An introduction to
Relativistic Quantum Chemistry

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Outline

● Why do we care about relativity in chemistry?
  ● What are relativistic effects?
  ● Relativistic effects in atoms
  ● Relativistic effects in molecules

● How can we include relativity in calculations?
  ● Perturbation theory of relativistic effects
  ● 2-component methods
  ● 4-component methods
  ● Effective Core Potentials

● Some recommendations / best practices
  ● Comparison light / heavy element calculations
  ● Importance of spin-orbit coupling
Assumptions in Quantum Chemistry

- **Born-Oppenheimer approximation**
  - Electronic and nuclear motion can be decoupled
  - Electronic energies for motion around clamped nuclei provide potential energy surfaces for nuclear motion
  - Coupling between surfaces is studied by perturbation theory

- **Nuclear charge distribution**
  - Point nucleus approximation
  - Nuclear deformations are treated in perturbation theory

- **Relativity**
  - The speed of electrons is always far below the speed of light
  - Goal is to find time-independent wave functions (stationary states)
  - Magnetic fields can be neglected or treated in perturbation theory
Dirac’s view on relativity

Dirac (1929)

- The general theory of quantum mechanics is now almost complete, the imperfection that still remain being in connection with the exact fitting in of the theory with relativistic ideas. These give rise to difficulties only when high speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei.

- The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.
Later insights

● Pekka Pyykkö and Jean-Paul Desclaux (1979)
  ● The chemical difference between the fifth row and the sixth row seems to contain large, if not dominant, relativistic contributions which, however, enter in an individualistic manner for the various columns and their various oxidation states, explaining, for example, both the inertness of Hg and the stability of Hg\textsuperscript{2+}. These relativistic effects are particularly strong around gold. A detailed understanding of the interplay between relativistic and shell-structure effects will form the impact of relativity on chemistry.

● Jan Almlöf & Odd Gropen (1996)
  ● While the incorporation of these effects sometimes increases the computation labor, the increase is generally reasonable, and certainly much less than in, e.g., the transition from semiempirical to ab initio methods for routine quantum chemistry applications. We predict, therefore, that relativistic corrections in one form or another will be included in the majority of all quantum chemistry calculations before the end of this decade.
The extra dimension

Development of relativistic molecular electronic structure theory
The hydrogenic atom: Energies

- The exact non-relativistic energy
  \[ E^{NR} = -\frac{Z^2}{2n^2} \]

- The exact relativistic energy
  \[
  E = mc^2 / \sqrt{1 + \left(1 - \frac{Z}{c} \sqrt{n - j - \frac{1}{2} + \sqrt{(j + 1/2)^2 - \frac{Z^2}{c^2}}} \right)^2}
  \]

- Spin-orbit coupling: \[ j = l \pm s \]
  Energy depends on orbital and spin variables
Orbital stabilization: increase in ionization energy

H, Li, Na, K, Rb, Cs, Fr, 119
Orbital contraction

- The outermost s-orbital shrinks substantially
Orbital destabilization and spin-orbit splitting

B, Al, Ga, In, Tl, 113

Zn, Cd, Hg, Cn

Group 13

Group 12

Np - orbital energy au

Nd - orbital energy au

Nuclear Charge
The outermost p- and d-orbitals expand
Ln-An contraction is partly caused by relativistic effects.

Trend expected from the atomic calculations can be checked by calculations on LnF, AnF, LnH$_3$ and AnH$_3$ molecules.
Atomization energies

- Example: Halogen molecules
- Molecular energy is hardly affected by SO-coupling (SO quenching)
- First order perturbation theory

Nonrelativistic

- \( \pi_g^* \)
- \( \pi_u \)
- \( \sigma_g \)

Relativistic

- \( \pi_{g,3/2}^* \)
- \( \pi_{u,3/2} \)
- \( \sigma_{g,1/2} \)
- \( \sigma_{u,1/2}^* \)
Atomization energies

- Atomic asymptotes are lowered by SO-coupling
- First order perturbation theory

Nonrelativistic

\[ p_x \quad p_y \quad p_z \]

Relativistic

\[ p_{1/2} \quad p_{3/2} \quad p_{3/2} \]
Spin-Orbit effect on atomization energies is well-reproduced by correcting only the separate atoms limit
Relativistic effect on vibrational frequencies (cm$^{-1}$)

