Relativistic Energy-consistent Ab Initio Pseudopotentials — New Developments for Actinides.

‘Stuttgart-(Dresden→Bonn→Cologne)‘ PPs: http://www.theochem.uni-stuttgart.de
• **Short introduction to energy-consistent relativistic pseudopotentials**

• **What we currently can provide for lanthanides and actinides:**

  Wood-Boring adjusted scalar-relativistic (one-component) large-core (Ln 4f-in-core, An 5f-in-core) and small-core (Ln 4f-in-valence, An 5f-in-valence) pseudopotentials, valence spin-orbit operators in the small core case and corresponding valence basis sets of different quality (VDZ to VQZ) and contraction schemes (segmented, generalized) based on ANOs.

  – some general considerations concerning the choice of the core:
    small-core vs. large-core PPs;
    f-in-core PPs (superconfiguration model (R.W.Field); feudal model (B.Bursten) ?)
  – calibration for atoms/molecules
  – examples for applications

• **What we would like to have for lanthanides and actinides:**

  Multi-configuration Dirac-Hartree-Fock/Dirac-Coulomb-Breit adjusted relativistic (two- and one-component) small-core pseudopotentials and corresponding correlation-consistent valence basis sets.
  At present only available for heavy main group and all d-transition elements.

• **Conclusions and outlook**
goal:
relativistic and correlated quantum chemical investigation of systems with (one or several) heavy elements

desireable:
• suitable for ground and excited states (unambiguous description in well-defined coupling scheme)
• suitable for all types of bonding (van der Waals, covalent, ionic, metallic) and systems (atoms, molecules, clusters, polymers, solids)

↓

wavefunction-based (ab initio) methods with the best available relativistic Hamiltonian!
(The right answer for the right reason ... and a very high computational cost)

also desireable:
• reduction of computational effort
• tolerable loss of accuracy
• control of underlying approximations
• possibility for systematic improvements

↓

approximate relativistic (ab initio/first principles) methods
(A reasonable answer for good reasons ... and a moderate computational cost)
Introduction: approximations in valence-only methods

approximation:

restriction of the explicit wavefunction-based quantum chemical ab initio treatment to the system of valence electrons

↓

frozen-core approximation and core-valence separation

↓

model potentials (MP), pseudopotentials (PP) and core-polarization potentials (CPP) *

*advantage:
reduction of computational effort
(simple inclusion of relativistic contributions)

*disadvantage:
reduction of accuracy

critical:
choice of the core (small, medium, large)
Introduction: approximations in valence-only methods

\[
\begin{align*}
\text{model potentials} & \\
\text{(Huzinaga, Klobukowski, Seijo, Barandiaran; Wahlgren, Gropen, Marian;...)} & \\
\text{valence orbitals} & \\
\text{(correct number of radial nodes)} & \\
\downarrow & \\
\text{pseudoorbital transformation} & \\
\downarrow & \\
\text{pseudopotentials}^* & \\
\text{(Hellmann; Preuß; Pitzer, Christiansen, ...; Durand, Barthelat, ...; Hay, Wadt; Stevens, ...; Stoll, Dolg, Schwerdtfeger, ...; ...)} & \\
\text{pseudo valence orbitals} & \\
\text{(reduced number of radial nodes)} & \\
\end{align*}
\]

\*advantage:
computational savings with respect to one-particle basis set

\*disadvantage:
formal transformation of (some) operators necessary, e.g., spin-orbit term, ...
overestimation of correlation energies?
methods of adjustment of ab initio pseudopotentials

orbital adjustment: shape-consistent PPs

reference data: all-electron valence orbitals and orbital energies
   (independent particle model)
   (Pitzer, Christiansen, ...; Durand, Barthelat, ...; Hay, Wadt; Stevens, ...)

energy adjustment: energy-consistent PPs*

reference data: all-electron total valence energies
   (quantum mechanical observables; independent particle model and beyond)
   (Stoll, Dolg, Schwerdtfeger, ...)

*advantage:
applicable for any quality of the wavefunction (SCF, MCSCF, CI, CC),
e.g., adjustment in intermediate coupling scheme possible

*disadvantage:
relatively high computational effort
problems with neutral or negative charged cores
Introduction: approximations in quantum chemical first-principles methods

Wanted: suitable compromise between accuracy and computational effort!

Note: ECPs lead to reductions in the sizes of the one- and many-electron basis sets!
ECPs are an approximate relativistic quantum chemical scheme and preferably should be used for medium-sized to large systems (including also periodic ones). Nevertheless many results for atoms and diatomics have been produced in the last decades, however more accurate schemes are available for theses cases nowadays.

- **(highly) accurate atomic results are not the ultimate goal of ECP calculations!**
  → E. Eliav, U. Kaldor, I. Grant, C. Froese-Fischer, P. Indelicato, ... can do it much better at the AE level, at least they get the right answer for the right reason.
  → atoms provide reference data and good test cases, e.g., for the balanced description of "chemically relevant" atomic configurations/states/levels.
  → An accuracy of $10^{-2}$ eV ($80 \text{ cm}^{-1}$) in excitation energies, ionization potentials, electron affinities usually sufficient.

- **(highly) accurate diatomic results are not the ultimate goal of ECP calculations!**
  → K. Faegri, K. Dyall, T. Saue, L. Visscher, ... could do it better at the AE level, at least if they apply large enough basis sets!
  → diatomics nevertheless provide good test cases for the transferability of the ECPs from the atom to the molecule (calibration studies).
  → An accuracy of $10^{-1}$ eV in $D_e$, $10^{-2}$ Å in $R_e$ and 10 cm$^{-1}$ in $\omega_e$ should at least be achieved.

Needed: "robust" (small-core) and highly transferable ECPs based on the best available relativistic many-electron Hamiltonian (e.g. Dirac-Coulomb-Breit) and series of valence basis sets with the possiblity to approach systematically the basis set limit.
MCDHF/DC+B-adjusted small-core PPs for actinides: Hamiltonian of reference all-electron calculations

All-electron Hamilton operator:

\[ \hat{H} = \sum_{i} \hat{h}(i) + \sum_{i<j} \hat{g}(i,j) + \sum_{\lambda<\mu} \frac{Z_{\lambda}Z_{\mu}}{r_{\lambda\mu}} \]

Dirac operator (correct to \(O(c^{-\infty})\)):

\[ h_D(i) = c\bar{\alpha}_i \vec{p}_i + (\beta_i - \mathbf{1}_4)c^2 + \sum_{\lambda} V_\lambda(r_{i\lambda}) \]

Coulomb operator:

\[ g_C(i,j) = \frac{1}{r_{ij}} \]

Coulomb-Gaunt operator (Lorentz or Feynman gauge), not even correct to \(O(c^{-2})\):

\[ g_{CG}(i,j) = \frac{1}{r_{ij}} - \frac{\bar{\alpha}_i \bar{\alpha}_j}{r_{ij}} \]

Coulomb-Breit operator (Coulomb gauge), correct to \(O(c^{-2})\):

\[ g_{CB}(i,j) = \frac{1}{r_{ij}} - \frac{1}{2r_{ij}} \left[ \bar{\alpha}_i \bar{\alpha}_j + \frac{(\bar{\alpha}_i \vec{r}_{ij})(\bar{\alpha}_j \vec{r}_{ij})}{r_{ij}^2} \right] \]

Considering the frequency of the exchanged photon (Coulomb gauge):

\[ g(i,j,\omega) = \frac{1}{r_{ij}} - \bar{\alpha}_i \bar{\alpha}_j \frac{e^{i\omega r_{ij}/c}}{r_{ij}} - (\bar{\alpha}_i \nabla_{r_{ij}})(\bar{\alpha}_j \nabla_{r_{ij}}) \frac{e^{i\omega r_{ij}/c}}{\omega^2 r_{ij}/c^2} - \frac{1}{\omega^2 r_{ij}/c^2} \]
MCDHF/DC+B-adjusted small-core PPs for actinides: Hamiltonian of reference all-electron calculations

In the low frequency limit $\omega r_{ij} << 1$ this reduces to the Breit interaction (magnetic interaction and retardation). Energy conservation requires $\omega = \epsilon_s - \epsilon_r = \epsilon_q - \epsilon_p$.

Dirac matrices:

$$\bar{\alpha} = \begin{pmatrix} \vec{\sigma} & \vec{0} \\ \vec{0} & \vec{\sigma} \end{pmatrix}$$
and

$$\beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}$$

Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

DCB Hamiltonian: one of the most accurate many-electron Hamiltonians ($O(c^{-2})$)!
Suitable for the generation of atomic reference data for relativistic valence-only schemes!

