Diracs equation and other prerequisites for achieving high accuracy in quantum chemistry

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Basic Theory

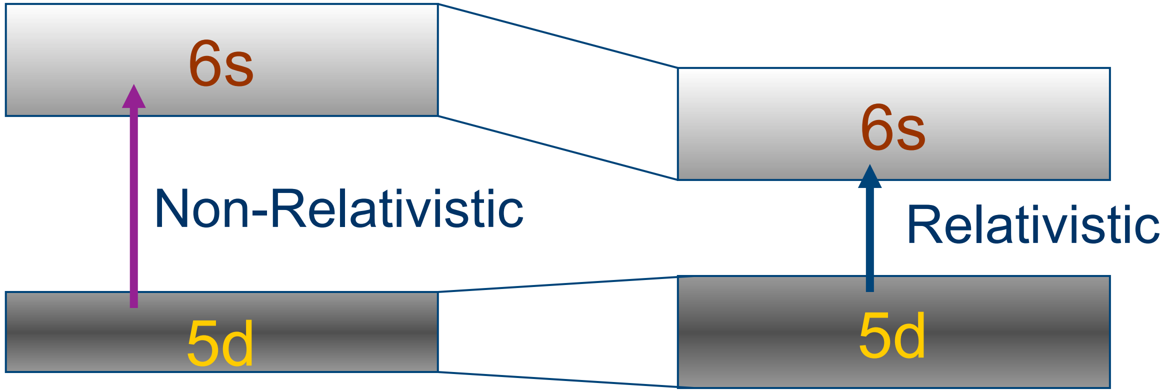
Dirac (1929)

- 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 wich 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.

Visible Relativistic Effects

- Non-relativistic gold is silver
  - The 5d-6s transition is shifted from the UV to the visible part of the spectrum by relativistic effects



6s

Non-Relativistic

5d

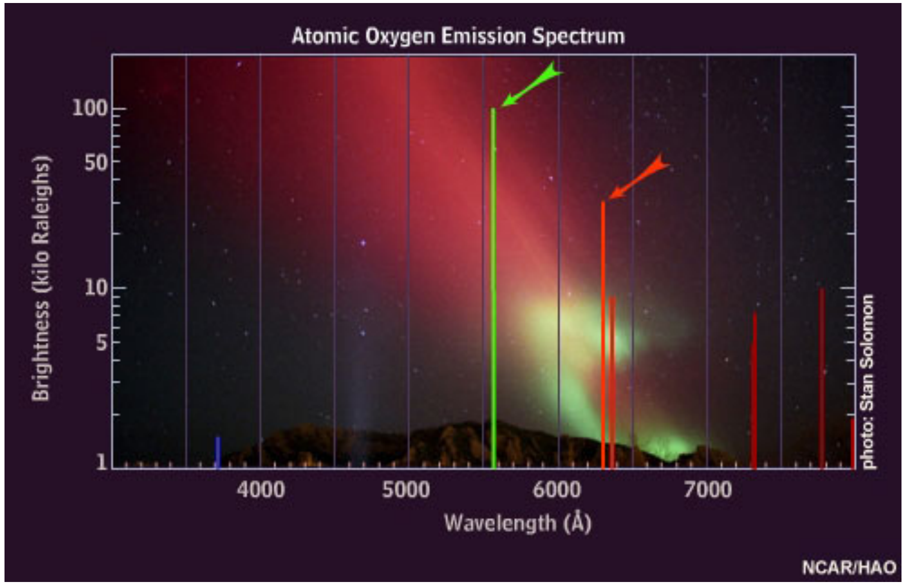
6s

Relativistic

5d

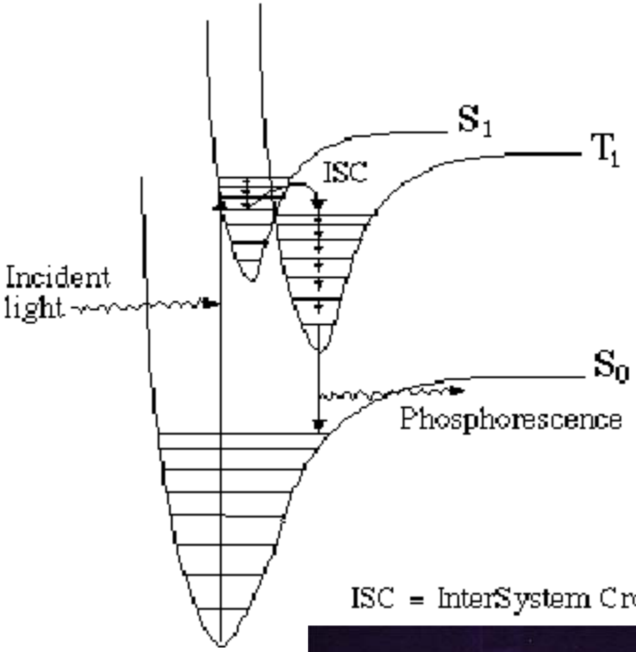
Visible Relativistic Effects

- Phosphoresence
  - Singlet-triplet transitions and intersystem crossing is allowed due to spin-orbit coupling: spin is not a good quantum number !

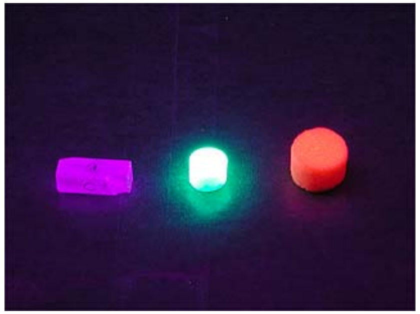


$$^1S_0 \rightarrow {}^1D_2 \qquad {}^1D_2 \rightarrow {}^3P_2$$

Lifetime 0.75 s   Lifetime 110 s



ISC = InterSystem Crossing



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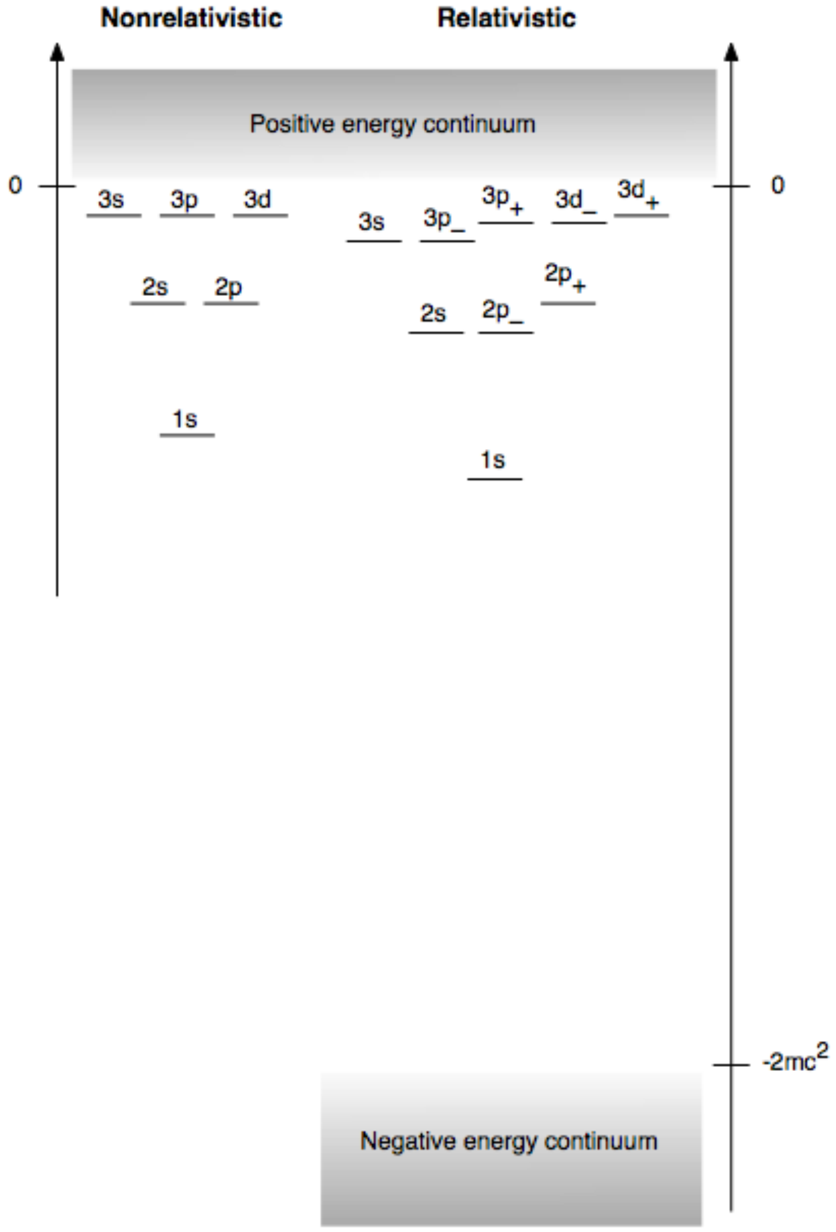
The hydrogenic atom

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

$$E = mc^2$$

- Spin-orbit couping : $\boxed{j = l \pm s}$


Nonrelativistic
Relativistic
Positive energy continuum
0
3s
3p
3d
2s
2p
1s
0
3s
$3p_-$
$3p_+$
$3d_-$
$3d_+$
2s
$2p_-$
$2p_+$
1s
$-2mc^2$
Negative energy continuum

Lecture 1: Basic theory, qualitative discussion

- Relativistic Quantum Theory
  - Special relativity
  - The Dirac equation
  - Relation to quantumelectrodynamics
  - Treatment of the electron-electron interaction

- Relativistic Effects in Chemistry
  - Orbital radii and energies
  - Reaction energies
  - Molecular structure

- Day 2: Approximate Hamiltonians, Frozen cores and ECPS

- Day 3: Wave function methods for accurate calculations
  Relativistic effects on molecular properties

