



Relativity, Spectroscopy and the EMSL Basis Set Library



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- Relativity
 - ◆ Intro into relativistic effects
 - ◆ Capabilities in NWChem to handle relativity

- Spectroscopy
 - ◆ NMR properties
 - ◆ Vibrational frequencies

- EMSL Basis Set Library

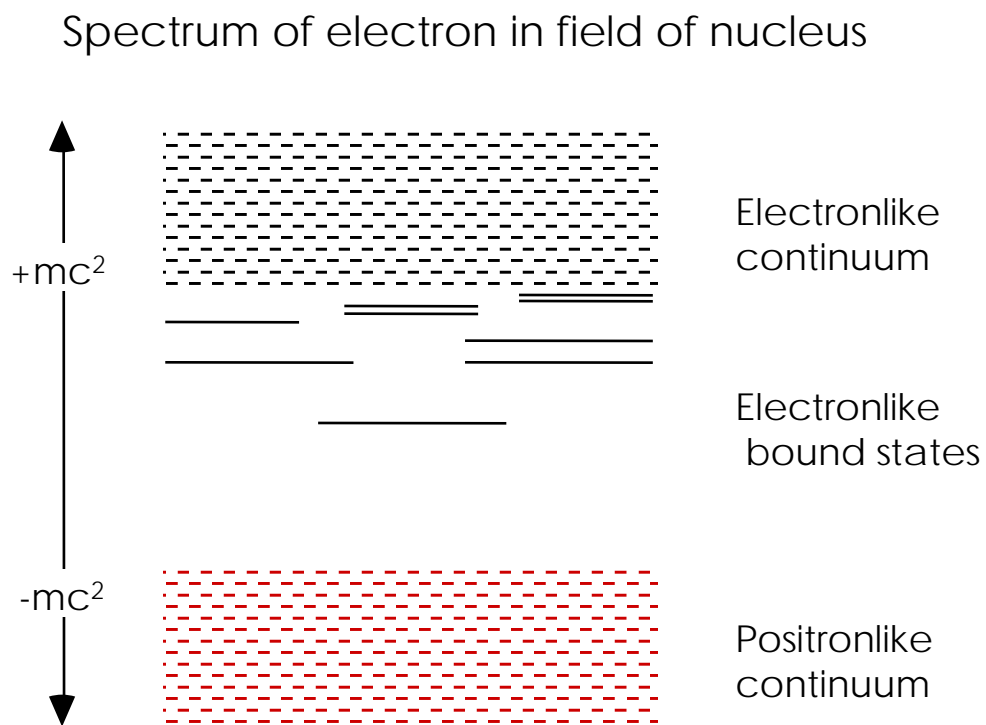
- Dirac Hamiltonian instead of Schrödinger Hamiltonian
 - ◆ Includes description of positron states

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

h_i^D

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

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

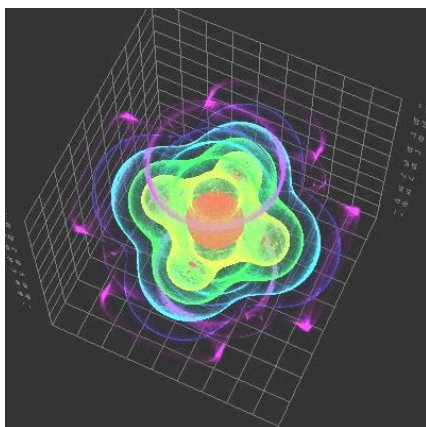


■ Scalar relativistic

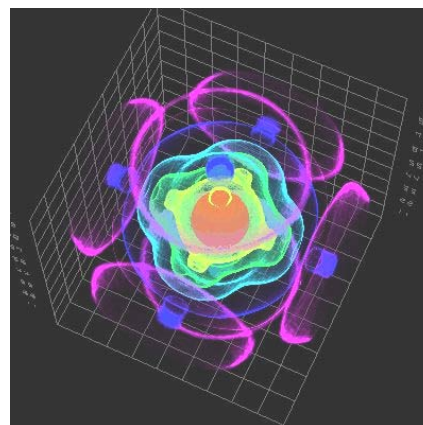
- ◆ Contraction and stabilization of s- and p-type orbitals
- ◆ Expansion and destabilization of d- and f-type orbitals

