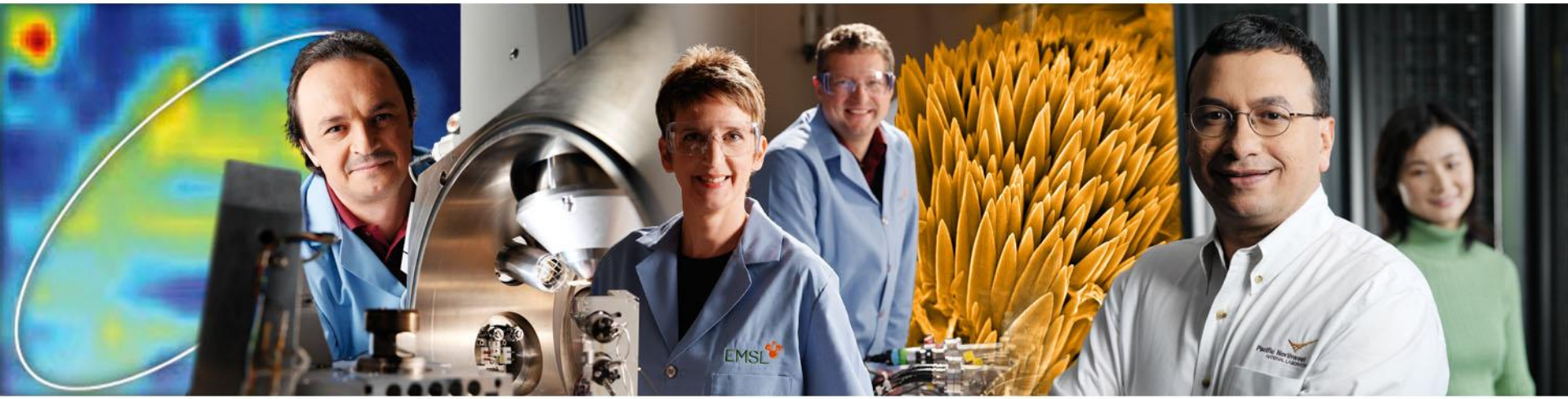
EMSL

# Relativity, Spectroscopy and the EMSL Basis Set Library

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# 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

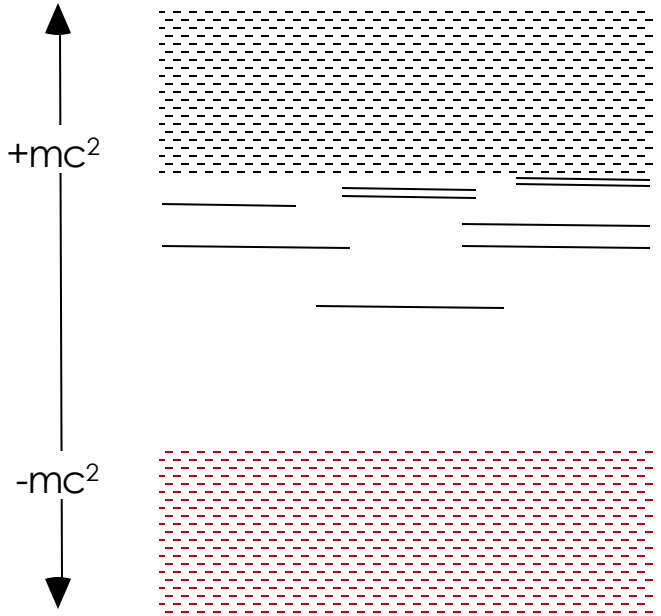
- Dirac Hamiltonian instead of Schrödinger Hamiltonian
  - Includes description of positron states

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

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

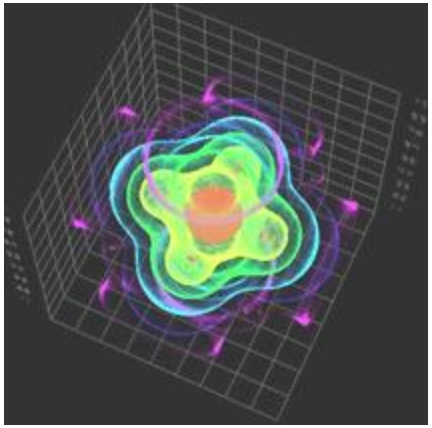
$$\hat{H} = \sum_i^N h_i^D + \tfrac{1}{2}\sum_{i\neq j}^N\left(\frac{1}{r_{ij}} - \frac{(\alpha_i\cdot\alpha_j)}{r_{ij}}\right)$$