Galilean transformation

- Consider 2 coordinate systems that move relative to each other with a velocity v in the x-direction
- Galilean transformation leaves distance invariant

$$x = x' + vt$$

$$y = y'$$

$$z = z'$$

$$r_{12} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$$

$$r'_{12} = \sqrt{(x'_1 - x'_2)^2 + (y'_1 - y'_2)^2 + (z'_1 - z'_2)^2}$$

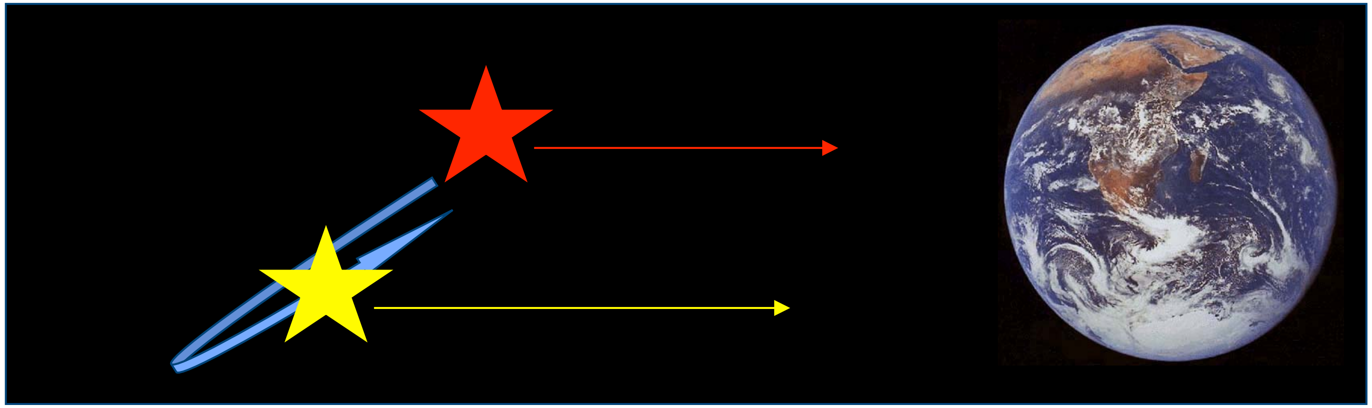
$$r_{12} = r'_{12}$$

- Simple addition of velocities, no speed limit

$$w = \frac{dx}{dt} = \frac{d(x' + vt)}{dt} = \frac{dx'}{dt} + v = w' + v$$

In a galaxy far far away…..

- Two rotating double stars A and B



- Does their light reach earth at different times ?
- Do we observe one star at two positions ?
- NO -> The speed of light (c) does not depend on the motion of the emitting stars
- Is there some immobile substance (ether) that transmits the radiation? NO -> Need better transformation of coordinates

Special relativity

- Measurement of c gives a constant value that is independent of the motion of the coordinate system

$$c = \frac{r_{12}}{t_{12}} = \frac{r'_{12}}{t'_{12}}$$

$$c^2 t_{12}^2 - r_{12}^2 = c^2 t_{12}'^2 - r_{12}'^2 = 0$$

- Define a new transformation to satisfy this condition

$$x = \gamma\left(x' + vt'\right) \longleftarrow \text{Scaling factor}$$

$$y = y'$$

$$z = z'$$

← No dependence on y and z because motion is in the x-direction

$$t = \alpha\left(t' + \beta x'\right) \longleftarrow \text{General expression for t}$$

Lorentz transformation

- Substitute this ansatz in the unprimed equations and solve

$$\alpha = \gamma = (1 - \frac{v^2}{c^2})^{-1/2} \qquad \beta = \frac{v}{c^2}$$

- Lorentz transformation

$$x = \gamma\left(x' + vt'\right)$$

$$y = y'$$

$$z = z'$$

$$t = \gamma\left(t' + \frac{v}{c^2}x'\right)$$

Generalize to 3d

$$\mathbf{r} = \mathbf{r}' + \mathbf{v}\left(\frac{\left(\mathbf{v}\cdot\mathbf{r}'\right)\left(\gamma - 1\right)}{v^2} + \gamma t'\right)$$

$$t = \gamma\left(t' + \frac{\left(\mathbf{v}\cdot\mathbf{r}'\right)}{c^2}\right)$$

- Time and spatial coordinates transform into each other
- 4-dimensional space-time coordinate system
- Nonrelativistic limit (c → ∞) gives Galileo transformation

Special relativity

Postulate 1: All inertial frames are equivalent

Postulate 2: The laws of physics have the same form in all inertial frames

Postulates hold for electromagnetism (Maxwells relations)

Postulates do not hold for Newtonian mechanics (invariant under Galilean transformations, not under Lorentz transformations)

Relativistic Quantum Mechanics

- 1905 : STR
  - Einstein : “E = mc^2”
- 1926 : QM
  - Schrödinger equation
- 1928 : RQM
  - Dirac equation
- 1949 : QED
  - Tomonaga, Schwinger & Feynman

Non-relativistic quantization 1

The nonrelativistic Hamilton function

$$H = T + V = \frac{p^2}{2m} + q\phi(\mathbf{r})$$

Quantization

$$H \rightarrow i\hbar\frac{\partial}{\partial t} \ ; \ \mathbf{p} \rightarrow -i\hbar\nabla$$

$$\hat{H}\,\psi(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t)$$

$$\hat{H} = -\frac{\hbar}{2m}\hat{\nabla}^2 + q\hat{\phi}(\mathbf{r})$$

Non-relativistic quantization 2

The nonrelativistic Hamilton function

$$H = T + V = \frac{\pi^2}{2m} + q\phi(\mathbf{r})$$

$$\pi = \mathbf{p} - q\mathbf{A}$$ ←

Mechanical (π) and canonical momentum (p)
Principle of minimal electromagnetic coupling

Quantization

$$H \rightarrow i\hbar\frac{\partial}{\partial t} \ ; \ \mathbf{p} \rightarrow -i\hbar\nabla$$

$$\hat{H}\psi(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t)$$

$$\hat{H} = -\frac{\hbar}{2m}\hat{\nabla}^2 + \frac{iq\hbar}{2m}\left(\hat{\nabla}\cdot\hat{\mathbf{A}} + \hat{\mathbf{A}}\cdot\hat{\nabla}\right) + \frac{q^2}{2m}\hat{\mathbf{A}}^2 + q\hat{\phi}(\mathbf{r})$$

Spin and non-relativistic quantization 1

We can, however, also write the the Hamilton function as

$$E = q\phi + \frac{\left(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\right)^2}{2m}$$

$$\boldsymbol{\sigma}_i\boldsymbol{\sigma}_j = \delta_{ij} + i\varepsilon_{ijk}\boldsymbol{\sigma}_k$$

$$\varepsilon_{xyz} = \varepsilon_{zxy} = \varepsilon_{yzx} = 1$$

$$\varepsilon_{xzy} = \varepsilon_{zyx} = \varepsilon_{yxz} = -1$$

← Kronecker delta and Levi-Civita tensor,
Summation over repeated indices

Quantization

$$\hat{H} = q\hat{\phi} + \frac{1}{2m}\left\{\boldsymbol{\sigma}\cdot\left(-i\hbar\hat{\nabla} + q\hat{\mathbf{A}}\right)\right\}^2$$

$$= q\hat{\phi} - \frac{\hbar^2}{2m}\left(\boldsymbol{\sigma}\cdot\hat{\nabla}\right)^2 + \frac{q^2}{2m}\left(\boldsymbol{\sigma}\cdot\hat{\mathbf{A}}\right)^2 + \frac{iq\hbar}{2m}\left[\left(\boldsymbol{\sigma}\cdot\hat{\nabla}\right),\left(\boldsymbol{\sigma}\cdot\hat{\mathbf{A}}\right)\right]_+$$

Spin and non-relativistic quantization 2

$$\boxed{(\sigma\cdot\mathbf{u})(\sigma\cdot\mathbf{v}) = (\mathbf{u}\cdot\mathbf{v}) + i\sigma\cdot(\mathbf{u}\times\mathbf{v})}$$

$$\begin{aligned}\hat{H} = & -\frac{\hbar}{2m}\hat{\nabla}^2 + q\hat{\phi} + \frac{q^2}{2m}\hat{\mathbf{A}}^2 \\ & + \frac{iq\hbar}{2m}\left(\hat{\nabla}\cdot\hat{\mathbf{A}} + \hat{\mathbf{A}}\cdot\hat{\nabla}\right) - \frac{q\hbar}{2m}\sigma\cdot\left(\hat{\nabla}\times\hat{\mathbf{A}} + \hat{\mathbf{A}}\times\hat{\nabla}\right)\end{aligned}$$

$$\hat{\nabla}\times\mathbf{A}(\mathbf{r})f(\mathbf{r}) = \hat{\nabla}\times\left(f(\mathbf{r})\mathbf{A}(\mathbf{r})\right)$$

← A is a multiplicative operator

$$= \left(\hat{\nabla}f(\mathbf{r})\right)\times\mathbf{A}(\mathbf{r}) + f(\mathbf{r})\hat{\nabla}\times\mathbf{A}(\mathbf{r})$$

← chain rule

$$= -\hat{\mathbf{A}}\times\left(\hat{\nabla}f(\mathbf{r})\right) + \mathbf{B}f(\mathbf{r})$$

← Use definition of B

$$\hat{H} = \hat{T} + q\hat{\phi} + iq\hat{\mathbf{A}}\cdot\hat{\nabla} + \frac{q^2}{2}\hat{\mathbf{A}}^2 - \frac{q}{2}\sigma\cdot\mathbf{B}$$

← in atomic units

Spin in NR quantum mechanics

The Pauli Hamiltonian in two-component form

$$\begin{pmatrix} -\frac{1}{2}\nabla^2 + q\phi + iq\mathbf{A}\cdot\nabla + \frac{q^2}{2m}A^2 - \frac{q}{2}B_z & -\frac{q}{2}\left(B_x - iB_y\right) \\ -\frac{q}{2}\left(B_x + iB_y\right) & -\frac{1}{2}\nabla^2 + q\phi + iq\mathbf{A}\cdot\nabla + \frac{q^2}{2m}A^2 + \frac{q}{2}B_z \end{pmatrix}$$

Second derivatives w.r.t. position, first derivative w.r.t. time
Linear in scalar, quadratic in vector potential
→ Can not be Lorentz-invariant

☹ *Ad hoc* introduction of spin.The anomalous g-factor (ratio of 2 between magnetic moment and intrinsic angular momentum) is not explained

☹ No interaction between angular momenta due to the orbital and spin : spin-orbit coupling is relativistic effect

Relativistic quantization 1

Take the classical relativistic energy expression

$$E - q\phi = \left[m^2c^4 + c^2\pi^2\right]^{1/2} \qquad \boxed{\text{"}E = mc^2\text{"}} \longleftarrow \text{Without EM-fields}$$

Quantization recipe gives

$$i\hbar\frac{\partial\psi}{\partial t} = q\phi\psi + \sqrt{m^2c^4 + c^2\pi^2}\;\psi$$

After series expansion of the square root this could provide relativistic corrections to the Schrödinger Equation

Disadvantage : Difficult to define the square root operator in terms of a series expansion (**A** and **p** do not commute). Not explored much.

