

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

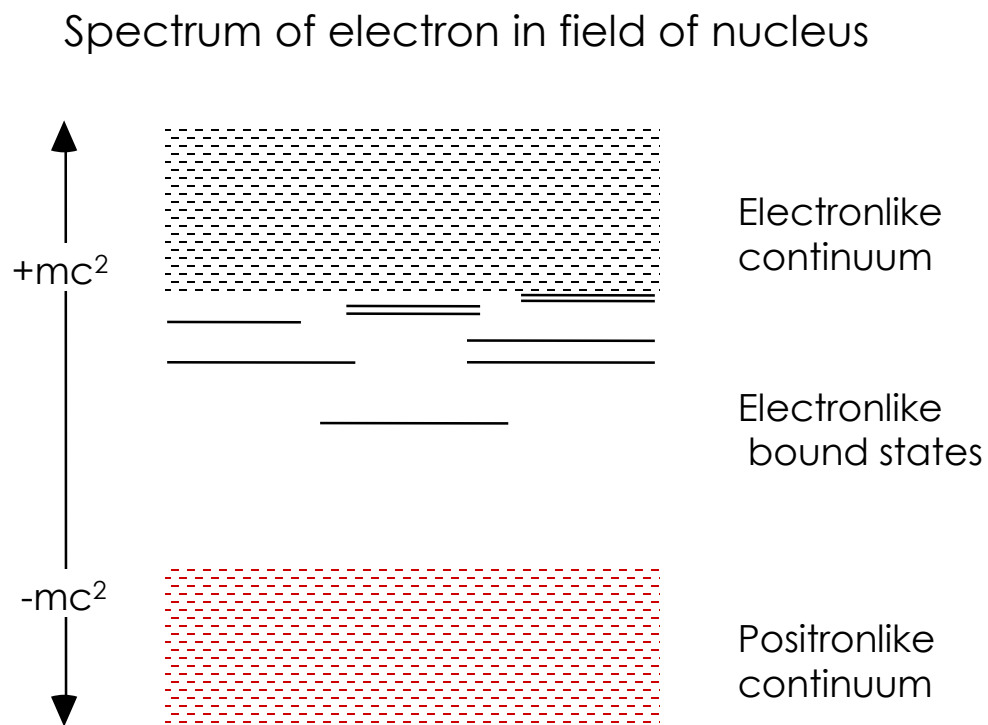
- Dirac Hamiltonian instead of Schrödinger Hamiltonian
 - ◆ Includes description of positron states

$$\left(\begin{array}{cc} V & c \sigma \cdot p \\ c \sigma \cdot p & V - 2mc^2 \end{array} \right) \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = \varepsilon \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix}$$

h_i^D

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

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

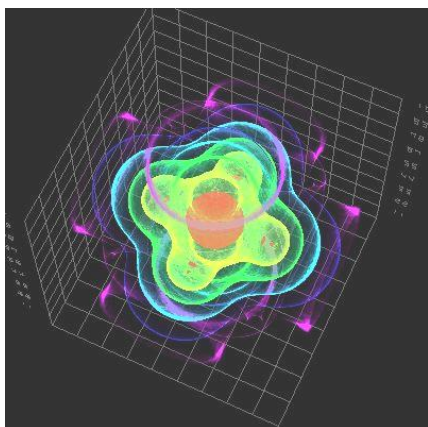


■ Scalar relativistic

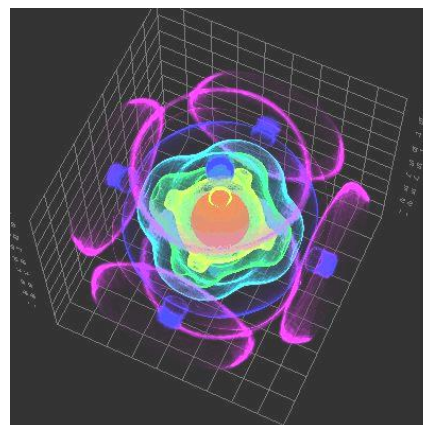
- ◆ Contraction and stabilization of s- and p-type orbitals
- ◆ Expansion and destabilization of d- and f-type orbitals