■ Spin-orbit splitting

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



Non-relativistic

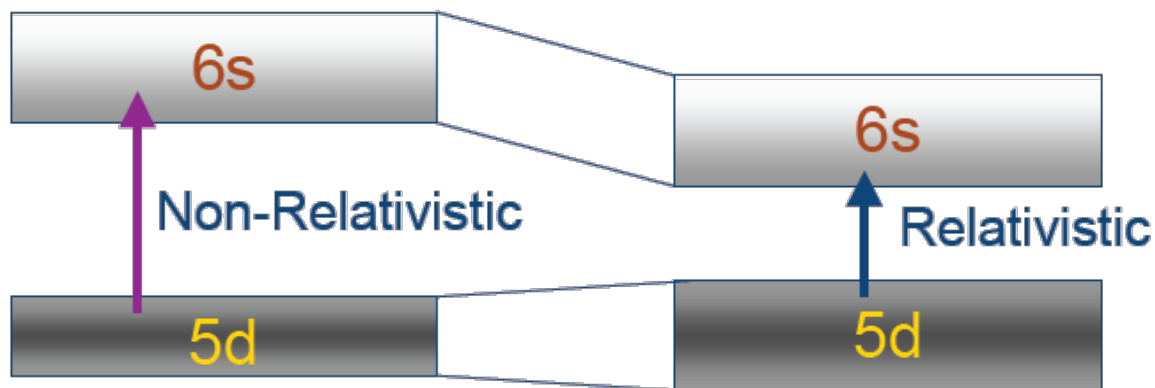


Relativistic

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

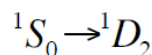
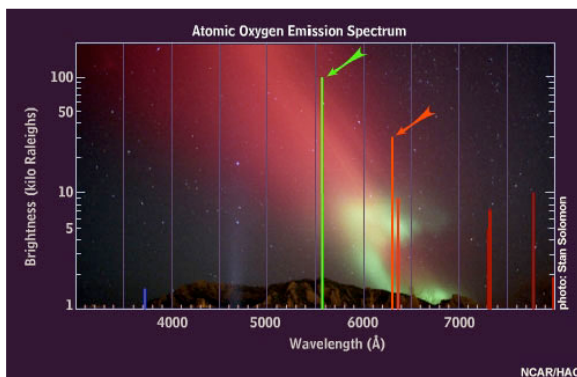
■ Non-relativistic gold has silver color

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

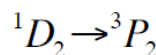


■ Phosphorescence

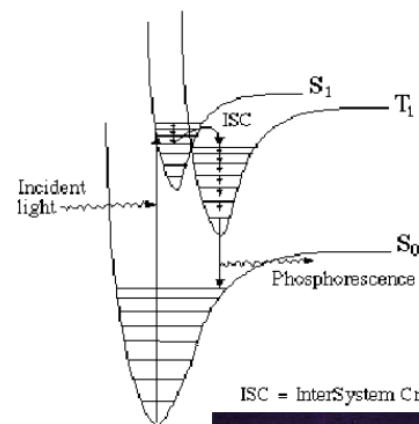
- ◆ Singlet-triplet transitions and surface crossings are allowed due to spin-orbit coupling, i.e. spin is not a good quantum number



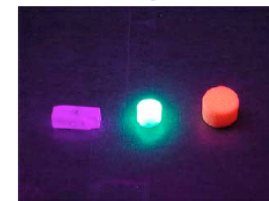
Lifetime 0.75 s



Lifetime 110 s



ISC = InterSystem Crossing



- ◆ 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          # 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"