Bond weakening due to admixture of the antibonding sigma orbital. This is also due to spin-orbit coupling.
Relativistic effect on equilibrium distances (Å)

Important and slightly method dependent for 6p elements
Relativistic effect on atomization energies (kcal/mol)

Make orbital diagram and identify possible SOC effects. Always include scalar effects.
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  ● Perturbation theory of relativistic effects
  ● 2-component methods
  ● 4-component methods
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  ● Importance of spin-orbit coupling
The nonrelativistic Hamiltonian

\[ H = T + V = \frac{p^2}{2m} + q\phi \]

Usually only electric field via scalar potential \( \phi \)

Magnetic fields via vector potential \( \mathbf{A} \):

\[ p \rightarrow \pi = p - q\mathbf{A} \quad \text{(minimal coupling substitution)} \]

\[ H = \frac{p^2}{2m} + q\phi - \frac{q}{m} \mathbf{A} \cdot \mathbf{p} + \frac{q^2}{m} A^2 \]

Zeeman interaction, but no spin-orbit coupling.
NR quantum mechanics with spin

Pauli Hamiltonian in two-component form

\[
\begin{pmatrix}
-\frac{1}{2} \nabla^2 + q\phi + iqA \cdot \nabla + \frac{q^2}{2m} A^2 - \frac{q}{2} B_z \\
-\frac{q}{2}(B_x + iB_y) \\
-\frac{q}{2}(B_x + iB_y) \\
-\frac{1}{2} \nabla^2 + q\phi + iqA \cdot \nabla + \frac{q^2}{2m} A^2 + \frac{q}{2} B_z
\end{pmatrix}
\]

Second derivatives w.r.t. position, first derivative w.r.t. time
Linear in scalar (electric), quadratic in vector (magnetic) potential

→ Is not Lorentz-invariant

😢 Ad hoc introduction of electron spin

😢 Ratio spin angular momentum and magnetic moment incorrect

😢 No spin-orbit coupling
Dirac equation

\[
\left( \beta mc^2 + c \alpha \cdot \pi + q \phi \right) \psi(r,t) = i\hbar \frac{\partial \psi(r,t)}{\partial t}
\]

- First derivatives with respect to time and position
- Linear in scalar and vector potentials
- Lorentz invariant
- \( \alpha \) and \( \beta \) are 4-component matrices

\[
\alpha_x = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} \quad \alpha_y = \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix} \quad \alpha_z = \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix} \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}
\]
The Dirac Hamiltonian

\[ \hat{H} = \beta mc^2 + c \mathbf{\alpha} \cdot \hat{\mathbf{\pi}} + q \phi \]

\[
\begin{pmatrix}
mc^2 + q\phi & 0 & c\pi_z & c(\pi_x - i\pi_y) \\
0 & mc^2 + q\phi & c(\pi_x + i\pi_y) & -c\pi_z \\
 c\pi_z & c(\pi_x - i\pi_y) & -mc^2 + q\phi & 0 \\
 c(\pi_x + i\pi_y) & -c\pi_z & 0 & -mc^2 + q\phi
\end{pmatrix}
\]

Four component wave function

1) Spin doubles the number of components

2) Relativity doubles the number of components again
Free particle Dirac equation

- Take simplest case: $\phi = 0$ and $A = 0$
- Use plane wave trial function

\[ \Psi(r) = e^{i k \cdot r} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} \]

Non-relativistic functional form with constants $a_i$ that are to be determined

\[
\begin{align*}
(E - mc^2)a_1 - c\hbar k_z a_3 - c\hbar k_z a_4 &= 0 \\
(E - mc^2)a_2 - c\hbar k_+ a_3 + c\hbar k_z a_4 &= 0 \\
-c\hbar k_z a_1 - c\hbar k_- a_2 + \left(E + mc^2\right)a_3 &= 0 \\
-c\hbar k_+ a_1 + c\hbar k_z a_2 + \left(E + mc^2\right)a_4 &= 0
\end{align*}
\]

After insertion into time-independent Dirac equation

\[ k_\pm = k_x \pm ik_y \]
Free particle Dirac equation

- Two doubly degenerate solutions
  \[
  \left( E^2 - m^2 c^4 - c^2 \hbar^2 k^2 \right) = 0
  \]
  \[
  E_+ = +\sqrt{m^2 c^4 + c^2 \hbar^2 k^2}
  \]
  \[
  E_- = -\sqrt{m^2 c^4 + c^2 \hbar^2 k^2}
  \]

