Chemistry of heavy elements

A different world….

<table>
<thead>
<tr>
<th></th>
<th>$\text{Au}_2$</th>
<th>$\text{C}<em>{20}\text{N}</em>{20}\text{H}_{12}$</th>
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<tbody>
<tr>
<td>electrons</td>
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<tr>
<td>total energy</td>
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<td>-987 Hartree</td>
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<tr>
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<td>48s38p24d18f2g 426 functions</td>
<td>240s108p24d 684 functions</td>
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<td>chemical bonds</td>
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<tr>
<td>Bond energy</td>
<td>0.1 Hartree 2.3 eV</td>
<td>10 Hartree 272 eV</td>
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</table>
Spectroscopy of f-elements

- Low-lying electronic states

<table>
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<tr>
<th></th>
<th>Eu$^{3+}$</th>
<th>C$_6$H$_6$</th>
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<tbody>
<tr>
<td>electrons</td>
<td>6 f-electrons</td>
<td>6 π-electrons</td>
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<tr>
<td>orbitals</td>
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<td>6</td>
</tr>
<tr>
<td>energies &lt; 0.125 Hartree</td>
<td>3 (with SOC: 8)</td>
<td>1</td>
</tr>
<tr>
<td>states &lt; 0.125 Hartree</td>
<td>159 (with SOC:58)</td>
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</table>

- Lanthanides: 4f is shielded from environment
- Actinides: 5f can participate in chemical bonding
Valence-Only approaches

- All-electron calculations are not always feasible or necessary

- Hierarchy of approximations for “core” electrons
  1. Correlate core electrons at a lower level of theory (e.g. MP2)
  2. Do not correlate core electrons at all (HF-only)
  3. Use atomic orbitals for core electrons (Frozen Core)
  4. Model frozen core by a Model Potential (AIMP)
  5. Model frozen core by a Effective Core Potential (ECP)
  6. Model frozen core by a Local Pseudopotential (LPP)

- Error correction and additional features
  1. Estimate higher order correlation effects in another basis set
  2.
  3. Use a core polarization potential
  4.
  5. Include valence relativistic effects in RECP
  6. Suitable for orbital-free DFT calculations
Consider the Fock operator

\[ F = \hbar^{\text{kinetic}} - \sum_{A} \frac{Z_{A}}{r_{A}} + \sum_{j} \left( J_{j} - K_{j} \right) \]

Identify localized (atomic) core orbitals and partition

\[ Z_{A}^{\text{core}} = Z_{A} - Z_{\text{Core}} \]

\[ F = \hbar^{\text{kinetic}} - \sum_{A} \frac{Z_{A}}{r_{A}} + \sum_{A} \sum_{c} J_{c}^{A} - K_{c}^{A} + \sum_{v} J_{v} - K_{v} \]

\[ F = \hbar^{\text{kinetic}} - \sum_{A} \frac{Z_{A}^{\text{core}}}{r_{A}} + \sum_{v} J_{v} - K_{v} + \sum_{A} \left( -\frac{Z_{A}^{\text{core}}}{r_{A}} + \sum_{c} J_{c}^{A} \right) - \sum_{A} \sum_{c} K_{c}^{A} \]

Coulomb potential goes to zero at large distance, contains correction due to imperfect screening of nuclei at short distance

Exchange potential depends on the overlap with the frozen atomic orbitals: short range

Approximation made: atomic core orbitals are not allowed to change upon molecule formation, other orbitals stay orthogonal to these AOs
Core polarization and overlap

- Polarizability of the core can be modeled by a classical core polarization correction (see also book II, formula 41.9)

\[ E_{CP}^A = -\frac{1}{2} \sum_A F_A^T \alpha_A F_A \]

Field from the electrons and the other nuclei at the position of core A

- Need a cut-off factor in the field since the multipole expansion is only valid outside the core
- Can be extended to model core-correlation and core-valence correlation as well

- The overlap between cores is assumed to be zero: the Pauli repulsion and Coulomb attraction between neighboring cores should be small
- For “large core” calculations an additional correction may be added
Ab Initio Model Potentials