$\Delta U_l = \frac{\hbar^2}{2I + 1} \Delta U_l$

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

- 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

- 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

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

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

- 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
```

- 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

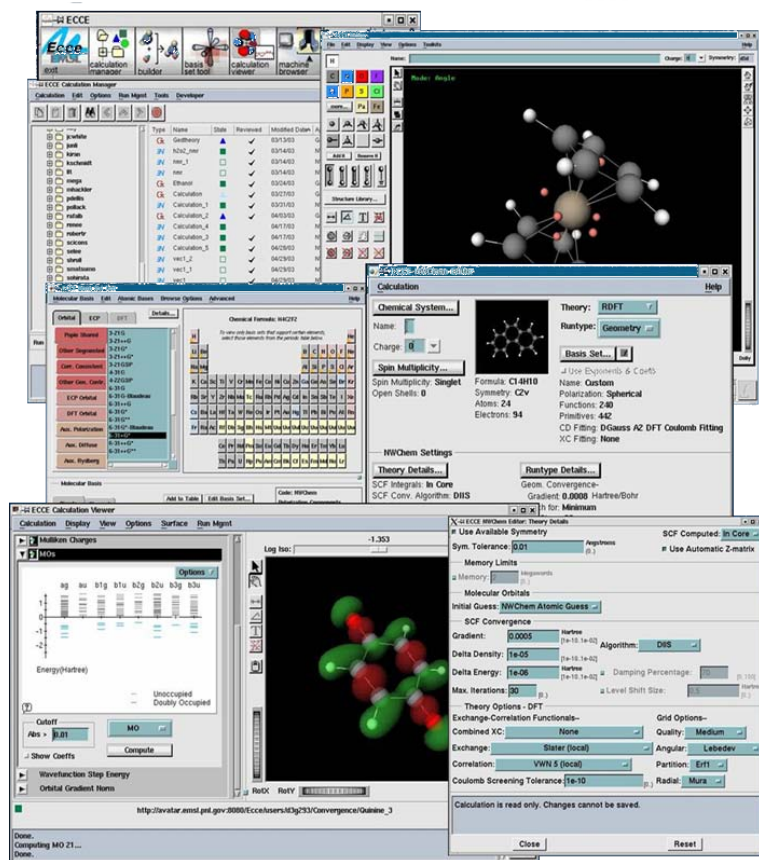
Maximum component (any atom: x,y, or z) displacement: 0.159

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

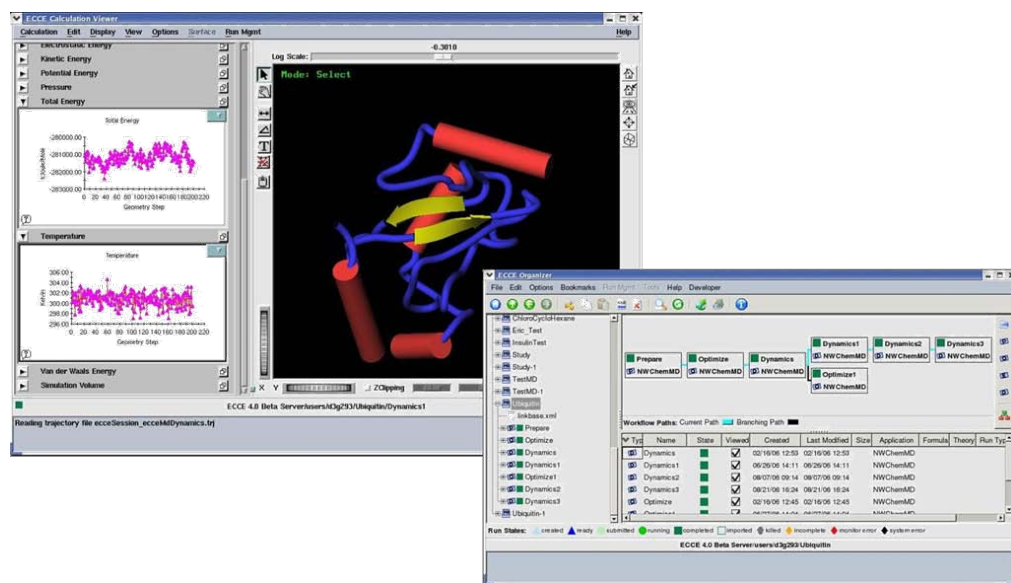
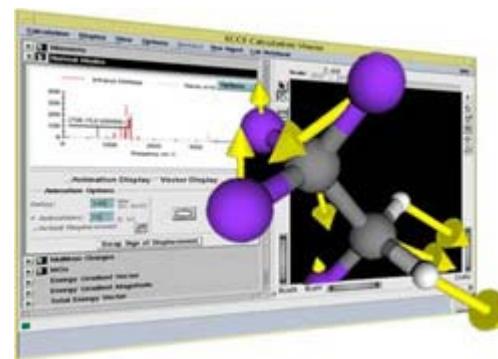
- Note: do not use raw step!

Visualizing normal modes

ECCE can be used to visualize normal modes



The screenshot shows the ECCE Calculation Manager interface. It features a tree view on the left with categories like 'Calculations', 'Molecular Models', and 'Molecular Orbitals'. The main window displays a 3D ball-and-stick model of a molecule. Below the model, there are several panels: 'Molecular Model' with 'Molecular Formula: H16C22', 'Molecular Weight: 240.32', and 'Molecular Weight: 240.32'; 'Molecular Orbitals' with a table of orbitals; and 'Molecular Orbitals' with a table of orbitals. The interface is complex and contains many buttons and options.



