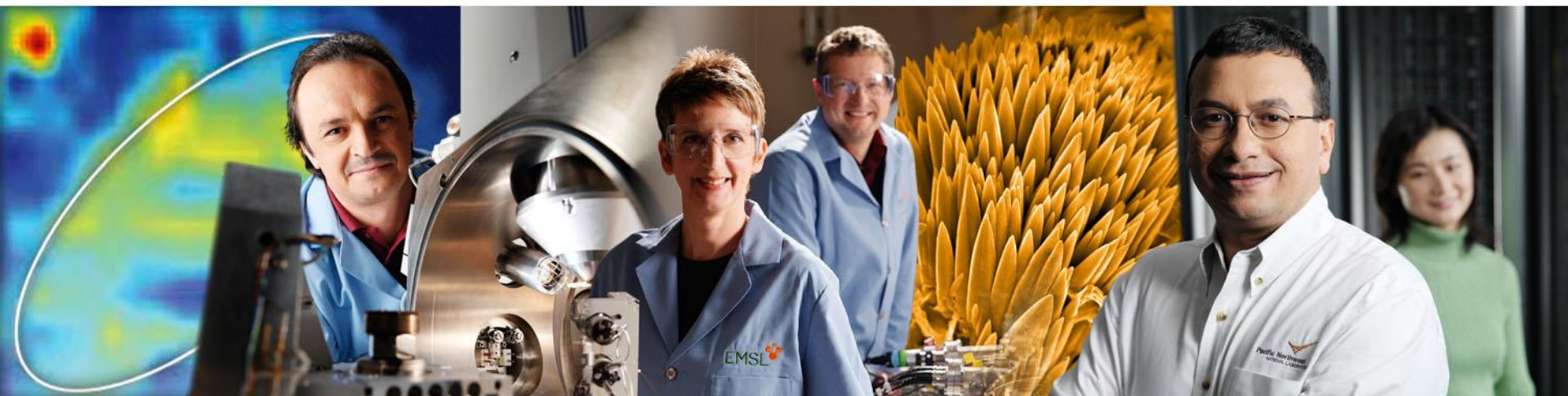


Relativity, Spectroscopy and the EMSL Basis Set Library



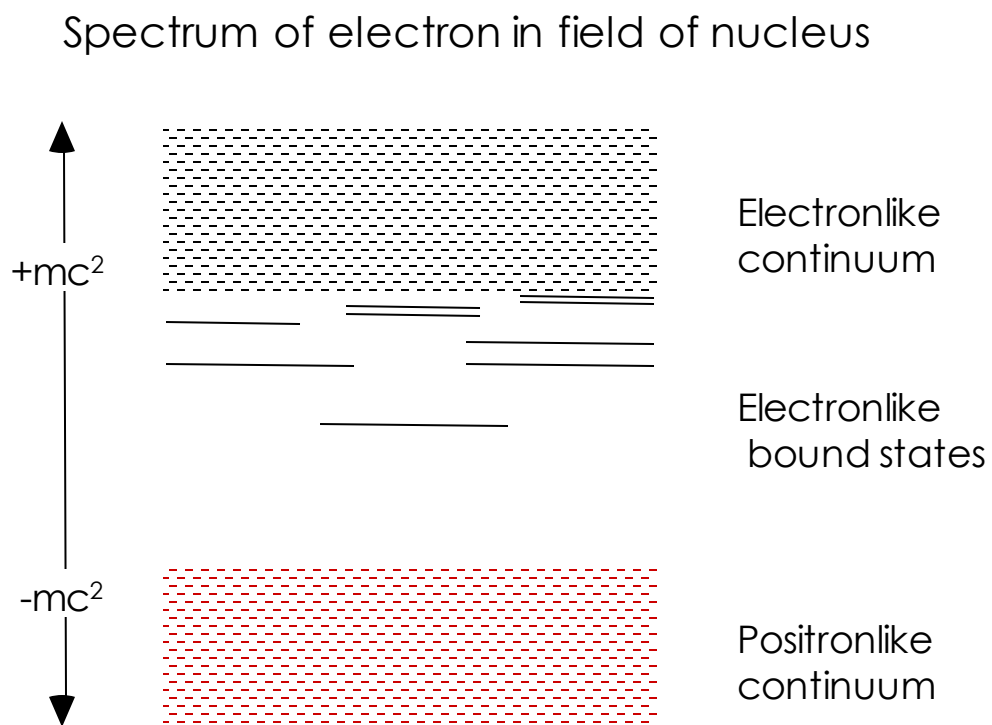
- Relativity
 - ◆ Intro into relativistic effects
 - ◆ Capabilities in NWChem to handle relativity
- Spectroscopy
 - ◆ NMR properties
 - ◆ Vibrational frequencies
- EMSL Basis Set Library