Replace the exact, non-local, frozen core potential by a model potential plus a projection operator

$$V_{\text{Frozen core}}^A = \sum_c^\text{core} \left( J_c^A - Z_{A,\text{core}}^c \right) - \sum_c^\text{core} K_c^A \approx V_{\text{Coul}}^A + V_{\text{Exch}}^A + P_{\text{Core}}^A$$

$$V_{\text{Coul}}^A = \frac{1}{r_A} \sum_i^\text{primitive} c_i^A e^{-\alpha_i^A r_A^2}$$  Density fit of spherical density, can be done to arbitrary precision

$$V_{\text{Exch}}^A = -\sum_c \sum_{r,s,t,u}^\text{core basis on A} \langle r \rangle S_{rs}^{-1} \langle s | K_c^A | t \rangle S_{tu}^{-1} \langle u \rangle$$  Resolution of identity with non-orthogonal functions

$$P_{\text{Core}}^A = \sum_c^\text{core} \langle c | B_c^A | c \rangle$$  Level shift that shifts the core solutions to high energies
Ab Initio Model Potentials

😊 No freely adjustable parameters
😊 Core solutions present but shifted to the virtual space
😊 Relativistic effects can be included in the reference Fock operator
  ● Cowan-Griffin Hamiltonian (scalar)
  ● Wood-Boring Hamiltonian (spin-orbit)
  ● Douglas-Kroll-Hess Hamiltonian
  ● X2C Hamiltonian
😊 Can also be used to generate “no-valence” MPs
  ● Improves description of ions in crystals
  ● May require iterative generation scheme
  ● Good results for e.g. calculations of lanthanide spectra by Seijo and coworkers
😊 Keeps nodal structure of the valence orbitals
Nodal structure

Radon ZORA-LDA TZP

ψ†(r)ψ(r)

6s orbital
1s orbital
2s orbital
3s orbital
4s orbital
5s orbital

r (Å)

ψ†(r)ψ(r)

-3 -2.5 -2 -1.5 -1 -0.5 0 0.5 1 1.5 2 2.5 3

-10.00 -8.00 -6.00 -4.00 -2.00 0.00 2.00 4.00 6.00 8.00 10.00
Valence density

Radon ZORA-LDA TZP

\[ \int_0^r 4\pi r'^2 \psi^\dagger(r')\psi(r') \, dr' \]

\[ 4\pi r^2 \psi^\dagger(r) \psi(r) \]
Valence orbitals

Radon ZORA-LDA TZP

\[ \psi^\dagger(\mathbf{r}) \psi(\mathbf{r}) \]
Pseudo orbitals

Radon ZORA-LDA TZP

Matching point

Matching point

r (Å)

6s orbital
6s pseudo orbital
Pseudopotentials in DFT

Easier to consider pseudo-orbitals in Density Functional Theory

\[
\left( \hat{T} - \frac{Z_A}{r_A} + J_A [\rho_A] + \hat{V}_A^{xc} [\rho_A] \right) \psi_i^A (\mathbf{r}) = \varepsilon_i^A \psi_i^A (\mathbf{r})
\]
Reference atomic calculation

\[
\left( \hat{T} + \hat{V}_A^{\text{eff}} \right) \psi_i^A (\mathbf{r}) = \varepsilon_i^A \psi_i^A (\mathbf{r})
\]
Orbitals are solution of a local effective potential

\[
\hat{V}_A^{\text{eff}} (\mathbf{r}) = \varepsilon_i^A - \frac{\nabla^2 \psi_i^A (\mathbf{r})}{2 \psi_i^A (\mathbf{r})}
\]
Potential can be constructed if the orbitals are known

\[
\left( \hat{T} + \hat{V}_A^{PP} \right) \phi_i^A (\mathbf{r}) = \varepsilon_i^A \phi_i^A (\mathbf{r})
\]
Equation that is to be fulfilled by the pseudo-orbital

\[
\hat{V}_A^{PP} (\mathbf{r}) = \varepsilon_i^A - \frac{\nabla^2 \phi_i^A (\mathbf{r})}{2 \phi_i^A (\mathbf{r})}
\]
Construction of the pseudopotential