Beyond the DCB Hamiltonian:
The lowest order Feynman diagrams: electron-electron interaction via exchange of a single virtual photon, vacuum polarization and self-energy correction (cf. book written by K.G.Dyall and K. Faegri). Suitable implementation and importance of the latter for actinides?
MCDHF calculations for U: various contributions

U AE DHF results (in cm\(^{-1}\)):

<table>
<thead>
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<th>result ----- deviation -----</th>
<th>result -- deviation --</th>
<th>result ----- deviation -----</th>
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(**) GRASP

→ importance: Breit interaction > finite nucleus > radiation corrections >> self-consistency of Breit term.
still unclear: importance of vacuum polarisation and self-energy corrections!
Valence-only Model-Hamilton operator:

\[ \hat{\mathcal{H}}_v = \sum_{i}^{n_v} \hat{h}_v(i) + \sum_{i<j}^{n_v} \hat{g}_v(i,j) + V_{cc} + V_{cpp} \]

with \( \hat{h}_v(i) = -\frac{1}{2} \Delta_i + V_{cv}(i) \) and \( \hat{g}_v(i,j) = \frac{1}{r_{ij}} \)

Core-electron interaction:

\[ V_{cv}(i) = \sum_{\lambda}^{N} \left( -\frac{Q_\lambda}{r_{\lambda i}} + \Delta V_{cv}^\lambda (r_{\lambda i}) \right) + \ldots \]

Core-core interaction:

\[ V_{cc} = \sum_{\lambda<\mu}^{N} \left( \frac{Q_\lambda Q_\mu}{r_{\lambda \mu}} + \Delta V_{cc}^{\lambda \mu} (r_{\lambda \mu}) \right) + \ldots \]

Semilocal (ab initio) pseudopotentials:

\[ \Delta V_{cv}^\lambda (r_{\lambda i}) = \sum_{l=0}^{L-1} \sum_{|j|=|l-1/2|}^{l+1/2} \left( V_{ij}^\lambda (r_{\lambda i}) - V_L^\lambda (r_{\lambda i}) \right) \sum_{m_j=-j}^{j} | \lambda l j m_j(i) \rangle \langle \lambda l j m_j(i) | + V_L^\lambda (r_{\lambda i}) \]

Spin-orbit-averaged (scalar-relativistic) form:

\[ \Delta V_{cv,av}^\lambda (r_{\lambda i}) = \sum_{l=0}^{L-1} \left( V_L^\lambda (r_{\lambda i}) - V_L^\lambda (r_{\lambda i}) \right) \sum_{m_l=-l}^{l} | \lambda l m_l > < \lambda l m_l | + V_L^\lambda (r_{\lambda i}) \]

Spin-orbit operator:

\[ \Delta V_{cv,so}^\lambda (r_{\lambda i}) = \sum_{l=1}^{L-1} \frac{\Delta V_{I}^{\lambda}(r_{\lambda i})}{2l+1} \left[ lP_{l,l+1/2}^{\lambda} - (l+1)P_{l,l-1/2}^{\lambda} \right] = \sum_{l=1}^{L-1} \frac{2\Delta V_{I}^{\lambda}(r_{\lambda i})}{2l+1} P_{l}^{\lambda} l s P_{l}^{\lambda} \]

with the difference potential

\[ \Delta V_I^\lambda (r_{\lambda i}) = V_{l,l+1/2}^\lambda (r_{\lambda i}) - V_{l,l-1/2}^\lambda (r_{\lambda i}) \]
Energy-consistent pseudopotentials: valence-only model Hamiltonian

Gaussian expansion of radial parts:

\[
V_{lj}^\lambda(r_{\lambda i}) = \sum_k A_{ljk}^\lambda r_{\lambda i}^{n_{ljk}^\lambda} \exp(-a_{ljk}^\lambda r_{\lambda i}^2)
\]

and

\[
V_{1l}^\lambda(r_{\lambda i}) = \sum_k A_{lk}^\lambda r_{\lambda i}^{n_{lk}^\lambda} \exp(-a_{lk}^\lambda r_{\lambda i}^2) \quad \text{and} \quad \Delta V_{1l}^\lambda(r_{\lambda i}) = \sum_k \Delta A_{lk}^\lambda r_{\lambda i}^{n_{lk}^\lambda} \exp(-a_{lk}^\lambda r_{\lambda i}^2)
\]

For large (polarizable) cores ...

Core-polarization potential:

\[
V_{cpp} = -\frac{1}{2} \sum_\lambda \alpha_\lambda f_\lambda^2
\]

Electrostatic field and cut-off factor:

\[
f_\lambda = -\sum_i \frac{r_{i\lambda}}{r_{i\lambda}^3}(1 - \exp(-\delta_c^\lambda r_{i\lambda}^2))^{n_c} + \sum_{\mu \neq \lambda} Q_{\mu} \frac{r_{\mu\lambda}}{r_{\mu\lambda}^3}(1 - \exp(-\delta_c^\lambda r_{\mu\lambda}^2))^{n_c}
\]

For large (mutually penetrating) cores ...

Core-core- and core-nucleus interaction correction:

\[
\Delta V_{cc}^{\lambda\mu}(r_{\lambda\mu}) = B_{\lambda\mu} \exp(-b_{\lambda\mu} r_{\lambda\mu})
\]

'Stuttgart pseudopotentials':

typically \( V_L^\lambda = 0 \) and \( n_{ljk}^\lambda = 0, n_{lk}^\lambda = 0 \) is chosen.
Energy-consistent pseudopotentials: multi-electron multi-state adjustment

Energy-adjustment $\rightarrow$ Energy-consistent pseudopotentials

Atomic adjustment of parameters $A_{ijk}, a_{ijk}$ respectively $A_{lk}, \Delta A_{lk}, a_{lk}$ to total valence energies $E_{I}^{AE,\text{valence}} = E_{I}^{AE} - E_{\text{core}}^{AE}$ of a multitude of 'chemically relevant' (low-lying) electronic configurations/states/levels of the neutral atom and low-charged ions!

$$S = \sum_{I} W_{I}(E_{I}^{AE,\text{valence}} - E_{I}^{PP,\text{valence}})^{2} := \min$$

Adjustment only to quantum mechanical observables (total valence energies = sums of excitation energies, ionization potentials, electron affinities)! Quantities defined within the independent particle approximation (orbitals, orbital energies, etc.) are not used.

In principle applicable to any computational method, in practice today adjustment to (average-level) multi-configuration Dirac-Hartree-Fock reference data based on the Dirac-Coulomb-Breit Hamiltonian (modified version of the atomic electronic structure program GRASP), i.e., use of an intermediate coupling scheme. (Previous parametrizations applied the scalar-relativistic Wood-Boring Hamiltonian in the LS coupling scheme.)


Recent development: allow for a variation $\Delta E_{\text{shift}}$ of the core energy:

$$E_{I}^{AE,\text{valence}} = E_{I}^{AE} - (E_{\text{core}}^{AE} + \Delta E_{\text{shift}})$$

$\rightarrow$ improvement of the quality of the fit (in case of 3d metals) by an order of magnitude!

Energy-consistent pseudopotentials: multi-electron multi-state adjustment

old sc–PP   new sc–PP

Sc(11+)     shift

Sc(3+)

Sc(2+)

Sc(1+)

Sc(0)

Sc(1−)

Quantities of interest

Reference data

WB  MCDHF

d3  s1d2  2G  7/2

s2d1  4F  5/2

2D  3/2

conf.  LS  J
“Chemical intuition“ (energetic separation): valence space Ce 4f, 5d, 6s; Th 5f, 6d, 7s.

Choice of the core: Ce valence orbital and core densities

Valence orbital densities and core densities of Ce

spatial separation: Ce valence space 4spdf 5spd 6s!

Choice of the core: Th valence orbital and core densities

Valence orbital densities and core densities of Th

spatial separation: Th valence space 5spdf 6spd 7s!

Choice of the core: AE MCDHF/DC (frozen core) results for Ce

Frozen core errors for Ce and Th
AE MCDHF/DC

Frozen core taken from Ce 4f\(^1\) 5d\(^1\) 6s\(^2\) and Th 6d\(^2\) 7s\(^2\).


→ core too large ! errors too large ! not useful !
frozen core taken from Ce 4f\(^1\) 5d\(^1\) 6s\(^2\) and Th 6d\(^2\) 7s\(^2\).


→errors acceptable within a given f occupation!

4f/5f-in-core Ln/An large-core PPs (LPPs).
frozen core taken from Ce \(4f^1\) \(5d^1\) \(6s^2\) and Th \(6d^2\) \(7s^2\).


→accurate also for changes of the f occupation!

\[4f/5f\text{-in-valence Ln/An small-core PPs (SPPs).}\]
**WB adjusted PPs: lanthanides and actinides**

<table>
<thead>
<tr>
<th>Ln 4f-in-valence PPs (1989*)</th>
<th>An 5f-in-valence PPs (1994*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>core: 1s-3d, valence: 4s-6s ...</td>
<td>core: 1s-4f, valence: 5s-7s ...</td>
</tr>
<tr>
<td>Q=29(La) bis 43(Lu)</td>
<td>Q=29(Ac) bis 43(Lr)</td>
</tr>
<tr>
<td>valence spin-orbit operators</td>
<td>valence spin-orbit operators</td>
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<tr>
<td>generalized contraction (ANO):</td>
<td>generalized contraction (ANO):</td>
</tr>
<tr>
<td>(14s13p10d8f6g)/[6s6p5d4f3g]</td>
<td>(14s13p10d8f6g)/[6s6p5d4f3g]</td>
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<tr>
<td>(pVQZ → pVTZ, pVDZ, mini)</td>
<td>(pVQZ → pVTZ, pVDZ, mini)</td>
</tr>
<tr>
<td>segmented contraction:</td>
<td>segmented contraction:</td>
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<tr>
<td>(14s13p10d8f6g)/[10s8p5d4f3g]</td>
<td>(14s13p10d8f6g)/[10s9p5d4f3g]</td>
</tr>
<tr>
<td>(’pVQZ’ quality)</td>
<td>(’pVQZ’ quality)</td>
</tr>
</tbody>
</table>

**Ln 4f-in-core PPs (1989*)**

| core: 1s-4f, valence: 5s-6s ... |
| Q=11(LnIII), Q=10(LnII), Q=12(LnIV) |
| segmented contraction: |
| (4s4p3d)/[2s2p2d], [3s3p2d], |
| (5s5p4d)/[2s2p2d], [3s3p3d], [4s4p3d], |
| (6s6p5d)/[2s2p2d], [3s3p3d], [4s4p4d] |
| for calculations on solids and |
| + ... 2s1p1d, e.g. (8s7p6d)/[6s5p5d], |
| for calculations on molecules |

**An 5f-in-core PPs (2006*)**

| core: 1s-5f, valence: 6s-7s ... |
| Q=11(AnIII), Q=10(AnII), Q=12(AnIV) |
| segmented contraction: |
| as for lanthanides ! |
| Q=13(AnV), Q=14(AnVI) ? |
| (in preparation) |
| See the poster of Anna Moritz ! |

*All valence basis sets were reoptimized after 2001, some PPs were newly adjusted or readjusted! PPs and basis sets available on http://www.theochem.uni-stuttgart.de
Calibration of Ln and An small-core PPs

Ln PP(28,WB) and An PP(60,WB), uncontracted spdf valence basis sets, HF with perturbative spin-orbit corrections vs. AE average-level (MC)DHF/DC+B, finite difference.