Relativistic quantization 2

Eliminate the square root before quantization

$$\left(E - q\phi\right)^2 = m^2c^4 + c^2\pi^2$$

Quantization

$$\left(i\hbar\frac{\partial}{\partial t} - q\hat{\phi}\right)^2\psi = \left(m^2c^4 + c^2\hat{\pi}^2\right)\psi$$

Klein-Gordon Equation

☺ Lorentz invariant
☹ No spin
☹ $\int \psi^*(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} = f(t)$ ← Charge is conserved, particle number is not

The KG-equation can be used for spinless particles

Relativistic quantization 3

Define a new type of "square root"

$$E - q\phi = \beta mc^2 + c\,\boldsymbol{\alpha}\cdot\boldsymbol{\pi}$$

$$\left[\alpha_i,\alpha_j\right]_+ = 2\delta_{ij} \quad \wedge \quad \left[\alpha_i,\beta\right]_+ = 0 \quad \wedge \quad \beta^2 = 1$$

Quantization

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

The Dirac equation

Suitable for relativistic description of electrons

The Dirac equation

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

☺ First derivatives with respect to time and position
☺ Linear in scalar and vector potentials

☺ Lorentz invariant (should be proved !)

Alpha and Beta are <u>conventionally</u> represented by the following set of 4-component matrices

$$\alpha_x = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} \quad \alpha_y = \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix} \quad \alpha_z = \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix} \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

Densities

- Charge density

$$\rho(\mathbf{r},t) = q\psi^{\dagger}(\mathbf{r},t)\psi(\mathbf{r},t)$$

- Current density

$$\mathbf{j}(\mathbf{r},t) = q\psi^{\dagger}(\mathbf{r},t)\, c\boldsymbol{\alpha}\, \psi(\mathbf{r},t)$$

← $c\alpha$ is the relativistic velocity operator

- Continuity relation

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t} + \nabla\cdot\mathbf{j}(\mathbf{r},t) = 0$$

Time-independent Dirac equation

- The nuclei do not move with relativistic speeds with respect to each other
- Take a stationary frame of reference (clamped-nucleus approximation)
- Separate the time and position variables

$$\hat{H}\psi(\mathbf{r},t) = i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t}$$

← Time dependent Dirac equation

$$\psi(\mathbf{r},t) = \Psi(\mathbf{r})\Phi(t)$$

$$\hat{H}\Psi(\mathbf{r}) = E\,\Psi(\mathbf{r})$$

← Time independent Dirac equation

$$\Phi(t) = e^{Et/i\hbar}$$

The Dirac Hamiltonian

$$\hat{H} = \beta mc^2 + c\boldsymbol{\alpha}\cdot\hat{\boldsymbol{\pi}} + q\phi$$

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

Four component wave function

1) Spin doubles the components

2) Negative energy solutions: $E < -mc^2$

Free particle Dirac equation

- Take simplest case : ϕ= 0 and **A** = 0
- Use plane wave trial function

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

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

$$\left(E - mc^2\right)a_1 - c\hbar k_z a_3 - c\hbar k_- a_4 = 0$$

$$\left(E - mc^2\right)a_2 - c\hbar k_+ a_3 + c\hbar k_z a_4 = 0$$

$$-c\hbar k_z a_1 - c\hbar k_- a_2 + \left(E + mc^2\right)a_3 = 0$$

$$-c\hbar k_+ a_1 + c\hbar k_z a_2 + \left(E + mc^2\right)a_4 = 0$$

← After insertion into time-independent Dirac equation

$$\boxed{k_\pm = k_x \pm ik_y}$$

Free particle Dirac equation

- Two doubly degenerate solutions

$$\left(E^2 - m^2c^4 - c^2\hbar^2k^2\right) = 0$$

$$E_+ = +\sqrt{m^2c^4 + c^2\hbar^2k^2}$$

$$E_- = -\sqrt{m^2c^4 + c^2\hbar^2k^2}$$

- Compare to classical energy expression

$$E = \sqrt{m^2c^4 + c^2p^2}$$

- Quantization (for particles in a box) and prediction of negative energy solutions

Free particle Dirac equation

- Wave function for E = E_+

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

$$\boxed{\hbar|k| \equiv p << mc}$$ ← For particles moving with “nonrelativistic” velocities

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

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

- Upper components are the “Large components”
- Lower components are the “Small components”

Free particle Dirac equation

- Wave function for E = E$_-$

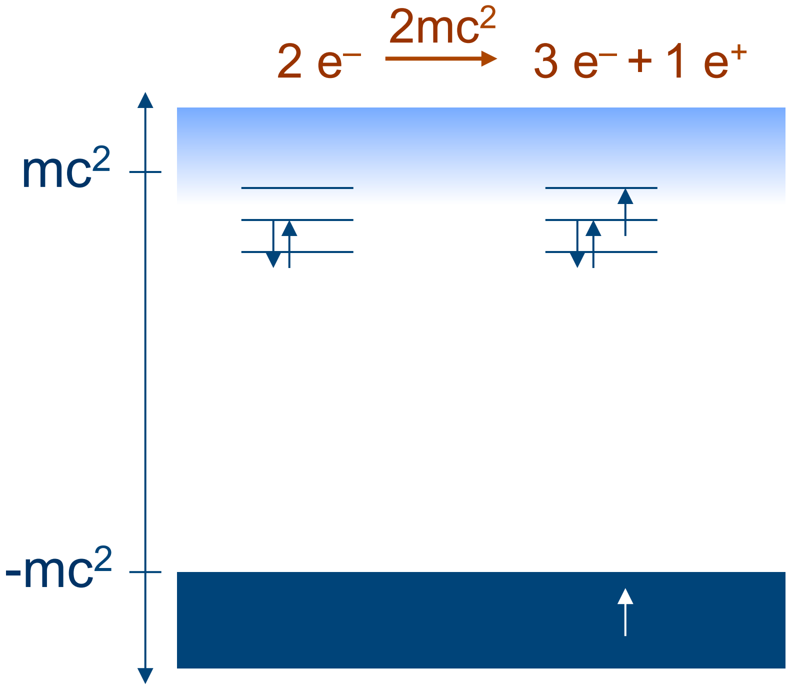
$$a_4 = 0$$

$$a_1 = a_3 \frac{c\hbar k_z}{E_- - mc^2} \approx a_3 \frac{p_z}{-2mc}$$

$$a_2 = a_3 \frac{c\hbar k_+}{E_- - mc^2} \approx a_3 \frac{p_+}{-2mc}$$

- Role of large and small components is reversed
- Charge conjugation symmetry
- Can we apply the variational principle ?
- Variational Collapse

Dirac sea of electrons



$$2\,e^- \xrightarrow{2mc^2} 3\,e^- + 1\,e^+$$

- All negative energy solutions are filled
- The Pauli principle forbids double occupancy
- ☺ Holes in the filled sea show up as particles with positive charge : positrons (discovered in 1933)
- ☹ Infinite background charge

Quantum Electro Dynamics

- Introduce a *m*-dimensional Fock space F(m)
  - States are defined by the occupation number vector **n**

$$|\mathbf{n}\rangle = |n_1, n_2, \ldots, n_m\rangle$$

$$n_i = 0,1$$

  - The vacuum has all n=0

$$|vac\rangle = |0,0,\ldots,0\rangle$$

  - We use an orthonormal basis

$$\langle \mathbf{n} | \mathbf{k} \rangle = \delta_{nk}$$

$$\langle vac | vac \rangle = 1$$

Second Quantization

- Second quantized operators
  - Creation operator

$$a_i^{\dagger}\left|n_1,\ldots,n_i,\ldots,n_m\right\rangle = 0 \;\; (n_i = 1)$$

$$a_i^{\dagger}\left|n_1,\ldots,n_i,\ldots,n_m\right\rangle = C_i\left|n_1,\ldots,1,\ldots,n_m\right\rangle \;\; (n_i = 0)$$

$$a_i^{\dagger}\left|vac\right\rangle = \left|0,\ldots,1,\ldots,0\right\rangle$$

  - Annihilation operator

$$a_i\left|n_1,\ldots,n_i,\ldots,n_m\right\rangle = C_i\left|n_1,\ldots,0,\ldots,n_m\right\rangle \;\; (n_i = 1)$$

$$a_i\left|n_1,\ldots,n_i,\ldots,n_m\right\rangle = 0 \;\; (n_i = 0)$$

$$a_i\left|vac\right\rangle = 0$$

  - Define all operators in terms of these elementary operators

$$\hat{\Omega} = \sum_{k,l=1}^{m} \Omega_{kl}\hat{a}_k^{\dagger}\hat{a}_l$$

Fock space Hamiltonian

Positive and negative energy solutions define a Fock space Hamiltonian

$$\hat{H}^{Total} = \hat{H}^{++} + \hat{H}^{+-} + \hat{H}^{-+} + \hat{H}^{--}$$

$$\hat{H}^{++} = \sum_{p,q}^{E \in E^{+}} H_{pq} \hat{a}_{p}^{\dagger} \hat{a}_{q} \qquad \hat{H}^{--} = \sum_{\alpha,\beta}^{E \in E^{-}} H_{\alpha\beta} \hat{a}_{\alpha}^{\dagger} \hat{a}_{\beta}$$

$$\hat{H}^{+-:pair\,creation} = \sum_{p}^{E \in E^{+}} \sum_{\alpha}^{E \in E^{-}} H_{p\alpha} \hat{a}_{p}^{\dagger} \hat{a}_{\alpha}$$

$$\hat{H}^{-+:pair\,annihilation} = \sum_{\alpha}^{E \in E^{-}} \sum_{p}^{E \in E^{+}} H_{\alpha p} \hat{a}_{\alpha}^{\dagger} \hat{a}_{p}$$