■ Spin-orbit splitting

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



Non-relativistic

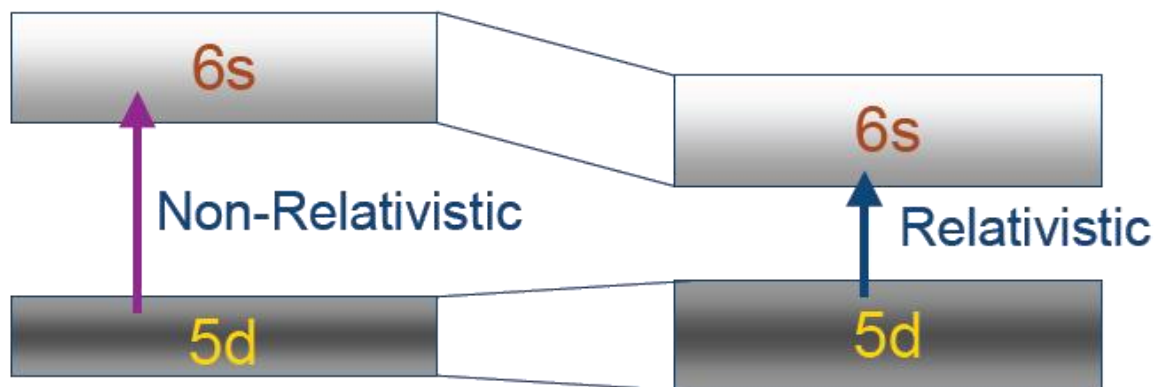


Relativistic

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

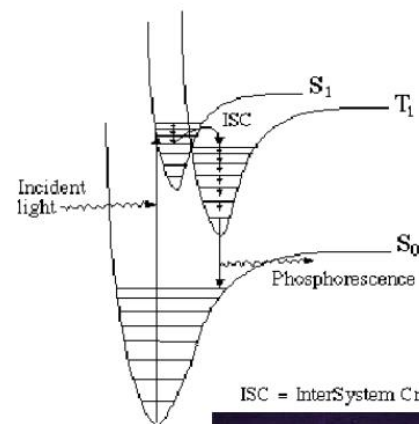
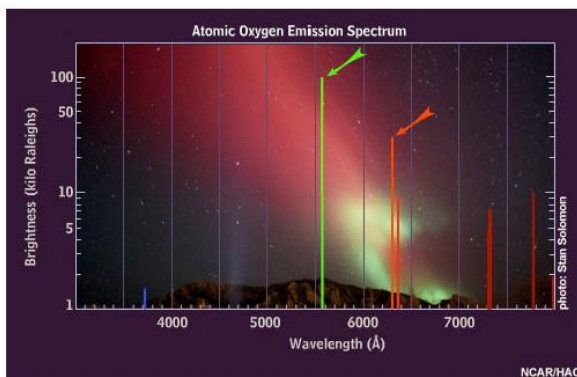
■ Non-relativistic gold has silver color

- ◆ 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

EMSL's Basis Set Exchange



EMSL Basis Set Exchange - Mozilla Firefox
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pnl.gov https://bse.pnl.gov/bse/portal
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Properties - NWChem EMSL Basis Set Exchange

EMSL Office of Science

BASIS SET EXCHANGE

Username: Password:

Basis Set Exchange: v1.2.7
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All
3-21++G
3-21++G*
3-21G
3-21G*
3-21G* Polarization
3-21GSP
4-31G
4-31G*
6-31++G
6-31++G*
6-31++G**
6-31+G
6-311++G (2d, 2p)
6-311++G (3d,f, 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

"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.