<table>
<thead>
<tr>
<th></th>
<th>IP₁</th>
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<tr>
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<td>0.07</td>
<td>0.09</td>
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<tr>
<td>Ln m.r.e. (%)</td>
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<td>0.7</td>
<td>0.4</td>
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<tr>
<td>An m.a.e. (eV)</td>
<td>0.03</td>
<td>0.06</td>
<td>0.28*</td>
<td>0.53*</td>
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<td>An m.r.e. (%)</td>
<td>0.6</td>
<td>0.5</td>
<td>1.4</td>
<td>1.5</td>
</tr>
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</table>

→ Ln, An small-core PPs reliable to 1 - 2% accuracy for low-ionized states.

Note: the relativistic and correlation contributions amount to several eV in many cases!

* PP adjustment restricted to Ln/An⁰,¹⁺, i.e. only IP₁ entered the fit explicitly!

* HF/WB approximates DHF/DC, i.e. mainly 4f/5f occupation number dependent Breit contributions (O(0.1 eV)) are not included!

→ improvement possible!

Readjustment at the MCDHF/DC+B level desireable → a task for the future!
Small-core PPs for lanthanides and actinides: calibration of pseudopotentials for atoms

Test case U IP₁ to IP₄

U \(5f^3\)\(6d^1\)\(7s^2\) \(J=6\) → U\(^+\) \(5f^3\)\(7s^2\) \(J=9/2\) → U\(^2+\) \(5f^4\) \(J=4\) → U\(^3+\) \(5f^3\) \(J=9/2\) → U\(^4+\) \(5f^2\) \(J=4\)

configurational averages (in eV)

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<tr>
<th></th>
<th>SPP, WB</th>
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</table>

SPP, WB vs. AE, WB: errors of the SPP 0.1 eV or less!

AE, WB vs. AE, DC: deviations of up to 0.3 eV! Note: IP₂+IP₃ AE,WB 28.8780 eV, AE DC 28.8673 eV → The problems mainly arise for changing f occupation numbers! AE, WB (usually) agrees even 'better' with AE, DC+B than with AE, DC.

lowest J-levels (in eV)

<table>
<thead>
<tr>
<th></th>
<th>SPP, WB</th>
<th>SPP, WB</th>
<th>AE, DC</th>
<th>AE, DC+B</th>
<th>SPP, DC+B</th>
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<tr>
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<td>5.5729</td>
<td>5.5380</td>
<td>5.5399</td>
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<tr>
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<td>11.5995</td>
<td>11.9457</td>
<td>11.8455</td>
<td>11.8451</td>
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<td>16.8616</td>
<td>16.9430</td>
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<td>31.5575</td>
<td>31.0744</td>
<td>31.1704</td>
<td>31.1853</td>
</tr>
</tbody>
</table>

The errors in excitation energies are usually smaller than in IPs, e.g., U \(5f^3\)\(6d^1\)\(7s^2\) → U \(5f^4\)\(7s^2\) WB 1.8651 eV, DC 2.0342 eV, DC+B 1.9568 eV, SPP WB 1.8779 eV.
Energy-consistent pseudopotentials: what’s new?

Present work on MCDHF-adjusted PPs

- **post-d main group elements:**

- **3d-transition elements:**

- **4d- and 5d-transition elements:**
  D. Figgen, PhD thesis (University of Stuttgart, 2007).

- **superheavy elements:**

The new pseudopotentials are/will be accompanied by correlation-consistent valence basis sets (collaboration with K. A. Peterson, PNNL, Washington)
**New: U MCDHF/DC+B PP: 100 configurations (yielding 30190 J-levels):**

<table>
<thead>
<tr>
<th>Configuration</th>
<th>J-levels</th>
<th>Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5s2 5p6 5d10 5f5 6s2 6p6 7s1</td>
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<td>20</td>
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<td>38</td>
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<tr>
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<td>9</td>
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<tr>
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<td>12</td>
</tr>
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<td>107</td>
<td>24</td>
</tr>
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</tr>
<tr>
<td>5s2 5p6 5d10 5f1 6s2 6p6 6d2</td>
<td>81</td>
<td>81</td>
</tr>
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</table>
## MCDHF/DC+B-adjusted small-core PPs for actinides: U reference states

<table>
<thead>
<tr>
<th>U(3+) ctnd.</th>
<th>U(5+) ctnd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5s2 5p6 5d10 5f1 6s2 6p6 6d1 7s1 39</td>
<td>5s2 5p6 5d10 6s2 6p6 7s1 2</td>
</tr>
<tr>
<td>5s2 5p6 5d10 5f1 6s2 6p6 6d1 7p1 113</td>
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</tr>
<tr>
<td>5s2 5p6 5d10 5f1 6s2 6p6 7s1 7p1 24</td>
<td>5s2 5p6 5d10 6s2 6p6 9s1 1</td>
</tr>
<tr>
<td>5s2 5p6 5d10 6s2 6p6 6d3 19</td>
<td>5s2 5p6 5d10 6s2 6p6 8p1 2</td>
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<tr>
<td>5s2 5p6 5d10 6s2 6p6 6d2 7s1 16</td>
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</tr>
<tr>
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<td>5s2 5p6 5d10 6s2 6p6 7d1 2</td>
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<tr>
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<tr>
<td>U(4+)</td>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>5s2 5p6 5d10 6s2 6p6 6d1 7s1 4</td>
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<td>5s2 5p6 5d10 6s2 6p5 2</td>
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<td>U(5+)</td>
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</tr>
<tr>
<td>5s2 5p6 5d10 6s2 6p6 6d1 2</td>
<td>5s2 5p6 5d10 6s2 6p5 2</td>
</tr>
</tbody>
</table>

Introduction of the core energy shift $\Delta E_{\text{shift}}$ allows the inclusion of higher ionized states to the reference data set, including some with holes in 5s, 5p, 5d, 6s and 6p semi-core orbitals.

MD, in preparation.

**Old:** U WB PP + $\Delta$DHF SO: 13 LS states of U and U$^+$; no holes in semi-core orbitals considered. Later augmented by multi-state multi-electron adjusted valence (5f, 6d, 7p) SO terms for use in either perturbation theory or variational calculations/spin-orbit CI.

MCDHF/DC+B-adjusted small-core PPs for actinides: U errors

U f.n. MCDF/DC+B(l.f.l.) PP Q=32
errors in valence energies of 100 non-relativistic configurations

maximum error 0.0067 eV
m.q.e. 16.1 cm$^{-1}$
MCDHF/DC+B-adjusted small-core PPs for actinides: U errors

U f.n. MCDHF/DC+B(l.f.l.) Q=32 PP
errors in total valence energies of 30190 J-levels (100 configurations)

- maximum error 0.267 eV
- 1218th J-level of $\text{U}(0)\ 5f^4\ 7s^1\ 7p^1$
- maximum error 0.036 eV
- $\text{U}(3+)\ 5f^3\ J=9/2$

- all 30190 J-levels of 100 configurations
- 16845 J-levels below 5eV relative energy
- Lowest J-level of each configuration

m.q.e. 306.3 cm$^{-1}$
'In our papers the conventional radially-local (semi-local) form of the RECP operator used by many groups up to now but suggested and first applied about 40 years ago was shown to be limited by accuracy and some nonlocal corrections to the RECP operator were suggested, which already allowed us to improve significantly the RECP accuracy.'

