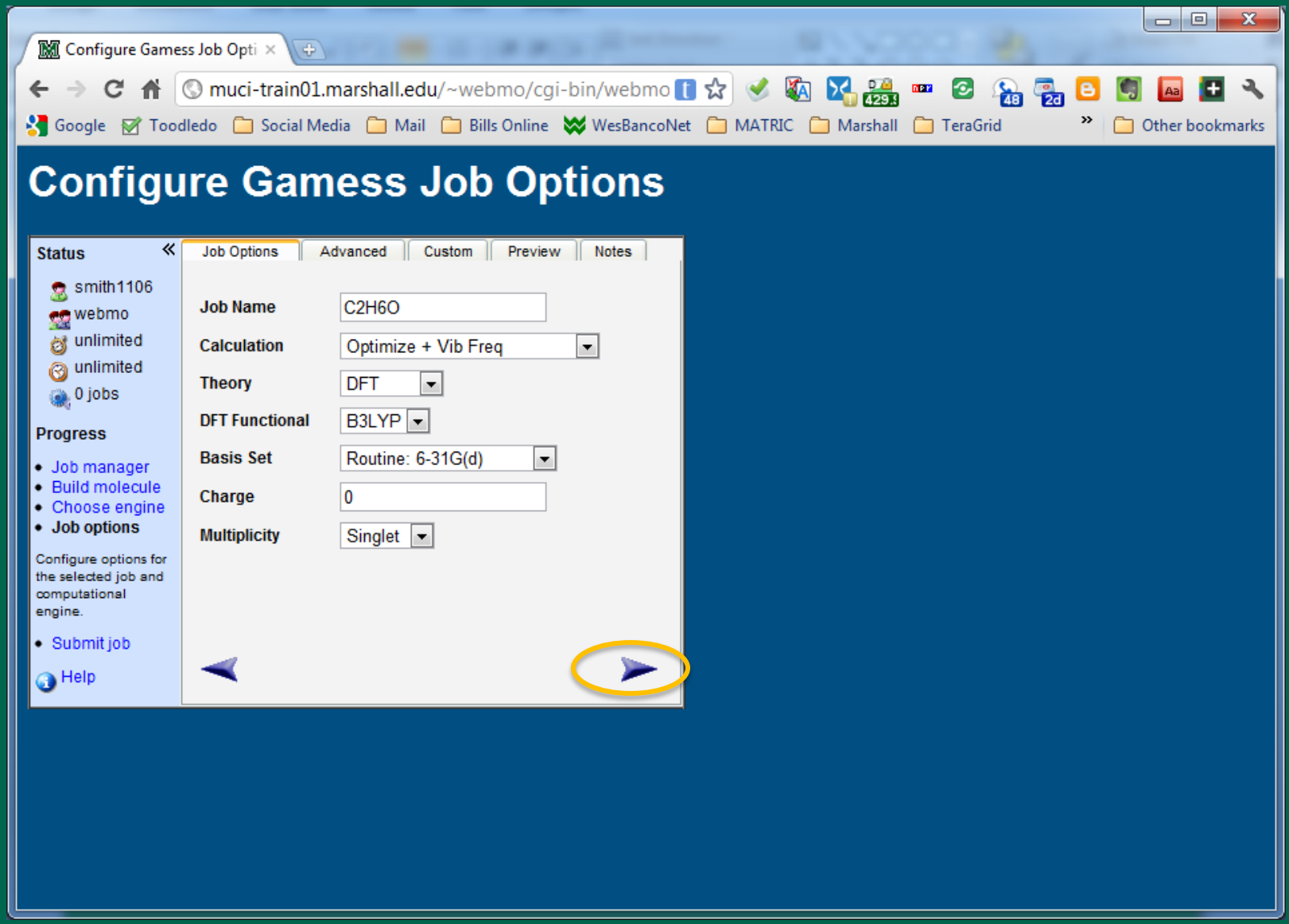
Submitting Jobs

- Choose Computational Engine
  - GAMESS, Gaussian, NWChem, MOPAC, Tinker
- Configure Job Options
  - Name
  - **Calculation Type**
  - Level of Theory
  - DFT Functional (for DFT)
  - Basis Set
  - Charge
  - Spin Multiplicity
- Submit to queue
- Monitor in Job Manager

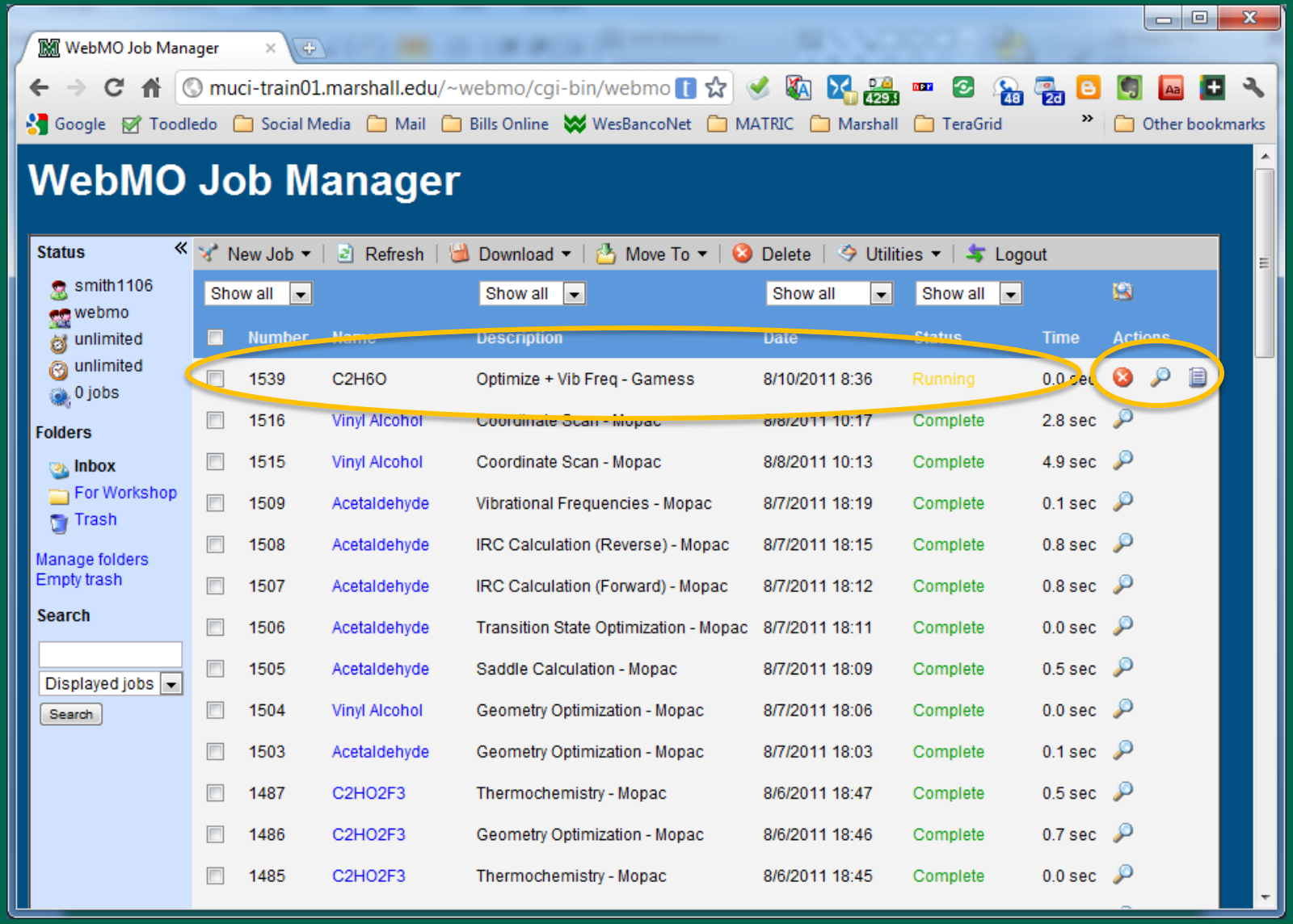
Submitting Jobs
Choose Computational Engine