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

https://bse.pnl.gov/

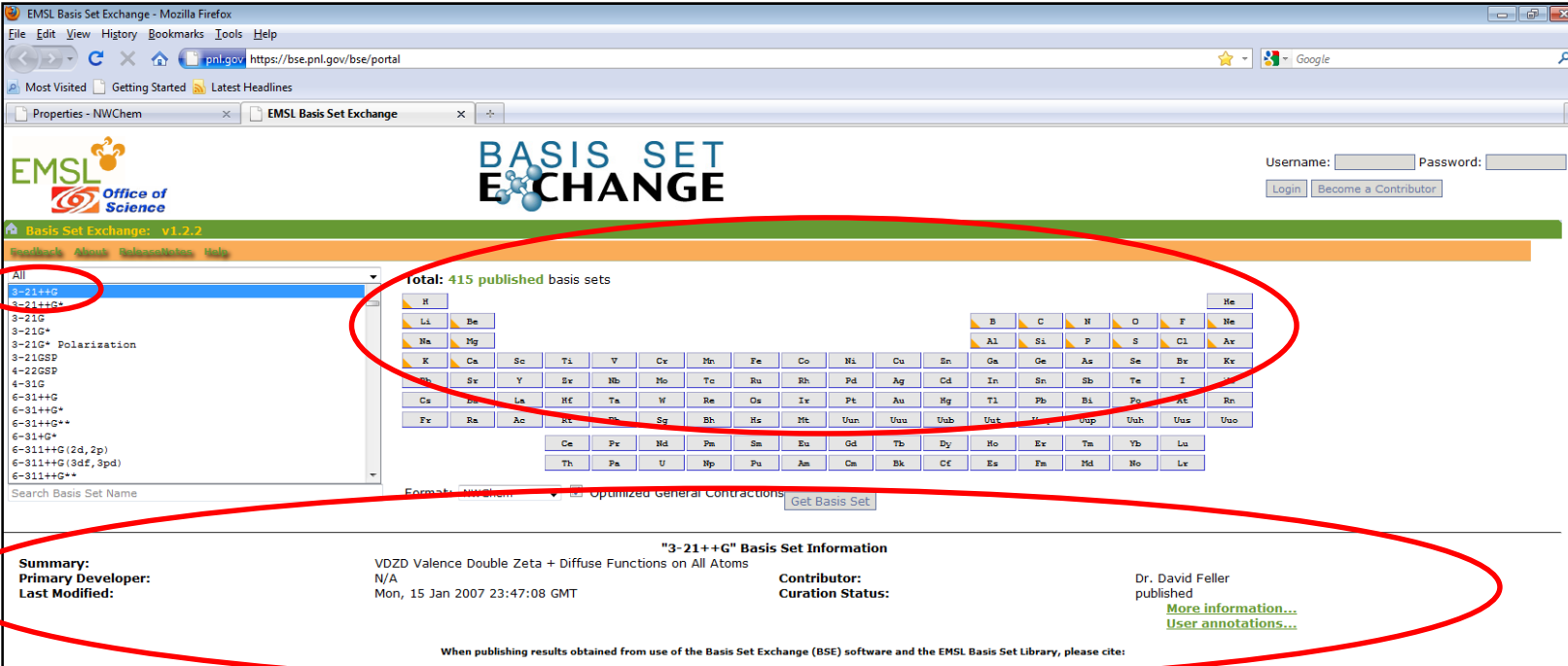


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- Basis Set Exchange is comprehensive online library containing Gaussian basis sets
 - ◆ Anyone can download basis sets in the format they want
 - Supporting formats other than NWChem
 - ◆ Anyone can contribute basis sets they have developed
 - Only 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 (BSE) portal. A dropdown menu on the left is set to "3-21++G". The main content area displays a periodic table where elements covered by this basis set are highlighted in blue. A summary section at the bottom provides details for the "3-21++G" basis set, including its primary developer (N/A), contributor (Dr. David Feller), and curation status (published).

