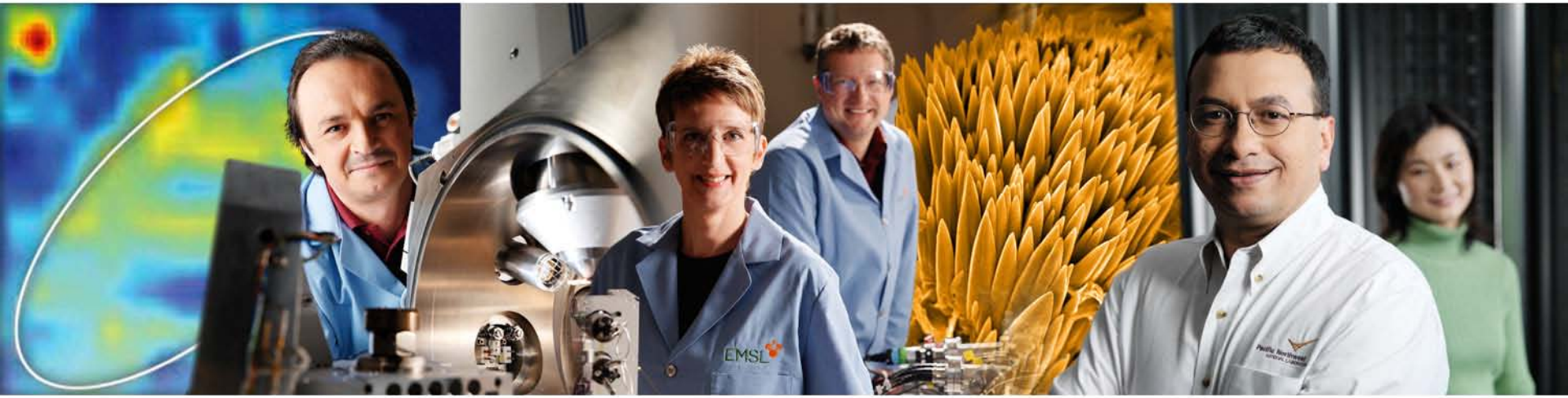
EMSL

Relativity, Spectroscopy and the EMSL Basis Set Library



www.emsl.pnl.gov

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

U.S. DEPARTMENT OF ENERGY

Outline

- Relativity
  - Intro into relativistic effects
  - Capabilities in NWChem to handle relativity
- Spectroscopy
  - NMR properties
  - Vibrational frequencies
- EMSL Basis Set Library

Quick introduction to relativity

- Dirac Hamiltonian instead of Schrödinger Hamiltonian
  - Includes description of positron states

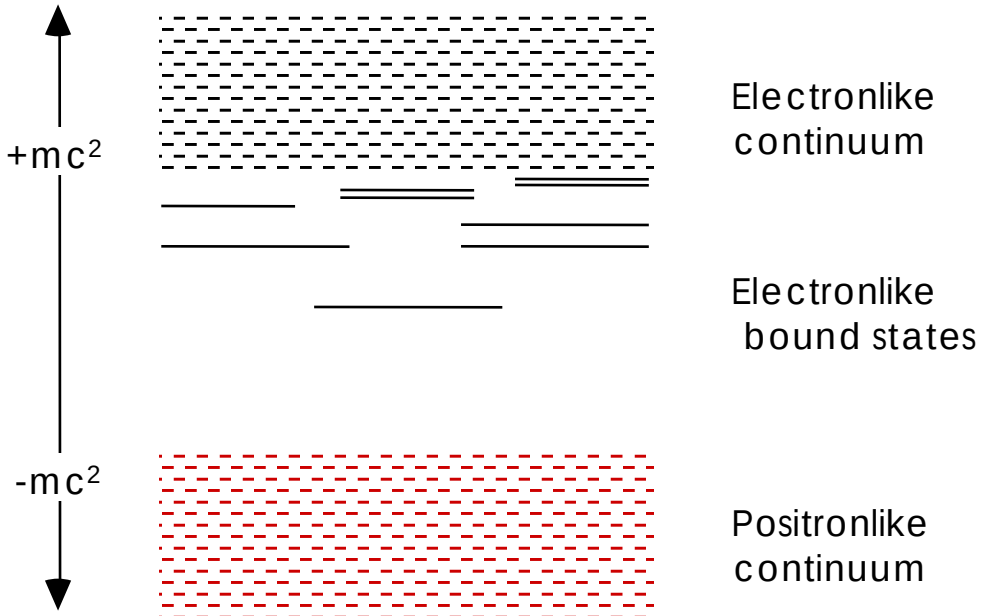
$$\begin{pmatrix} V & c\sigma\cdot p \\ c\sigma\cdot p & V-2mc^2 \end{pmatrix}\begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = \varepsilon\begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix}$$

$$h_i^D$$

$$\hat{H}\begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix} = E\begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix}$$