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

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

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

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

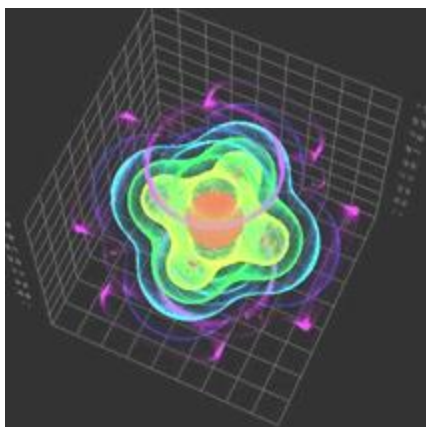


■ Scalar relativistic

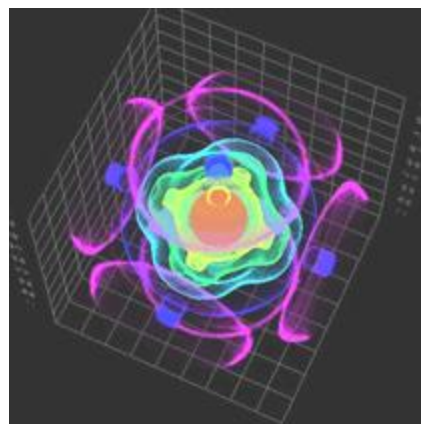
- ◆ Contraction and stabilization of s- and p-type orbitals
- ◆ Expansion and destabilization of d- and f-type orbitals

■ Spin-orbit splitting

- ◆ Orbitals with angular momentum $l > 0$ split into subshells $l \pm \frac{1}{2}$
- ◆ Coupling between electronic states