Renormalization

1. Subtract energy from the occupied negative energy states

$$\hat{H}^{QED} = \hat{H}^{Total} - E^{0} = \hat{H}^{Total} - \left\langle \quad \middle| \hat{H}^{Total} \middle| \quad \right\rangle$$

2. Re-interpretation

$$\hat{a}_p^{\dagger} = \hat{b}_p^{\dagger} \qquad \hat{a}_p = \hat{b}_p$$

$$\hat{a}_\alpha^{\dagger} = \hat{b}_\alpha \qquad \hat{a}_\alpha = \hat{b}_\alpha^{\dagger}$$

3. Normal ordered Hamiltonian

Due to the anticommutation relation

$$\hat{H}^{QED} = \sum_{p,q}^{electrons} H_{pq}\hat{b}_p^{\dagger}\hat{b}_q + \sum_{p}^{el.}\sum_{\alpha}^{pos.}\left(H_{p\alpha}\hat{b}_p^{\dagger}\hat{b}_\alpha^{\dagger} + H_{\alpha p}\hat{b}_\alpha\hat{b}_p\right) \overset{\downarrow}{-} \sum_{\alpha,\beta}^{positrons} H_{\alpha\beta}\hat{b}_\alpha^{\dagger}\hat{b}_\beta$$

Quantum Electro Dynamics

- Positive energy for positrons

$$E(1p;0e) = \langle \ldots, \underset{\text{Neg.}}{1,\ldots};\underset{\text{Pos.}}{\ldots} \,|\, \hat{H}^{QED} \,|\, \underset{\text{Neg.}}{\ldots,1,\ldots};\underset{\text{Pos.}}{\ldots} \rangle$$

$$= \langle \ldots,1,\ldots;\ldots | - \sum_{\alpha,\beta}^{\substack{positron\\ states}} H_{\alpha\beta} b_{\alpha}^{\dagger} b_{\beta} | \ldots,\underset{\gamma}{1},\ldots;\ldots \rangle = -E_{\gamma} \geq mc^{2}$$

- Total charge is also redefined

$$Q_{vac}^{QED} = -e\langle vac|\hat{N}^{QED}|vac\rangle$$

$$= -e\langle vac| \sum_{p}^{\substack{electron\\ states}} b_{p}^{\dagger} b_{p} - \sum_{\alpha}^{\substack{positron\\ states}} b_{\alpha}^{\dagger} b_{\alpha} |vac\rangle = 0$$

Dressed particles

- The QED Hamiltonian depends on the positive and negative energy solutions of the Dirac equation. The Dirac equation depends on the external potential

- Common choices
  - Free particle solutions (Feynman,1948)
  - Fixed external potential (Furry,1951)
  - External + some mean-field potential (“fuzzy”)

- Particles in one representation are quasiparticles (dressed with ep-pairs) in another representation

- Different no-pair approximations possible

Electron-electron interaction

- Quantize also the EM-field

$$|\ \rangle = |p-states; e-states; photons\rangle$$

$$\hat{H}^{QED,full} = \hat{H}^{e+p} + \hat{H}^{photons} + \hat{H}^{e+p,photons}$$

- Electron-electron interaction is automatically retarded by the finite velocity of light

- Corrections to the Dirac equation and the instantaneous Coulomb interaction can be derived
  - Feynman (NP 1965) diagrams
    - Breit interaction (1929) (Order c^{-2})
    - Vacuum Polarization + Self Energy = Lamb shift (NP 1955) (c^{-3})

Electron-electron interaction

- Three terms up to order c^{-2}

$$g^{Coulomb-Breit}(1,2) = \frac{1}{r_{12}} - \frac{1}{c^2 r_{12}} c\alpha_1 \cdot c\alpha_2 - \frac{1}{2c^2}\left(c\alpha_1 \cdot \nabla_1\right)\left(c\alpha_2 \cdot \nabla_2\right) r_{12}$$

- Coulomb, Gaunt and retardation terms
  - First correction describes the current-current interaction
  - Second correction describes retardation

The hydrogenic atom

- Starting point for the LCAO approach
- Like the S.E. the D.E. can be solved exactly by separating the radial and angular variables (various textbooks, e.g. Dyall & Faegri, Reiher & Wolf)

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

- Knowing the properties of the exact solutions helps in devising basis set approaches and in understanding the chemical bonding in the relativistic regime

Hydrogenic orbitals

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

$$\begin{pmatrix}\psi^L(\mathbf{r})\\ \psi^S(\mathbf{r})\end{pmatrix}=\frac{1}{r}\begin{pmatrix}P_{n\kappa}(r)\xi_{\kappa,m}(\vartheta,\varphi)\\ iQ_{n\kappa}(r)\xi_{-\kappa,m}(\vartheta,\varphi)\end{pmatrix}$$

- Solutions to the radial equation

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

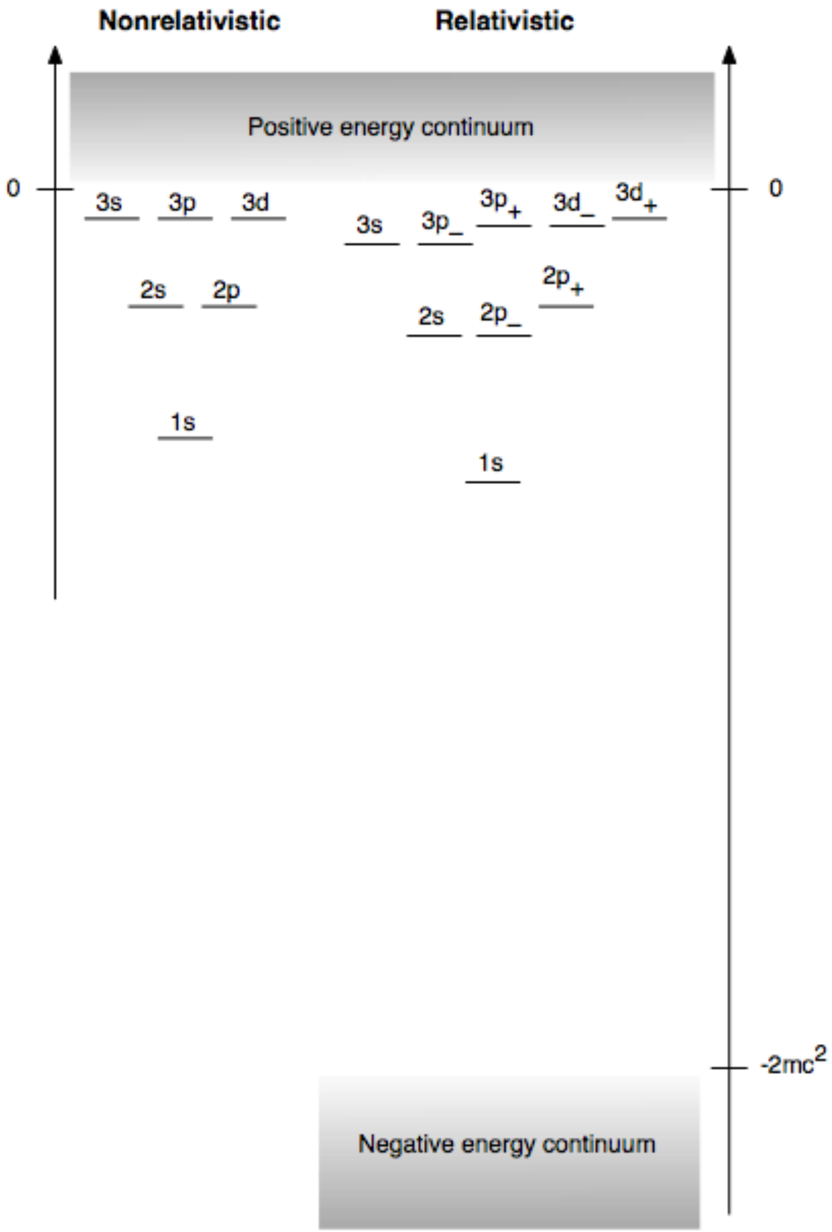
$$\gamma=\sqrt{\kappa^2-\frac{Z^2}{c^2}}<|\kappa|$$

$$P_{n\kappa}(r)=N^P_{n\kappa}e^{-\lambda r}r^{\gamma}\left(F_1(r)+F_2(r)\right)$$ Large component

$$Q_{n\kappa}(r)=N^Q_{n\kappa}e^{-\lambda r}r^{\gamma}\left(F_1(r)-F_2(r)\right)$$ Small component