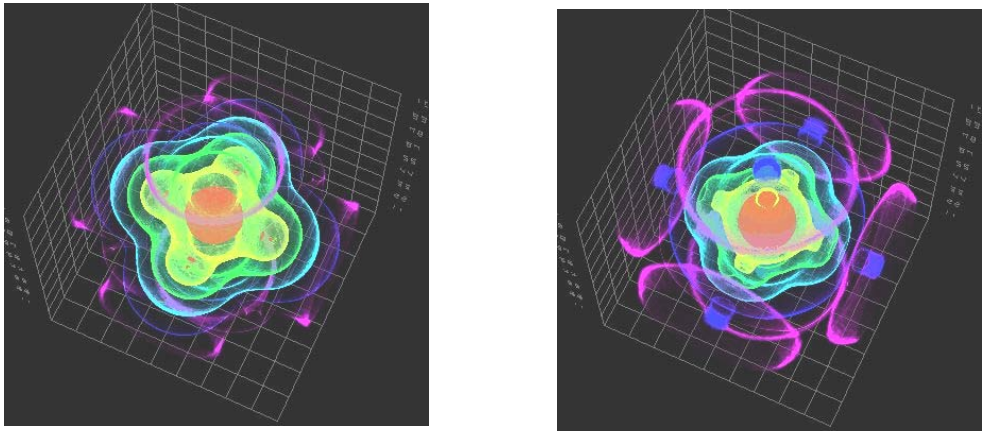
$$\hat{H} = \sum_i^N h_i^D + \tfrac{1}{2}\sum_{i\neq j}^N \left(\frac{1}{r_{ij}} - \frac{(\alpha_i \cdot \alpha_j)}{r_{ij}} \right)$$

Spectrum of electron in field of nucleus



Effects of relativity

- Scalar relativistic
  - Contraction and stabilization of s- and p-type orbitals
  - Expansion and destabilization of d- and f-type orbitals
- Spin-orbit splitting
  - Orbitals with angular momentum $l > 0$ split into subshells $l \pm ½$
  - Coupling between electronic states

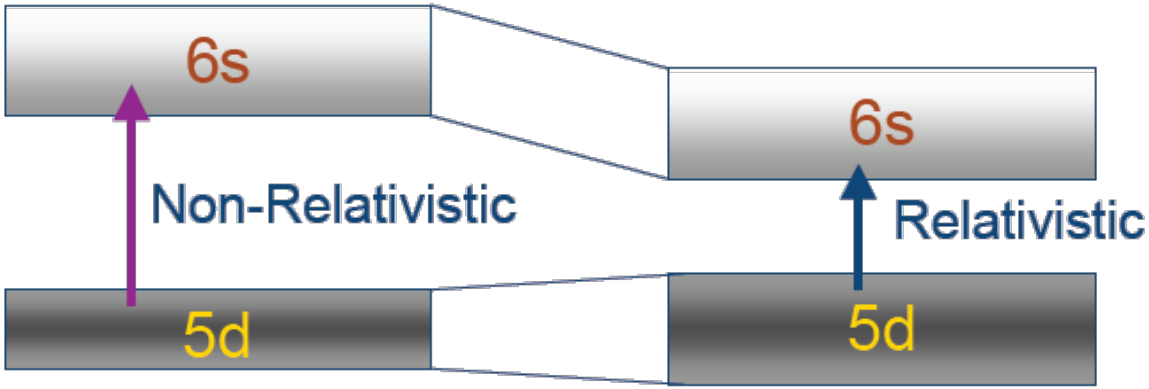


Non-relativistic Relativistic

Electron density plot of the $7\gamma_{6g}$ spinor in UF_6

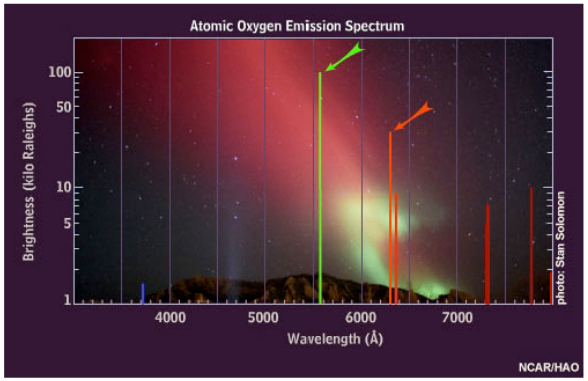
Relativity in every day life

- Non-relativistic gold has silver color
  - Stabilization of s-band and destabilization d-band shifts absorption via d-s transition from UV to Vis



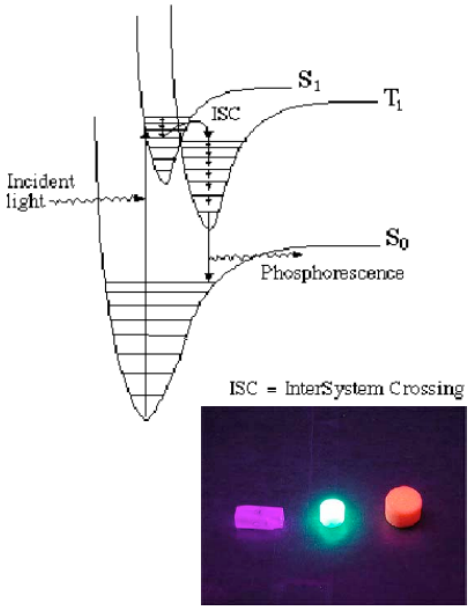
Relativity in every day life

- Phosphorescence
  - Singlet-triplet transitions and surface crossings are allowed due to spin-orbit coupling, i.e. spin is not a good quantum number



$^1S_0 \rightarrow {}^1D_2$ $^1D_2 \rightarrow {}^3P_2$

Lifetime 0.75 s Lifetime 110 s



  - Street lights work with "forbidden" spectroscopic transition $^3P_1$ to $^1S_0$

Relativity in NWChem

- NWChem can handle both scalar and spin-orbit effects at the DFT level

task sodft energy

task sodft optimize

task sodft frequencies

- New capabilities under development include
  - Spin-orbit TDDFT for excited states
  - NMR properties (Autschbach, University of Buffalo, USA)

Effective core potentials: scalar

```
basis
  U library crenbl_ecp                  # basis set associated with ECP
  O library aug-cc-pvdz
end

ecp
  U library crenbl_ecp                  # effective core potential
end

task dft optimize
```