Non-relativistic

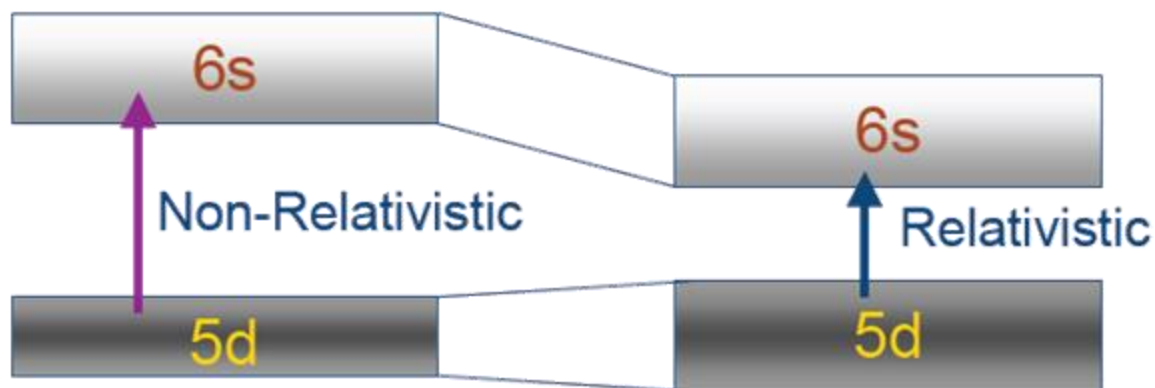


Relativistic

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

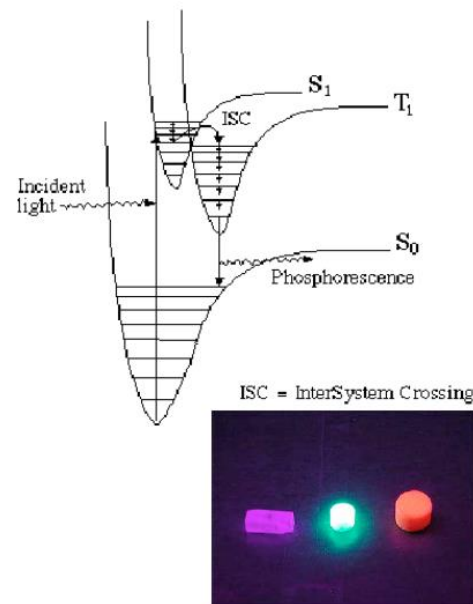
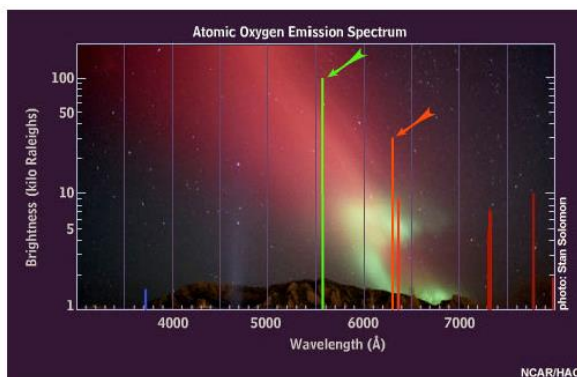
■ Non-relativistic gold has silver color

- ◆ Stabilization of s-band and destabilization d-band shifts absorption via d-s transition from UV to Vis



■ Phosphorescence

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



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

- 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)

basis

U library crenbl_ecp

O library aug-cc-pvdz

end

basis set associated with ECP

ecp

U library crenbl_ecp

end

effective core potential

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

- 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
```

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

relativistic

douglas-kroll on

douglas-kroll dkh

douglas-kroll dk3full

end

Use Douglas-Kroll approximation

Default is Douglas-Kroll-Hess

Third-order Douglas-Kroll

relativistic

zora on

end

zora approximation will be used

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

- 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

■ 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

- 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

- NWChem uses the most common masses for elements

task scf frequencies

freq

reuse

mass hydrogen 2.014101779

mass 3 3.021234

end

task scf frequencies

Reuse Hessian

Change the mass for H to D

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

- 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

Normal mode frequencies output

Normal Eigenvalue Mode [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)!

- Sometimes you get imaginary modes

Normal Eigenvalue Mode [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

- 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
```