- Compare to classical energy expression
  \[
  E = \sqrt{m^2 c^4 + c^2 p^2}
  \]

- Quantization (for particles in a box) and prediction of negative energy solutions
Free particle Dirac equation

- Wave function for $E = E_+$

$$a_2 = 0; \quad a_3 = a_1 \frac{c\hbar k_z}{E_+ + mc^2}; \quad a_4 = a_1 \frac{c\hbar k_+}{E_+ + mc^2}$$

$\hbar k \equiv p \ll mc$  \hspace{1cm} For particles moving with “nonrelativistic” velocities

$$a_3 = a_1 \frac{cp_z}{mc^2 + \sqrt{m^2 c^4 + c^2 p^2}} \approx a_1 \frac{p_z}{2mc}$$

$$a_4 \approx a_1 \frac{p_+}{2mc}$$

- Upper components are the “Large components”
- Lower components are the “Small components”
Dirac sea of electrons

- Negative energy solutions are all occupied
- Pauli principle applies
- Holes in this sea of electrons are seen as particles with positive charge: positrons (1933)
- Infinite background charge
- QED (Quantum Electrodynamics) to properly account for contribution of negative energy states
- No-pair approximation

\[ 2\, e^- \xrightarrow{2mc^2} 3\, e^- + 1\, e^+ \]
The hydrogenic atom

- Starting point for the LCAO approach
- Can be solved by separating the radial and angular variables (see Dyall & Faegri or Reiher & Wolf)

\[
\begin{pmatrix}
mc^2 - \frac{Z}{r} & \mathbf{c} \mathbf{\sigma} \cdot \mathbf{p} \\
\mathbf{c} \mathbf{\sigma} \cdot \mathbf{p} & -mc^2 - \frac{Z}{r}
\end{pmatrix}
\begin{pmatrix}
\psi^L (\mathbf{r}) \\
\psi^S (\mathbf{r})
\end{pmatrix}
= E
\begin{pmatrix}
\psi^L (\mathbf{r}) \\
\psi^S (\mathbf{r})
\end{pmatrix}
\]

- The exact solutions help in devising basis set approaches and in understanding the chemical bonding in the relativistic regime
The hydrogenic atom: orbitals

- Write orbitals as product of radial and angular (2-spinor functions)

\[
\begin{align*}
\psi^L(r) &= \frac{1}{r} \left( P_{n\kappa} (r) \xi_{\kappa,m} (\vartheta, \varphi) \right) \\
\psi^S(r) &= \frac{1}{r} \left( i Q_{n\kappa} (r) \xi_{-\kappa,m} (\vartheta, \varphi) \right)
\end{align*}
\]

- Solutions to the radial equation

\[
\begin{align*}
P_{n\kappa} (r) &= N_{n\kappa}^P e^{-\lambda r} \gamma \left( F_1(r) + F_2(r) \right) \quad \text{Large component} \\
Q_{n\kappa} (r) &= N_{n\kappa}^Q e^{-\lambda r} \gamma \left( F_1(r) - F_2(r) \right) \quad \text{Small component} \\
R_{nl}(r) &= N_{nl}^R e^{-\frac{\sqrt{2}E}{mc^2}r} r^{l+1} F(r) \quad \text{Nonrelativistic}
\end{align*}
\]

\[
\lambda = -\sqrt{-2E \left( 1 + \frac{E}{2mc^2} \right)}
\]

\[
\gamma = \sqrt{\kappa^2 - \frac{Z^2}{c^2}} < |\kappa|
\]

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More than one electron

- General form of a time-independent Hamiltonian
  \[ \hat{H} = \sum_{i=1}^{N} \hat{h}_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \hat{g}_{ij} \]

- Wave function
  \[ \Psi(1, \ldots, N) \quad \text{N x 4 components} \]
  \[ \Psi(\ldots, i, \ldots, j, \ldots) = -\Psi(\ldots, j, \ldots, i, \ldots) \quad \text{anti-symmetry} \]

- Difference between relativistic and non-relativistic calculations is in the calculation of integrals over \( h \) and \( g \)