N.S. Mosyagin, A.N. Petrov, A.V. Titov, I.I. Tupitsyn,

\[
U^{N_i} = E^{N_i}_{\text{core}} + U^{N_i}_{n_v LJ}(r) + \sum_{l=0}^{L} \sum_{j=|l-1/2|}^{l+1/2} \left\{ [U^{N_i}_{n_v l j}(r) - U^{N_i}_{n_v L J}(r)] P_{l j} \right\}
+ \sum_{n_c} [U^{N_i}_{n_c l j}(r) - U^{N_i}_{n_v l j}(r)] \tilde{P}^{N_i}_{n_c l j} + \sum_{n_c} \tilde{P}^{N_i}_{n_c l j} [U^{N_i}_{n_c l j}(r) - U^{N_i}_{n_v l j}(r)]
- \sum_{n_{c, n_{c}'}} \tilde{P}^{N_i}_{n_c l j} \left\{ \frac{U^{N_i}_{n_c l j}(r) + U^{N_i}_{n_{c}' l j}(r)}{2} - U^{N_i}_{n_v l j}(r) \right\} \tilde{P}^{N_i}_{n_{c}' l j},
\]

\[
P_{l j} = \sum_{m=-j}^{j} \langle l j m | l j m \rangle,
\]

\[
\tilde{P}^{N_i}_{n_c l j} = \sum_{m=-j}^{j} |(n_c l j m)^{N_i}\rangle \langle (n_c l j m)^{N_i}|,
\]
MCDHF/DC+B-adjusted small-core PPs for actinides: comparison to GRECP

U MCDHF/DC+B Q=32 PP vs. DHF/DCB Q=32 GRECP (in cm\(^{-1}\)):

56 parameters for s,p,d,f (adjusted to 30190 J-levels from 100 configurations):

<table>
<thead>
<tr>
<th>f</th>
<th>d</th>
<th>s</th>
<th>p</th>
<th>DHF/DC+B</th>
<th>error</th>
<th>SPP</th>
<th>Fermi n.</th>
<th>GRECP</th>
<th>error(*)</th>
<th>Fermi n.</th>
<th>error(*)</th>
</tr>
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<tbody>
<tr>
<td>5</td>
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<tr>
<td>4</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>49575(*)</td>
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<td>49572</td>
<td>-357</td>
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<tr>
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<td>1</td>
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<tr>
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<tr>
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</tr>
</tbody>
</table>

spread of errors: 16

| 3  | 1  | 4  | 1  | 38779.7  | -13.8 | 38781|          |       |          |          |          |
| 3  | 2  | 1  | 15119(*)| -5    | 15120| -350    |       |          |          |          |
| 3  | 2  | 1  | 13124(*)| -9    | 13124| -7      |       |          |          |          |
| 3  | 1  | 1  | 54575.2 | -6.3  | 54576| -6      |       |          |          |          |
| 3  | 1  | 2  | 17220(*)| -4    | 17200| -1      |       |          |          |          |
| 3  | 1  | 0  | 0    | 0.0   | 0     | 0       |       |          |          |          |
| 3  | 1  | 0  | 42327.6| -5.8  | 42328| 0       |       |          |          |          |
| 3  | 2  | 1  | 7516.2 | -4.6  | 7516  | 5       |       |          |          |          |
| 3  | 2  | 1  | 36289.0| -13.6  | 36289| 9       |       |          |          |          |
| 3  | 1  | 1  | 61569.4| -17.5 |       |          |       |          |          |          |

spread of errors: 37

The (self-consistent treatment of the) Breit interaction contributes at most with \(\approx\)1800 (4) cm\(^{-1}\) !

MCDHF/DC+B-adjusted small-core PPs for actinides: comparison to GRECP

U MCDHF/DC+B Q=32 PP vs. DHF/DCB Q=32 GRECP (in cm⁻¹):

56 parameters for s,p,d,f (adjusted to 30190 J-levels from 100 configurations):

<table>
<thead>
<tr>
<th>J</th>
<th>5f- 3 6d- 1 7s+ 2</th>
<th>5f- 2 6d- 2 7s+ 2</th>
<th>5f- 3 5f+ 1 7s+ 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fermi n. error</td>
<td>0 10767.4 366.0 10767 416</td>
<td>0 39561.1 422.6 39562 724</td>
<td>1 6029.5 162.4 6030 176</td>
</tr>
<tr>
<td>Fermi n. error</td>
<td>1 29342.5 311.6 29343 553</td>
<td>1 20452.5 101.2 20453 292</td>
<td>2 10428.7 285.3 10429 335</td>
</tr>
<tr>
<td>Fermi n. error</td>
<td>2 20477.0 413.4 20477 556</td>
<td>2 24250.8 228.8 24252 422</td>
<td>3 8870.1 249.4 8870 285</td>
</tr>
<tr>
<td>Fermi n. error</td>
<td>3 18515.7 208.6 18516 359</td>
<td>3 15905.0 -38.9 15906 126</td>
<td>4 9498.0 266.7 9498 310</td>
</tr>
<tr>
<td>Fermi n. error</td>
<td>4 17458.4 194.0 17458 339</td>
<td>4 13548.7 -20.7 13549 86</td>
<td>5 8814.8 254.8 8815 293</td>
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<tr>
<td>Fermi n. error</td>
<td>5 2762.4 -55.4 2762 -23</td>
<td>5 7017.3 -116.5 7018 -30</td>
<td>6 10635.9 296.3 10636 357</td>
</tr>
<tr>
<td>Fermi n. error</td>
<td>6 0.0 0.0 0 0</td>
<td>6 0.0 0.0 0 0</td>
<td>7 0.0 0.0 0 0</td>
</tr>
<tr>
<td>Fermi n. error</td>
<td>8 488.3 21.8 488 27</td>
<td>8</td>
<td>254.7</td>
</tr>
</tbody>
</table>


m.a.e. refer to the term energies excluding the ground level.

→ We conclude that the semilocal ansatz is alive and well!
Small-core PPs for lanthanides and actinides: calibration of basis sets for atoms

Test of valence basis sets for Ln and An small-core PPs
Ln PP(28,MWB) and An PP(60,MWB), (14s13p10d8f)/[6s6p5d4f] ANO basis sets, HF vs. corresponding PP finite difference results.

<table>
<thead>
<tr>
<th></th>
<th>IP₁</th>
<th>IP₂</th>
<th>IP₃</th>
<th>IP₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ln m.a.e. (eV)</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
<td>&lt; 0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>m.r.e. (%)</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>An m.a.e. (eV)</td>
<td>0.02</td>
<td>0.01</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>m.r.e. (%)</td>
<td>0.4</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

→ basis sets describe low-lying ionization states of Ln, An at the HF level quite reliably.

Test of pseudopotentials and valence basis sets for Ln (and An) small-core PPs
Ln PP(28,MWB), spin-orbit corrected CASSCF/ACPF vs. experimental results.

<table>
<thead>
<tr>
<th></th>
<th>IP₁</th>
<th>IP₂</th>
<th>IP₃</th>
<th>IP₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>La-Gd m.a.e. (eV)¹</td>
<td>0.18</td>
<td>0.06</td>
<td>0.44</td>
<td>0.38</td>
</tr>
<tr>
<td>Tb-Lu</td>
<td>0.25</td>
<td>0.22</td>
<td>0.77</td>
<td>0.65</td>
</tr>
<tr>
<td>La-Gd m.a.e. (eV)²</td>
<td>0.14</td>
<td>0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb-Lu</td>
<td>0.42</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La-Gd exp. error bars</td>
<td>&lt; ±0.01</td>
<td>±0.06</td>
<td>±0.15</td>
<td>±0.39</td>
</tr>
<tr>
<td>Tb-Lu</td>
<td>&lt; ±0.01</td>
<td>±0.12</td>
<td>±0.10</td>
<td>±0.29</td>
</tr>
</tbody>
</table>

¹ (14s13p10d8f6g)/[6s6p5d4f3g] ANO standard basis set; 4s,4p,4d frozen.
² (16s15p12d10f8g8h8i) basis set limit extrapolation using 1/t³, all orbitals correlated.

→ results of a similar quality are expected for actinides; lack of experimental data!
Small-core PPs for lanthanides and actinides: basis set extrapolation

IP$_4$ of Ce, Th (Exp. Ce 36.76 eV, Th 28.65 eV)
PP(small core, WB)+SO, CCSD(T), basis set extrapolation

Ce: (16s15p12d10f8g8h8i)
Th: (14s13p10d8f6g6h6i)

corr.coeff. -0.9999923

corr.coeff. -0.9999955

Correlation contributions (%):

Ce

Th

Compare: (CASSCF)/ACPF errors Ce -0.61 eV, Th -0.20 ± 0.02 eV
Small-core PPs for actinides: calibration for molecules, ThO

Spectroscopic constants of ThO $^1\Sigma^+$ from pseudopotential (PP), all-electron (AE) Dirac-Hartree-Fock-Roothaan (DHFR), reduced frozen-core approximation (RFCA) and ab initio model potential (AIMP) calculations in comparison to experimental data.

<table>
<thead>
<tr>
<th>method</th>
<th>$R_e$ (Å)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$D_e$ (eV)</th>
<th>$D_0^e$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(WB,30),SCF$^a$</td>
<td>1.817/1.817</td>
<td>956/955</td>
<td>6.26/6.24</td>
<td></td>
</tr>
<tr>
<td>AIMP(CG,12),SCF$^b$</td>
<td>1.819/</td>
<td>956/</td>
<td>5.99/</td>
<td></td>
</tr>
<tr>
<td>AE, DFR$^c$</td>
<td>1.874/</td>
<td>937/</td>
<td>7.61/</td>
<td></td>
</tr>
<tr>
<td>RFCA, MRCI$^d$</td>
<td>1.891/</td>
<td>892/</td>
<td>8.48/</td>
<td></td>
</tr>
<tr>
<td>EC-PP(WB,30), CCSD(T)$^a$</td>
<td>1.839/1.845</td>
<td>898/891</td>
<td>9.58/9.38</td>
<td>9.16/8.96</td>
</tr>
<tr>
<td>Exp.</td>
<td>1.840</td>
<td>896</td>
<td>9.00±0.09</td>
<td></td>
</tr>
</tbody>
</table>

The notation .../... refers to results without/with counterpoise correction of the BSSE. $^a$Th (14s13p10d8f6g)/[6s6p5d4f3g] ANO, O aug-cc-PVQZ (spdfg); this work. $^b$AIMP for Th with [Xe] 4f$^4$5d$^1$ core and for O with [He] core; Seijo 2001. $^c$Th (24s20p16d12f)/[19s15p12d5f], O (10s6p1d)/[7s4p1d] Watanabe 2002. $^d$Th (19s16p13d9f)/[9s8p7d6f], O(9s6p1d)/[6s4p1d] Watanabe 2002. $^e$ $D_e$ values are corrected for molecular (0.03 eV) and atomic (Th 0.38 eV, O 0.01 eV) spin-orbit lowerings; the zero-point energy (0.06 eV) was subtracted.