Submitting Jobs
Configure Job Options



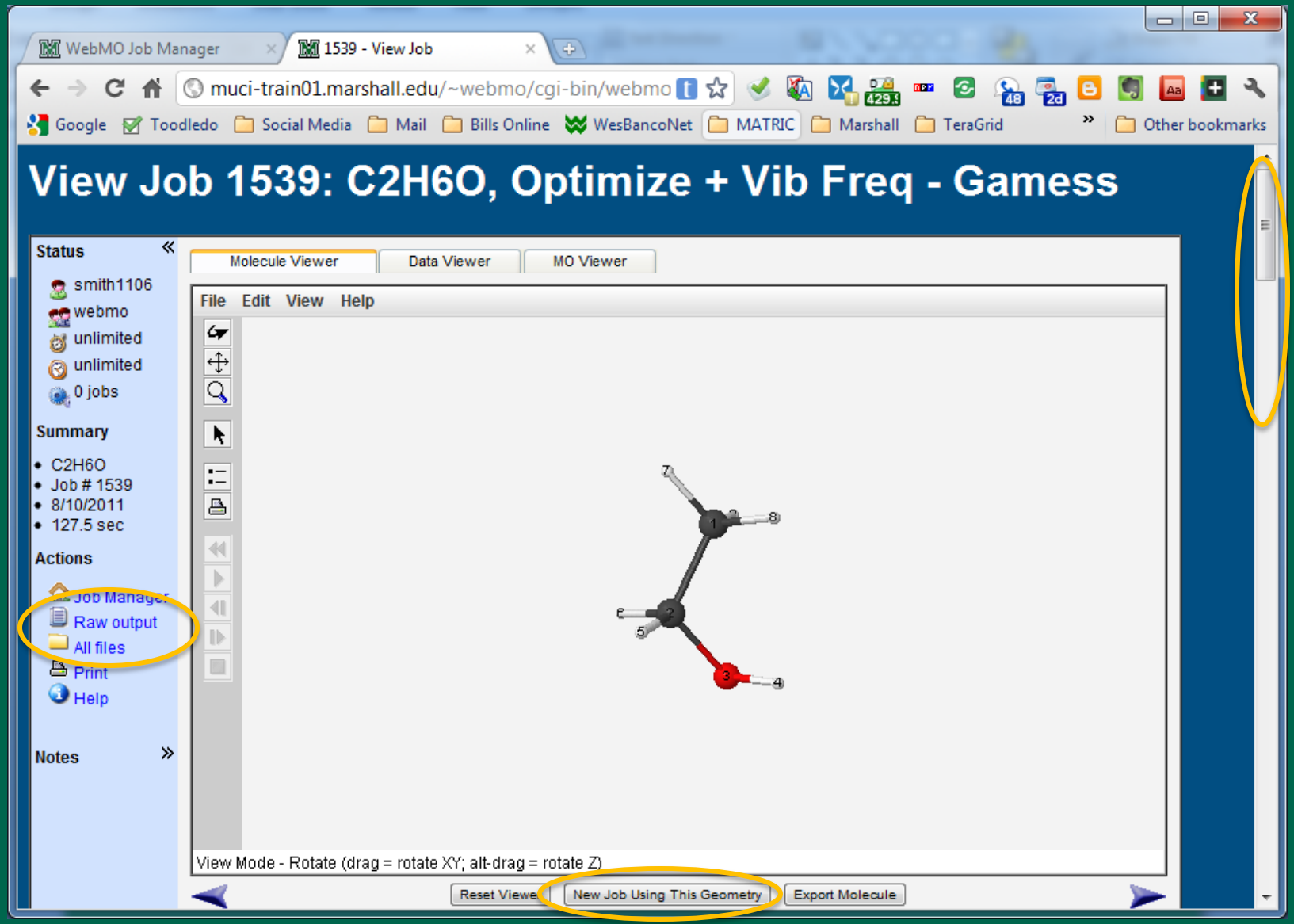
Submitting Jobs
Monitor Status



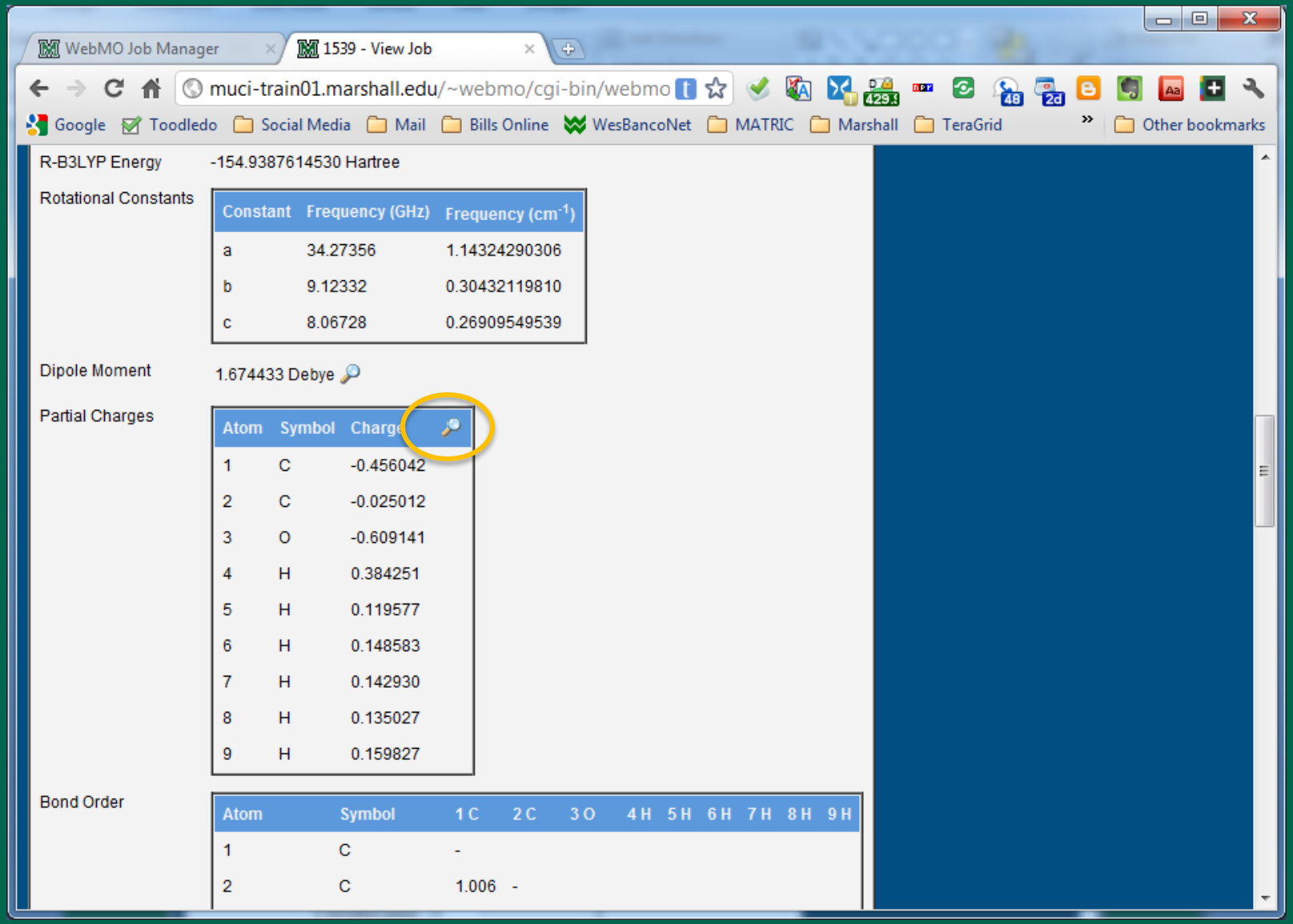
Viewing Results

- Molecular Viewer
  - Final structure
  - View properties
    - Partial charges, dipole moment
  - Animation
    - Geometry optimization, vibrational modes
  - Input for next job
- Data Viewer
  - Linear plots
  - Spectra (IR, UV-Vis, NMR)
  - 2D maps
- MO Viewer (tabbed)
  - Isosurfaces of MO's and density
  - Texturing with other properties
    - Electrostatic potential
    - Frontier density (electrophilic, nucleophilic and radical susceptabilities)

Viewing Results
Molecular Viewer



Viewing Results
Calculated Quantities



R-B3LYP Energy -154.9387614530 Hartree

Rotational Constants

Constant	Frequency (GHz)	Frequency (cm^{-1})
a	34.27356	1.14324290306
b	9.12332	0.30432119810
c	8.06728	0.26909549539