PP depends on a specific $\varepsilon$ and $\phi$
Representation in terms of grid in $\mathbf{r}$
Nonlocal norm-conserving pseudopotentials

Define a local and a *nonlocal* potential

\[
\left( \hat{T} + \hat{V}_A^L (\mathbf{r}) + \hat{V}_A^{NL} \right) \phi_i^A = \varepsilon_i^A \phi_i^A
\]

\( \varepsilon \) takes care of the long range (screened) nuclear attraction, is identical to \( V_{\text{eff}} \) for \( r > R \)

\[
\left| \chi_i^A \right> = \left( \varepsilon_i^A - \hat{T} - \hat{V}_A^L (\mathbf{r}) \right) \phi_i^A
\]

Wavefunction that is only non-zero for \( r < R \)

\[
\hat{V}_A^{NL} = \frac{\left< \chi_i^A \right| \chi_i^A \left| \chi_i^A \right> - \left< \chi_i^A \right| \phi_i^A \left| \phi_i^A \right> \left< \phi_i^A \right| \chi_i^A \left| \chi_i^A \right>}{\left< \chi_i^A \right| \phi_i^A \left| \phi_i^A \right>}
\]

\( \hat{V}_{\text{NL}} \) serves to model short range repulsive interactions, is zero for \( r > R \)

To use more than one pseudo orbital one can introduce a generalized norm-conserving condition \( Q \) that should be fulfilled

\[
Q_{ij} = \left< \psi_i^A \left| \psi_j^A \right> \right>_R - \left< \phi_i^A \left| \phi_j^A \right> \right>_R = 0
\]

Makes sure orthonormality of the original orbitals is also obeyed by the pseudo-orbitals

\[
\hat{V}_A^{NL} = \sum_{i,j} B^{-1}_{ij} \chi_i^A \left< \chi_i^A \right| \chi_j^A \left| \chi_j^A \right> \quad \text{with} \quad B_{ij} = \left< \phi_i^A \left| \chi_j^A \right> \right>
PPs in plane-wave expansions

- Required in condensed matter DFT calculations that employ a plane-wave basis. Need to smoothen (soften) wave function and potentials as much as possible.

- Abandon normalization condition and work with generalized eigenvalue problem.

- The more complicated formalism pays off since the number of plane-wave basis functions can be drastically reduced.

- Common to also "pseudoize" the lowest solutions of a given symmetry (e.g. 2p).
Effective Core Potentials

In molecular LCAO calculations it is sufficient to reduce the basis set used to describe the valence orbitals.

\[ F_v \rightarrow F_v + \sum_c (\epsilon_v - \epsilon_c) \langle c \rangle \langle c \rangle \]

Phillips and Kleinman: shift core orbitals to make them degenerate with the valence orbitals.

\[ \{ \psi_v \} \rightarrow \{ \widetilde{\psi}_v \} \]

Make nodeless pseudo-orbital by mixing core and valence spinors.

\[ V^A_{\text{Frozen core}}(r_A) \approx M^A_L(r_A) + \sum_{l=0}^{L-1} \sum_{m_i=-l}^{l} |lm_i\rangle f^A_l(r_A) \langle lm_i| \]

Scalar

\[ V^A_{\text{Frozen core}}(r_A) \approx M^A_L(r_A) + \sum_{l=0}^{L-1} \sum_{j=\lfloor l/2 \rfloor}^{l+1/2} \sum_{m_i=-l}^{l} |ljm_j\rangle f^A_{ij}(r_A) \langle ljm_j| \]

Spin-Orbit

These *nonlocal pseudopotentials* are determined via a fitting procedure that optimizes the potential for each \( l \)-value. Takes care of Coulomb and Exchange and core-valence orthogonality.
Shape consistent ECPs

- “American school”: Christiansen, Ermler, Pitzer
- “French school”: Barthelat, Durand, Heully, Teichteil
- Make nodeless pseudo-orbitals that resemble the true valence orbitals in the bonding region

\[
\psi_v(r) \rightarrow \tilde{\psi}_v(r) = \begin{cases} 
\psi_v(r) & (r \geq R) \\
\tilde{f}_v(r) & (r < R) 
\end{cases}
\]