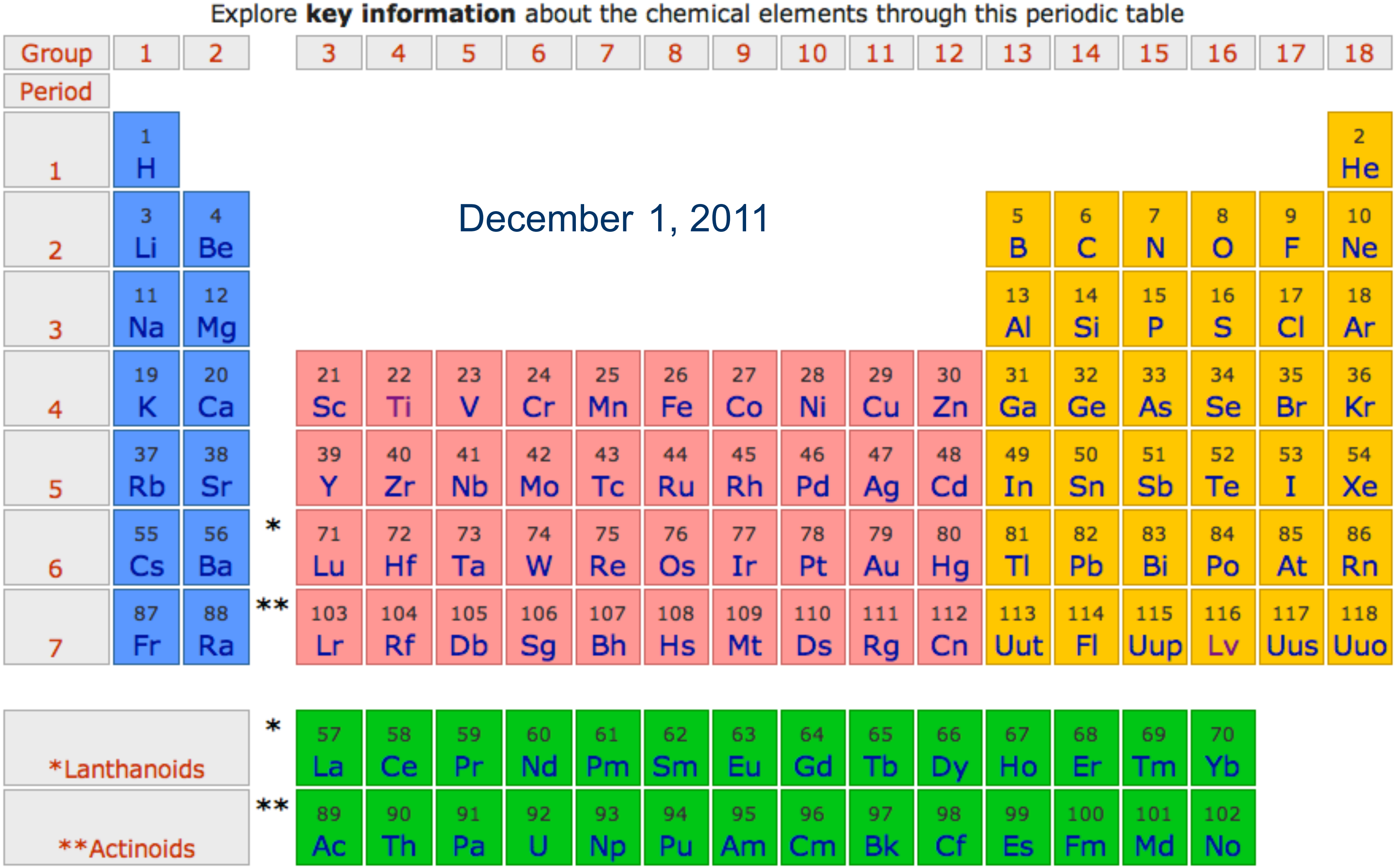
$$R_{nl}(r)=N^R_{nl}e^{-\left(\sqrt{-2E}\right)r}r^{l+1}F(r)$$ Nonrelativistic

l	0	1	1	2	2	3	3
j	1/2	1/2	3/2	3/2	5/2	5/2	7/2
κ	-1	1	-2	2	-3	3	-4
	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$


Nonrelativistic
Relativistic
Positive energy continuum
0
3s
3p
3d
2s
2p
1s
0
3s
3p_
3p+
3d_
3d+
2s
2p_
2p+
1s
-2mc2
Negative energy continuum

Relativity and the periodic table

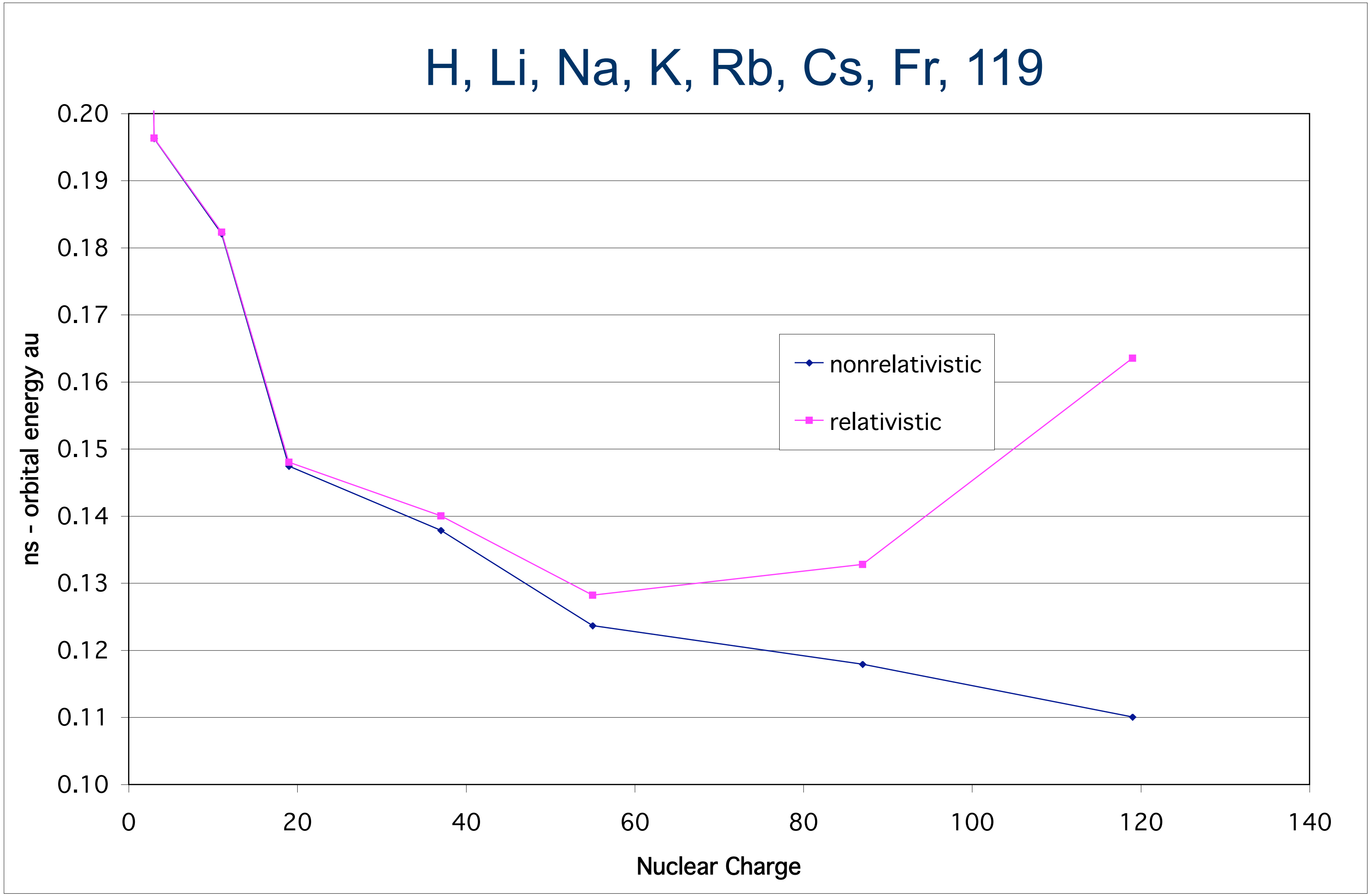
December 1, 2011



Explore **key information** about the chemical elements through this periodic table