- Note: use DFT instead of TDDFT for calculations without spin-orbit coupling

Manual input scalar ECP

```
ecp
  O nelec 2                                  # ecp replaces 2 electrons on O
  O ul      # d
    1      80.0000000      -1.60000000
    1      30.0000000      -0.40000000
    2       1.0953760      -0.06623814
  O s       # s - d
    0       0.9212952       0.39552179
    0      28.6481971       2.51654843
    2       9.3033500      17.04478500
  O p       # p - d
    2      52.3427019      27.97790770
    2      30.7220233     -16.49630500
end
```

- Note: For Stuttgart ECPs there is no local term, and you can leave it out or use "**2 1.0 0.0**"

$$\Delta U_l = \frac{}{2l+1}\Delta U_l$$

Spin-orbit coupling

- In addition to scalar relativistic ECP you need to define a spin-orbit potential

```
ecp
  u library stuttgart_rsc_1997_ecp
end
so
  u p
  2        9.06055606      14.90142409
  u d
  2        8.83183198       2.72712409
  u f
  2        7.01851629       0.65455772
end
```

- Note: make sure that
  - The spin-orbit potential belongs with ECP
  - Coefficients are correctly scaled

All-electron methodologies

- NWChem can handle both scalar and spin-orbit effects at the DFT level

```
relativistic
    douglas-kroll on          # Use Douglas-Kroll approximation
    douglas-kroll dkh         # Default is Douglas-Kroll-Hess
    douglas-kroll dk3full     # Third-order Douglas-Kroll
end
```

```
relativistic
    zora on                   # zora approximation will be used
end
```

- Note: You will need all-electron basis sets for ALL elements

Spectroscopy with NWChem

- NWChem has a suite of capabilities for calculating spectroscopic properties
  - NMR properties
    - Electric field gradient (expectation value)
    - Hyperfine coupling (expectation value)
    - Shielding (response property)
    - Spin-spin coupling (response property)
  - Electric polarizability and optical rotation(response property)
- Vibrational frequencies
- UV-Vis already covered earlier

NMR properties

- Expectation values

```
property
  efieldgrad          # gets you the electric field gradient tensor
  hyperfine           # gets you the hyperfine coupling tensor
end
```

- Response properties

```
property
  shielding   2   1 2   # calculate shielding tensor for first two atoms
  spinspin    1   3 4   # calculate spin-spin coupling tensor between
                          atoms 3 and 4
end
task property           # tell NWChem to run the properties module
```

Shielding vs Chemical Shift

- Experiments measure the chemical shift instead of the shielding
  - Chemical shift (δ) is relative to a standard molecule
  - Example, oxygen chemical shift is relative to oxygen in water

$$\delta = \sigma_{water} - \sigma_{your\ molecule}$$

  - Properties are tensors!!
    - You can visualize directions of tensor components with ECCE

Calculating vibrational frequencies

- First optimize your molecule's geometry!!!!

```
driver
  maxiter 20          # number of geometry optimization steps
  tight               # tight convergence for floppy molecules
 end
 task dft optimize    # tell NWChem to do the optimization
```

- You can also optimize at the SCF, MP2, TDDFT, and coupled cluster level of theory
  - Optimize excited state geometries with TDDFT
  - Caution: Coupled cluster optimization will be done using numerical gradients and will be expensive

Masses and intensities

- NWChem uses the most common masses for elements

```
task scf frequencies

freq
  reuse                              # Reuse Hessian
  mass hydrogen 2.014101779          # Change the mass for H to D
  mass 3 3.021234
end
task scf frequencies
```

- NWChem only calculates IR intensities
  - Raman intensities are coming soon

Frequencies output

- NWChem prints out two sets of frequencies
  - Raw normal modes
  - Projected normal modes with translations and rotations projected out
  - Use the projected normal modes!

NORMAL MODE EIGENVECTORS IN CARTESIAN COORDINATES

(Projected Frequencies expressed in cm-1)

	1	2	3	4	5	6
P.Frequency	0.00	0.00	0.00	0.00	0.00	0.00
1	0.00109	-0.01197	0.12020	-0.07402	0.01164	-0.00799
2	0.00970	0.20350	-0.00123	0.00184	-0.02448	-0.00288
3	0.00624	-0.00875	-0.00516	0.10368	0.00269	0.13042
4	0.00596	-0.00529	0.11985	-0.06716	0.00152	-0.00732
5	-0.03405	0.13917	-0.00045	-0.00078	0.07045	-0.00172

Frequencies output: Eigenvalues

- Normal mode frequencies output

Normal Mode	Eigenvalue [cm**-1]	Projected Infra Red Intensities [atomic units]	[(debye/angs)**2]	[(KM/mol)]	[arbitrary]
1	0.000	0.000042	0.001	0.041	0.013
2	0.000	0.003341	0.077	3.257	1.032
3	0.000	0.000007	0.000	0.007	0.002
4	0.000	0.004245	0.098	4.138	1.311
5	0.000	0.002836	0.065	2.764	0.876
6	0.000	0.000063	0.001	0.061	0.019
7	127.737	0.000163	0.004	0.159	0.050
8	170.851	0.000049	0.001	0.048	0.015
9	232.061	0.000973	0.022	0.948	0.300

- Note: Three rotational and translational modes are zero (projected out)!