- Second-quantized form of equations is identical to non-relativistic theory when using the no-pair approximation
Electron-electron interactions

- In molecular calculations:
  
  \[ g_{\text{Coulomb–Breit}}^{12} = \frac{1}{r_{12}} = \frac{1}{r_{12}} \]
  
  Coulomb: diagonal operator

  \[ -\frac{1}{c^2 r_{12}} c\alpha_1 \cdot c\alpha_2 \]
  
  Gaunt: off-diagonal operator

  \[ -\frac{1}{2c^2} \left( c\alpha_1 \cdot \nabla_1 \right) \left( c\alpha_2 \cdot \nabla_2 \right) r_{12} \]
  
  Retardation

- Coulomb, Gaunt and retardation terms
  - Zeroth order is the instantaneous electrostatic interactions
  - First correction describes the magnetic interactions
  - Second correction describes retardation of the interaction
Expansion of the energy expression

- The exact Hydrogenic energy expression

\[ E = mc^2 / \left( 1 + \sqrt{1 + \left( \frac{Z}{c} \right)^2 \left( n - j - \frac{1}{2} + \sqrt{(j + 1/2)^2 - \frac{Z^2}{c^2}} \right)} \right)^2 \]

- Can be expanded to

\[ E = mc^2 - \frac{Z^2}{2n^2} + \frac{Z^4}{2n^4 c^2} \left\{ \frac{3}{4} - \frac{n}{j + \frac{1}{2}} \right\} + O \left( \frac{Z^6}{c^4} \right) \]
Breit-Pauli Hamiltonian applied to hydrogenic atom

\[ \hat{H}_{BP}^{\text{BP}} = \hat{T} + \hat{V} - \frac{p^2 V}{8 m^2 c^2} - \frac{p^4}{8 m^3 c^2} + \frac{i \sigma \cdot (p V) \times p}{4 m^2 c^2} \]

Darwin  Mass-Velocity  Spin-Orbit

\[ < \hat{H}_{\text{Darwin}} > = \frac{Z^4}{2 n^3 c^2} \quad (l = 0) \quad \text{Positive: reduces nuclear attraction} \]

\[ < \hat{H}_{\text{Darwin}} > = 0 \quad (l > 0) \quad \text{Operator is delta-function for } V = -Z/r \]

\[ < \hat{H}_{\text{MV}}^{\text{MV}} > = \frac{Z^4}{2 n^4 c^2} \left\{ \frac{3}{4} - \frac{n}{l + \frac{1}{2}} \right\} \quad \text{Always negative: decreases kinetic energy} \]

\[ < \hat{H}_{\text{SO}}^{\text{SO}} > = \frac{Z^4}{2 n^3 c^2} \frac{l}{l(2l+1)(l+1)} \quad (j = l+1/2) \quad \text{Splitting larger for small } n \text{ and/or } l \text{ and large } Z \]

\[ < \hat{H}_{\text{SO}}^{\text{SO}} > = \frac{Z^4}{2 n^3 c^2} \frac{-l-1}{l(2l+1)(l+1)} \quad (j = l-1/2) \]
The wish list for a relativistic Hamiltonian:

1. It should describe the scalar relativistic effects
2. It should describe the spin-orbit coupling effect
3. There should be a lowest eigenvalue (variational stability)
4. Interpretation: comparison with Schrödinger picture
5. Implementation: easy integrals, efficient coding
6. Errors should be small and systematically improvable
What is wrong with the BP approach? The expansion parameter!

\[ K(E,r) = \left[ 1 + \frac{(E-V)}{2mc^2} \right]^{-1} = 1 - \frac{(E-V)}{2mc^2} + O(c^{-4}) \]

- E should be small relative to 2mc²
  - Orbital energies vary over a range of -0.1 to 5,000 au
  - Twice the rest mass energy is 37,558 au
  - This difference should be large enough

- V should be small relative to 2mc²
  - The potential is dominated by the nuclear attraction close to the nuclei
    \[ V \approx -\frac{Z}{r} \]
  - Take \( r = 10^{-4} \) au and \( Z=6 \) (carbon): \( V = 60,000 \) au
  - Is this inside the nucleus? No: the nuclear radius is 4.7 \( 10^{-5} \) au for C.
0\textsuperscript{th} order regular approximation: ZORA