- 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

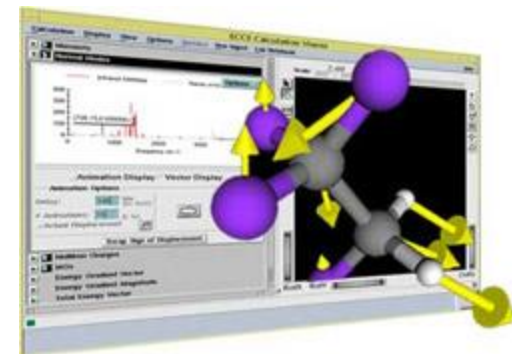
- Translational = 2.979 cal/mol-K

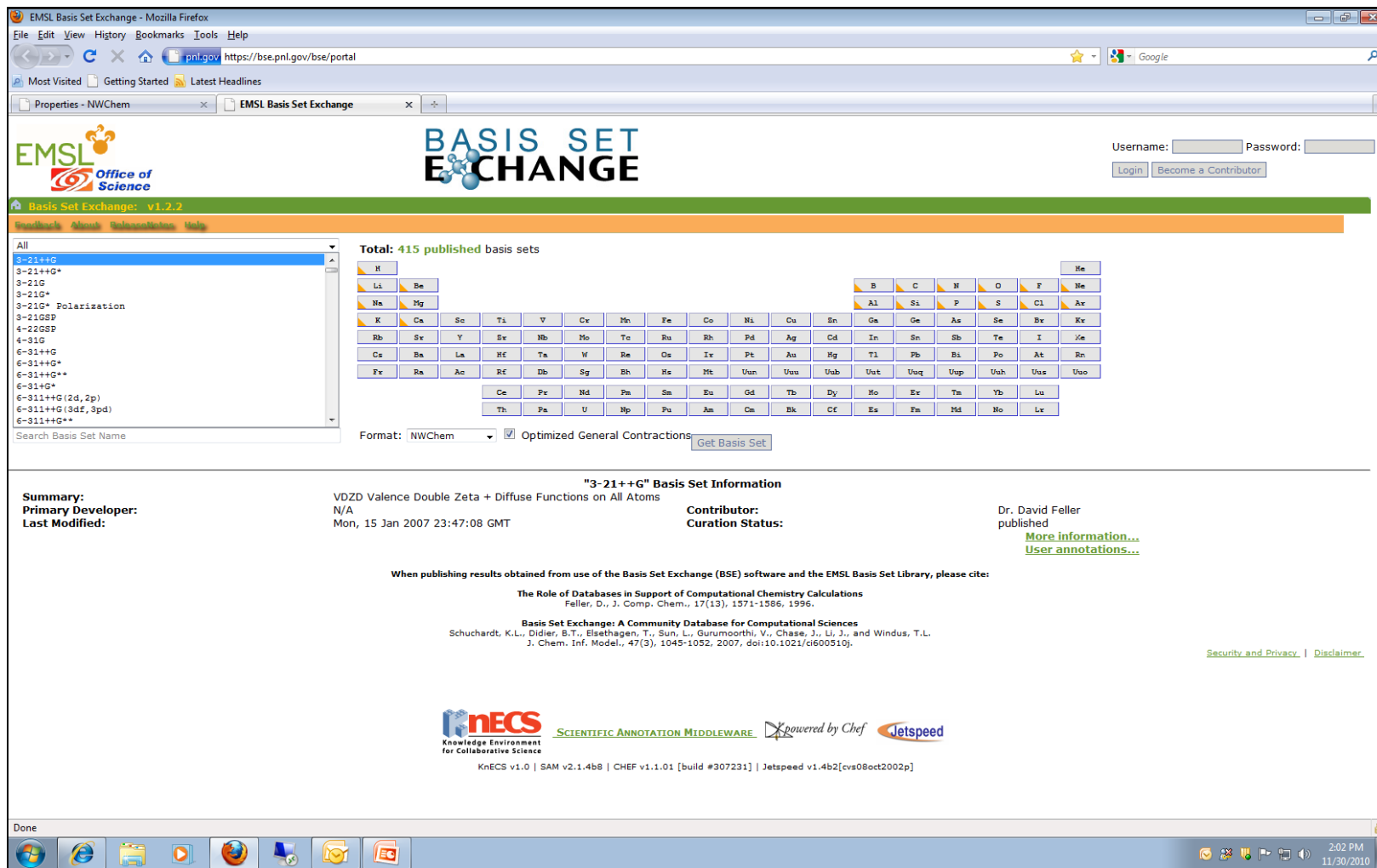
- Rotational = 2.979 cal/mol-K

- Vibrational = 14.026 cal/mol-K

- Note: Different temperature can be set in input

- 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 in Cube format (E.g. Molden, Molekel, Avogadro, VMD, OpenGMol, Gaussview)





EMSL Basis Set Exchange - Mozilla Firefox

File Edit View History Bookmarks Tools Help

pnl.gov https://bse.pnl.gov/bse/portal

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EMSL Office of Science

BASIS SET EXCHANGE

Username: Password:

Login Become a Contributor

Basis Set Exchange: v1.2.2

Feedback About ReleaseNotes Help

All

- 3-21++G
- 3-21+G*
- 3-21G
- 3-21G*
- 3-21G* Polarization
- 3-21GSP
- 4-22GSP
- 4-31G
- 6-31++G
- 6-31+G*
- 6-31+G**
- 6-31+G*
- 6-311++G (2d, 2p)
- 6-311++G (3d, 3pd)
- 6-311++G**

Search Basis Set Name

Total: 415 published basis sets

H	He																
Li	Be	B	C	N	O	F	Ne										
Na	Mg	Al	Si	P	S	Cl	Ar										
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

Format: NWChem Optimized General Contractions [Get Basis Set](#)

"3-21++G" Basis Set Information

Summary: VDZD Valence Double Zeta + Diffuse Functions on All Atoms
Primary Developer: N/A
Last Modified: Mon, 15 Jan 2007 23:47:08 GMT

Contributor: Dr. David Feller
Curation Status: published



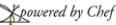

[More information...](#)
[User annotations...](#)

When publishing results obtained from use of the Basis Set Exchange (BSE) software and the EMSL Basis Set Library, please cite:

The Role of Databases in Support of Computational Chemistry Calculations
Feller, D., J. Comp. Chem., 17(13), 1571-1586, 1996.