U-F bond length $R_e$ (Å), infrared frequencies $\nu_i$ (cm$^{-1}$) and bond dissociation energy $D_e$ (kcal/mole) of UF$_6$ from various pseudopotential (SPP) density functional theory calculations. The intensities of the main peaks are listed in parentheses.

<table>
<thead>
<tr>
<th>method</th>
<th>$R_e$</th>
<th>$\nu_1$</th>
<th>$\nu_2$</th>
<th>$\nu_3$</th>
<th>$\nu_4$</th>
<th>$\nu_5$</th>
<th>$\nu_6$</th>
<th>$D_e$</th>
<th>ref.</th>
</tr>
</thead>
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<td>541</td>
<td>655</td>
<td>199</td>
<td>221</td>
<td>143</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.985</td>
<td>741</td>
<td>546</td>
<td>659</td>
<td>(1064)</td>
<td>201</td>
<td>(83)</td>
<td>222</td>
<td>143</td>
</tr>
<tr>
<td>SVWN</td>
<td>1.989</td>
<td>661</td>
<td>546</td>
<td>627</td>
<td>171</td>
<td>183</td>
<td>130</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.993</td>
<td>660</td>
<td>548</td>
<td>628</td>
<td>(594)</td>
<td>173</td>
<td>(30)</td>
<td>184</td>
<td>130</td>
</tr>
<tr>
<td>BLYP</td>
<td>2.035</td>
<td>611</td>
<td>509</td>
<td>579</td>
<td>176</td>
<td>187</td>
<td>130</td>
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<tr>
<td>BPW91</td>
<td>2.019</td>
<td>624</td>
<td>517</td>
<td>591</td>
<td>176</td>
<td>187</td>
<td>131</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>2.021</td>
<td>625</td>
<td>519</td>
<td>593</td>
<td>(562)</td>
<td>176</td>
<td>(32)</td>
<td>186</td>
<td>131</td>
</tr>
<tr>
<td>B3LYP</td>
<td>2.007</td>
<td>657</td>
<td>530</td>
<td>613</td>
<td>184</td>
<td>196</td>
<td>138</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.011</td>
<td>656</td>
<td>532</td>
<td>613</td>
<td>(685)</td>
<td>186</td>
<td>(41)</td>
<td>198</td>
<td>139</td>
</tr>
<tr>
<td>B3PW91</td>
<td>1.996</td>
<td>666</td>
<td>535</td>
<td>622</td>
<td>184</td>
<td>195</td>
<td>139</td>
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</tr>
<tr>
<td>PBE0</td>
<td>1.993</td>
<td>677</td>
<td>532</td>
<td>631</td>
<td>(735)</td>
<td>186</td>
<td>(40)</td>
<td>198</td>
<td>140</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>2.002</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>exp.</td>
<td>1.999</td>
<td>667</td>
<td>534</td>
<td>626</td>
<td>(750)</td>
<td>186</td>
<td>(38)</td>
<td>200</td>
<td>143</td>
</tr>
<tr>
<td></td>
<td>1.996</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>69±5</td>
</tr>
</tbody>
</table>

f-electrons tend to cause a lot of problems (e.g., large number of states, large contributions of electron correlation and relativity, high computational demands, ...). Why not simply get rid of them by putting them into the PP core? → 4f- and 5f-in-core PPs!

<table>
<thead>
<tr>
<th>n</th>
<th>LS</th>
<th>J</th>
<th>det</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,13</td>
<td>1</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>2,12</td>
<td>7</td>
<td>13</td>
<td>91</td>
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<tr>
<td>3,11</td>
<td>17</td>
<td>41</td>
<td>364</td>
</tr>
<tr>
<td>4,10</td>
<td>27</td>
<td>107</td>
<td>1001</td>
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<tr>
<td>5,9</td>
<td>73</td>
<td>198</td>
<td>2002</td>
</tr>
<tr>
<td>6,8</td>
<td>119</td>
<td>295</td>
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</tr>
<tr>
<td>7</td>
<td>119</td>
<td>327</td>
<td>3432</td>
</tr>
</tbody>
</table>

f-projector by construction still allows participation of 4f/5f in chemical bonding as an electron acceptor, i.e. \((4f/5f^n)^{+\Delta n}\), \(0 \leq \Delta n < 1\) is still allowed!

**Warning:**

The following calculations reported here have been performed by an experienced LPP user. Do not try to do similar work without previously reading the instructions and warnings in e.g. A. Moritz, X. Cao, M.D., Theor. Chem. Acc. 117 (2007) 473. In all cases perform a single point SPP or AE SCF calculation to verify the assumption about the 4f/5f occupancy!
Energy-consistent pseudopotentials: 4f-in-core vs. 4f-in-valence PPs for CeO

First ('historical') test calculations on CeO ($\text{Ce}^{2+}$ 4f$^1$ 6s$^1$ O$^{2-}$)

Concept of a superconfiguration: all states resulting from a valence substate and a 4f subconfiguration have similar spectroscopic constants and belong to the same superconfiguration. For example: CeO has a 4f$^1$ subconfiguration and a $\sigma^1$ 2$\Sigma$ valence substate, resulting in a 4f$^1$ $\sigma^1$ superconfiguration with 8 $\Lambda\Sigma$ states ($^{1,3}\Sigma, \Pi, \Delta, \Phi$) and 16 $\Omega$ states.


| 4f$^1$ 6sp$^1$ $^3\Phi$ ground state, CISD+SCC results |
|---|---|---|---|---|
| method | $R_e$ (Å) | $\omega_e$ (cm$^{-1}$) | $D_e$ (eV) | $T_e$ (eV) |
| PPc | 1.819 | 834 | 7.25 (88%) |
| PPv avg. | 1.821 | 836 | 7.16 (87%) |
| exp. | 1.820 | 824 | 8.22 (100%) |
| PPv $^3\Phi$ | 1.827 | 838 | 7.28 (89%) |
| PPv $^1\Phi$ | 1.827 | 837 | 0.04 |
| PPv $^3\Delta$ | 1.819 | 840 | 0.10 |
| PPv $^1\Delta$ | 1.818 | 836 | 0.15 |
| PPv $^3\Pi$ | 1.819 | 833 | 0.17 |
| PPv $^1\Pi$ | 1.826 | 829 | 0.21 |
| PPv $^3\Sigma$ | 1.816 | 835 | 0.18 |
| PPv $^1\Sigma$ | 1.821 | 834 | 0.31 |

Contribution of 4f orbitals to chemical bonding: $\Delta R_e \approx -0.11$ Å, $\Delta D_e \approx -0.9$ eV (estimated from calculations with different PP f projectors: 4f$^1$ vs. 4f$^{1+x}$).

Term energies of states belonging to the 4f$^1$ 6sp$^1$ $^3\Phi$ superconfiguration, SOCI results (cm$^{-1}$)

<table>
<thead>
<tr>
<th>$\Omega$</th>
<th>exp.</th>
<th>PPv</th>
<th>PPc</th>
</tr>
</thead>
<tbody>
<tr>
<td>X$_{12}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>X$_{23}$</td>
<td>80</td>
<td>119</td>
<td>101</td>
</tr>
<tr>
<td>W$_{11}$</td>
<td>812</td>
<td>913</td>
<td>923</td>
</tr>
<tr>
<td>W$_{22}$</td>
<td>912</td>
<td>1045</td>
<td>968</td>
</tr>
<tr>
<td>V$_{10^-}$</td>
<td>1679</td>
<td>1396</td>
<td>1589</td>
</tr>
<tr>
<td>V$_{21}$</td>
<td>1870</td>
<td>1476</td>
<td>1679</td>
</tr>
<tr>
<td>U$_{10^+}$</td>
<td>1932</td>
<td>1715</td>
<td>1769</td>
</tr>
<tr>
<td>X$_{34}$</td>
<td>2040</td>
<td>2139</td>
<td>2302</td>
</tr>
<tr>
<td>X$_{43}$</td>
<td>2141</td>
<td>2286</td>
<td>2487</td>
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<tr>
<td>W$_{33}$</td>
<td>2617</td>
<td>2872</td>
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<tr>
<td>W$_{42}$</td>
<td>2772</td>
<td>3039</td>
<td>3165</td>
</tr>
<tr>
<td>V$_{32}$</td>
<td>3463</td>
<td>3386</td>
<td>3771</td>
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<tr>
<td>V$_{41}$</td>
<td>3646</td>
<td>3391</td>
<td>3766</td>
</tr>
<tr>
<td>T$_{10^-}$</td>
<td>3822</td>
<td>3476</td>
<td>4120</td>
</tr>
<tr>
<td>U$_{21}$</td>
<td>4133</td>
<td>3605</td>
<td>4249</td>
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<td>U$_{30^+}$</td>
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<tr>
<td>m.a.e.</td>
<td>210</td>
<td>192</td>
<td></td>
</tr>
</tbody>
</table>

Actinide polyflourides $\text{AnF}_n$ as test cases

$\text{AnF}_2$ (An=Pu–No) $C_{2v}$: LPP HF in comparison to SPP state-averaged MCSCF results.