Spectrum of electron in field of nucleus

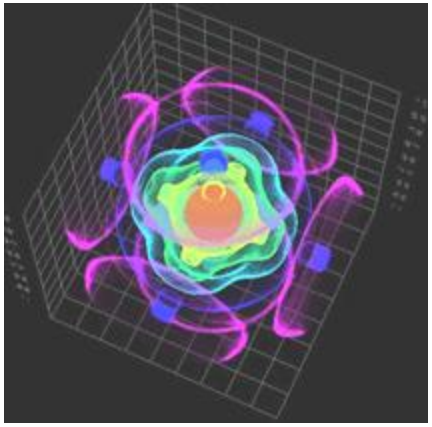


# Effects of relativity

- 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 $l \pm \frac{1}{2}$
  - Coupling between electronic states



Non-relativistic

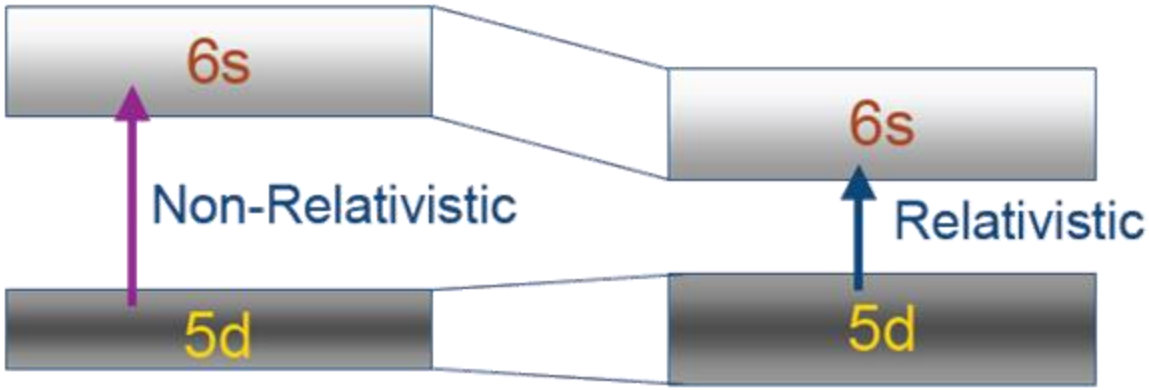


Relativistic

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

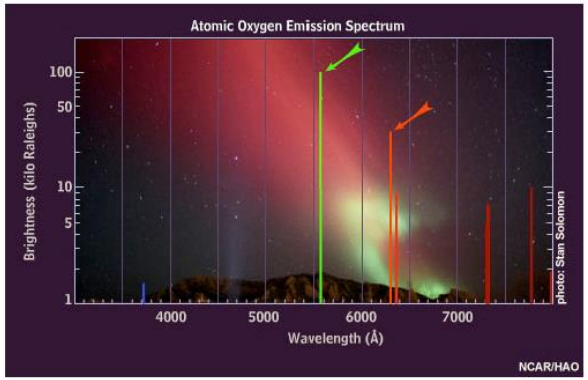
# Relativity in every day life

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



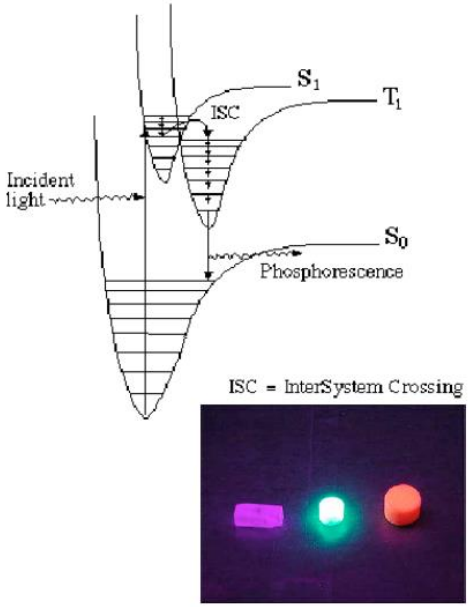

# Relativity in every day life

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




$^1S_0 \rightarrow {}^1D_2$ Lifetime 0.75 s

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

# 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
```

# 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
```

# 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

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- 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