Basis Set Exchange: A Community Database for Computational Sciences
Schuchardt, K.L., Didier, B.T., Elsethagen, T., Sun, L., Gurumoorthi, V., Chase, J., Li, J., and Windus, T.L.
J. Chem. Inf. Model., 47(3), 1045-1052, 2007, doi:10.1021/ci600510j.

[Security and Privacy](#) | [Disclaimer](#)

KnECS v1.0 | SAM v2.1.4b8 | CHEF v1.1.01 [build #307231] | Jetspeed v1.4b2[cvs08oct2002p]

Done

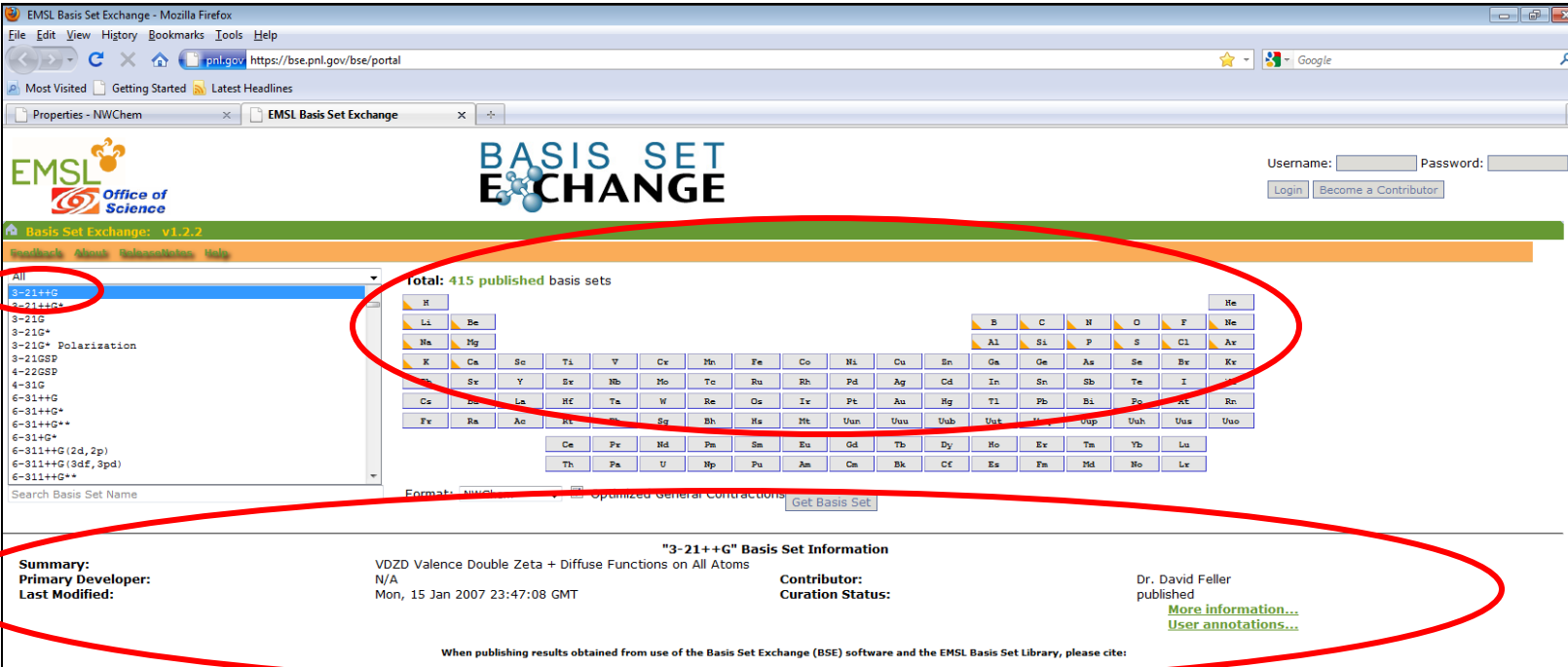
2:02 PM
11/30/2010

<https://bse.pnl.gov/>

- 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



The screenshot shows the EMSL Basis Set Exchange portal. A red circle highlights the '3-21++G' basis set selected in the