<table>
<thead>
<tr>
<th>An</th>
<th>$R_e$ (Å)</th>
<th>$\angle F$–An–F (°)</th>
<th>$E_{bond}$ (eV)</th>
<th>Mulliken $f$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LPP</td>
<td>SPP</td>
<td>LPP</td>
<td>SPP</td>
</tr>
<tr>
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<td>2.212</td>
<td>2.152</td>
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<td>106.5</td>
</tr>
<tr>
<td>Am</td>
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<td>2.163</td>
<td>121.0</td>
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<td>113.6</td>
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<tr>
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<td>2.178</td>
<td>2.155</td>
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<td>117.8</td>
</tr>
<tr>
<td>Cf</td>
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<td>123.5</td>
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<tr>
<td>Es</td>
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<td>2.134</td>
<td>124.6</td>
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<tr>
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<td>2.122</td>
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</tbody>
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LPP (7s6p5d2f1g)/[6s5p4d2f1g];
SPP (14s13p10d8f6g)/[6s6p5d4f3g]; F aug-cc-pVTZ
AnF$_3$ (An=Ac–Lr) $C_{3v}$: LPP HF in comparison to SPP state-averaged MCSCF results.

<table>
<thead>
<tr>
<th>An</th>
<th>$R_e$ (Å)</th>
<th>$\angle$F–An–F (°)</th>
<th>$E_{bond}$ (eV)</th>
<th>Mulliken f</th>
</tr>
</thead>
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<td>SPP</td>
<td>LPP</td>
<td>SPP</td>
</tr>
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<td>2.06</td>
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m.a.e. 0.027  4.1  0.09

*LPP (7s6p5d2f1g)/[5s4p3d2f1g]; SPP (14s13p10d8f6g)/[10s9p5d4f3g]; F aug-cc-pVQZ.
AnF$_4$ (An=Th–Cf) T$_d$: LPP HF in comparison to SPP state-averaged MCSCF results.

<table>
<thead>
<tr>
<th>An</th>
<th>$R_e$ (Å)</th>
<th>$E_{\text{bond}}$ (eV)</th>
<th>Mulliken f</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>LPP</td>
<td>SPP</td>
<td>LPP</td>
</tr>
<tr>
<td>Th</td>
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<td>Bk</td>
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<td>2.017</td>
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<tr>
<td>Cf</td>
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<td>2.001</td>
<td>5.11</td>
</tr>
<tr>
<td>m.a.e.</td>
<td>0.018</td>
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</tbody>
</table>

LPP (7s6p5d2f1g)/[6s5p4d2f1g];
SPP (14s13p10d8f6g)/[6s6p5d4f3g]; F aug-cc-pVQZ.

AnF$_5$ (An=Pa–Am) C$_{4v}$: LPP HF in comparison to SPP state-averaged MCSCF results.

<table>
<thead>
<tr>
<th>An</th>
<th>$R_e^{ax}$ (Å) LPP</th>
<th>$R_e^{eq}$ (Å) LPP</th>
<th>$\angle F^{ax}$–An–F$^{eq}$ (°) LPP</th>
<th>$E_{bond}$ (eV) LPP</th>
<th>$E_{bond}$ (eV) SPP</th>
<th>Mulliken f LPP</th>
<th>Mulliken f SPP</th>
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<td>2.022</td>
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m.a.e. 0.007 0.011 2.6 0.09

LPP (7s6p5d2f)/[6s5p4d2f];
SPP (14s13p10d8f)/[6s6p5d4f]; F (11s6p3d)/[5s4p3d]
A. Moritz, preliminary results.

AnF$_6$ (An=..., U, ... ?) O$_h$: LPPs not yet available; limited range of applications.

→ 5f-in-core PPs are at least useful for getting (quickly) a rough picture of structure and energetics (errors in bond lengths < 0.05 Å, in bond angles < 10°, in binding energies < 0.15 eV.
→ Together with reduced valence basis sets the 5f-in-core PPs are also applicable in solid state calculations using e.g. the program CRYSTAL (Roetti, Dovesi, Pisani, ...), which otherwise (still) cannot deal with f-element atoms.
An-O bond length of An$^{3+}$OH$_2$ (An=Ac-Lr)
LPP (5f-in-core PPs); SPP (5f-in-valence PPs), VTZ

deviation of LPP/RHF from SPP/RHF:
maximum deviation: 0.028 Angstrom
average deviation: 0.015 Angstrom

An (30s25p19d13f2g); H, O cc-pVDZ
Binding energy of $\text{An}^{3+}\text{OH}_2$ (An=Ac-Lr)

LPP (5f-in-core PP); SPP (5f-in-valence PP); VTZ

Largest deviation of LPP/RHF from SPP/RHF:
- average over all states: 0.13 eV
- lowest state: 0.25 eV

Estimated BSSE in $D_e$ for AE/DHF at least 0.2 eV?
(calculated for Ln$^{3+}\text{OH}_2$; errors in total energies of An twice as large as for Ln!
largest errors in SPP valence energies a factor of 10 smaller than for the AE case.)


An (30s25p19d13f2g); H, O cc-pVDZ
5f-in-core PPs for actinides: calibration for $\text{An}^{3+}\text{H}_2\text{O}$

Binding energy of $\text{An}^{3+}\text{OH}_2$ ($\text{An}=$Ac-Lr)

LPP (5f-in-core PP); SPP (5f-in-valence PP); VDZ

$D_e$ (An-OH$_2$, eV)


An (30s25p19d13f2g); H, O cc-pVDZ
About equal participation of 5f (e2u) and 6d (e2g) orbitals to metal-ring bonding in uranocene \( \text{U(C}_8\text{H}_8)_2 \) is well established: can 5f-in-core PPs deal with such (slight) involvement of some 5f orbitals bonding?

Metal-ring distance in actinocenes

Hartree-Fock and selected correlated results

An: LPP (7s6p5d2f1g)/[6s5p4d2f1g], SPP (14s13p10d8f6g)/[6s6p5d4f3g]; C: cc-pVTZ (in HF), cc-pVDZ (in CCSD(T)), TZVP in DFT.

Quality of the metal-ring interaction energies estimated from ionic binding energies
$\text{An} (\text{C}_8\text{H}_8)_2 \rightarrow \text{An}^{4+} + 2 \text{C}_8\text{H}_8^{2-}$.

<table>
<thead>
<tr>
<th>Mulliken f population (HF)</th>
<th>An</th>
<th>LPP</th>
<th>SPP</th>
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<tr>
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<th>SPP</th>
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An: LPP (7s6p5d2f1g)/[6s5p4d2f1g], SPP (14s13p10d8f6g)/[6s6p5d4f3g]; C: cc-pVTZ.
Texaphyrins = “Expanded porphyrins from Texas!
(coordinating core with 5 N instead of 4 N; core 20% larger)
(J. Sessler et al., Inorg. Chem. 32 (1993) 3175)

- stable (water-soluble) complexes with larger cations, e.g., Ln(III) ions
- accumulation in tumors, ...
- highly-paramagnetic (Gd(III) texaphyrin)
- absorption in far-red visible spectrum
- reversible and easy reduction: Ln-Tex$^{2+}$ – Ln-Tex$^{1+}$ – Ln-Tex;
  production/removal of reactive oxygen species (ROS), e.g., singlet oxygen, hydroxyl radical, superoxide anion, ...
- medical applications of Gd-Tex$^{2+}$ (XYCYTRIN), Lu-Tex$^{2+}$ (LUTRIN), ... in cancer, heart attack and stroke therapy (cf. Pharmacynics, Inc.; Nasdaq: PCYC):
  - X-ray radiation therapy (XRT)
  - magnetic resonance imaging (MRI)
  - photodynamic therapy (PDT)
  - photoangioplasty (PA)
  - light-based treatment of age-related macular degeneration (AMD)

Texaphyrins: two -O(CH$_2$)$_3$OH side chains, Motexafins: two -O(CH$_2$CH$_2$O)$_3$OH side chains.

**Questions for theory:** structure, stability, electron affinity, spectrum in the long-wavelength region (La - Gd - Lu); existence of An(III) complexes (U(III)-Motex$^{2+}$)?

**Attempted answers:** DFT and TDDFT (BP) calculations using 4f-in-core and 5f-in-core PPs (TURBOMOLE)
In the gasphase $\text{Gd-Motex}^{2+}$ is (probably) the most stable f-element motexafin. Binding energies $10.3(9.6), 11.2(8.9), 10.6(8.1)$ eV for La(Ac), $\text{Gd(Cm)}, \text{Lu(Lr)}$; similar to Gd-Tex$^{2+}$

In polar solvents Ac-Motex$^{2+}$ is (probably*) the most stable f-element motexafin. Binding energies: 3.91(4.80), 4.09(3.94), 4.15(2.12) eV for La(Ac), Gd(Cm), Lu(Lr).

* hydration/solvation energies of An$^{3+}$ (if those are stable ...)?

5f-in-core PPs for actinides: application to $\text{An}^{3+}$-hydration

1-3: models for first hydration sphere; no minimum corresponding to $h=10$ found.  
4-5: models for the influence of the second hydration sphere on the first sphere.

PP DFT/BP; structures: An (7s6p5d2f)/[6s5p4d2f], H, O aug-cc-pVDZ, C$_1$ symmetry;  
energies: MP2 as above, DFT An (7s6p5d2f1g)/[6s5p4d2f1g], H, O aug-cc-pVQZ;  
TURBOMOLE.