Frequencies output: Imaginary modes

- Sometimes you get imaginary modes

Normal Mode	Eigenvalue [cm**-1]	Projected Infra Red Intensities [atomic units]	[(debye/angs)**2]	[(KM/mol)]	[arbitrary]
1	-67.461	0.000411	0.009	0.401	0.086
2	-56.947	0.000814	0.019	0.794	0.171
3	-34.343	0.004494	0.104	4.381	0.942
4	-13.396	0.001548	0.036	1.509	0.324
5	0.000	0.001474	0.034	1.436	0.309
6	0.000	0.001367	0.032	1.333	0.286
7	0.000	0.001035	0.024	1.009	0.217
8	0.000	0.001463	0.034	1.426	0.307
9	0.000	0.001567	0.036	1.528	0.328
10	0.000	0.001901	0.044	1.853	0.398
11	28.105	0.006869	0.158	6.696	1.439
12	36.721	0.000162	0.004	0.158	0.034

Imaginary modes: Dealing with them

- Causes for imaginary modes:
  - Small eigenvalues in floppy molecules may require tight geometry optimization
  - If you are searching for a transition state, you should find one imaginary mode
- Side bar: Transition state searches

```
freq
  firstneg          # follow first imaginary mode
  vardir 4          # search along internal variable 4
  moddir 1          # search along normal mode 1
end
task scf saddle
```

Imaginary modes: Multiple large modes

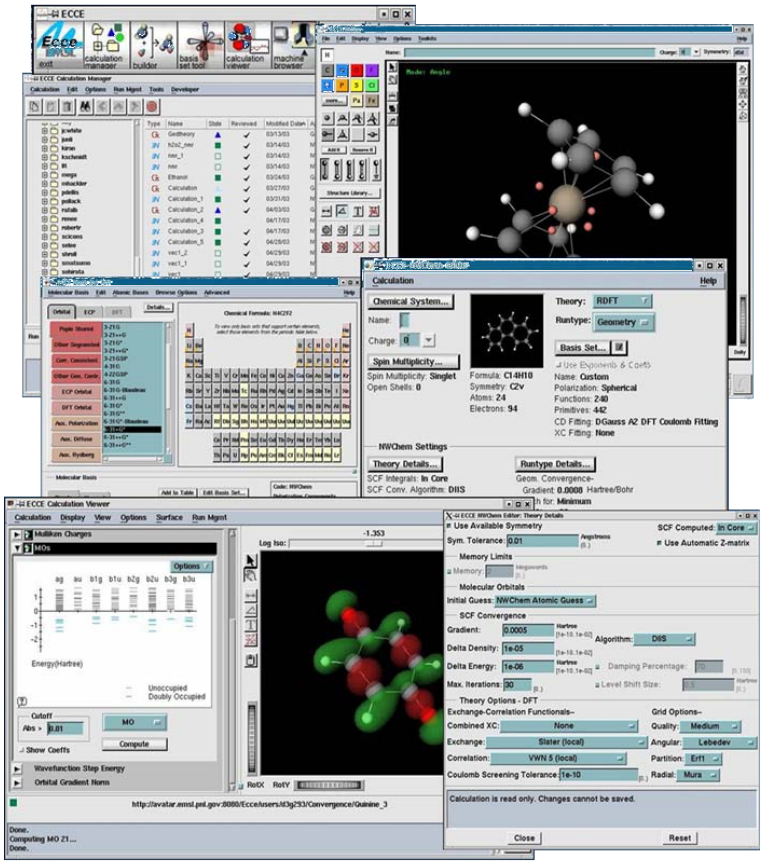
- Larger modes suggest that geometry not in minimum
  - Output provides information about imaginary modes
  - Use information as start for geometry optimization

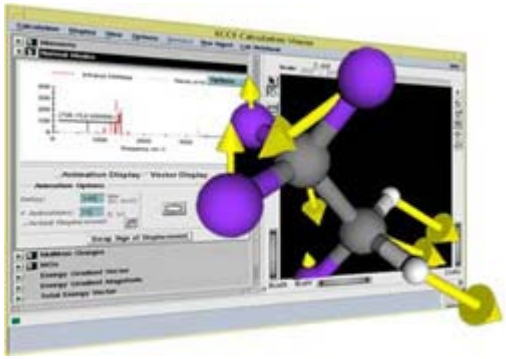
```
============================================================
   Negative Nuclear Hessian Mode    1  Eigenvalue =    -21.49 cm**(-1)
------------------------------------------------------------------------------

Geometry after  100.0% step for mode  1; Step length =  0.253 angstroms
  Maximum component (any atom: x,y, or z) displacement:  0.159
   1 U          92.0000    0.08537830    0.05333786    0.44684301
   2 O           8.0000   -0.25738246    1.78398570    0.24182943
   3 O           8.0000    0.45360974   -1.67855648    0.57102659
   4 O           8.0000   -2.27645631   -0.41108121    0.73211136
   5 O           8.0000   -0.28916140   -0.09890107   -1.94856070
   6 O           8.0000    2.43515585    0.36500624   -0.06284980
   7 C           6.0000   -3.04960523   -0.53147913    1.70513397
```

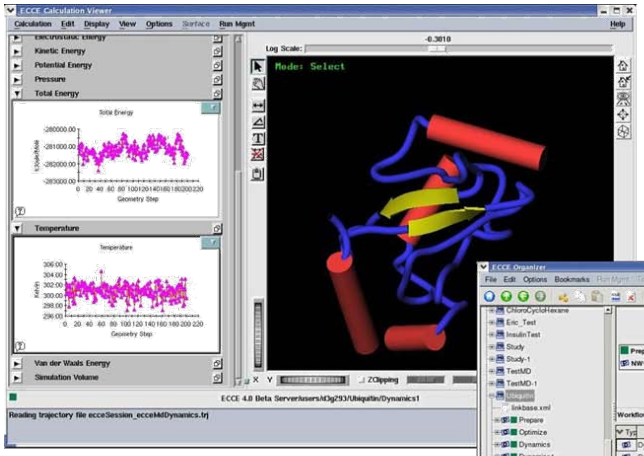
- Note: do not use raw step!