dropdown menu. Another red circle highlights the periodic table of elements, which is color-coded to show which elements are covered by the selected basis set. A third red circle highlights the 'Summary' section for the '3-21++G' basis set, which includes the primary developer (Dr. David Feller), the last modified date (Mon, 15 Jan 2007 23:47:08 GMT), and the contributor (N/A). The summary also includes a 'Curation Status' and a note about citing the software and library.

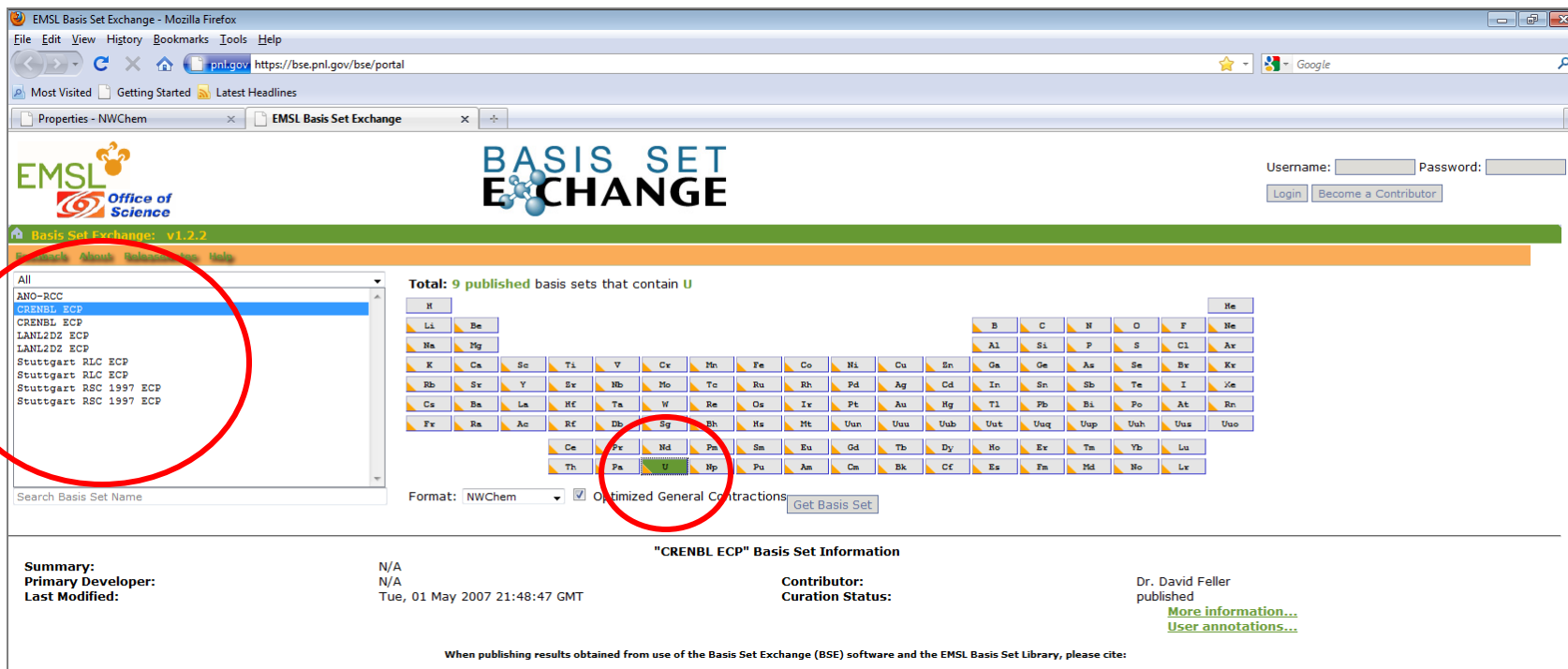
Summary:
Primary Developer: Dr. David Feller published
Last Modified: Mon, 15 Jan 2007 23:47:08 GMT
Contributor: N/A
Curation Status: published