Dipole Moment 1.674433 Debye

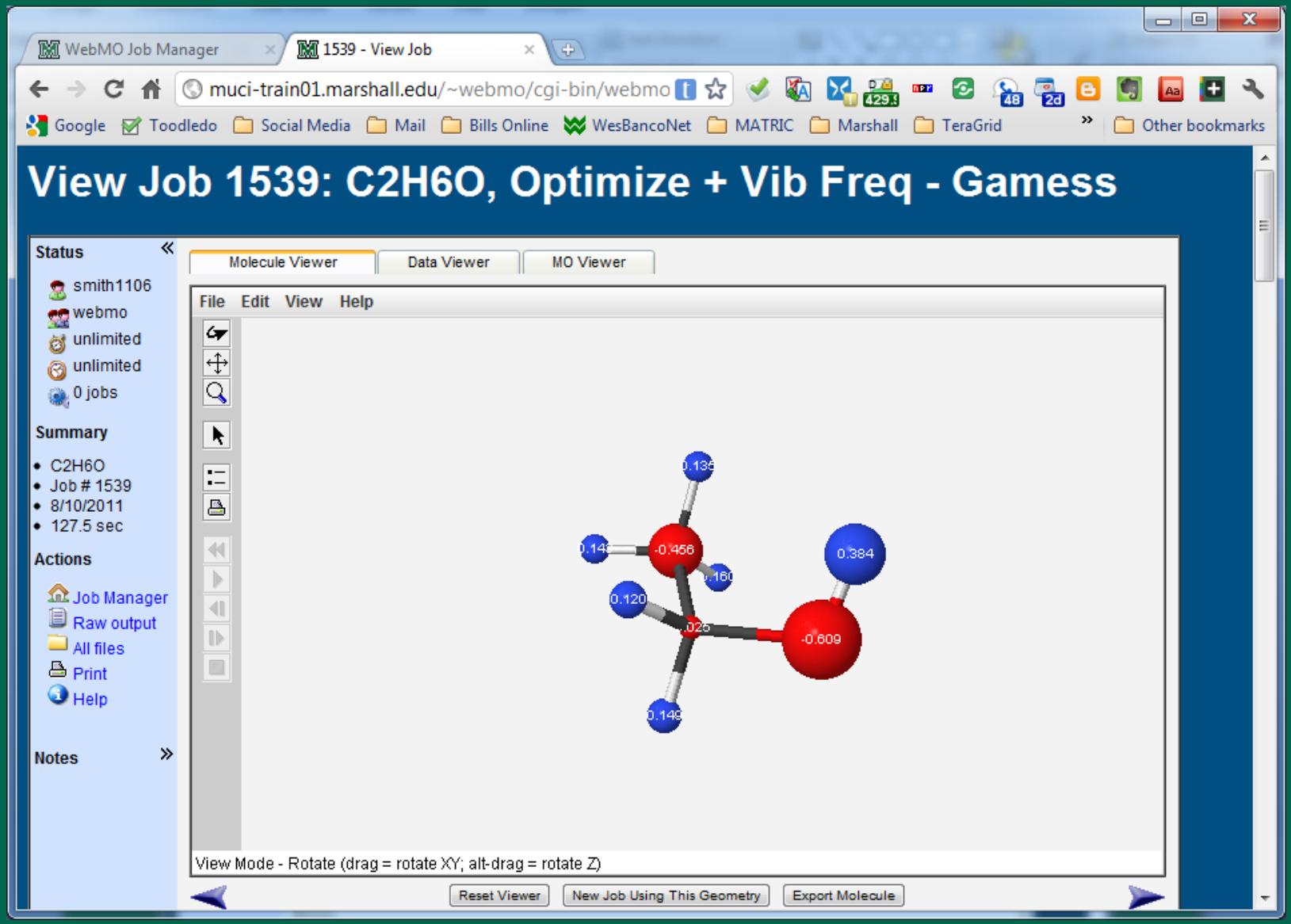
Partial Charges

Atom	Symbol	Charge
1	C	-0.456042
2	C	-0.025012
3	O	-0.609141
4	H	0.384251
5	H	0.119577
6	H	0.148583
7	H	0.142930
8	H	0.135027
9	H	0.159827