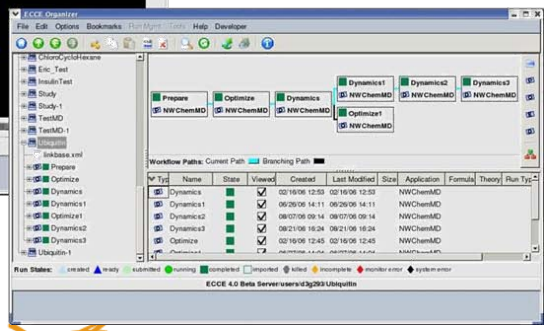
Visualizing normal modes

- ECCE can be used to visualize normal modes









Frequencies output: Zero-point energy

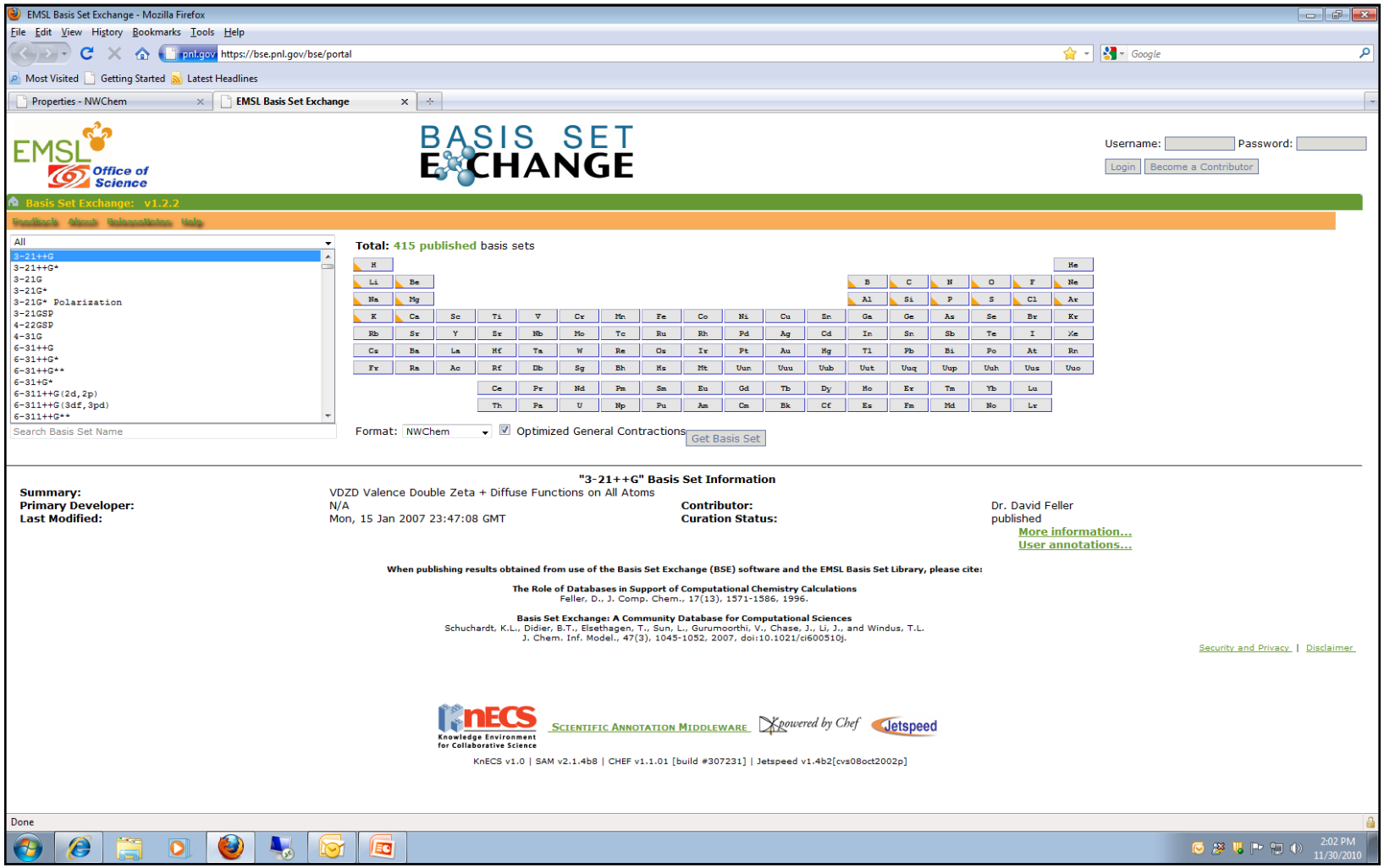
EMSL

- NWChem prints out zero-point energy and other thermodynamic properties

```
Temperature                    =   298.15K

Zero-Point correction to Energy  =   63.909 kcal/mol  (  0.101845 au)
Thermal correction to Energy     =   67.730 kcal/mol  (  0.107934 au)
Thermal correction to Enthalpy   =   68.322 kcal/mol  (  0.108878 au)

Total Entropy                  =   75.958 cal/mol-K
  - Translational              =   38.765 cal/mol-K (mol. weight =  73.0528)
  - Rotational                 =   25.463 cal/mol-K (symmetry #  =       1)
  - Vibrational                =   11.730 cal/mol-K

Cv (constant volume heat capacity) =   19.985 cal/mol-K
  - Translational              =    2.979 cal/mol-K
  - Rotational                 =    2.979 cal/mol-K
  - Vibrational                =   14.026 cal/mol-K
```