Explicit treatment of the first hydration sphere; simple modelling of the second, ... hydration sphere using COSMO, a conductor-like screening model. An\(^{3+}\) cavity radii obtained by fitting to the semiempirical standard free enthalpies of hydration \(\Delta G_H^o\) values provided by David, Vokhmin, New. J. Chem. 27 (2003) 1627. Unfortunately, minimum structures including COSMO have only been found for some \([\text{An}(\text{H}_2\text{O})_9]^{3+}\) complexes \(\rightarrow\) approximate derivation of the hydration energy \(\Delta E_H\)!
5f-in-core PPs for actinides: application to An$^{3+}$-hydration

Prefered CN $h$: BP: $h=8$ for all actinides; MP2: $h=9$ for Ac - Md, $h=8$ for No -Lr;
Note: energy differences too small to point to the preference of a single $h$ value!
Errors partly due to neglect of influence of second coordination sphere! An-O distance in $[\text{An}(\text{H}_2\text{O})_{h-1}\text{H}_2\text{O}]^{3+} \approx 23.1$ and 21.0 pm less than in $[\text{An}(\text{H}_2\text{O})_{h-1}]^{3+}$ for $h=8$ and 9, respectively.
COSMO recovers a part of the estimated effect of the second hydration sphere. Correct?
Convergence problems for coordination numbers of 7 and 8 → picture incomplete!
→ future work should (at least) include the second coordination sphere explicitly...
An$^{\text{III}}$ cavity radii $r$ (in pm) used in COSMO, estimated Gibbs free energies of hydration $\Delta G_{\text{H}}^\circ$ (in kJ mol$^{-1}$) for different $h$, and semiempirical reference An$^{\text{III}}$ Gibbs free energies of hydration (in kJ mol$^{-1}$).

<table>
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<tr>
<th></th>
<th>$\Delta G_{\text{H}}^\circ$</th>
<th>$\Delta G_{\text{H}}^\circ$*</th>
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Approximation: $\Delta G_{\text{H}}^\circ \approx \Delta H_{\text{H}}^\circ - T\Delta S_{\text{H}}^\circ \approx \Delta E_{\text{H}} - T\Delta S^\circ$;

H$^\circ$ data not available for An$^{3+}$ (g); $\Delta S^\circ$ refers to the gas phase entropy change.
Conclusions

- Electron correlation usually is a more difficult problem than relativity, especially for systems containing open f shells.

- The 4f- and 5f-in-valence PP approach is usually reliable, efficient and thus competitive to relativistic all-electron methods, at least when ‘chemical accuracy’ is sufficient.

- 4f-in-core PPs for lanthanides are well established and were frequently tested/applied with success in the last 15 years.

- 5f-in-core PPs for actinides are at least useful for special applications.

Outlook

- Two-component MCDHF/DC+B adjusted small-core PPs for lanthanides (4f-in-valence) and actinides (5f-in-valence) have to be derived in order to model correctly corresponding four-component all-electron calculations. Corresponding parametrizations for the main group and d transition metals are essentially complete. Initial results for uranium look promising.

- Development of a (simple) model valence-only Hamiltonian with two-electron contributions in order to overcome the unpleasant consequences of the pseudoorbital transformation. (?)
Acknowledgement

- Hermann Stoll (Universität Stuttgart, Stuttgart)
- Ulrich Wedig (Stuttgart; 198?) many-electron adjustment (nrel.)
- Peter Schwerdtfeger (Stuttgart, ..., Auckland; 198? - ...) relativistic PPs, PPs for super-heavy elements
- Dirk Andrae (Stuttgart; 199?) WB PPs 4d transition metals
- Ulrich Häussermann (Stuttgart; 199?) WB PPs 5d transition metals
- Wolfgang Küchle (Stuttgart, Dresden; 1991 - 1998) WB PPs for main group elements and actinides
- Bernhard Metz (Stuttgart; 1998 - 2002) MCDHF PPs for main group elements
- Xiaoyan Cao (Bonn, Köln; 2000 - ...) basis sets for lanthanide and actinide PPs
- Detlef Figgen (Stuttgart; 2003 - 2007) MCDHF PPs for 4d and 5d transition metals
- Jun Yang (Köln; 2003 - 2007) basis sets for lanthanide 4f-in-core PPs
- Mark Burkatzki (Köln; 2004 - ...) QMC adapted WB PPs for main group elements
- Anna Moritz (Köln; 2005 - ...) 5f-in-core WB PPs for actinides
- Jonas Wiebke (Köln; 2006 - ...) applications to hydrated actinide ions
- and others

- Kirk Peterson (Pullman) cc-pVxZ basis sets
- Ken Dyall (Schrödinger Inc.) GRASP

- DFG, DAAD, FCI, OSC, MPG, NSC
- Univ. Stuttgart, OSU, MPI-PKS, Univ. Bonn, Univ. zu Köln

Thank you for your attention!
Any questions left open?

Appendix
The Relativistic Many Body Problem in Molecular Theory


Pseudopotential calculations are less accurate than all-electron calculations, but they simulate the results of the latter often surprisingly well, for substantially smaller expenses. It is therefore not astonishing that in the chemistry of heavy atoms, relativistic pseudopotential theory is practically the method of choice. It is certainly the most successful of all approximate relativistic molecular theories.
Simplified summary of relativistic effects for valence shells of many-electron atoms

- **direct effect** (dominates for valence s and p shells)
  \[\rightarrow\text{stabilization, contraction}\]

- **indirect effect** (dominates for valence d and f shells)
  \[\rightarrow\text{destabilization, expansion}\]

- **spin-orbit splitting** (of p, d, f, \ldots shells)
  \[\rightarrow\text{change of symmetry properties, i.e., single point group }\rightarrow\text{double point group}\]

relativity stabilizes occupation of shells in the order \(f < d < p < s\).

consequences for chemical bonding, e.g., bond length contraction or expansion, bond stabilization or destabilization, \ldots
many articles on the subject, e.g., Pyykkö, Chem. Rev. 88 (1988) 563

Electron correlation effects in many-electron atoms

correlation stabilizes occupation of shells in the order \(f > d > p > s\).
Relativistic and electron correlation effects for IP$_{3,4}$ of Ac - Lr
AE HF vs. DHF and PP ACPF results with basis set extrapolation
Electronic ground state and configurations for the lanthanides Ln$^{n+}$ (n = 0 – 4).

<table>
<thead>
<tr>
<th></th>
<th>M</th>
<th>M$^{1+}$</th>
<th>M$^{2+}$</th>
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<td>2F$_{5/2}$</td>
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<td>15I$_{15/2}$</td>
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Color code: 4f$^n$ (as in Ln g.s.); 4f$^{n+1}$; 4f$^{n-1}$; 4f$^{n-2}$.
Electronic states of actinides

Electronic ground state and configurations for the actinides An^{n+} (n = 0 – 4).

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<th>M^{3+}</th>
<th>M^{4+}</th>
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Color code: 5f^n (as in An g.s.); 5f^{n+}; 5f^{n-}; 5f^{n-2}.
WB-adjusted PPs

Quite reliable (at least) for scalar-relativistic calculations. At present our only option/offer for lanthanides and actinides, due to too high (?) computational effort for MCDHF adjustment ($O(10^4 - 10^5)$ reference J-levels !)

- 4f/5f-in-valence (small-core) Ln/An PPs (SPPs)


- 4f/5f-in-core (large-core) Ln/An PPs (LPPs)

Choice of the core: AE MCDHF/DC (frozen core) results for U

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frozen cores: U Q=6: 1s - 5d, 6s, 6p; Q=14: 1s - 5d; Q=32: 1s - 4d.
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frozen cores: U Q=6: 1s - 5d, 6s, 6p; Q=14: 1s - 5d; Q=32: 1s - 4d.
Choice of the core: AE MCDHF/DC (frozen core) results for U

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frozen cores: U Q=6: 1s - 5d, 6s, 6p; Q=14: 1s - 5d; Q=32: 1s - 4d.
Choice of the core: AE MCDHF/DC (frozen core) results for U

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frozen cores: U Q=6: 1s - 5d, 6s, 6p; Q=14: 1s - 5d; Q=32: 1s - 4d.
Spin-Orbit contributions to IP₃ of Ln, An
Small-core PPs for lanthanides: $\Delta IP_4$, spin-orbit contributions

Spin-Orbit contributions to $\Delta IP_4$ of Ln, An

$\Delta IP_4$ (eV)

La/Ac

Gd/Cm

Lu/Lr
U $5f^3 \ 6d^1 \ 7s^2$ (AE MCDHF vs. ECP60MWB + SO(5f,6d))

PP: state averaged relativistic MCHF (5s,5p,5d,6s,6p scalar-relativistic and frozen)
MCDHF/DC+B-adjusted small-core PPs for actinides: U errors

U p.n. DHF/DC+B(f.d.) Q=32 PP
m.a.e. in 98 nonrelativistic configurations (red), 30035 J-levels (blue)
MCDHF/DC+B-adjusted small-core PPs for actinides: U errors

U p.n. DHF/DC+B(f.d.) Q=32 PP

largest deviations in total valence energies of 30035 J-levels

U 5f⁴ 7s² (107)

U 5f⁴ 7s² 7p¹ (1218)

U 5f⁴ (107)

U 5f⁴ 7s² (5)

U 5f⁴ 7s¹ 7p¹ (333)

U (2⁺) 5f⁴ (107)

U (7⁺) 5d⁹ (1)

U (7⁺) 5d⁹ (1)

U (1⁺) 5f⁴ 7p¹ (1218)

number of parameters for s, p, d, f potential

largest deviations (cm⁻¹)
Overview over current status of fitting for U MCDHF SPPs.