- Can we use a better expansion parameter? Yes!

\[ K(E,r) = \left[ 1 + \frac{(E - V)}{2mc^2} \right]^{-1} = \left( 1 - \frac{V}{2mc^2} \right)^{-1} \left( 1 + \frac{E}{2mc^2 - V} \right)^{-1} \]

- E should be small relative to $2mc^2 - V$
  - V is negative which improves the expansion close to the nuclei

- Zeroth order in this expansion

\[ \left\{ \frac{1}{2m} (\sigma \cdot p) \left( 1 - \frac{V}{2mc^2} \right)^{\text{-1}} (\sigma \cdot p) + V \right\} \psi_{ZORA}(r) = E\psi_{ZORA}(r) \]

- Zeroth order equation does describe SO-coupling and scalar relativistic corrections

- Gauge dependence of the energy
  - Affects ionization energies, structures
  - Can be avoided by keeping potential in the denominator fixed

\[ V \rightarrow V + C \quad E \rightarrow E + C - \frac{EC}{2mc^2} \]
Uranium atom

1s orbital

- DIRAC
- ZORA
- NR

Slide: courtesy Erik van Lenthe, SCM
Uranium atom

7s orbital

- **DIRAC**
- **ZORA**
- **NR**

Picture change: nodes absent in Dirac density
Four-component methods

- **Idea**
  - Expand Dirac equation in basis set
  - Use kinetic balance condition to prevent “variational collapse”

- **Advantages-Disadvantages**
  - 😊 No approximations made
  - 😊 Matrix elements over the operators are easily evaluated
  - 😞 Many more two-electron integrals
  - 😞 The Fock matrix is twice as large
  - 😊 No picture change
Electron Density of Uranyl

Large component

Small component
Foldy-Wouthuysen transformations

- Define energy-independent unitary transformation to decouple the large and small component equations

\[
UH^D U^{-1} U\psi^D_i = EU\psi^D_i
\]

\[
H^{FW} = U\hat{H}^D U^{-1} = \begin{pmatrix}
H^+ & 0 \\
0 & H^-
\end{pmatrix}
\]

\[
\psi^{FW(+)}_i = U\psi^{D(+)}_i = \begin{pmatrix}
\psi^{FW}_i \\
0
\end{pmatrix}
\]

\[
\hat{U} = \begin{pmatrix}
(1 + X^\dagger X)^{-1/2} & (1 + X^\dagger X)^{-1/2} X^\dagger \\
-(1 + XX^\dagger)^{-1/2} X & (1 + XX^\dagger)^{-1/2}
\end{pmatrix}
\]

- Exact operator expressions are only known for the free particle problem

\[
X = \frac{1}{2mc} K(\sigma \cdot p)
\]
eXact 2-Component (X2C) theory

Idea: Decouple a matrix representation of the Dirac equation

1. Define a 4-component basis and compute matrix elements over the one-electron operators
2. Find exact solution to the Dirac equation in this matrix representation
3. Use the eigenvectors to construct an exact decoupling operator in matrix form
4. Transform all other one-electron operators to this decoupled representation
5. Add two-electron Coulomb operator in unmodified form (accept picture change error for this operator)
Matrix-based X2C approaches

- Fully equivalent to the matrix Dirac equation in the no-pair approximation
- 2-component picture is easily compared to the non-relativistic Schrödinger picture
- Errors made by neglecting corrections to the 2-electron operators are small

- The necessary diagonalization and other matrix manipulations are done before the SCF procedure
- Decoupling from molecular Hartree-Fock solutions: molecular mean-field (X2C-MMF) approach
- 4-component property matrices can be readily transformed to the 2-c picture
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

\[ F = \hbar^\text{kinetic} - \sum_A \frac{Z_A}{r_A} + \sum_{\text{A nuclei}} J^A_c - K^A_c + \sum_{\text{valence}} J_v - K_v \]

\[ F = \hbar^\text{kinetic} - \sum_A \frac{Z^*_A}{r_A} + \sum_{\text{valence}} J_v - K_v + \sum_{\text{Nuclei}} \left( \frac{Z^\text{core}}{r_A} + \sum_{\text{core}} J^A_c \right) - \sum_{\text{Nuclei core}} K^A_c \]