Summary:
Primary Developer: N/A
Last Modified: Mon, 15 Jan 2007 23:47:08 GMT

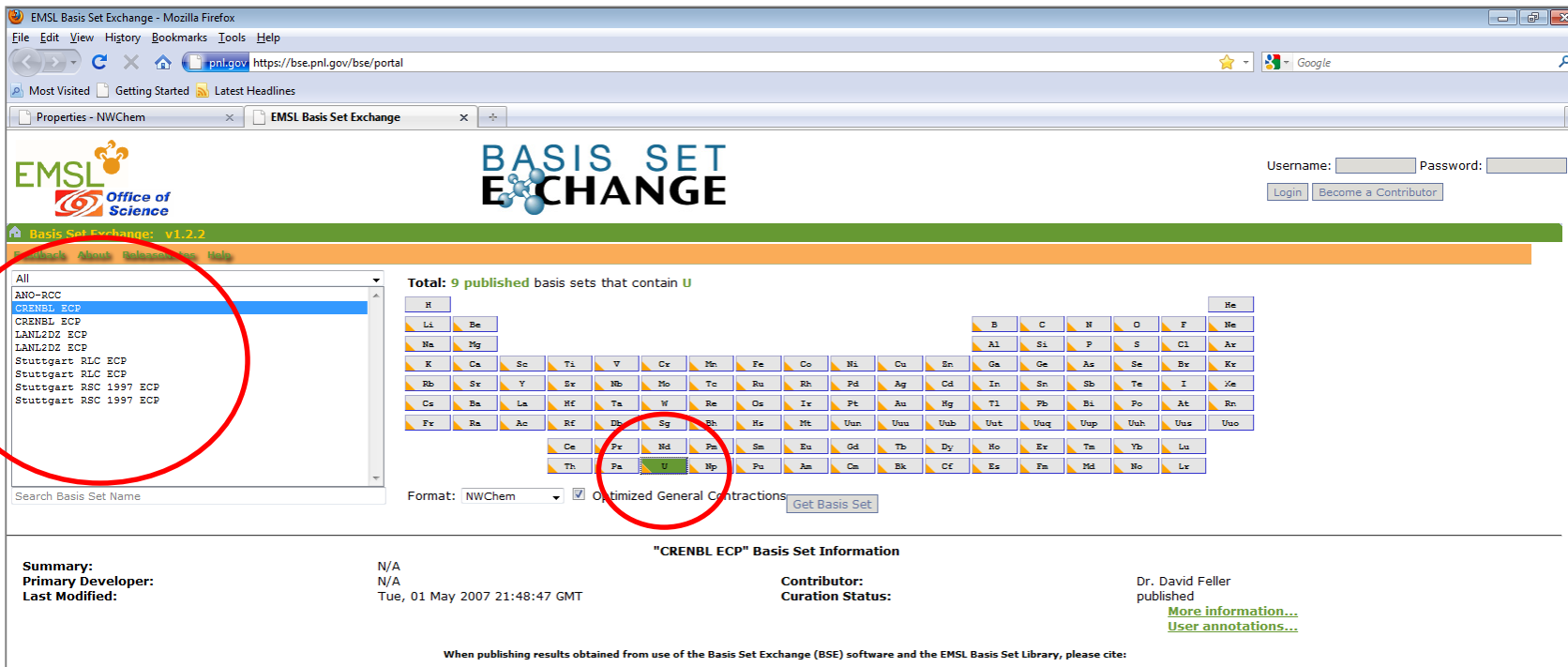
"3-21++G" Basis Set Information
VDZD Valence Double Zeta + Diffuse Functions on All Atoms
Contributor: Dr. David Feller published
Curation Status: published

[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. A search for 'U' (Uranium) is performed, resulting in 9 published basis sets. The element 'U' is highlighted in the periodic table, and the search results list includes 'CRENBL ECP' and 'LANL2DZ ECP'. The 'CRENBL ECP' basis set is selected, and its information is displayed below.

EMSL Office of Science

BASIS SET EXCHANGE

Username: Password:
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Basis Set Exchange: v1.2.2

Feedback About Releases Help

All
ANO-RCC
CRENBL ECP
CRENBL 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 [Get Basis Set](#)

"CRENBL ECP" Basis Set Information

Summary:	N/A	Contributor:	Dr. David Feller
Primary Developer:	N/A	Curator Status:	published
Last Modified:	Tue, 01 May 2007 21:48:47 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:

■ 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 a total of 9 published basis sets. The 'Format' dropdown menu is set to 'NWChem'. The 'Get Basis Set' button is highlighted. The summary information for the selected basis set is shown below the search results.