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Orbital stabilisation



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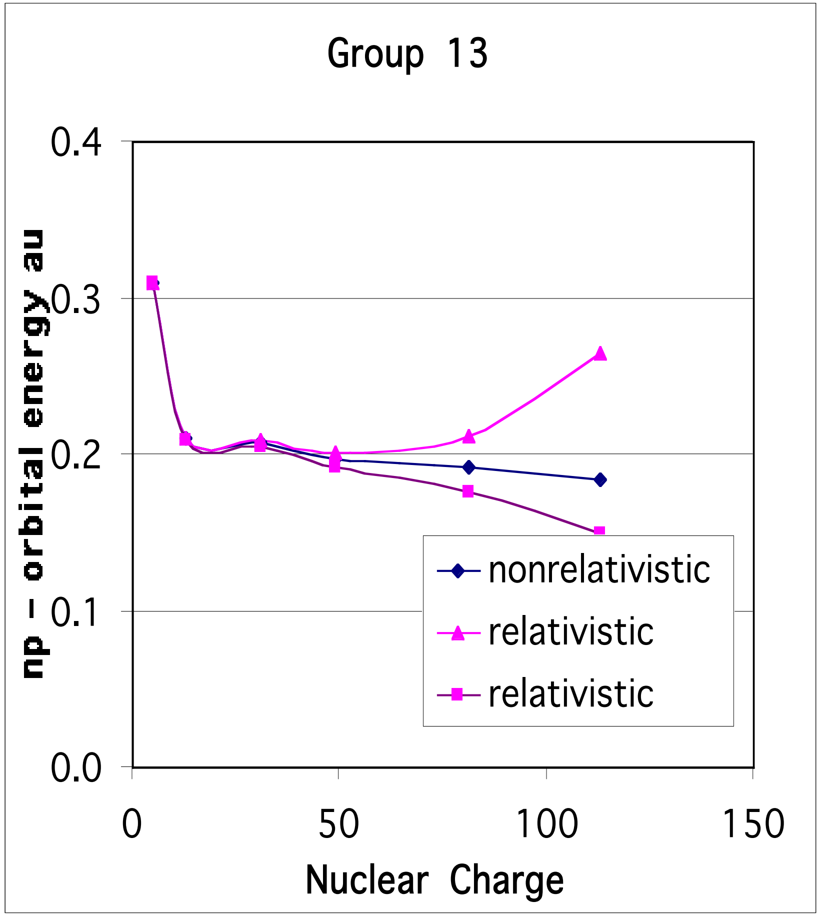
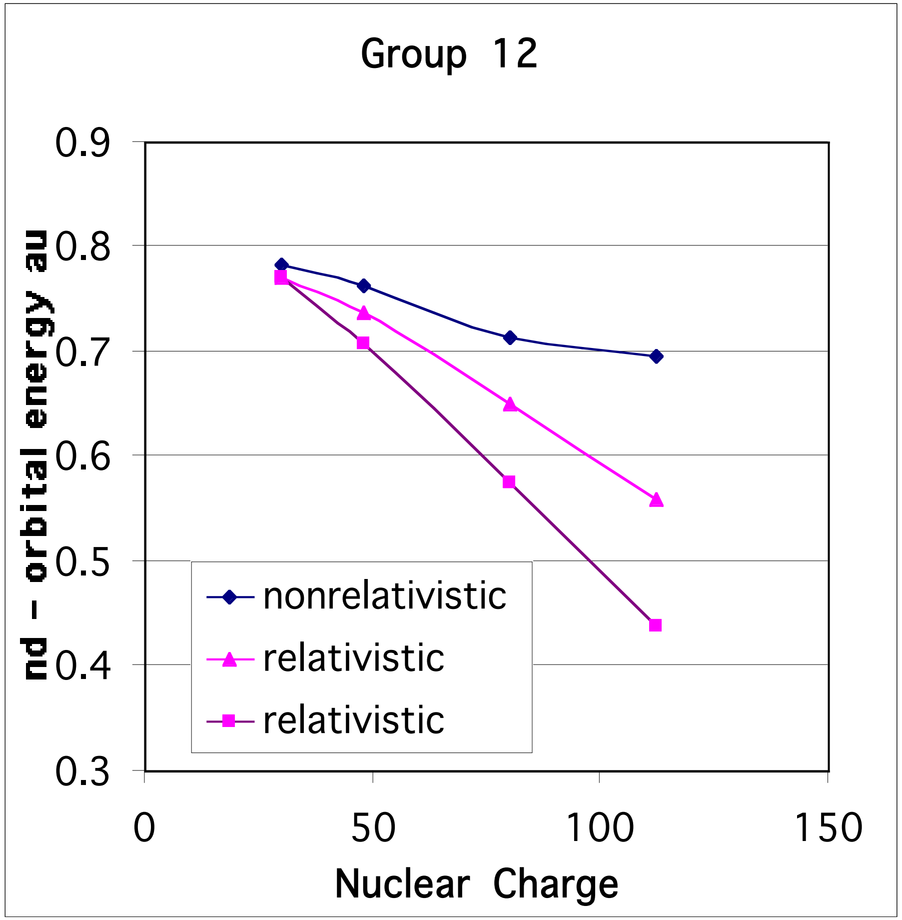
Orbital destabilization and spin-orbit splitting

B, Al, Ga, In, Tl, 113

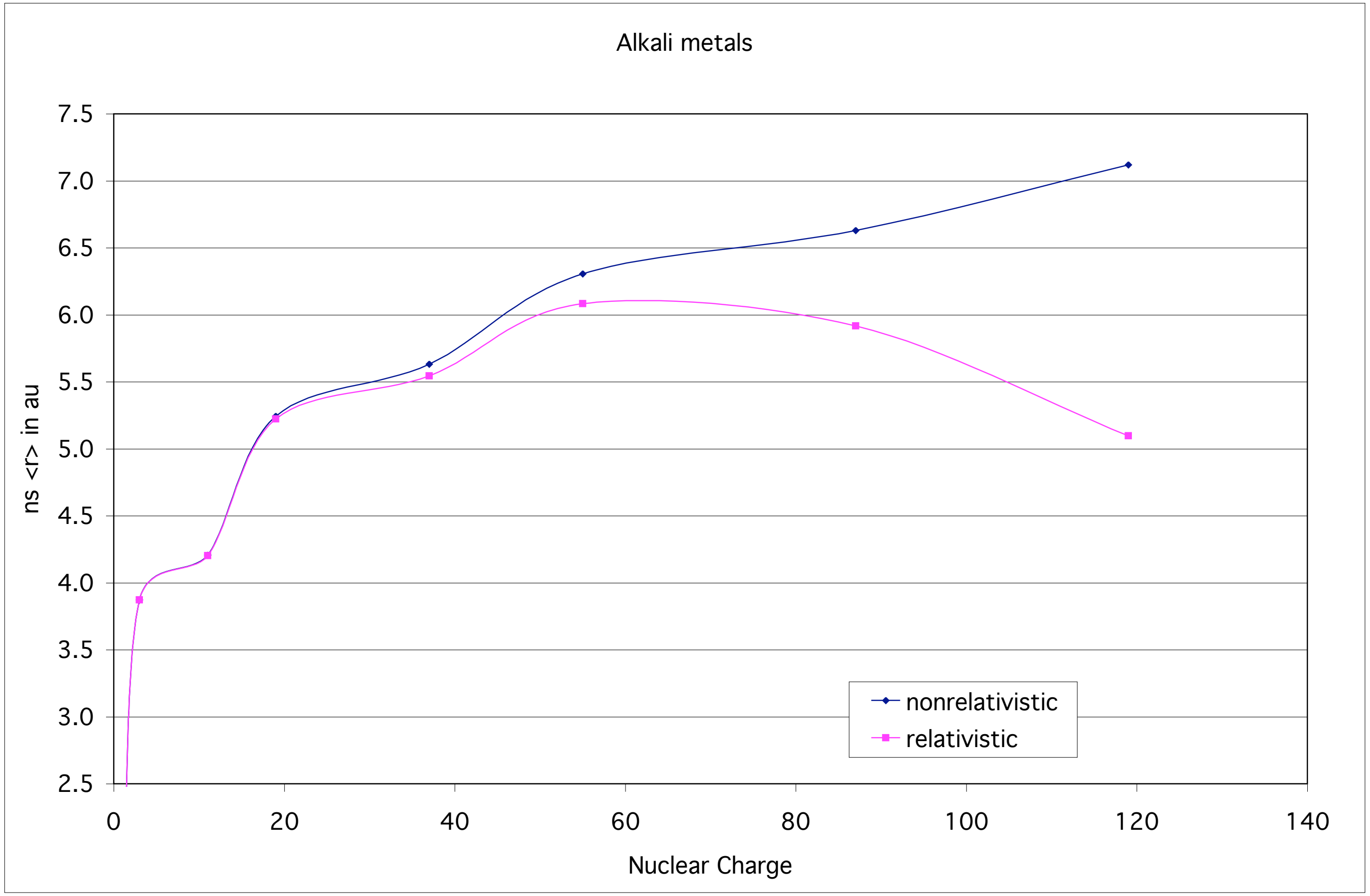
Zn, Cd, Hg, 112





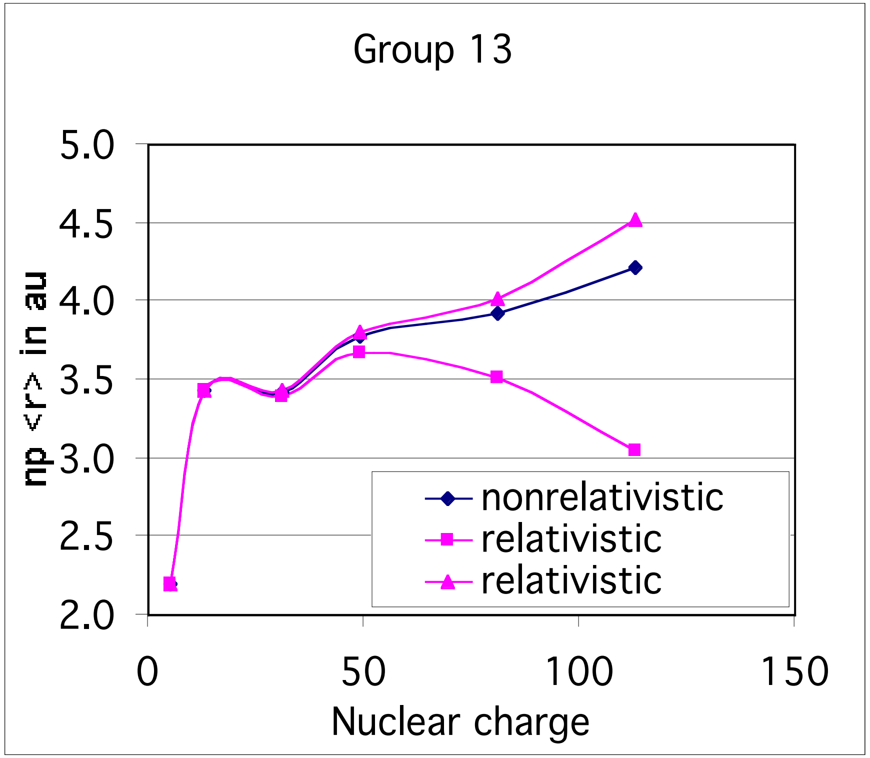
Orbital contraction

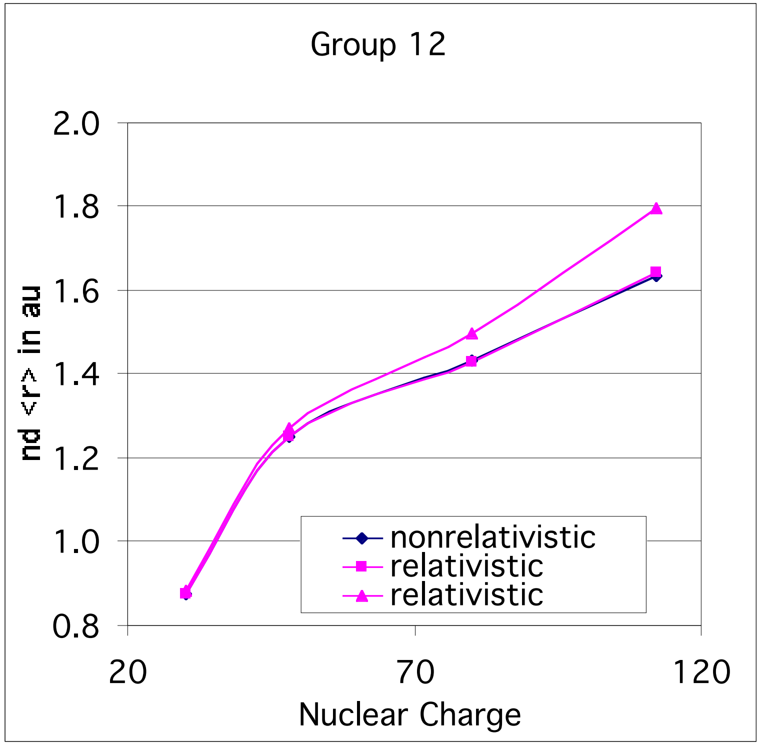
- The outermost s-orbital becomes more compact



