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

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

Spectrum of electron in field of nucleus

- Electronlike continuum
- Electronlike bound states
- Positronlike continuum

\[
\hat{H} = \sum_{i} h_i^D + \frac{1}{2} \sum_{i \neq j} \left( \frac{1}{r_{ij}} - \frac{(\alpha_i \cdot \alpha_j)}{r_{ij}} \right)
\]
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
Electron density plot of the $7\gamma_{6g}$ spinor in UF$_6$

Relativistic
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

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

\[ ^1S_0 \rightarrow ^1D_2 \quad ^1D_2 \rightarrow ^3P_2 \]

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
  O library aug-cc-pvdz
end

ecp
  U library crenbl_ecp
end

task dft optimize
```

- **Note**: use DFT instead of TDDFT for calculations without spin-orbit coupling
Manual input scalar ECP

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>30.7220233</td>
<td>-16.49630500</td>
<td></td>
<td></td>
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</tbody>
</table>

# ecp replaces 2 electrons on O

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

```plaintext
relativistic
do Douglas-Kroll on
relativistic
do Douglas-Kroll dkh
relativistic
do Douglas-Kroll dk3full
end
```

- ZORA approximation will be used:

```plaintext
relativistic
zora on
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**

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

**Response properties**

```plaintext
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 ($\delta$) 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.
Calculating vibrational frequencies

First optimize your molecule’s geometry!!!!

```plaintext
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.

```plaintext
task scf frequencies

freq
  reuse
  mass hydrogen 2.014101779
  mass 3 3.021234
end

# Reuse Hessian
# Change the mass for H to D

task scf frequencies
```

NWChem only calculates IR intensities.

- Raman intensities are coming soon.
NWC hem prints out two sets of frequencies
- Raw normal modes
- Projected normal modes with translations and rotations projected out
- Use the projected normal modes!

<table>
<thead>
<tr>
<th></th>
<th>P.Frequency</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
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<td>0.12020</td>
<td>-0.07402</td>
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<td>-0.00799</td>
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<tr>
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<td>0.20350</td>
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<td>-0.02448</td>
<td>-0.00288</td>
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<tr>
<td>3</td>
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<td>0.10368</td>
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<tr>
<td>4</td>
<td>0.00596</td>
<td>-0.00529</td>
<td>0.11985</td>
<td>-0.06716</td>
<td>0.00152</td>
<td>-0.00732</td>
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<td>5</td>
<td>-0.03405</td>
<td>0.13917</td>
<td>-0.00045</td>
<td>-0.00078</td>
<td>0.07045</td>
<td>-0.00172</td>
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Normal mode frequencies output

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

Note: Three rotational and translational modes are zero (projected out)!
Sometimes you get imaginary modes

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

task scf saddle
```

# follow first imaginary mode
# search along internal variable 4
# search along normal mode 1
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

---

<table>
<thead>
<tr>
<th>Negative Nuclear Hessian Mode</th>
<th>1</th>
<th>Eigenvalue = (-21.49) cm**((-1))</th>
</tr>
</thead>
</table>

Geometry after 100.0% step for mode 1; Step length = 0.253 angstroms
Maximum component (any atom: x, y, or z) displacement: 0.159

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 U</td>
<td>92.000</td>
<td>0.08537830</td>
<td>0.05333786</td>
</tr>
<tr>
<td>2 O</td>
<td>8.0000</td>
<td>-0.25738246</td>
<td>1.78398570</td>
</tr>
<tr>
<td>3 O</td>
<td>8.0000</td>
<td>0.45360974</td>
<td>-1.67855648</td>
</tr>
<tr>
<td>4 O</td>
<td>8.0000</td>
<td>-2.27645631</td>
<td>-0.41108121</td>
</tr>
<tr>
<td>5 O</td>
<td>8.0000</td>
<td>-0.28916140</td>
<td>-0.09890107</td>
</tr>
<tr>
<td>6 O</td>
<td>8.0000</td>
<td>2.43515585</td>
<td>0.36500624</td>
</tr>
<tr>
<td>7 C</td>
<td>6.0000</td>
<td>-3.04960523</td>
<td>-0.53147913</td>
</tr>
</tbody>
</table>

Note: do not use raw step!
ECCE can be used to visualize normal modes.
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.
https://bse.pnl.gov/
Basis Set Exchange is a 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, and 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 a source for NWChem basis set library.
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
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 basis in
- Click “Get Basis Set”
You can add basis sets you have developed to the exchange for download by others

Get an account and start adding
Questions?