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- 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
```

# Calculating vibrational frequencies

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- 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
```

# Frequencies output: Zero-point energy

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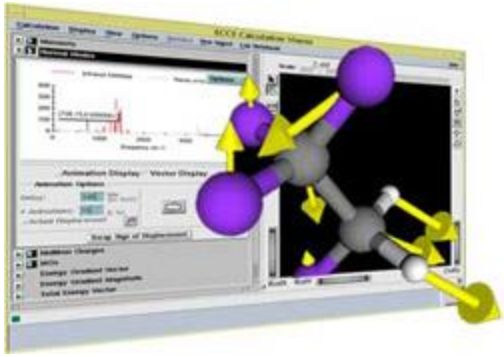
- NWChem prints out zero-point energy and other thermodynamic properties

```
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

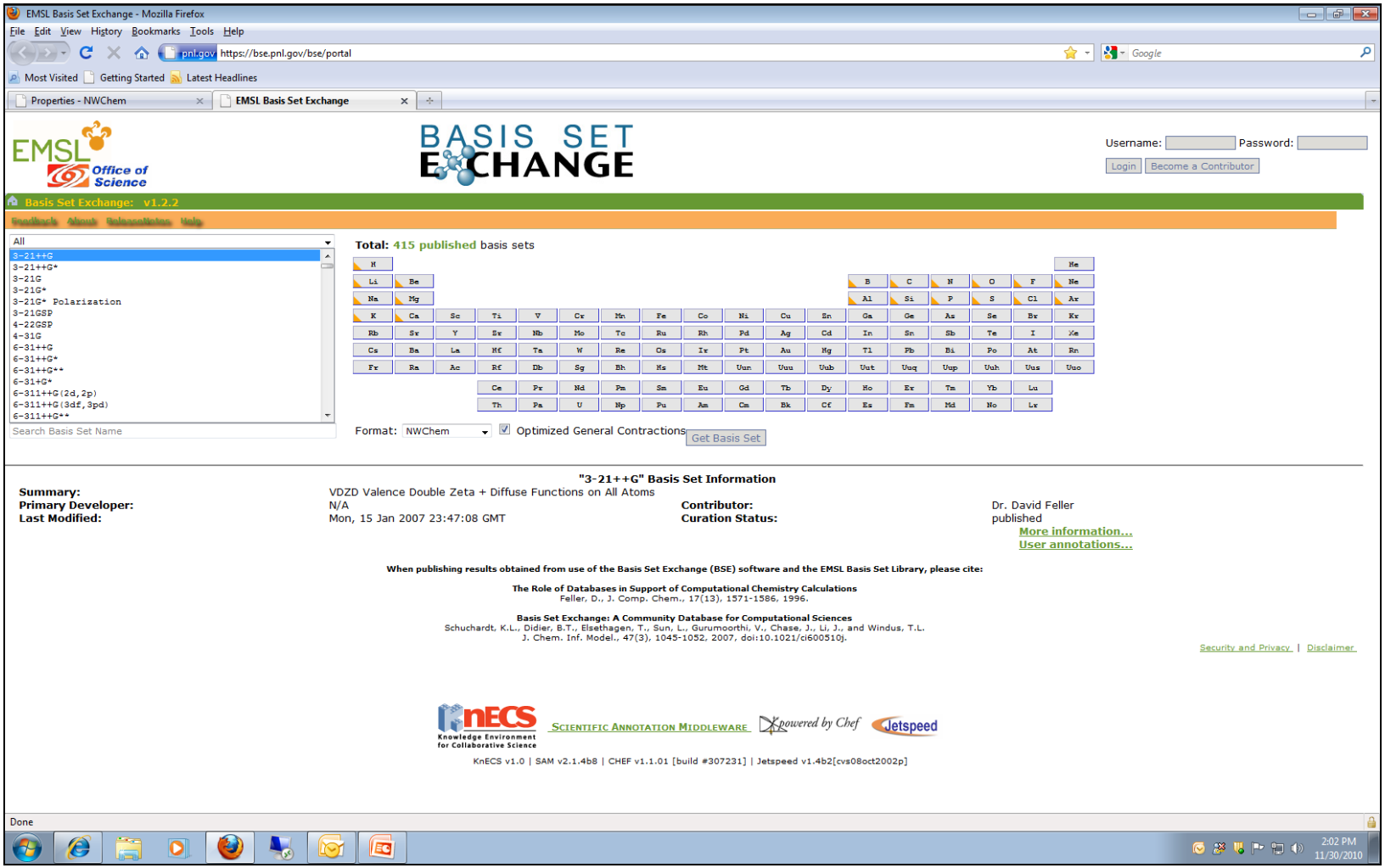
# Visualizing normal modes



- ECCE can be used to visualize normal modes

- Other visualizers can be used to visualize NWChem results. Molecular orbitals and charge/spin densities are written un Cube format (E.g. Molden, Molekel, Avogadro, VMD, OpenGMol, Gaussvuew)