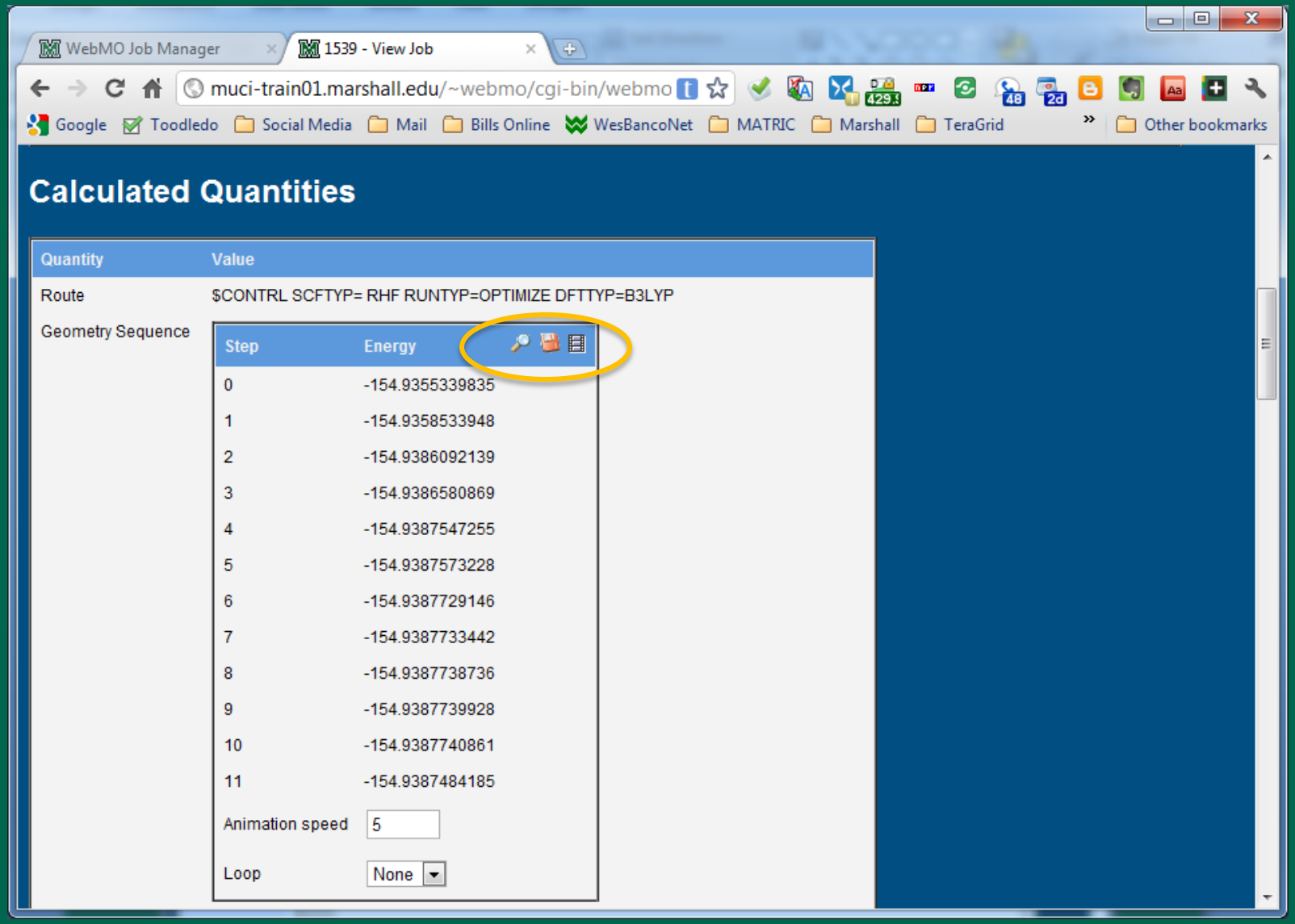
Bond Order

Atom	Symbol	1 C	2 C	3 O	4 H	5 H	6 H	7 H	8 H	9 H
1	C	-								
2	C	1.006	-							

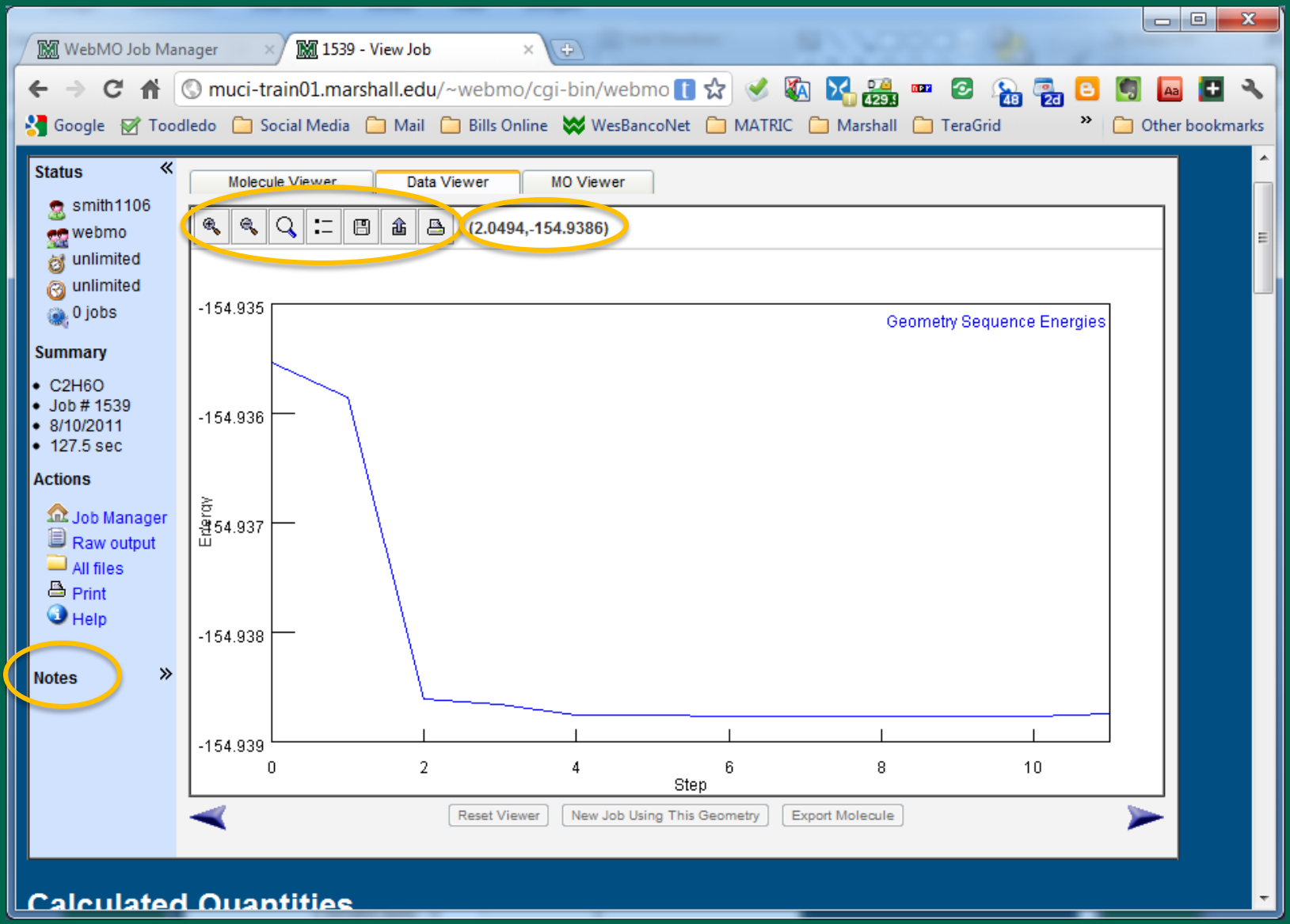
Viewing Results
Partial Charges



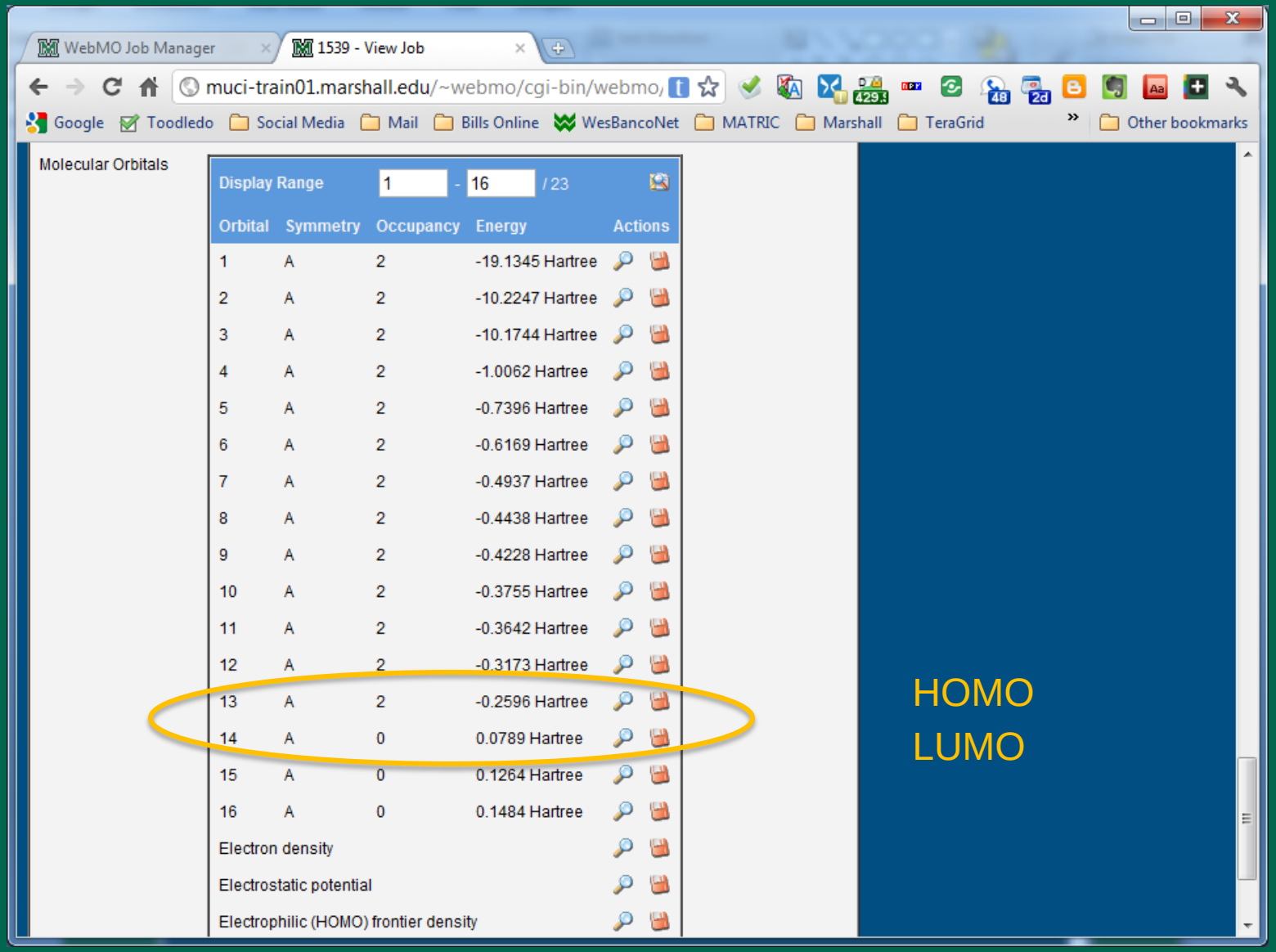
Viewing Results
Geometry Optimization



Viewing Results
Data Viewer

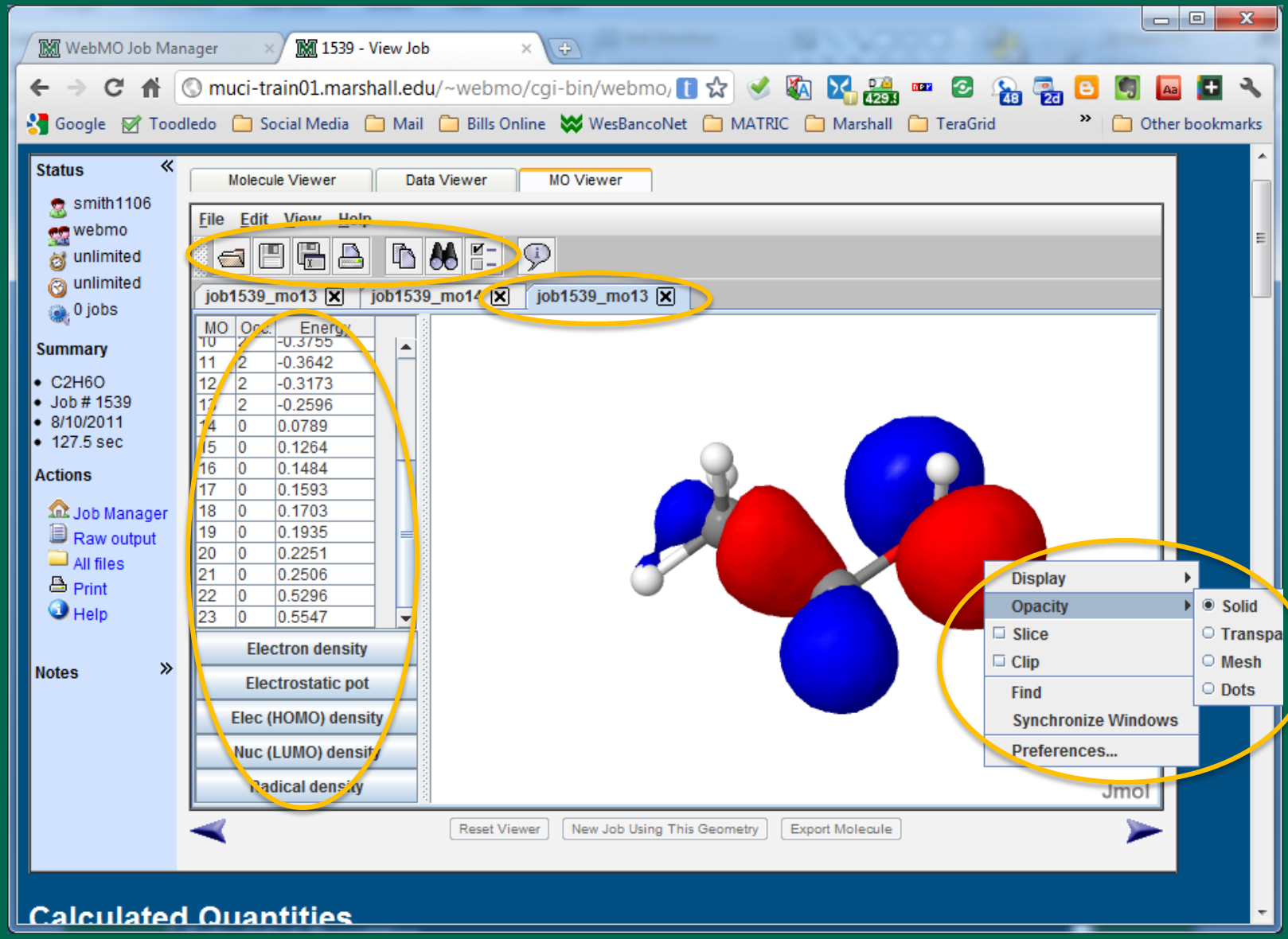


Viewing Results
Molecular Orbitals

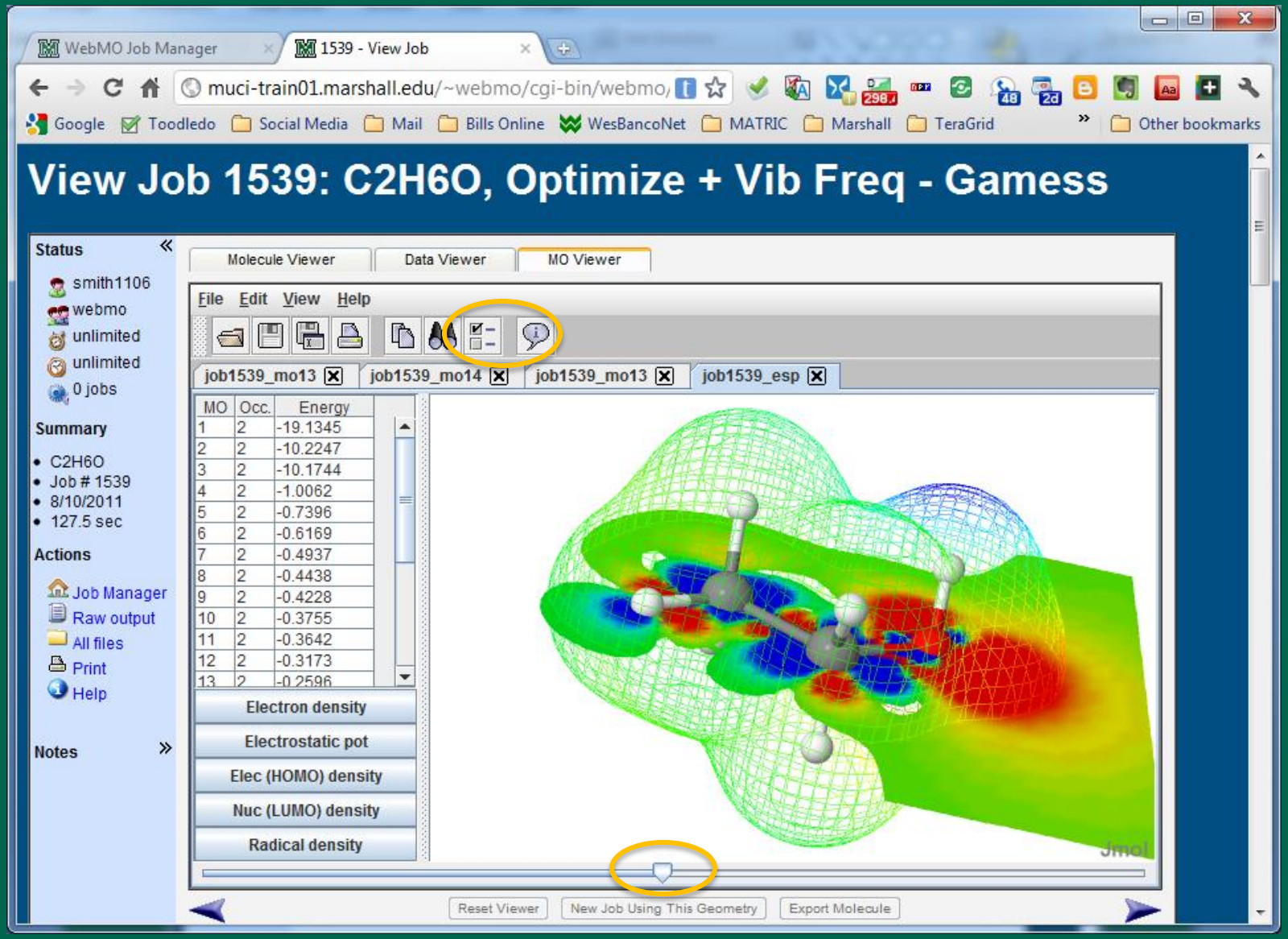


Viewing Results

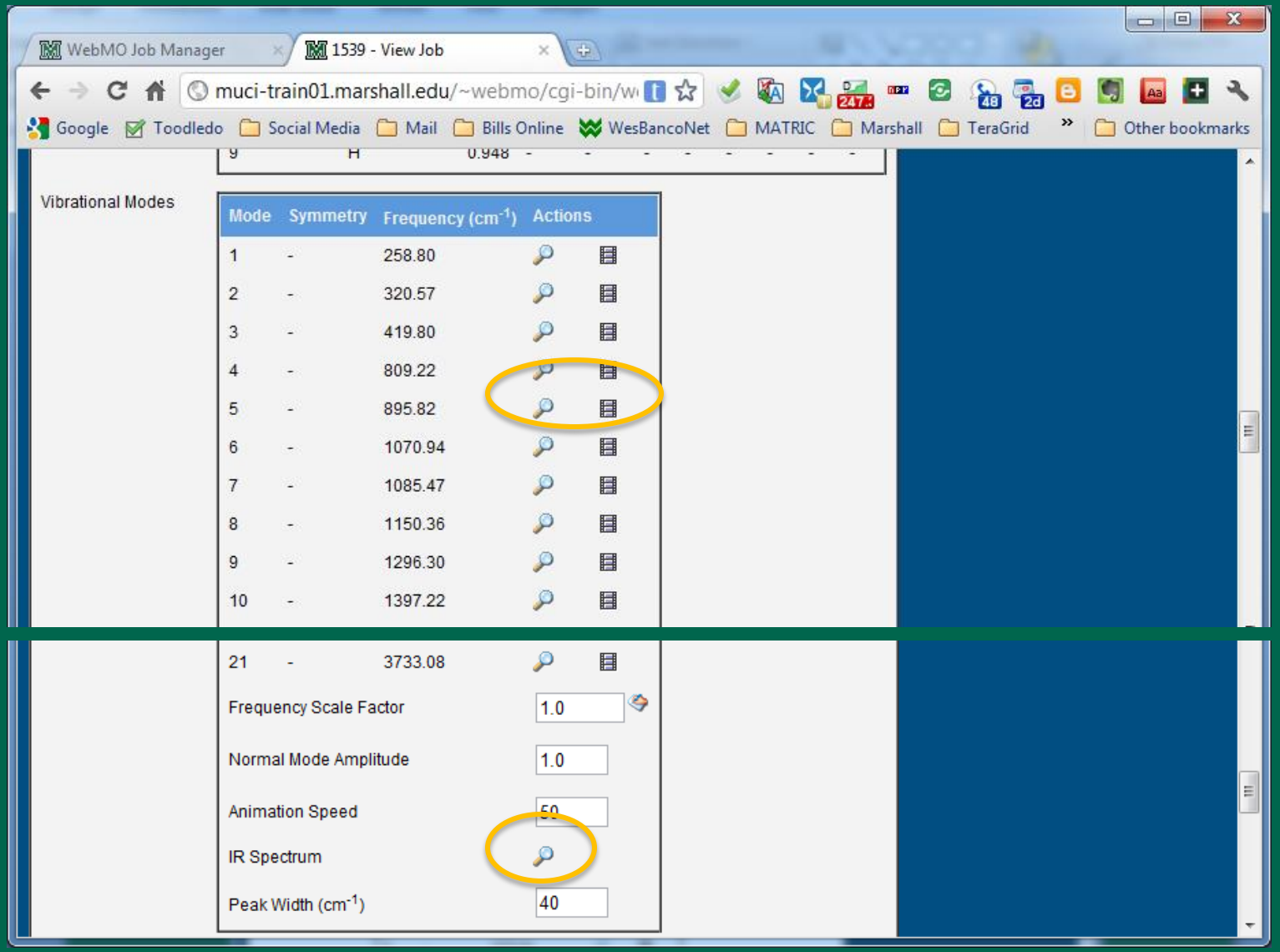
MO Viewer



Viewing Results
Display Options

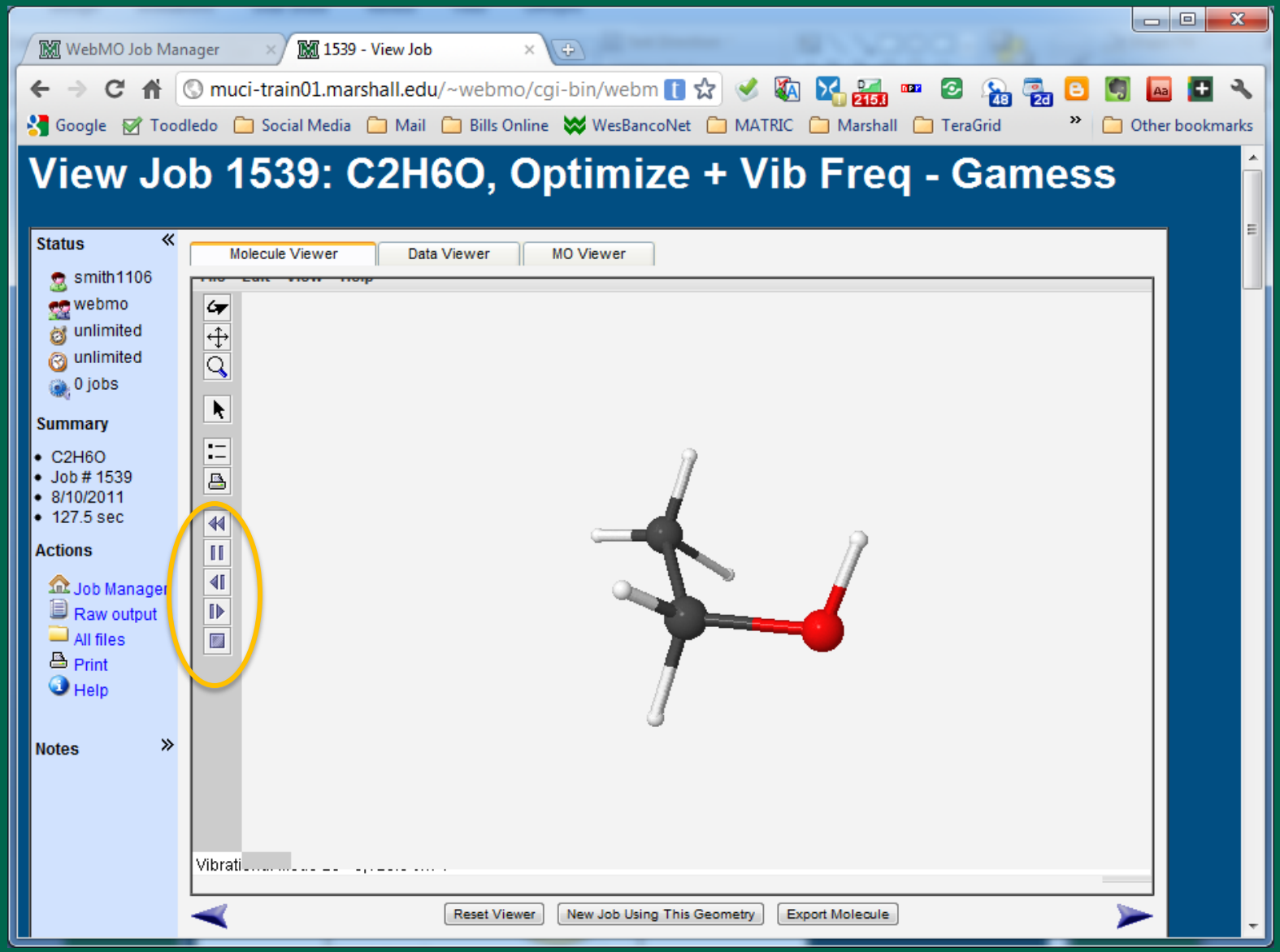


Viewing Results
Vibrational Modes

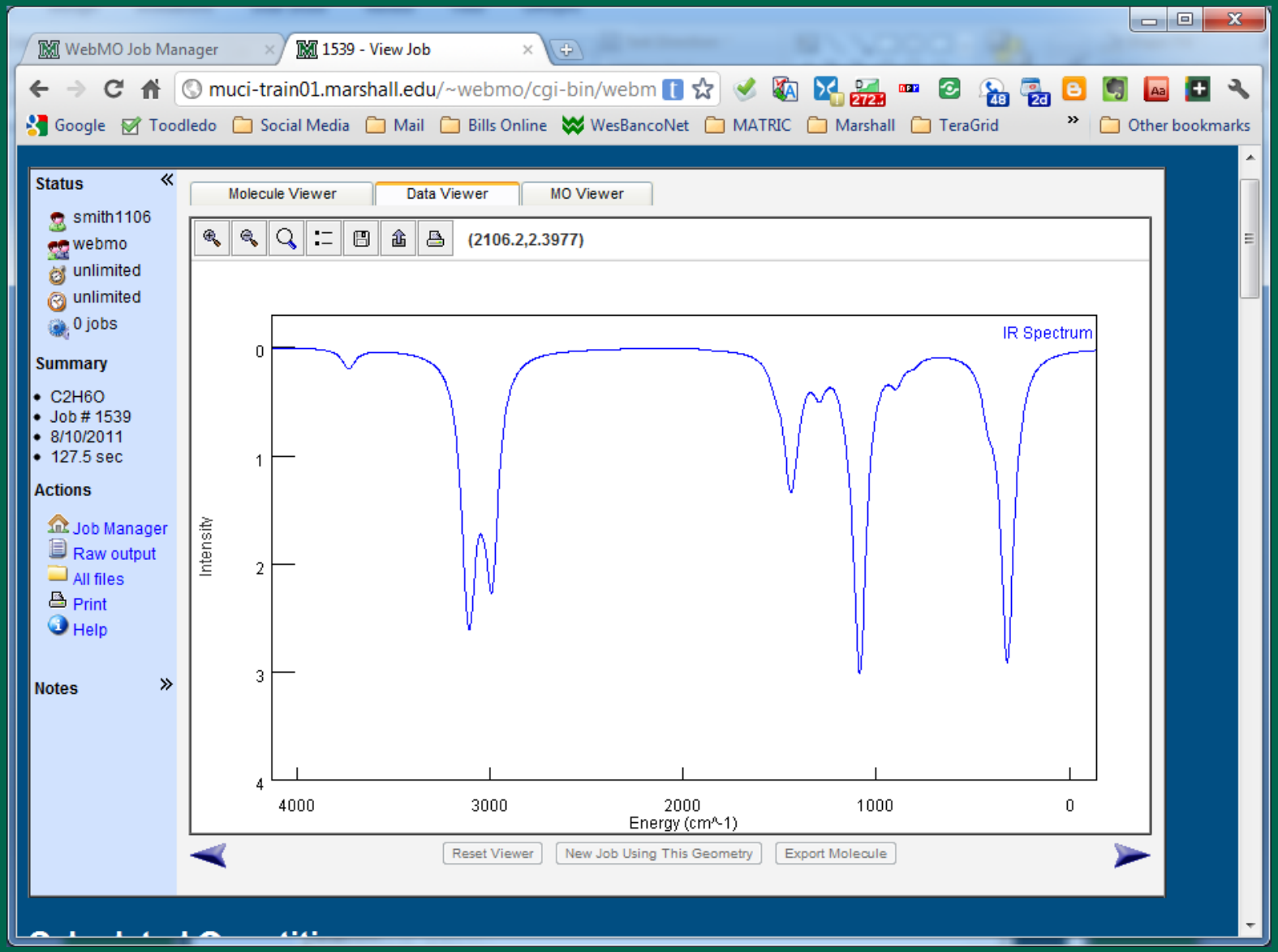


Viewing Results

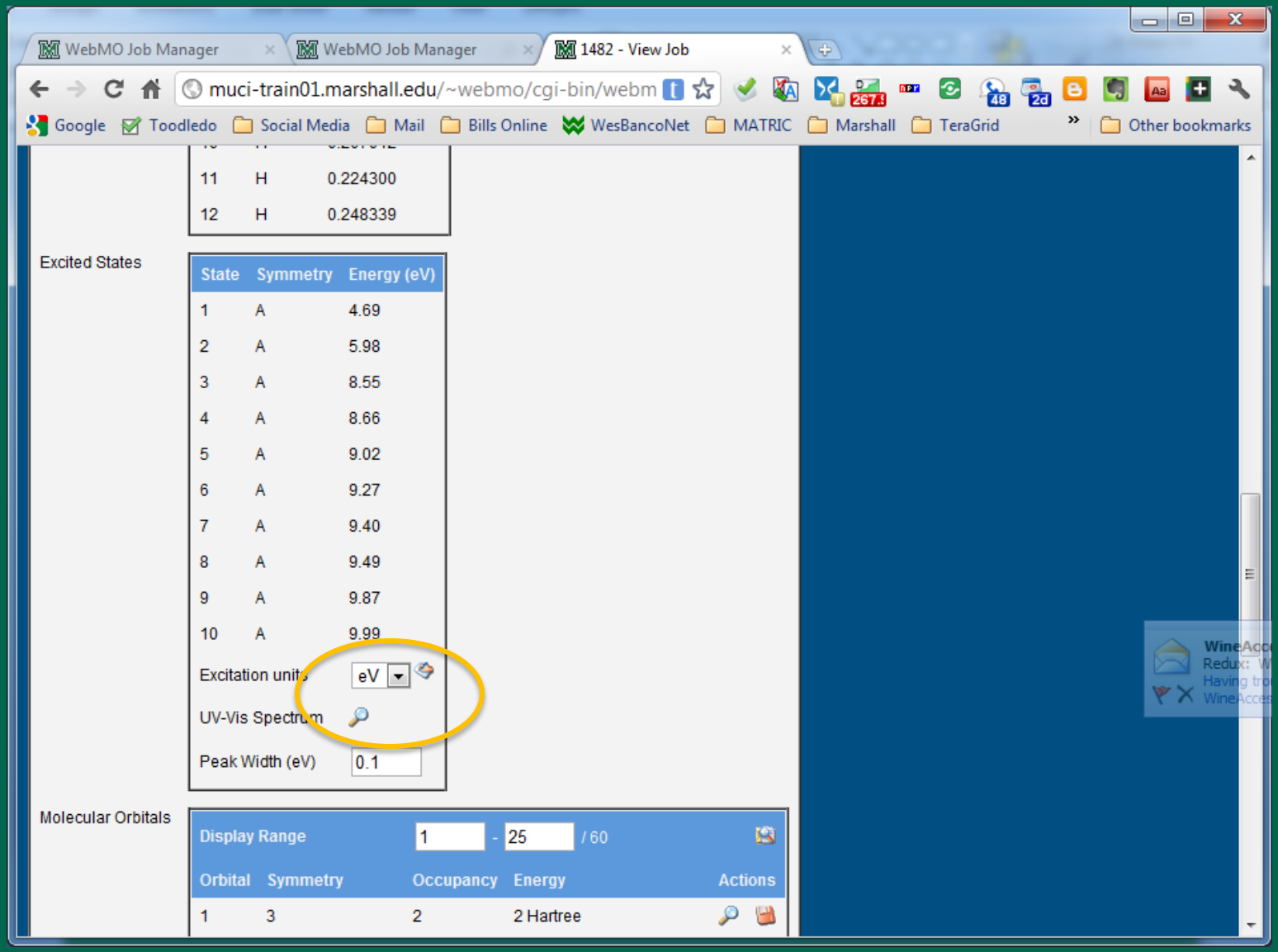
Animation of Vibrational Mode



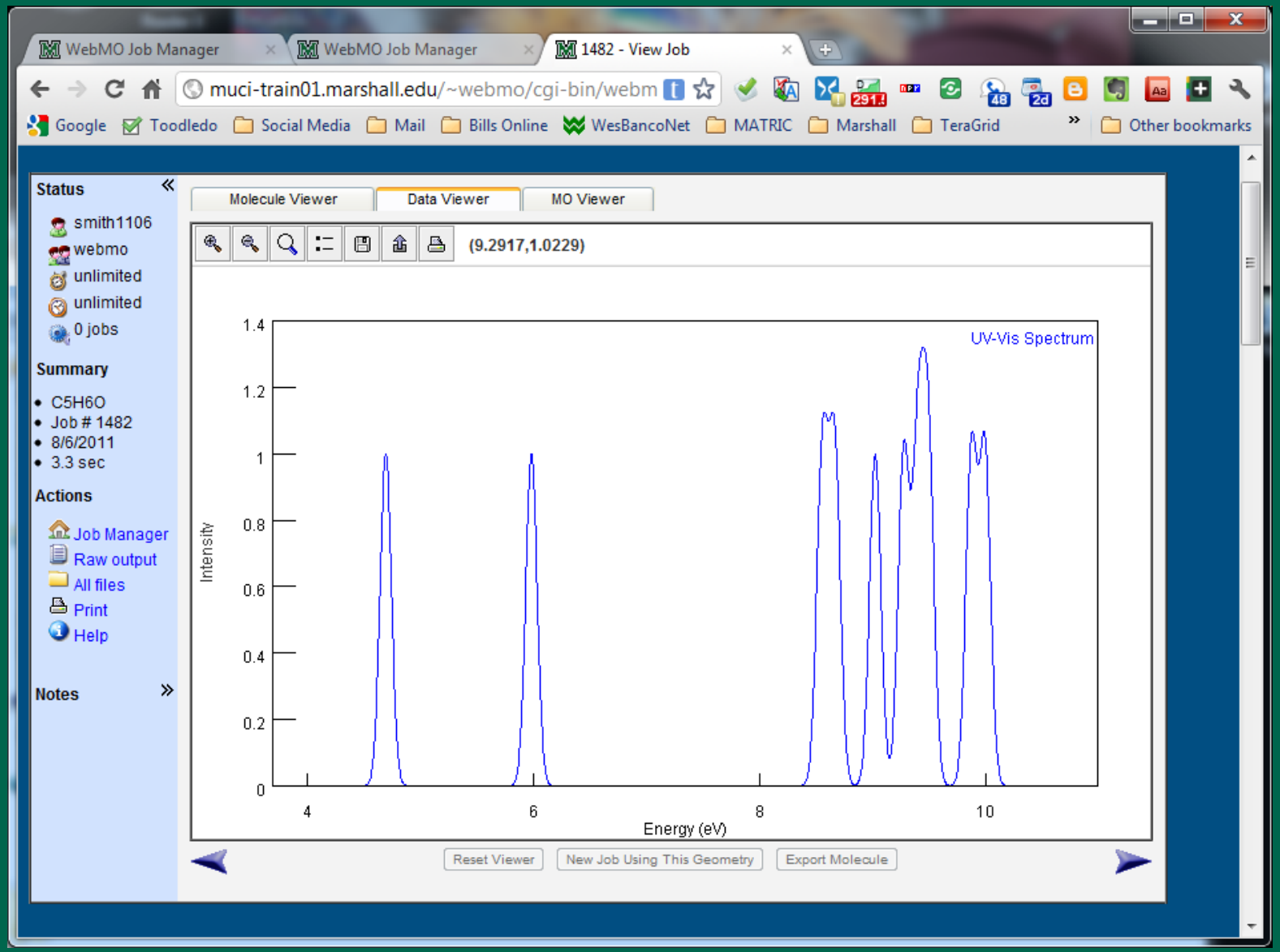
Viewing Results
IR Spectrum



Viewing Results
Single (UV-Vis) Excitations