- Note: Different temperature can be set in input

EMSL's Basis Set Exchange



https://bse.pnl.gov/

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

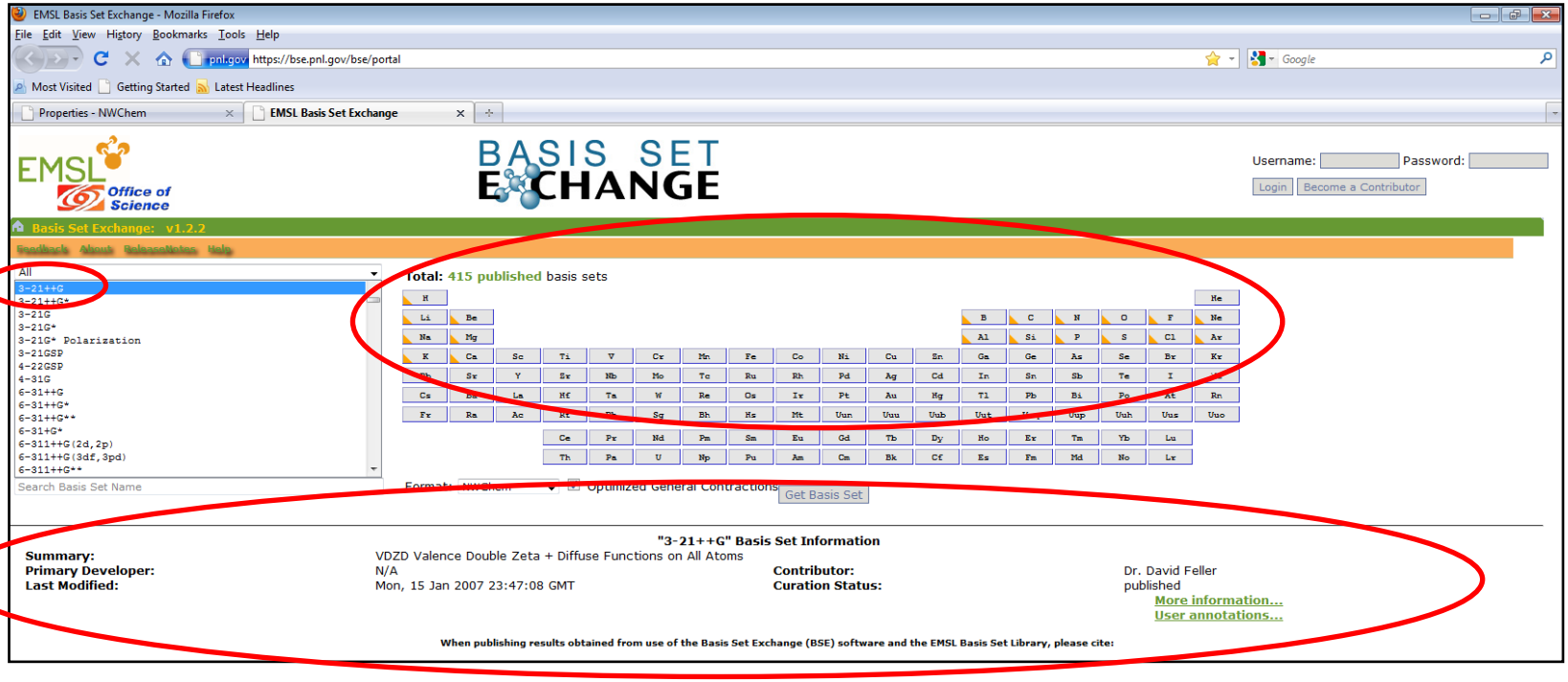
U.S. DEPARTMENT OF ENERGY

EMSL's Basis Set Exchange

EMSL

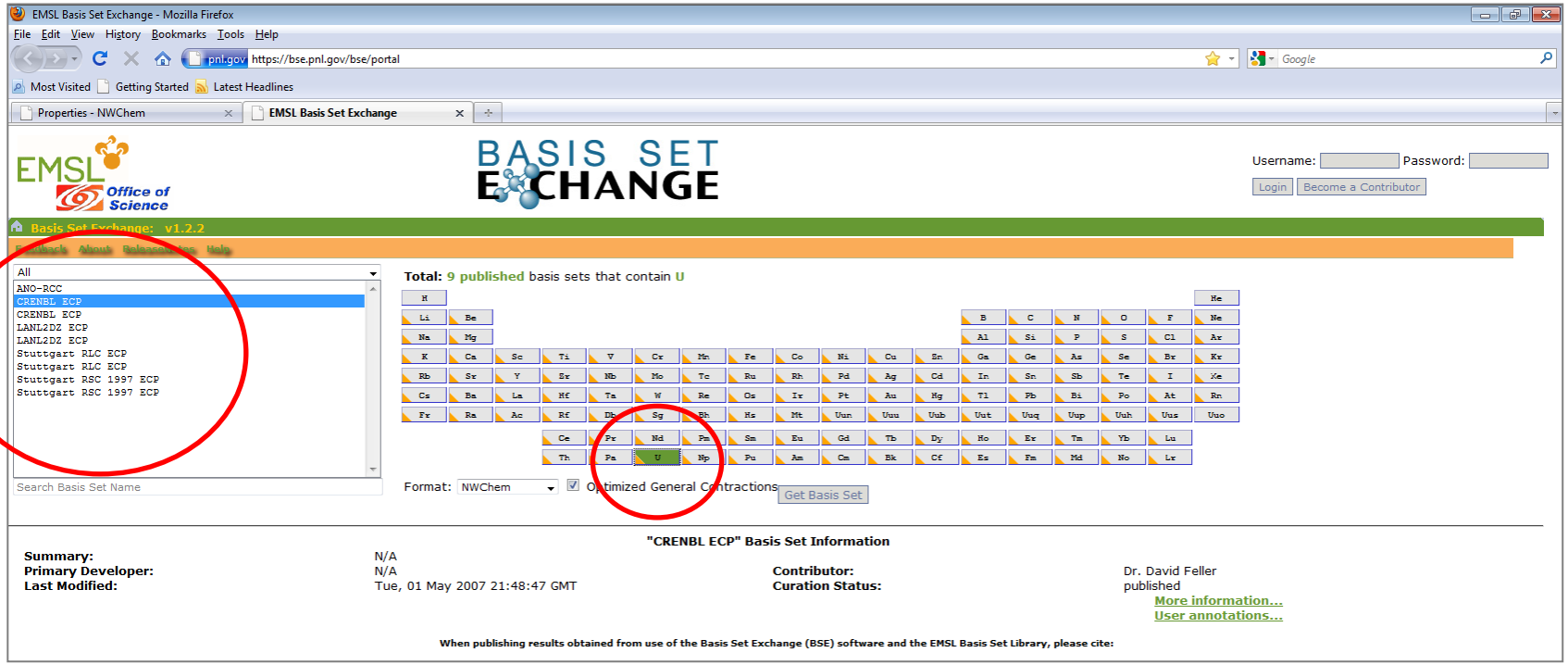
- Basis Set Exchange is comprehensive online library containing Gaussian basis sets
  - Anyone can download basis sets in the format they want
    - Supporting formats other than NWChem