# EMSL's Basis Set Exchange

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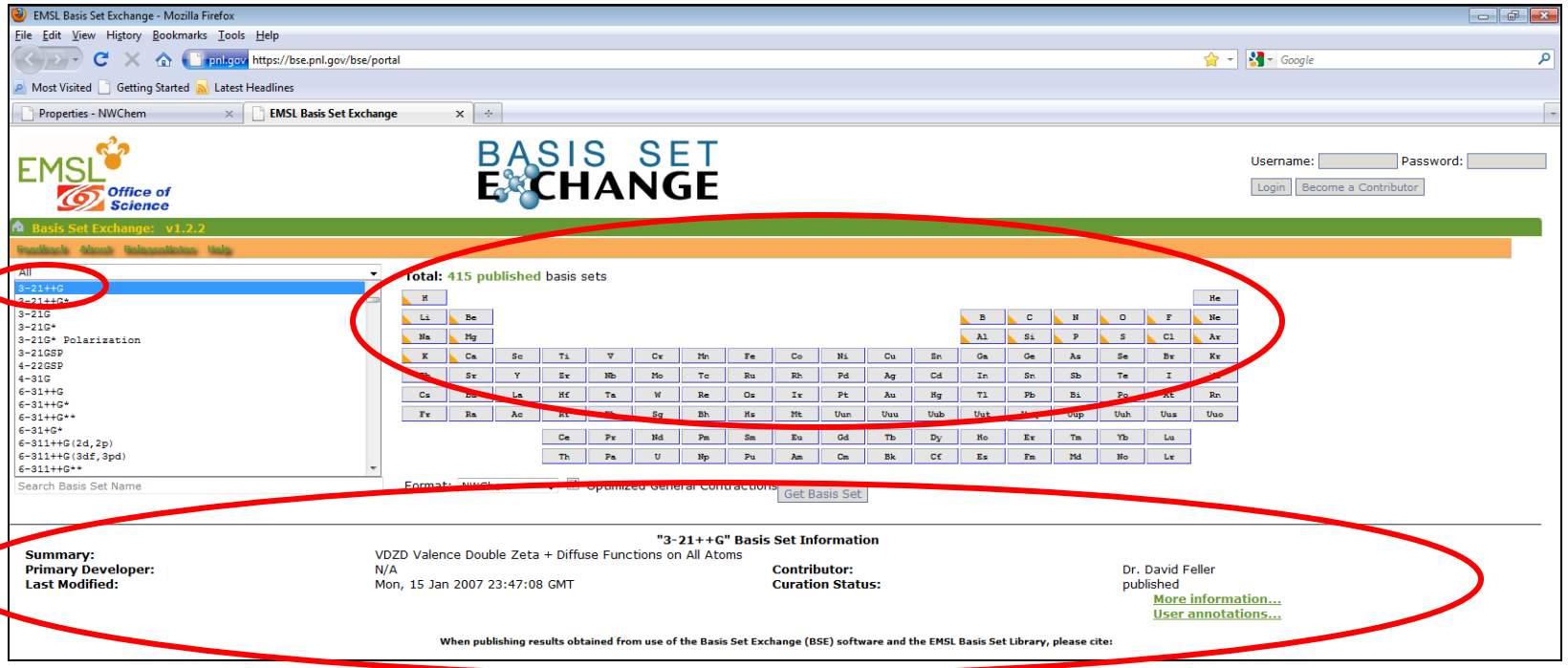
# EMSL's Basis Set Exchange

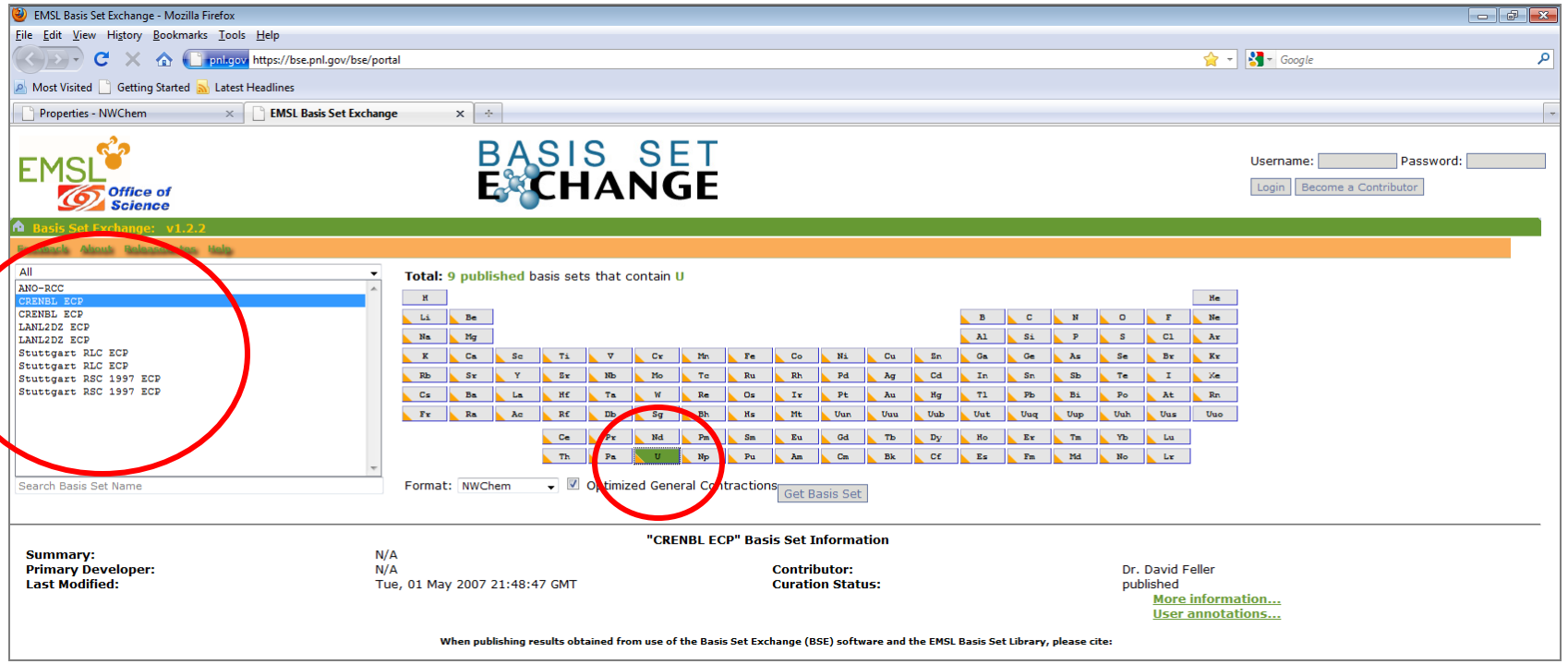
- Basis Set Exchange is comprehensive online library containing Gaussian basis sets
  - Anyone can download basis sets in the format they want
    - Supporting formats other than NWChem
  - Anyone can contribute basis sets they have developed