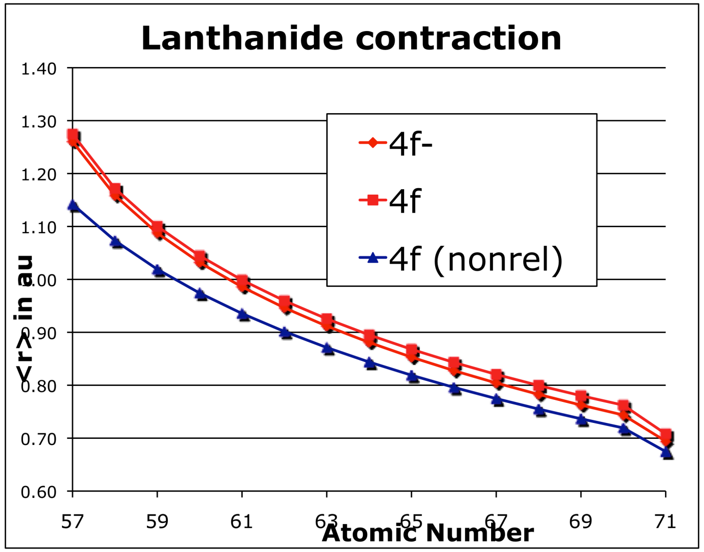
Orbital expansion

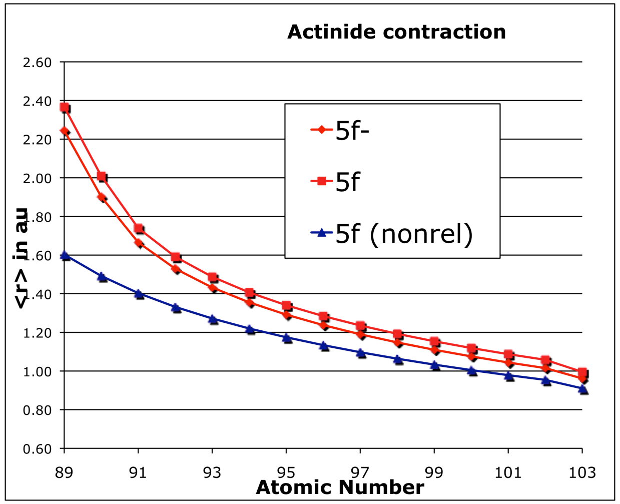
- The outermost p- and d-orbitals expand





Ln-An contraction





- Ln-An contraction is partly caused by relativistic effects
- Trend expected from the atomic calculations is indeed seen in calculations on LnF, AnF, LnH_3 and AnH_3 molecules.

Scalar Relativistic Effects

- Spectroscopy
  - Energy levels are shifted (s down, f up)

- Molecular structure
  - s-orbitals more compact, f-orbitals expand
  - bond distances are shorter

- Other
  - Polarizability decreases systems with outermost s and p
  - Retardation of electron-electron interaction (weakening of van der Waals interaction to r^{-7} dependence)

Spin-Orbit coupling

- Spectroscopy
  - Energy levels are split
  - Spin selection rules are broken

- Molecular structure
  - The hybridization that occurs when chemical bonds are formed makes the effects on structure usually only relevant when comparing to high-precision experiments
  - But: bonds to heavy and “superheavy” elements can be qualitatively different if SOC is included

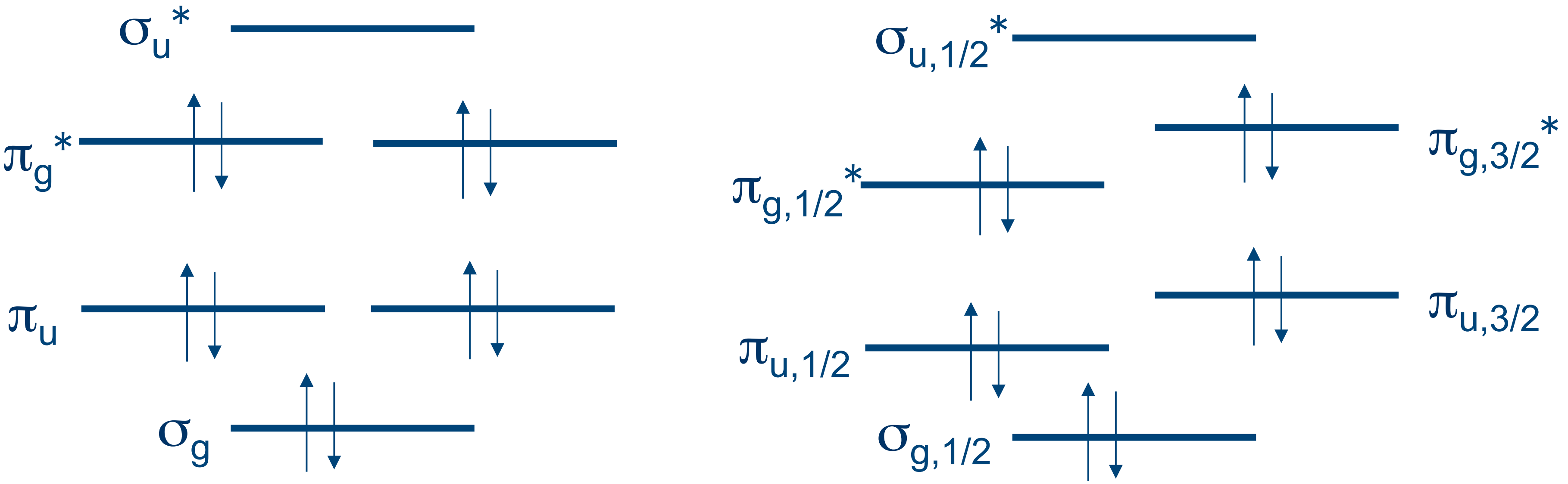
- Thermochemistry, reaction barriers
  - Lowering of open shell states (atomization energies)
  - Coupling between singlet and triplet surfaces, intersystem crossing

Atomization energies

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

Nonrelativistic

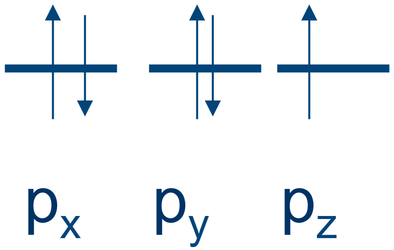
Relativistic



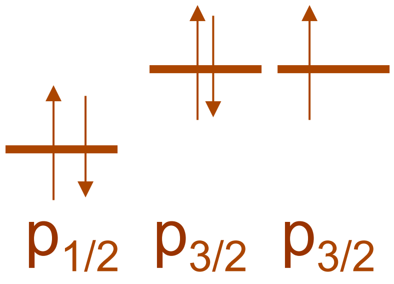
Atomization energies

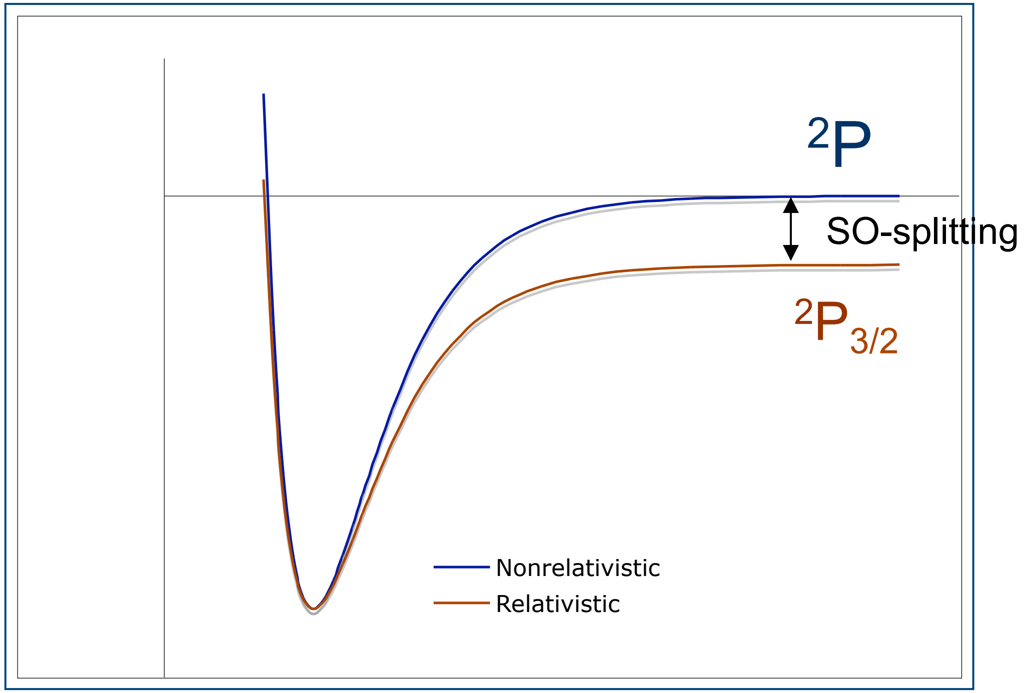
- Atomic asymptotes are lowered by SO-coupling
- First order perturbation theory