- Original orbital in the outer region
- Smooth polynomial expansion in the inner region

- Fit is sometimes done to the large component of Dirac wave function (picture change error)
- Creating a normalized shape consistent orbital necessarily mixes in virtual orbitals
- Intermolecular overlap integrals are well reproduced
- Gives rather accurate bond lengths and structures
ECPs and electron correlation

- Integrals are calculated over pseudospinors
- Consider the MP2 valence energy expression

\[ E^{MP2} = \sum_{i,j}^{\text{occupied}} \sum_{a,b}^{\text{virtual}} \frac{|\langle ij \parallel ab \rangle|^2}{\varepsilon_i + \varepsilon_i - \varepsilon_a - \varepsilon_b} \]

\[ \langle ij \parallel ab \rangle^{\text{pseudo}} - \langle ij \parallel ab \rangle^{\text{original}} \neq 0 \]

\[ \varepsilon_i^{\text{original}} - \varepsilon_a^{\text{original}} > \varepsilon_i^{\text{pseudo}} - \varepsilon_a^{\text{pseudo}} \]

- Orbital energy spectrum is compressed and in particular the intra-atomic 2-electron integrals will be different from the reference all-electron calculation

- Absolute correlation energy may be overestimated relative to correlation calculations done with the unmodified orbitals

- Example: for Pt the radial maximum of the 5d is very close to a node of the 6s. Pseudoizing the 6s will remove this node and overestimate the correlation energy. Remedy: takes also the 5s in the valence
Energy consistent ECPs

- “German school”: Stoll, Preuss, Dolg
- Initially semi-empirical, later *ab initio* approach that tries to reproduce the low-energy atomic spectrum (using correlated calculations)
  
  \[
  \min \left( \sum_{I} w_I \left( E_I^{PP} - E_I^{Reference} \right)^2 \right)
  \]

- Provides good accuracy for many elements and bonding situations
  - Difference in correlation energy due to the nodeless valence orbitals is automatically included in the fit
  - Small cores may still be necessary to obtain stable results
  - Cheap core description allows for good valence basis sets
  - Available in many program packages (a.k.a. “SDD”)
ECPs and molecular properties

- Valence electric and/or magnetic properties (multipoles, polarizabilities, circular dichroisms, etc.)
  - Unmodified operators can be used

- NMR shielding and spin-spin couplings
  - ECPs are valid for the neighboring atoms, not for the ones for which the shielding or couplings are to calculated

- Reconstruction of original wave function
  - Allows calculation of core properties or excitations (mostly applied in solid-state approaches, but some molecular applications have also been reported)

- Spin-Orbit coupling between states
  - Apply SOC-operator that is derived for the ECP that is employed (usually AREP and SOREP)
SO-operator in CI (CC) approaches

1. First order quasi-degenerate perturbation theory (inclusion after CI step)
   - Can also be used with unbound operators (Pauli form)
   - Is computationally efficient (one step procedure)
   - Offers convenient (conventional) interpretation scheme
   - Important couplings to excited states may be missed

2. Limited variational theory (inclusion in CI step)
   - Unbound operators (Pauli form) are acceptable
   - Does only increase the CI effort, no influence on HF and MO-transformation
   - Interpretation is non-conventional
   - Accuracy is limited when orbital relaxation effects are important

3. Variational theory (inclusion in SCF step)
   - Can only be used with bound operators
   - Is computationally demanding (symmetry change already in SCF)
   - Interpretation is non-conventional
   - Should be the most accurate theory
2-Step treatment of SO-coupling

- Use the proper spin-orbit integrals!
  - 2-electron integrals are usually not explicitly considered: atomic mean field integrals (AMFI)
  - ECPs: come with SO-operators suitable for evaluation over pseudo-orbitals

- Basis for perturbative treatment
  - CI/CASSCF: select limited set of wave functions and form effective Hamiltonian. Diagonalization of this small matrix provides the final wave function
  - CASPT2: shift diagonal matrix elements of effective Hamiltonian matrix by adding PT2 correction prior to the diagonalization
“Best” method depends on system studied
See exercise (and answer) 10