All energy values in in cm$^{-1}$

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np: number of parameters  
nc: number of (nonrelativistic) configurations  
nJl: number of J levels  
m.q.e.: mean quadratic error  
m.n.d.: maximum negative deviation  
m.p.d.: maximum positive deviation

A better account for QED effects (self-energy correction) is needed/under investigation.
MCDHF/DC+B-adjusted small-core PPs for actinides: U errors

Total AE Valence Energy (eV)

Error in Total PP Valence Energy (eV)

U p.n. MCDF/DC+B(f.d.) PP Q=32
errors in valence energies of 98 non-relativistic configurations

m.q.e. 16.3 cm$^{-1}$
U p.n. MCDHF/DC+B(f.d.) Q=32 PP
errors in total valence energies of 30035 J-levels

- maximum error 0.268 eV
- 1218th J-level of \( \text{U}(0) \ 5f^4 \ 7s^1 \ 7p^1 \)

- all 30035 J-levels of 98 configurations
- 16718 J-levels below 5eV relative energy
- 98 lowest J-levels of each configuration

m.q.e. 305.2 cm\(^{-1}\)
**MCDHF/DC+B-adjusted small-core PPs for actinides: comparison to GRECP**

U MCDHF/DC+B Q=32 PP vs. DHF/DCB Q=32 GRECP (in \( \text{cm}^{-1} \)):

56 parameters for s,p,d,f (adjusted to 30035 J-levels from 98 configurations):

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spread of errors: 13 6

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<th>s</th>
<th>p</th>
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<th>error</th>
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<th>error(*)</th>
<th>point</th>
<th>Fermi</th>
<th>n.</th>
<th>SPP</th>
<th>Fermi</th>
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</table>

spread of errors: 33 31

spread of errors: 15 15

The (self-consistent treatment of the) Breit interaction contributes at most with \( \approx 1800 (2) \text{ cm}^{-1} \)!

MCDHF/DC+B-adjusted small-core PPs for actinides: comparison to GRECP

U MCDHF/DC+B Q=32 PP vs. DHF/DCB Q=32 GRECP (in cm\(^{-1}\)):

56 parameters for s,p,d,f (adjusted to 30035 J-levels from 98 configurations):

<table>
<thead>
<tr>
<th></th>
<th>J DHF/DC+B</th>
<th>PP</th>
<th>J DHF/DCB(<em>)GRECP(</em>)</th>
<th>point</th>
<th>n. error</th>
<th>Fermi</th>
<th>n. error</th>
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<td>309.9</td>
<td>29343</td>
<td>553</td>
<td>20447.5</td>
<td>98.8</td>
<td>20453</td>
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<td>2</td>
<td>20468.5</td>
<td>413.2</td>
<td>20477</td>
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<td>0.0</td>
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<td>0</td>
</tr>
</tbody>
</table>

m.a.e. 257.8 374.3 m.a.e. 154.7 280.0 m.a.e. 220.1 254.7


m.a.e. refer to the term energies excluding the ground level.

→ We conclude that the semilocal ansatz is alive and well!

Further evidence is on the way and will be published asap...
Is the superconfiguration/feudal* model useful for actinides? Can actinide 5f-in-core LPPs yield reasonable results? → Some test calculations on UH:

Low-lying electronic states:
U\(^{+}\) 5f\(^3\)7s\(^2\) 4I H\(^{-}\) 1s\(^{2}\) 1S → \(4\Lambda\) (\(\Lambda = 0 - 6\); e.g. \(4\)I, \(4\)H, \(4\)\(\Gamma\), \(4\)\(\Phi\), \(4\)\(\Delta\), \(4\)\(\Pi\), \(4\)\(\Sigma\));
lowest levels of U\(^{+}\) 5f\(^3\)6d\(^{1}\)7s\(^{1}\), 5f\(^3\)6d\(^{2}\) and 5f\(^{1}\)7s\(^{1}\) at 289, 4585 and 4664 cm\(^{-1}\), respectively → further possible low-lying states.

Question of the ground state:
Balasubramanian et al. (2003) CASSCF/SOCI \(4\)I ground state, \(6\)\(\Lambda\) excited state; single reference schemes yield a \(6\)\(\Lambda\) ground state; spin-orbit effects not included.

Hamiltonian and basis sets:
U: AE DKH (30s26p18d14f7g)/[10s9p7d5f3g] ANO; SPP (14s13p10d8f6g)/[6s6p5d4f3g] ANO;
5f\(^{3}\)-in-core LPP (7s6p5d2f1g)/[5s4p3d2f1g]. H: aug-cc-pVQZ (spdf) Dunning.
(adding U (3h)/[1h]: MRCI \(\Delta R_e = -0.005\) Å, \(\Delta \omega_e = +12\) cm\(^{-1}\); no change in CASSCF).

CASSCF reference wavefunction:
Minimum active space: U 5f → 3 electrons in 7 orbitals!
Ideal active space: U 5f, 6d, 7s and 7p, H 1s → 7 electrons in 17 orbitals!
Applied reduced active space: lower \(\sigma^2\) kept doubly occupied, 4 weakly occupied orbitals excluded → 5 electrons in 12 orbitals! 1282 CSFs leading to \(36 \times 10^6\) contracted (\(498 \times 10^6\) uncontracted) configurations in MRCI. (CASSCF 5,12→7,17: \(\Delta R_e = -0.003\) Å, \(\Delta \omega_e = -11\) cm\(^{-1}\)).

* feudal = \(f\) essentially unaffected, \(d\) accommodates ligands.
Selected results for the UH $5f^3 \sigma^2 \sigma^2$ superconfiguration

<table>
<thead>
<tr>
<th>method</th>
<th>configuration/state</th>
<th>$R_e$ (Å)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>LPP/HF</td>
<td>$5f^3 \sigma^2 \sigma^2$ avg. (1 det.)</td>
<td>2.186</td>
<td>1291</td>
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<tr>
<td>SPP/CASSCF$^a$</td>
<td>$5f^3 \sigma^2 \sigma^2$ avg. (364 det.)</td>
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<td>SPP/CASSCF$^a$</td>
<td>lowest doublet state</td>
<td>2.171</td>
<td>1331</td>
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<tr>
<td>SPP/CASSCF$^a$</td>
<td>lowest quartet state ($^4I$)</td>
<td>2.159</td>
<td>1330</td>
</tr>
<tr>
<td>SPP/CASSCF$^b$</td>
<td>lowest quartet state ($^4I$)</td>
<td>2.076</td>
<td>1442</td>
</tr>
<tr>
<td>SPP/CASSCF$^c$</td>
<td>lowest quartet state ($^4I$)</td>
<td>2.073</td>
<td>1431</td>
</tr>
<tr>
<td>LPP/CASSCF$^d$</td>
<td>$5f^3 \sigma^2 \sigma^2$ avg.</td>
<td>2.127</td>
<td>1378</td>
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</tbody>
</table>

$^a$ Minimum active space in CASSCF: 3 electrons in 7 orbitals (U 5f).

$^b$ Applied active space in CASSCF: 5 electrons in 12 orbitals.

$^c$ Ideal active space in CASSCF: 7 electrons in 17 orbitals (U 5f, 6d, 7s, 7p, H 1s)

$^d$ Active space in CASSCF: 4 electrons in 10 orbitals (U 6d, 7s, 7p, H 1s)

Possible reasons for the deviations:

U 5f shell not completely core-like:
singly occupied orbitals: $\phi$, $\delta$ 100 % U f; $\pi$ 99 % U f, 1 % U d; $\sigma$ 96 % U f, 3 % U d.
f occupation number 2.995, i.e., slightly below the occupation of 3+x ($x > 0$) which the f projector is constructed for.

→ more favorable cases than UH for the application of 5f-in-core LPPs exist!
### Selected results for the UH $^4$I ground state

<table>
<thead>
<tr>
<th>method</th>
<th>configuration/state</th>
<th>$R_e$ (Å)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$D_e$ (eV)</th>
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<tbody>
<tr>
<td>LPP/CISD+Q</td>
<td>$5f^3 \sigma^2 \sigma^2$</td>
<td>2.069</td>
<td>1430</td>
<td>3.06</td>
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<tr>
<td>LPP/MRCI+Q</td>
<td></td>
<td>2.078</td>
<td>1421</td>
<td></td>
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<tr>
<td>SPP/MRCI+Q</td>
<td>$5f^3 \sigma^2 \sigma^2$ $^4$I</td>
<td>2.008</td>
<td>1501</td>
<td>2.97, 3.06$^c$</td>
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<tr>
<td>DKH/MRCI+Q</td>
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<td>2.019</td>
<td>1495</td>
<td>2.87, 2.99$^c$</td>
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<tr>
<td>SPP/MRCI+Q/SO $\Omega = 9/2$</td>
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<tr>
<td>DKH/MRCI+Q/SO</td>
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<td>2.021</td>
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<td>exp.$^a$</td>
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<td>PP/SOCI$^b$</td>
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$^a$ Andrews and coworkers (1997), UH in Argon matrix; $^b$ Balasubramanian et al. (2003).

$^c$ calculated wrt neutral atoms (U, H) in separate calculations and ions (U$^+$, H$^-$) at large distance in one calculation.

Small-core PPs for actinides: calibration for molecules, UH

\[
\begin{align*}
\text{UH } f^3 \sigma^2 \sigma^2 & \text{ Superconfiguration: Term Energies} \\
\text{CASSCF and MRCI results for PP and DKH}
\end{align*}
\]

\[
\begin{array}{cccc}
\text{CASSCF} & \text{MRCI} & \text{SOCI} \\
\text{SPP} & \text{DKH} & \text{SPP} & \text{DKH} & \text{SPP+SO} & \text{DKH+BP} \\
\end{array}
\]

\[
\begin{align*}
^6K, ^6\Lambda & > 0.3 \text{ eV} & \text{others} & > 0.3 \text{ eV}
\end{align*}
\]

Note: only the contributions of the listed ΛS states to the 5 lowest Ω states were considered!

Small-core PPs for actinides: calibration for molecules, UH

UH f^3 \sigma^2 \sigma^2 Superconfiguration: Bond Lengths
CASSCF and MRCI results for PP and DKH

Small-core PPs for actinides: calibration for molecules, UH