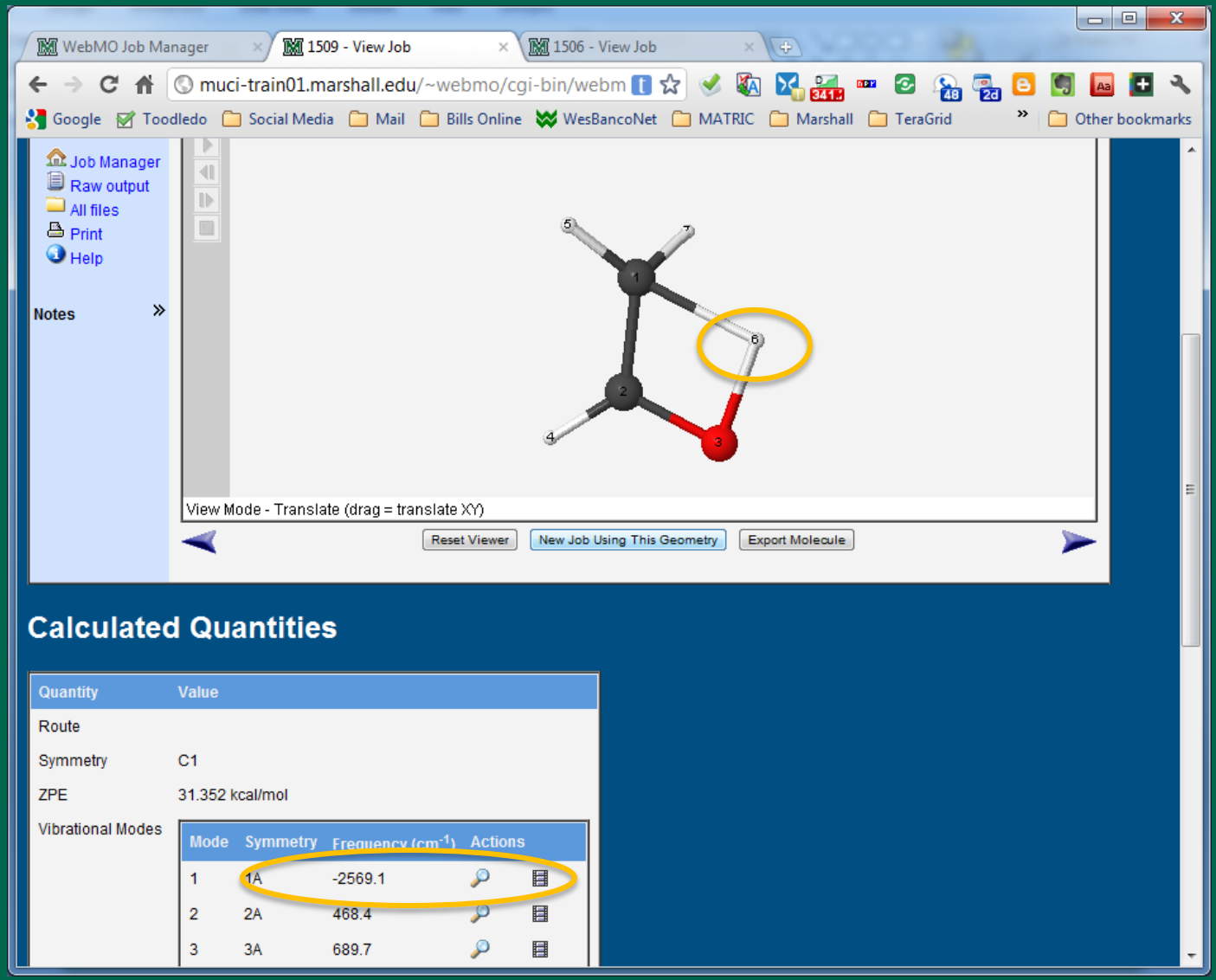
Viewing Results
UV-Vis Spectrum



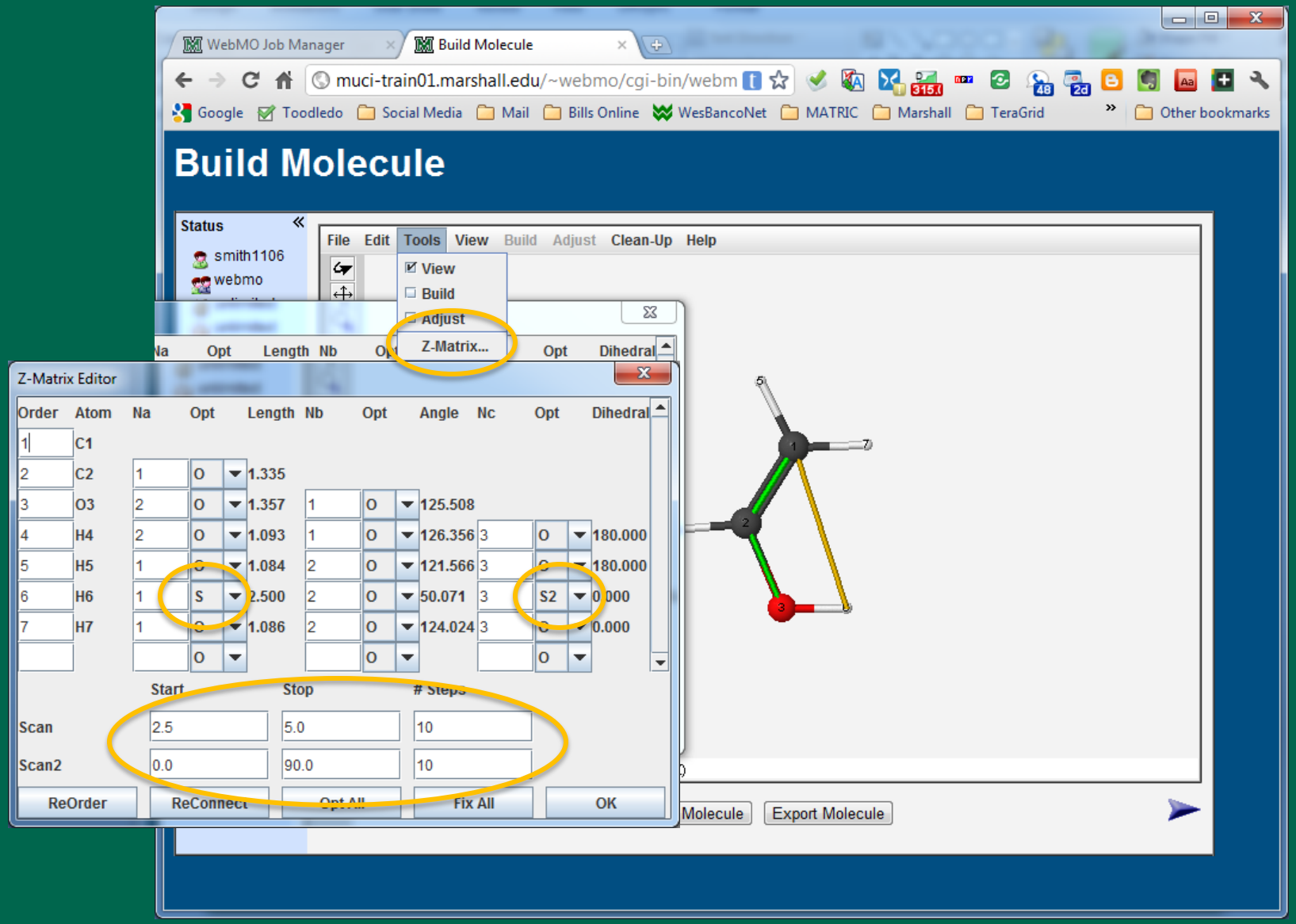
Potential Energy Surface

- Geometry scans (PES)
  - 1 or 2 internal coordinates (distance, angle, dihedral)
- Transition state optimization
  - Saddle point
  - Gradient minimization
  - Confirm one imaginary frequency
- Reaction Coordinate (path)
  - IRC: Intrinsic, kinetic energy dissipated
  - DRC: Dynamic, T+V conserved – *not in WebMO*!

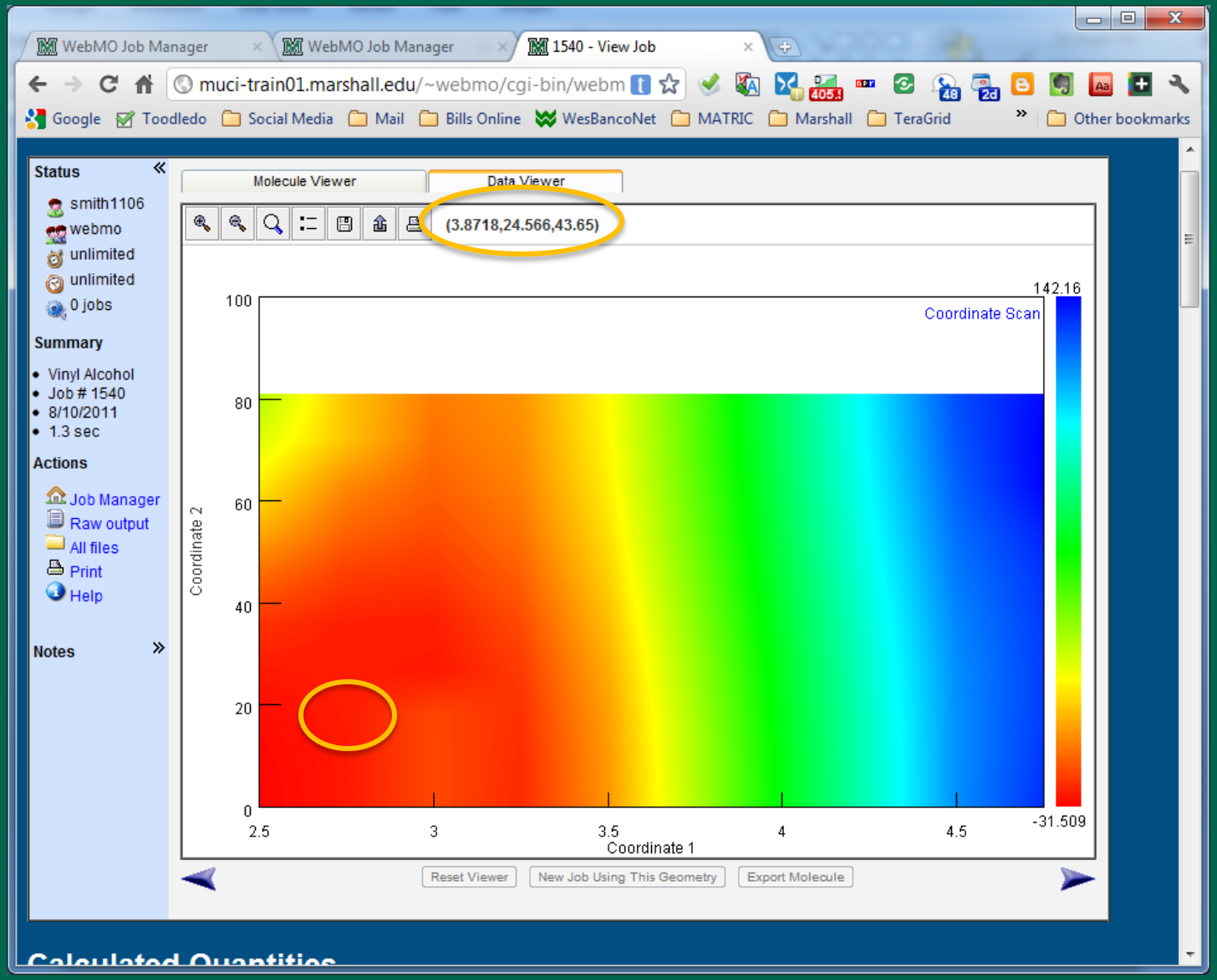
Viewing Results
Transition State



Viewing Results
2-D Geometry Scan



Viewing Results
2-D Geometry Scan



Potential Future Topics

- Periodic Systems and Materials Modeling
  - Quantum ESPRESSO, VASP
- Reactivity, QSAR/QSPR
- Spectroscopy and Excited States
- Thermochemistry and Model Chemistries
- Solvation
- Kinetics
- Computational Chemistry – Theory & Practice