    - Only published online after work has been published in literature
- 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



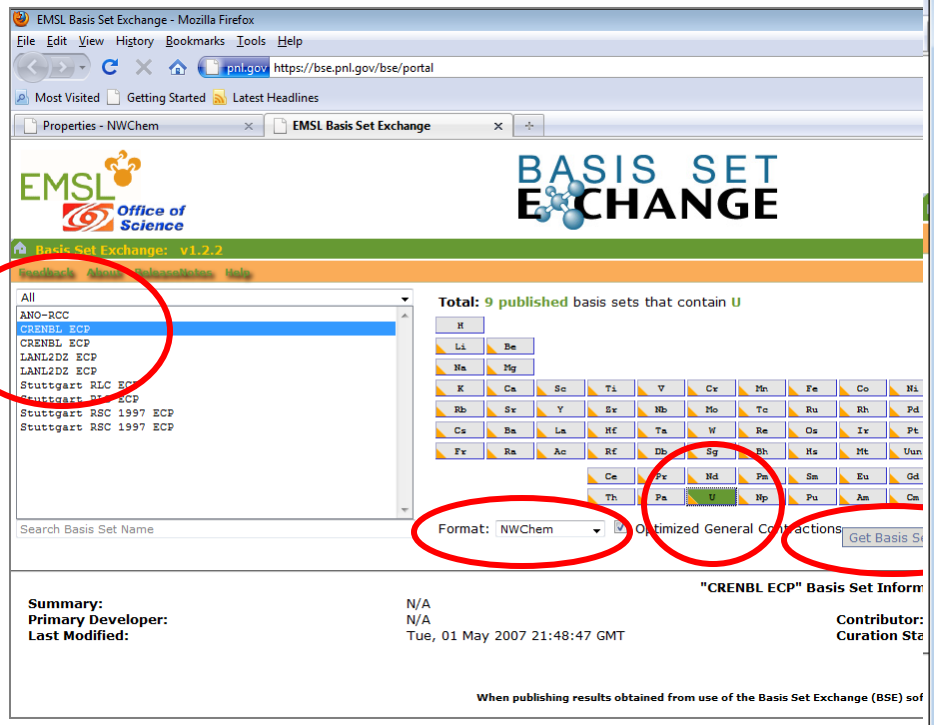

- When you select a basis set
  - You see the elements that are covered by the basis set
  - You can get more details about the basis set itself

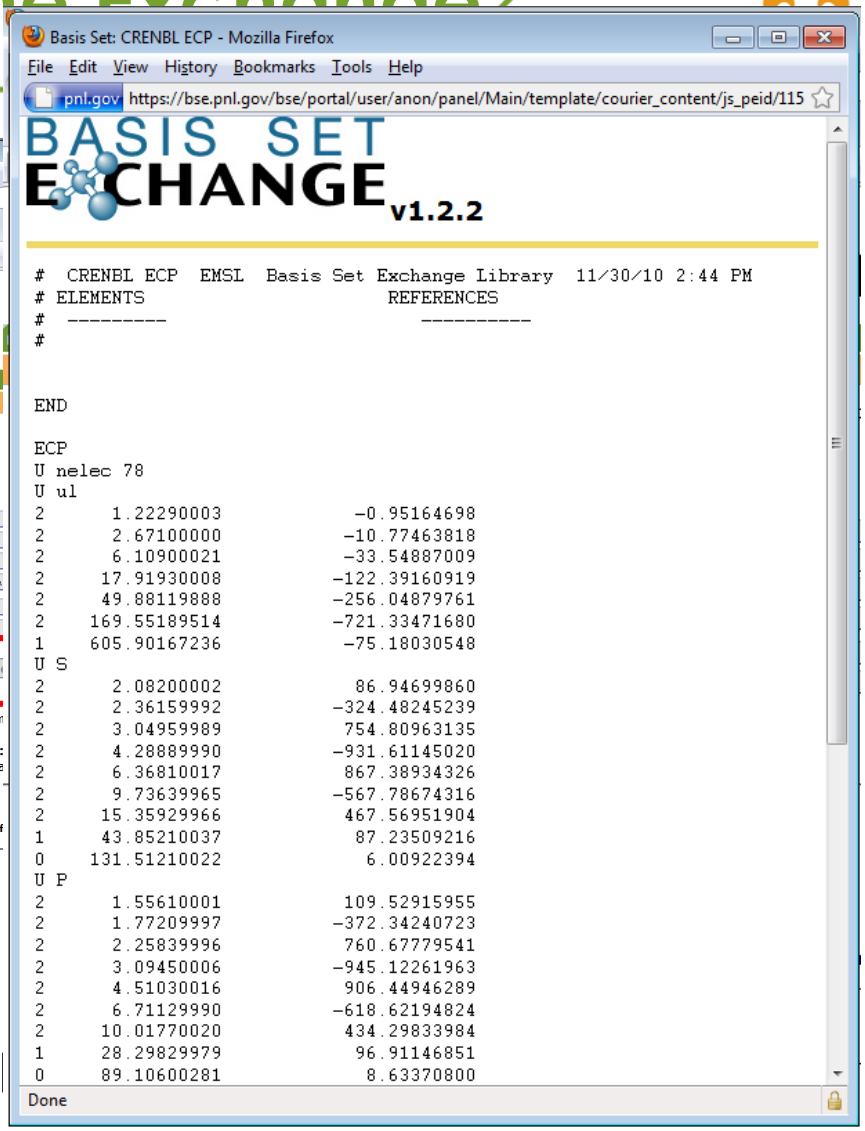