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

\[ Z^*_A = Z_A - Z_{\text{Core}} \]
Ab Initio Model Potentials

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

\[
V_{\text{Frozen core}}^A = \sum_c^\text{core} \left( J^A_c - Z^\text{core}_A \right) - \sum_c^\text{core} K^A_c \approx V_{\text{Coul}}^A + V_{\text{Exch}}^A + P_{\text{Core}}^A
\]

\[
V_{\text{Coul}}^A = \frac{1}{r^A_i} \sum_i c^A_i e^{-\alpha^A_i r^A_i}
\]

Density fit of spherical density, can be done to arbitrary precision

\[
V_{\text{Exch}}^A = -\sum_c \sum_{r,s,t,u}^{\text{primitive basis on } A} \langle r | S^{-1}_{rs} s | K^A_c | t \rangle S^{-1}_{st} \langle u |
\]

Resolution of identity with non-orthogonal functions

\[
P_{\text{Core}}^A = \sum_c^\text{core} |c\rangle B^A_c \langle c|
\]

Level shift that shifts the core solutions to high energies
Nodal structure

Radon ZORA-LDA TZP

\[ \psi^+(r) \psi(r) \]

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

\[ \text{r (Å)} \]

-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

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

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

r (Å)
Pseudo orbitals

Radon ZORA-LDA TZP

Matching point

Matching point

r (Å)
Effective Core Potentials

Effective Core Potentials allow reduction of the basis set used to describe the valence orbitals by creating smoother orbitals.

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

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

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

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

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

Scalar

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

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

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

- 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

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

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

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

- 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)

$$\min \left( \sum_{\text{Lowlying Levels}} w_i \left( E_i^{PP} - E_i^{Reference} \right)^2 \right)$$

- 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”)

\[ \text{Reference}(2) \]
Why do we care about relativity in chemistry?
- What are relativistic effects?
- Relativistic effects in atoms
- Relativistic effects in molecules

How can we include relativity in calculations?
- Perturbation theory of relativistic effects
- 2-component methods
- 4-component methods
- Effective Core Potentials

Some recommendations / best practices
- Comparison light / heavy element calculations
- Importance of spin-orbit coupling
Some recommendations

- “Best” method depends on system and property that is calculated!

- 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 to decide on the electronic structure method

- Two comparison between heavy/light element calculations
- Two examples in which spin-orbit coupling is important
Chemistry of heavy elements

- A different world….

<table>
<thead>
<tr>
<th></th>
<th>Au$_2$</th>
<th>C$<em>{20}$N$</em>{20}$H$_{12}$</th>
</tr>
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<tbody>
<tr>
<td>electrons</td>
<td>178</td>
<td>160</td>
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<tr>
<td>total energy</td>
<td>-36,870 Hartree</td>
<td>-987 Hartree</td>
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<td>basis functions</td>
<td>48s38p24d18f2g</td>
<td>240s108p24d684 functions</td>
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<tr>
<td>chemical bonds</td>
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</tr>
<tr>
<td>Bond energy</td>
<td>0.1 Hartree</td>
<td>10 Hartree</td>
</tr>
<tr>
<td></td>
<td>2.3 eV</td>
<td>272 eV</td>
</tr>
</tbody>
</table>

- Structure and valence properties: frozen core / ECPs
- XPS, NMR, EFG, Mössbauer: all-electron methods
Spectroscopy of f-elements

- Low-lying electronic states

<table>
<thead>
<tr>
<th></th>
<th>Eu$^{3+}$</th>
<th>C$_6$H$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrons</td>
<td>6 f-electrons</td>
<td>6 π-electrons</td>
</tr>
<tr>
<td>orbitals</td>
<td>7</td>
<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>
<td>1</td>
</tr>
</tbody>
</table>

- Lanthanides: 4f is shielded from environment, possible to work with f-in-core ECPs to get structures
- Actinides: 5f can participate in chemical bonding, small-core ECP or all-electron approach may be necessary
Fine structure splitting in radicals

- Valence iso-electronic systems $\text{O}_2^-$, FO, ClO
- Breit interaction and correlation should be included for accurate results

NMR: $^1$H shielding trends

![Graph showing NMR $^1$H shielding trends for HF, HCl, HBr, and HI.]

Further reading

Relativistic Quantum Mechanics

Relativistic Quantum Chemical methods

Applications