- Beyond WebMO
  - Molecular Dynamics
  - Biomolecules (proteins, nucleic acids)
  - Hybrid QM/MM Techniques

Exercise #1

Triflouroacetic acid (TFA): CF_3COOH

- **Build molecule in 3D editor**
- **Optimize geometry at different levels of theory**
  - MM3 (Tinker), **PM3 (MOPAC)**, RHF/3-21G, DFT/B3LYP/6-31G(d) (GAMESS)
  - **Visualize optimization**
  - **Visualize partial charges (especially acidic H), dipole moment**
  - **Visualize orbitals, total and frontier densities, electrostatic potential**
  - Browse output files
- Perform geometry scan of C-C-O-H dihedral
  - Visualize scan and confirm low-energy conformation
- **Compute and visualize IR spectrum**
  - **Animate vibrational nodes**
- Compute deprotonation energy
  - CF_3COOH [+ H_2O] → CF_3COO^- [+ H_3O^+]
- Repeat with solvent (H_2O)

Use **MOPAC (PM3)**

Bonus: Compare acidities of $CF_nH_{3-n}COOH$ (n=0,3)

Exercise #2

Conjugated aldehyde (enal): $H_2C(=CH\text{-}CH)_n=O$

- **For n = 1 (acrolein)**
  - **Build and optimize structure**
    - **Use MOPAC (PM3)**
  - **Compute and visualize HOMO and LUMO orbitals (and those nearby)**
    - **Use GAMESS: Molecular Orbitals, DFT/B3LYP/6-31G(d)**
    - **Calculate HOMO-LUMO gap (1 hartree = 27.2107 eV) and save**
  - **Compute and visualize UV-Vis (excitation) spectrum**
    - **Use GAMESS: UV-Vis Spectrum, 6-31G(d) -- *ignores level of theory***
    - **Look at raw output for excitation details (e.g., HOMO → LUMO)**
  - **Compare excitation energies with** HOMO-LUMO gap
    - $1240/\lambda(nm) = 1$ eV
- Repeat above for n = 2, 3
  - Save results in a spreadsheet and plot HOMO-LUMO gap vs excitation energies
  - Save results as HTML (web pages) and view in browser
- **Compare with experiment: 209**, 221, 251 (nm)

Bonus: Predict and test results for n > 3

Exercise #3

Keto-enol tautomerization (proton migration)

H_3C-C=O (acetaldehyde) → H_2C=C-OH (vinyl alcohol)

All at the **MOPAC (PM3)** Level

- Build and optimize acetaldehyde structure
- Convert acetaldehyde to vinyl alcohol
  - Adding, deleting, and changing bonds only – no adding/deleting atoms
  - Clean hybridization and geometry only – do not add Hydrogens
- Optimize vinyl alcohol structure
  - Remember job#
- Return to acetaldehyde structure and compute the Saddle Point
  - Use job# of vinyl alcohol results as second geometry
- Edit such that H-O-C-C forms a 4-membered ring of single bonds
- Optimize as a Transition State (TS)
- Compute vibrational frequencies
  - Look for one negative (imaginary) frequency and animate it
- Compute IRCs from the TS to both acetaldehyde and vinyl alcohol