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

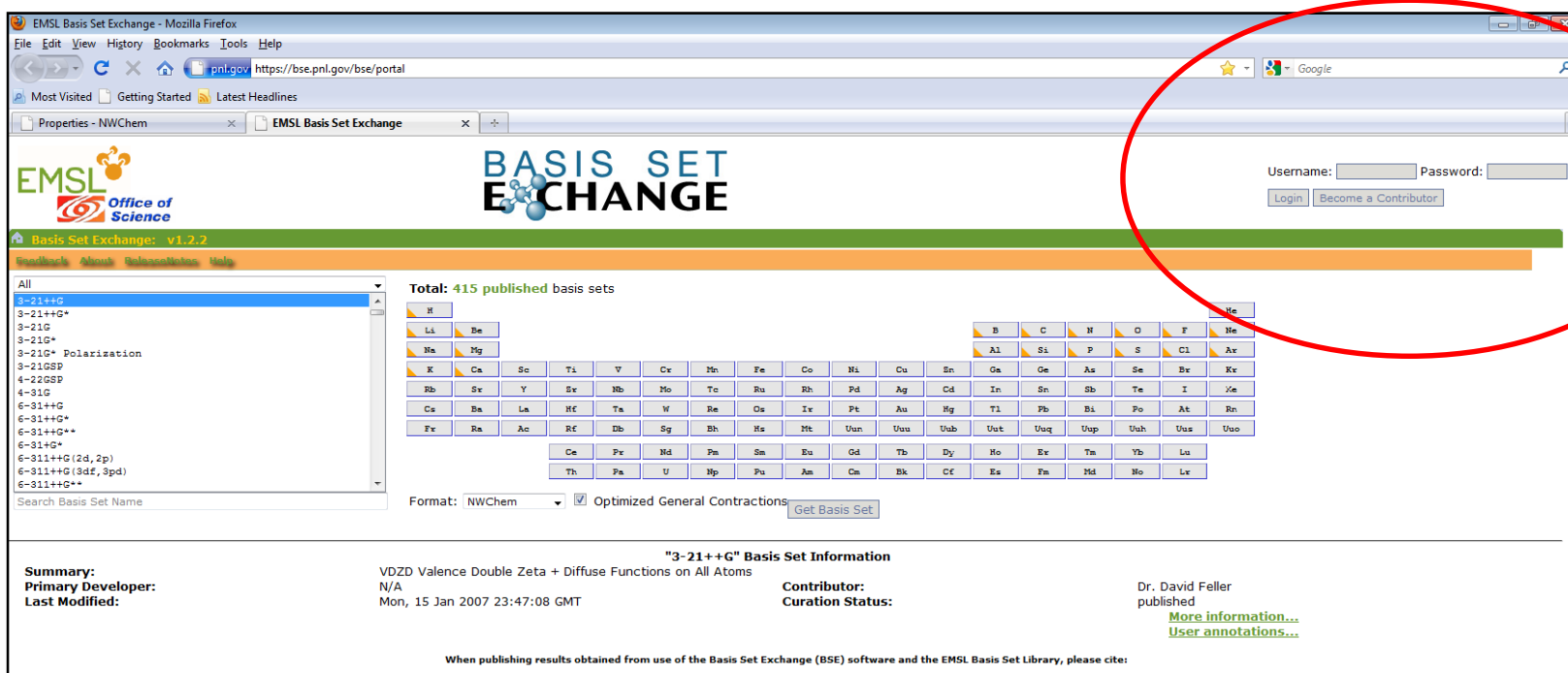
The screenshot shows the Basis Set Exchange v1.2.2 interface. The output of the 'Get Basis Set' action is displayed, showing the basis set name, the number of elements, and the basis set definition. The output is as follows:

```
# 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
```

- 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 in a Mozilla Firefox browser. The URL is <https://bse.pnl.gov/bse/portal>. The page features the EMSL Office of Science logo and the 'BASIS SET EXCHANGE' title. A search bar on the left contains '3-21++G'. The main content area displays 'Total: 415 published basis sets' and a periodic table with highlighted elements corresponding to the search criteria. A red circle highlights the login and registration area on the right side of the page.

Username: Password:

"3-21++G" Basis Set Information

Summary:	VDZD Valence Double Zeta + Diffuse Functions on All Atoms	Contributor:	Dr. David Feller
Primary Developer:	N/A	Curator 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