Closed shells and simple open shells
- Use a size-extensive and economical method
- SOC-inclusive method may be required

Complicated open shells, bond breaking
- CASSCF/PT2, Multi-Reference CI or MR-CC
- SOC-inclusive methods are usually required
- Mean-field description of SO (AMFI) is usually sufficient

Use “best practice” and experience from calculations on light elements

Some examples...
Make orbital diagram and identify possible SOC effects. Always include scalar effects.
• Valence iso-electronic systems $O_2^-$, FO, ClO
• Breit interaction and correlation should be included for accurate results
NMR: $^1$H shielding trends
NMR spin-spin couplings

Why are SOC effects so important for NMR

- Shielding and sin-spin couplings can be written as a second derivative of the energy relative to the internal/external magnetic fields

\[ E_K^{(11)} = \frac{d^2E}{dM_K dB} = -I_3 + \sigma_K \]  

**Shielding**

\[ E_{KL}^{(02)} = \frac{d^2E}{dM_K dM_L} = \frac{\mu_0 R_{KL}^2 I_3 - 3R_{KL} R_{KL}^T}{4\pi R_{KL}^5} + K_{KL} \]  

**Indirect nuclear spin-spin coupling**

\[ E_K^{(11)} = \langle 0 | H^{(11)} | 0 \rangle + \sum_S \frac{\langle 0 | H^{(10)} | S \rangle \langle S | H^{(01)} | 0 \rangle}{E_0 - E_S} \]

\[ E_{KL}^{(02)} = \langle 0 | H^{(02)} | 0 \rangle + \sum_S \frac{\langle 0 | H^{(01)} | S \rangle \langle S | H^{(01)} | 0 \rangle}{E_0 - E_S} + \sum_T \frac{\langle 0 | H^{(01)} | T \rangle \langle T | H^{(01)} | 0 \rangle}{E_0 - E_T} \]

- Programs that can handle third derivatives (a.k.a quadratic response) can handle such higher order contributions.
Why are SOC effects so important for NMR

- Shielding and sin-spin couplings can be written as a second derivative of the energy relative to the internal/external magnetic fields

\[
E^{(11)}_K = \frac{d^2 E}{dM_K dB} = -I_3 + \sigma_K
\]

Shielding

\[
E^{(02)}_{KL} = \frac{d^2 E}{dM_K dM_L} = \frac{\mu_0 R^2_{KL} I_3 - 3R_{KL}R^T_{KL}}{R^5_{KL}} + K_{KL}
\]

Indirect nuclear spin-spin coupling

\[
E^{(11)}_K = \langle 0 | H^{(11)} | 0 \rangle + \sum_S \frac{\langle 0 | H^{(10)} | S \rangle \langle S | H^{(01)} | 0 \rangle}{E_0 - E_S} + \sum_S \sum_T \frac{\langle 0 | H^{(10)} | S \rangle \langle S | H^{SO} | T \rangle \langle T | H^{(01)} | 0 \rangle}{(E_0 - E_S)(E_0 - E_T)}
\]

\[
+ \sum_S \sum_T \frac{\langle 0 | H^{(10)} | S \rangle \langle S | H^{(01)} | T \rangle \langle T | H^{SO} | 0 \rangle}{(E_0 - E_S)(E_0 - E_T)}
\]

- Programs that can handle third derivatives (a.k.a quadratic response) can handle such higher order contributions.
### Reaction energies: \( \text{HgF}_2 + \text{F}_2 \rightarrow \text{HgF}_4 \)

<table>
<thead>
<tr>
<th>Hamiltonian</th>
<th>Basis</th>
<th>Method</th>
<th>Reaction energy (kJ/mol)</th>
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<tbody>
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<td>sc-ECP</td>
<td>aug-QZ</td>
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</table>


Confirmed 1993 prediction of Hg(IV) by Kaupp, compound observed by Andrews in 2007.
Further reading

**Relativistic Quantum Mechanics**


**Relativistic Quantum Chemical methods**


**Applications**