  - Anyone can contribute basis sets they have developed
    - Only published online after work has been published in literature and after curation
- All basis sets that are online are also in the NWChem basis set library
  - Basis Set Exchange is source for NWChem basis set library

Elements covered by basis set



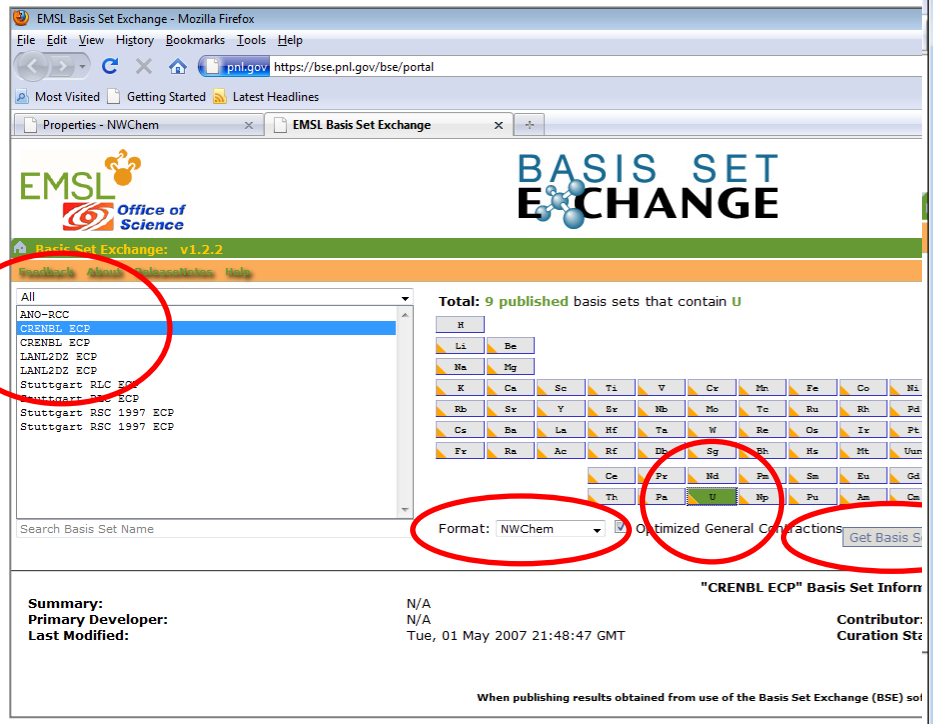
- When you select a basis set
  - You see the elements that are covered by the basis set
  - You can get more details about the basis set itself