The screenshot shows two windows from the ECCE software. The 'ECCE Calculation Viewer' window displays energy profiles for 'Kinetic Energy', 'Potential Energy', 'Pressure', and 'Total Energy' over a 'Geometry Step'. The 'ECCE Organizer' window shows a workflow path with steps like 'Prepare', 'Optimize', 'Dynamics', and 'TestMD'. It also includes a table of workflow steps with columns for Name, State, Viewed, Created, Last Modified, Size, Application, Formula, Theory, Run, and Type.

- 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
File Edit View History Bookmarks Tools Help
pnl.gov https://bse.pnl.gov/bse/portal
Most Visited Getting Started Latest Headlines
Properties - NWChem EMSL Basis Set Exchange

EMSL Office of Science

BASIS SET EXCHANGE

Username: Password:

Basis Set Exchange: v1.2.7
[Feedback](#) [About](#) [ReleaseNotes](#) [Help](#)

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 (3df, 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	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:

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

https://bse.pnl.gov/

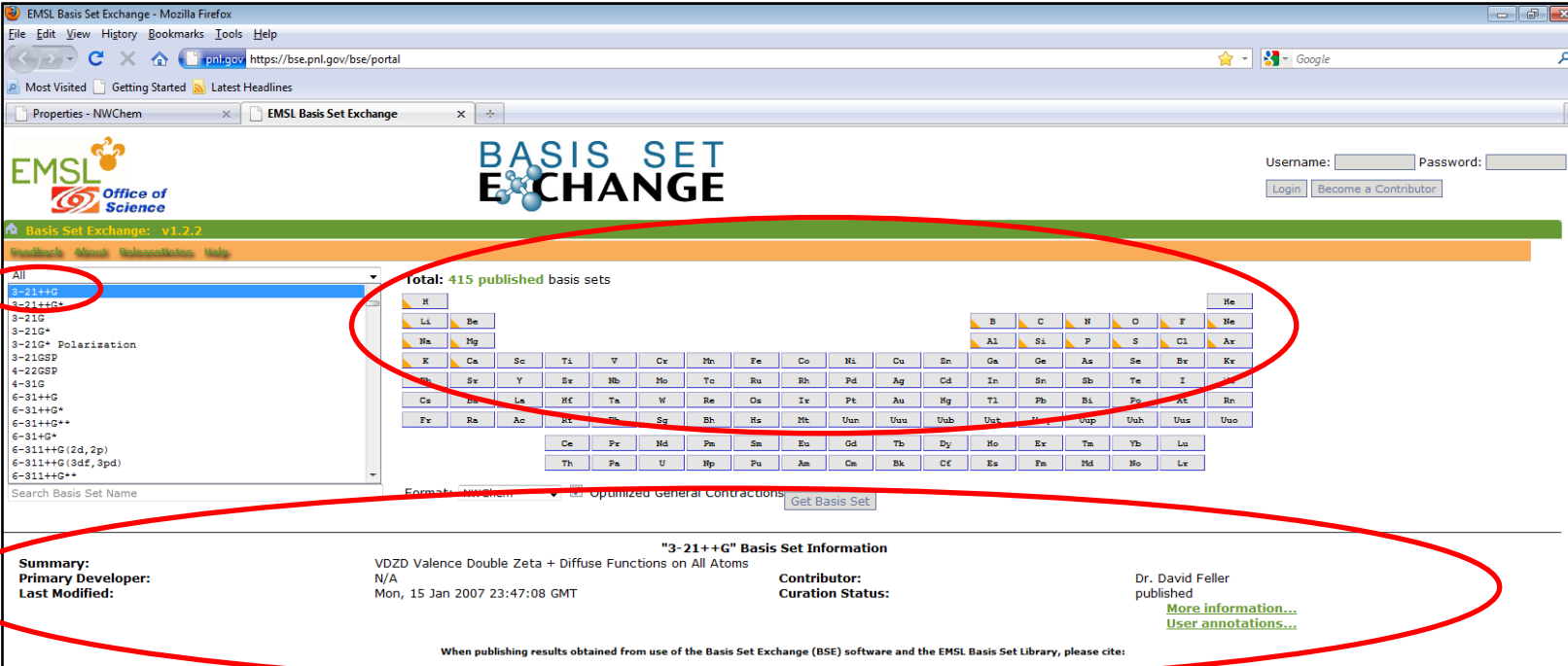


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- Basis Set Exchange is comprehensive online library containing Gaussian basis sets
 - ◆ Anyone can download basis sets in the format they want
 - Supporting formats other than NWChem
 - ◆ Anyone can contribute basis sets they have developed
 - Only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



The screenshot shows the EMSL Basis Set Exchange website. The browser address bar displays <https://bse.pnl.gov/bse/portal>. The page title is "Basis Set Exchange" and the version is "v1.2.2". A search bar on the left shows "3-21++G" selected. The main content area displays "Total: 415 published basis sets" and a periodic table where elements covered by the selected basis set are highlighted in red. The 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

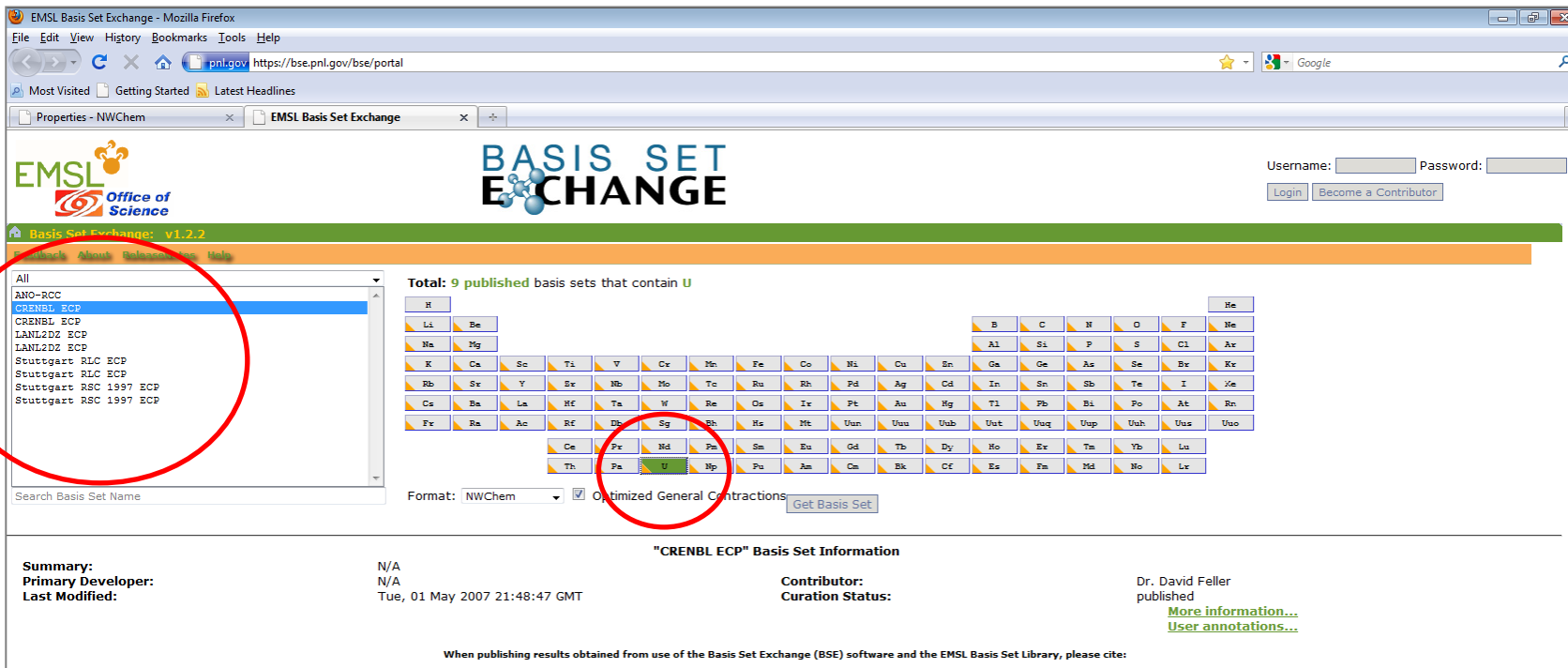
"3-21++G" Basis Set Information
VDZD Valence Double Zeta + Diffuse Functions on All Atoms
Contributor: Dr. David Feller
Curation Status: published

[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 search results for 'CRENBL ECP' are listed on the left, with 'CRENBL ECP' selected. The periodic table shows 'U' (Uranium) highlighted. The search results are as follows:

Search Basis Set Name
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 with a red circle. The 'CRENLB ECP' basis set is selected in the list.

EMSL Office of Science

BASIS SET EXCHANGE v1.2.2

Feedback Admin Database Help

Basic Set Exchange: v1.2.2

All

- ANO-RCC
- CRENLB ECP**
- CRENLB ECP
- LANL2D2 ECP
- LANL2D2 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](#)

"CRENLB ECP" Basis Set Inform

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

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

The screenshot shows the Basis Set: CRENLB ECP - Mozilla Firefox window. The page displays the basis set data for 'CRENLB ECP' in the EMSL Basis Set Exchange Library. The data is presented as a table with columns for the basis set name, the number of elements, and the number of references. The basis set is defined by the following elements and their corresponding basis functions:

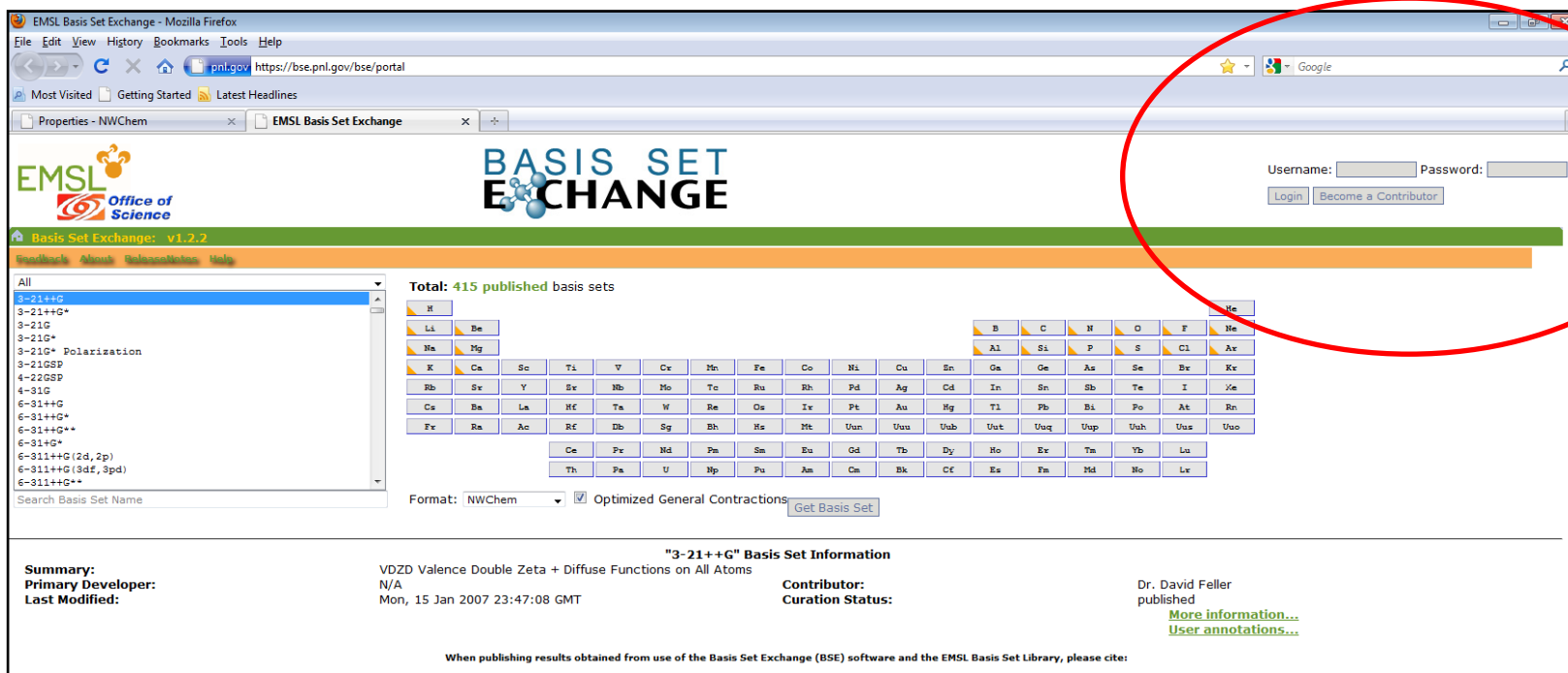
```
# CRENLB ECP EMSL Basis Set Exchange Library 11/30/10 2:44 PM
# ELEMENTS REFERENCES
# -----
#
END
ECP
U nelec 78
U ul
2 1.22290003 -0.95164698
2 2.67100000 -10.77463818
2 6.10900021 -33.54887009
2 17.91930008 -122.39160919
2 49.88119888 -256.04879761
2 169.55189514 -721.33471680
1 605.90167236 -75.18030548
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 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 red circle highlights the login area, which includes fields for "Username:" and "Password:", along with "Login" and "Become a Contributor" buttons. Below the header, there is a navigation bar with links for "Feedback", "About", "ReleaseNotes", and "Help". The main content area displays a list of basis sets on the left, a periodic table in the center, and a search bar at the bottom. The periodic table is color-coded by groups. The search bar contains the text "3-21++G" and a "Get Basis Set" button. Below the periodic table, there is a section titled "3-21++G" Basis Set Information, which includes a summary, primary developer, last modified date, contributor, and curation status. A disclaimer at the bottom states: "When publishing results obtained from use of the Basis Set Exchange (BSE) software and the EMSL Basis Set Library, please cite:"

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 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:

Questions?