# Basis set for certain element




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

# Getting a basis set from the Exchange

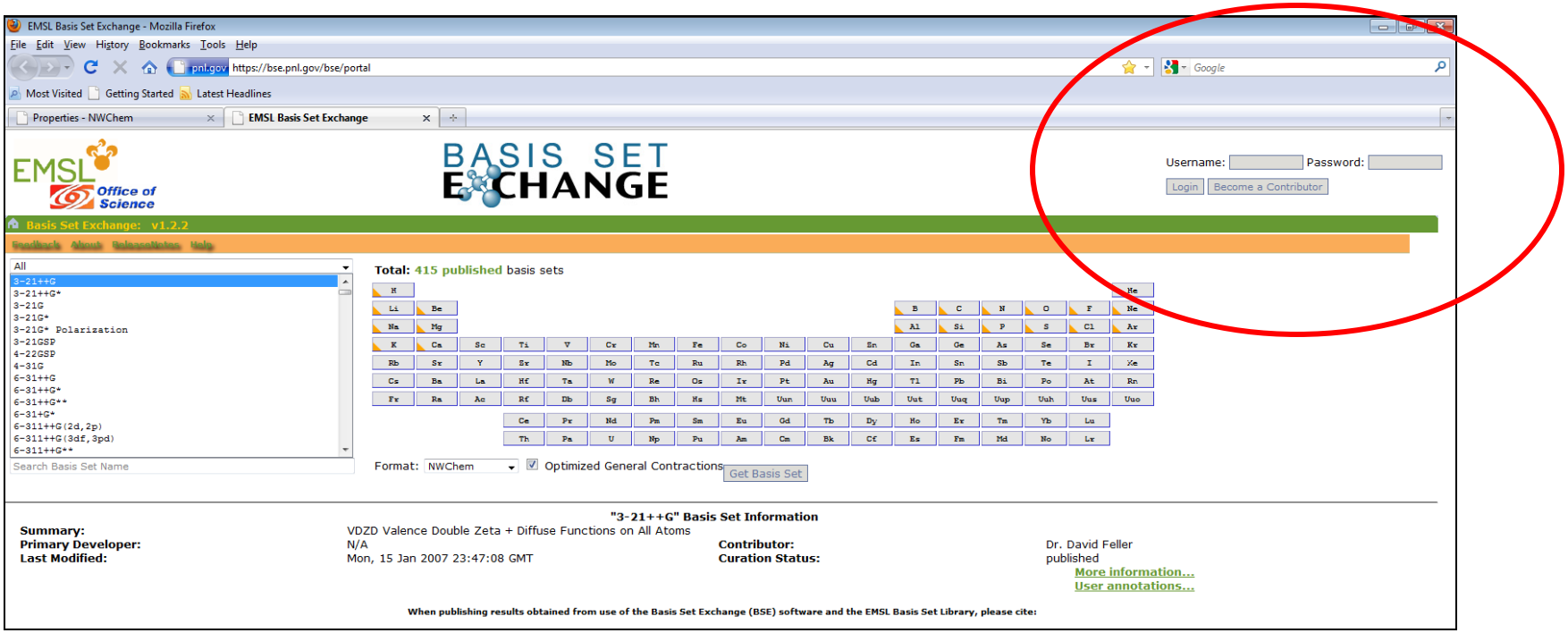



- Select an element
  - Select a basis from the list
  - Select a format you want the
  - Click "Get Basis Set"

# 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

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# Questions?

## Community forum:
## www.nwchem-sw.org