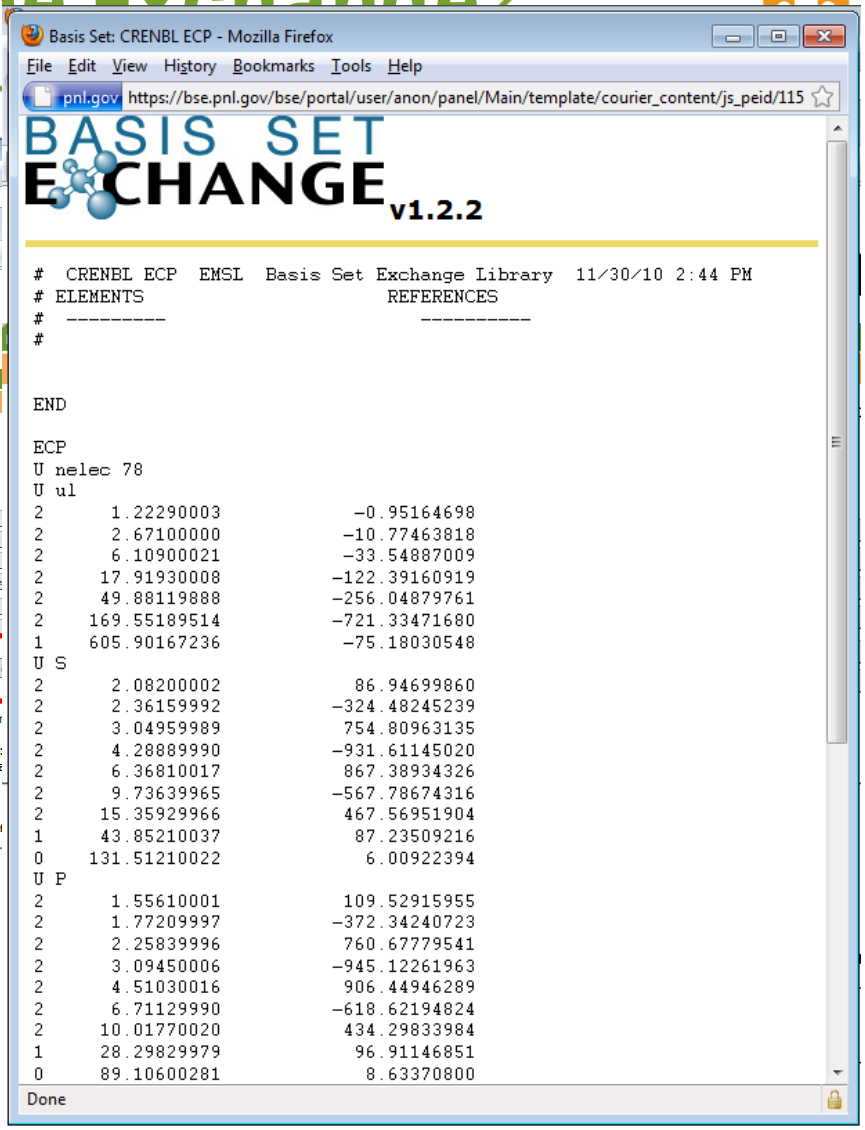
Basis set for certain element



- Select an element
  - And find the basis sets available for this element

Getting a basis set from the Exchange

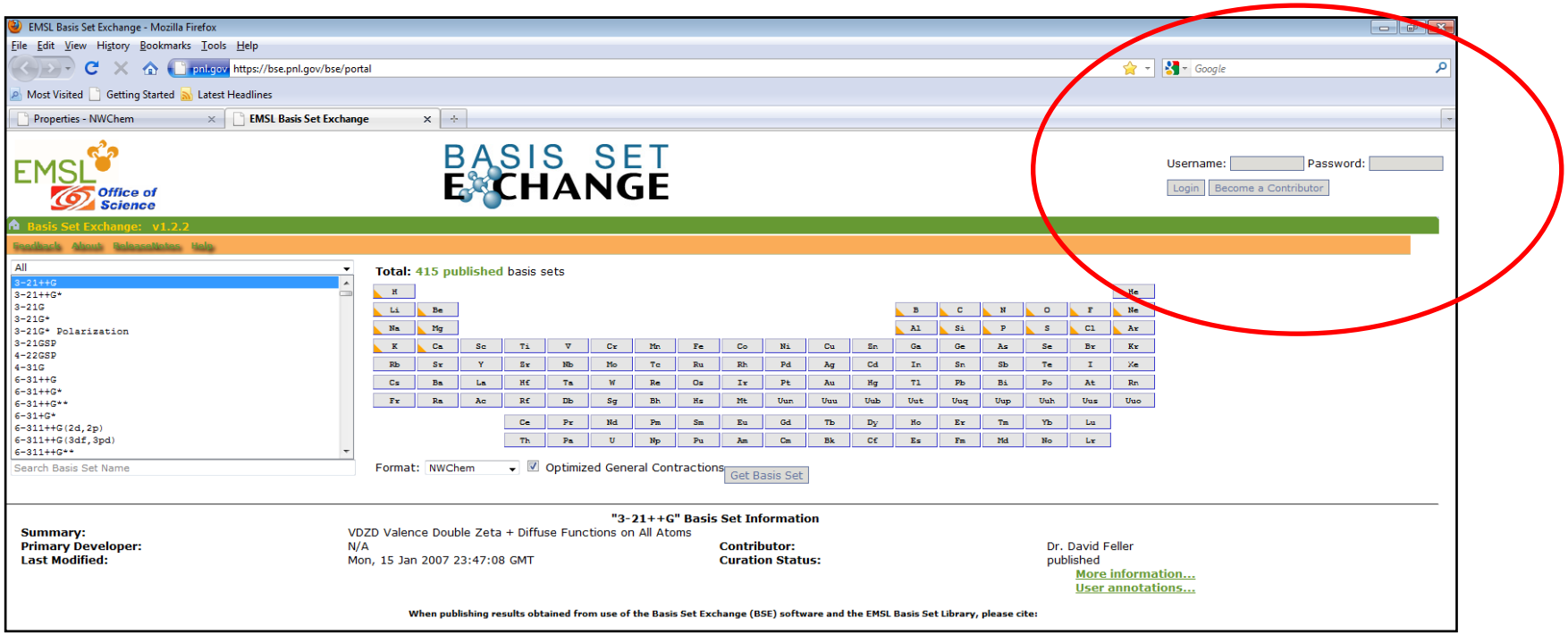




- Select an element
  - Select a basis from the list
  - Select a format you want the
  - Click “Get Basis Set”

Adding Basis Sets to the Exchange

- You can add basis sets you have developed to the exchange for download by others
  - Get an account and start adding



EMSL

Questions?