[More information...](#)
[User annotations...](#)

When publishing results obtained from use of the Basis Set Exchange (BSE) software and the EMSL Basis Set Library, please cite:

- 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



The screenshot shows the EMSL Basis Set Exchange website. The browser address bar displays <https://bse.pnl.gov/bse/portal>. The page header includes the EMSL Office of Science logo and the text "BASIS SET EXCHANGE". A search bar on the left is circled in red, containing a list of basis sets: ANO-RCC, CRENL ECP, LANL2DZ ECP, Stuttgart RLC ECP, Stuttgart RSC 1997 ECP, and Stuttgart RSC 1997 ECP. The main content area shows a periodic table with the element Sg circled in red. Below the periodic table, the text "Total: 9 published basis sets that contain U" is visible. A search bar at the bottom left contains the text "Search Basis Set Name".

Summary:
Primary Developer: N/A
Last Modified: N/A Tue, 01 May 2007 21:48:47 GMT

"CRENL ECP" Basis Set Information
Contributor: Dr. David Feller published
Curation Status: [More information...](#)
[User annotations...](#)

When publishing results obtained from use of the Basis Set Exchange (BSE) software and the EMSL Basis Set Library, please cite:

■ Select an element

◆ And find the basis sets available for this element

Getting a basis set from the Exchange

The screenshot shows the EMSL Basis Set Exchange website. The search results for 'CRENLB ECP' are displayed, showing 9 published basis sets. The 'Format' dropdown menu is set to 'NWChem'. The 'Get Basis Set' button is highlighted. The 'CRENLB ECP' basis set is selected in the list.

EMSL Office of Science

BASIS SET EXCHANGE v1.2.2

Feedback Admin Database/Status Help

All

- ANO-RCC
- CRENLB ECP**
- CRENLB ECP
- LANL2DZ ECP
- LANL2DZ ECP
- Stuttgart RLC ECP
- Stuttgart RLC ECP
- Stuttgart RSC 1997 ECP
- Stuttgart RSC 1997 ECP

Total: 9 published basis sets that contain U

Format: NWChem Optimized General Contractions

"CRENLB ECP" Basis Set Information

Summary:	N/A	Contributor:	
Primary Developer:	N/A	Curation Status:	
Last Modified:	Tue, 01 May 2007 21:48:47 GMT		

When publishing results obtained from use of the Basis Set Exchange (BSE) software

The screenshot shows the Basis Set Exchange v1.2.2 interface. The output of the 'Get Basis Set' action is displayed, showing the basis set name, the number of elements, and the basis set definition. The output is as follows:

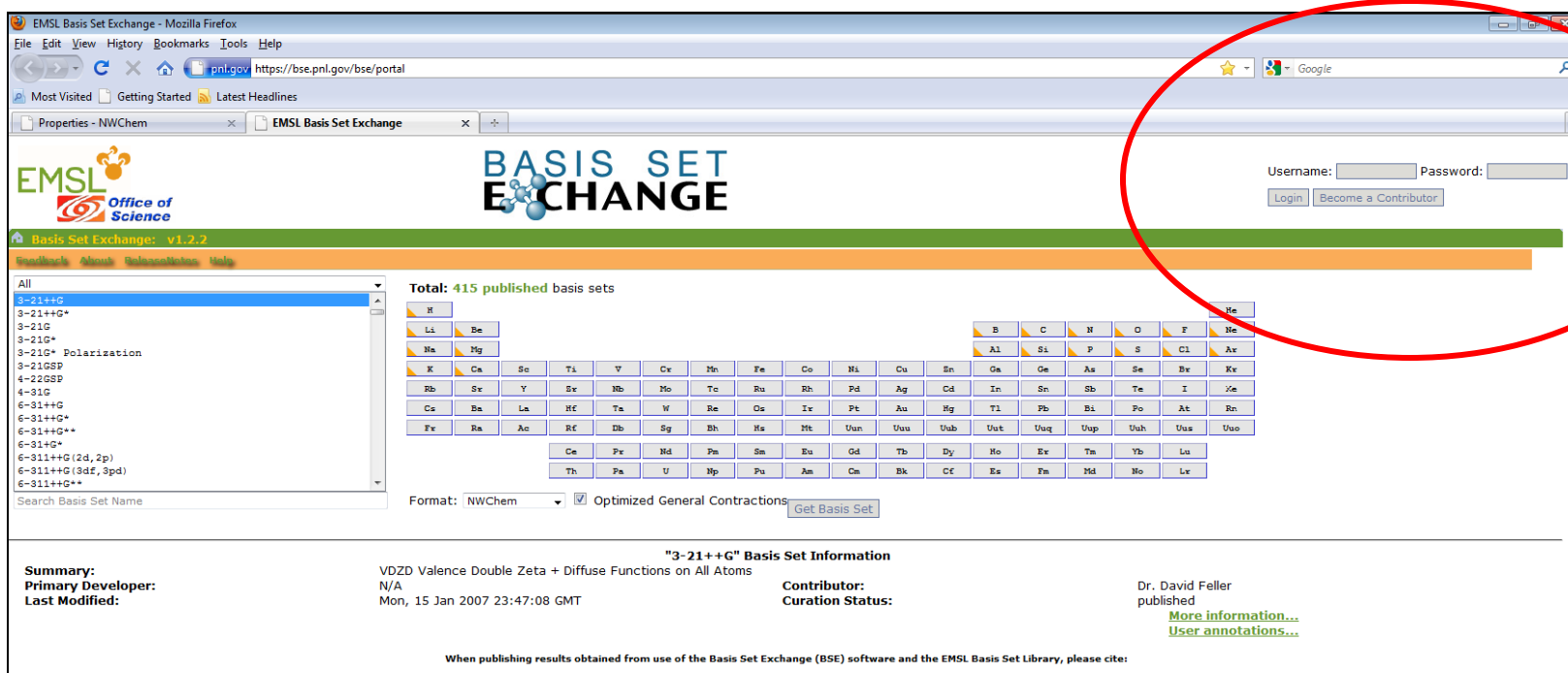
```
# CRENLB ECP EMSL Basis Set Exchange Library 11/30/10 2:44 PM
# ELEMENTS REFERENCES
# -----
#
END
ECP
U nelec 78
U ul
2 1 22290003 -0.95164698
2 2 67100000 -10.77463818
2 6 10900021 -33.54887009
2 17 91930008 -122.39160919
2 49 88119888 -256.04879761
2 169 55189514 -721.33471680
1 605 90167236 -75.18030548
U S
2 2 08200002 86.94699860
2 2 36159992 -324.48245239
2 3 04959989 754.80963135
2 4 28889990 -931.61145020
2 6 36810017 867.38934326
2 9 73639965 -567.78674316
2 15 35929966 467.56951904
1 43 85210037 87.23509216
0 131 51210022 6.00922394
U P
2 1 55610001 109.52915955
2 1 77209997 -372.34240723
2 2 25839996 760.67779541
2 3 09450006 -945.12261963
2 4 51030016 906.44946289
2 6 71129990 -618.62194824
2 10 01770020 434.29833984
1 28 29829979 96.91146851
0 89 10600281 8.63370800
```

Done

- 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



The screenshot shows the EMSL Basis Set Exchange website. The top navigation bar includes the EMSL logo and the text "Basis Set Exchange". A search bar and a "Get Basis Set" button are visible. A list of basis sets is shown on the left, with "3-21++G" selected. The main content area displays a periodic table and a detailed view of the "3-21++G" basis set information.

3-21++G Basis Set Information

Summary:	VDZD Valence Double Zeta + Diffuse Functions on All Atoms	Contributor:	Dr. David Feller
Primary Developer:	N/A	Curation Status:	published
Last Modified:	Mon, 15 Jan 2007 23:47:08 GMT		More information... User annotations...

When publishing results obtained from use of the Basis Set Exchange (BSE) software and the EMSL Basis Set Library, please cite:

Questions?

Community forum: www.nwchem-sw.org