Nonrelativistic



Relativistic





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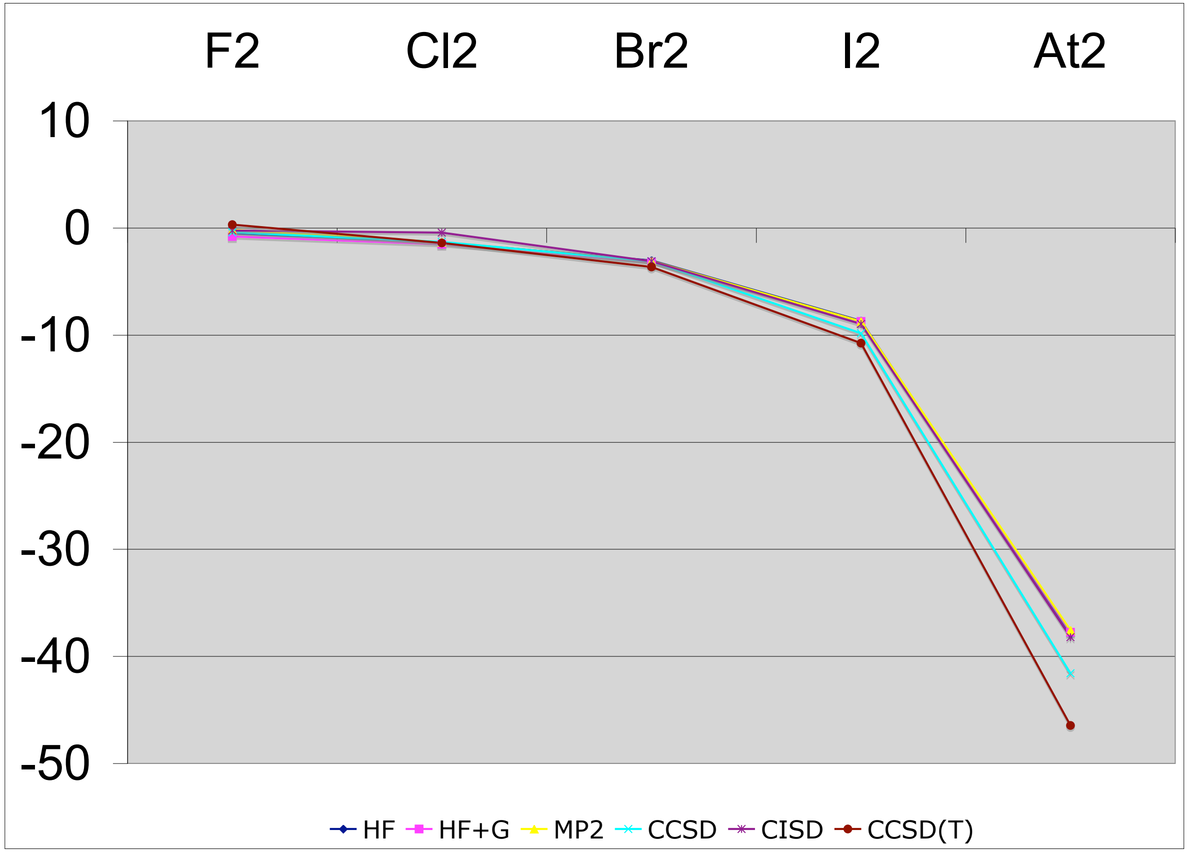
Relativistic effect on atomization energies (kcal/mol)

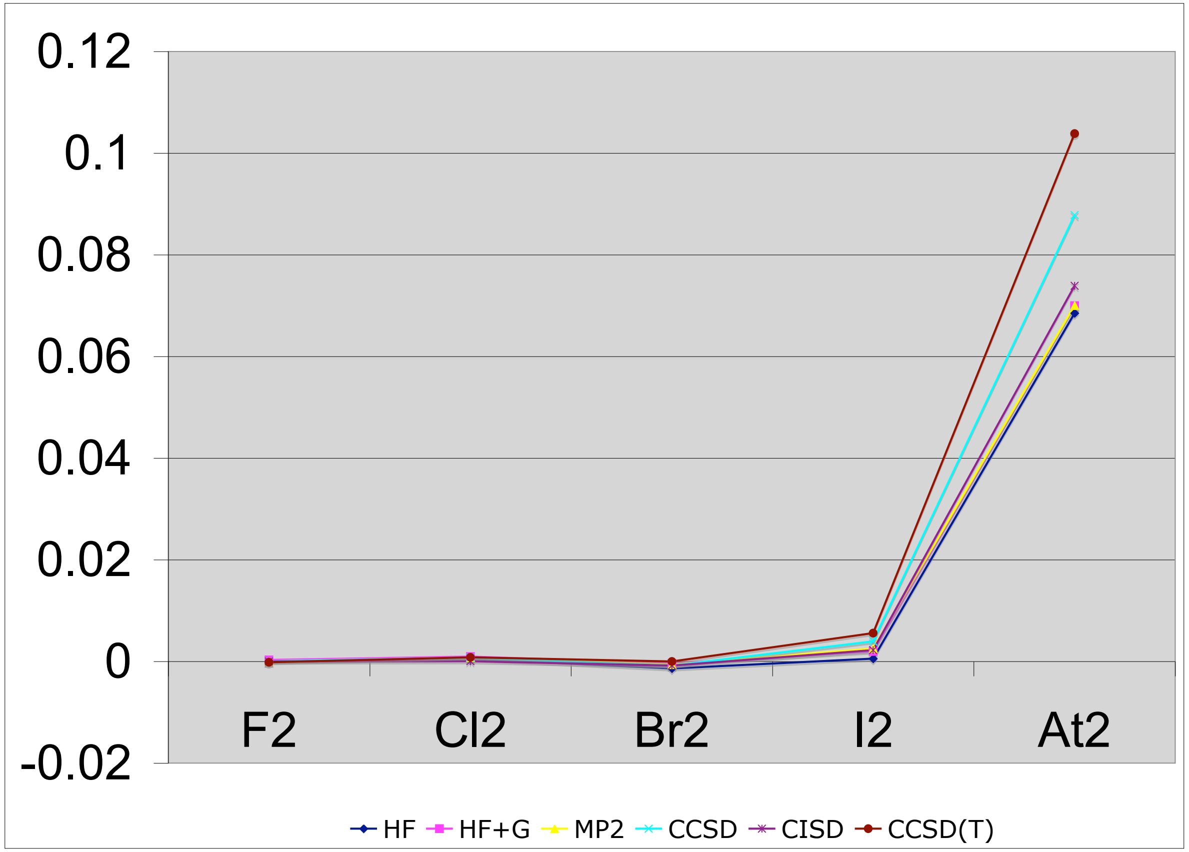
Relativistic effect on atomization energies is well-reproduced by correcting only the asymptote

Relativistic effect on harmonic frequencies (cm^{-1})



Bond weakening due to admixture of the antibonding sigma orbital. This is also due to spin-orbit coupling.

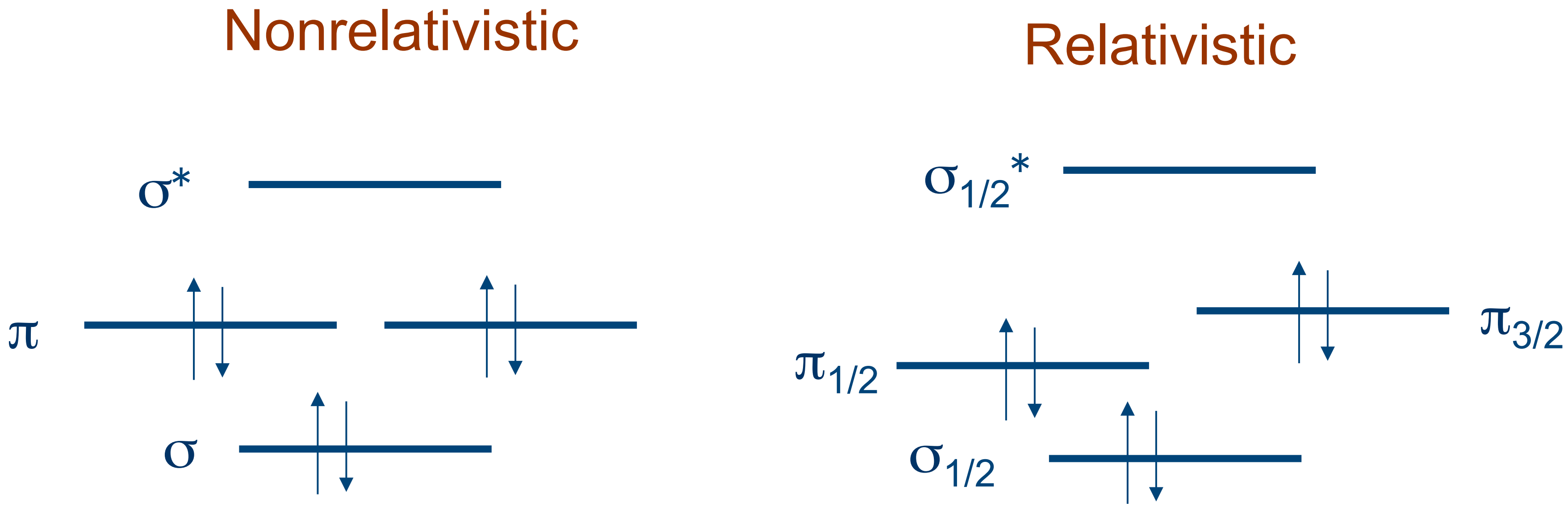
Relativistic effect on equilibrium distances (Å)



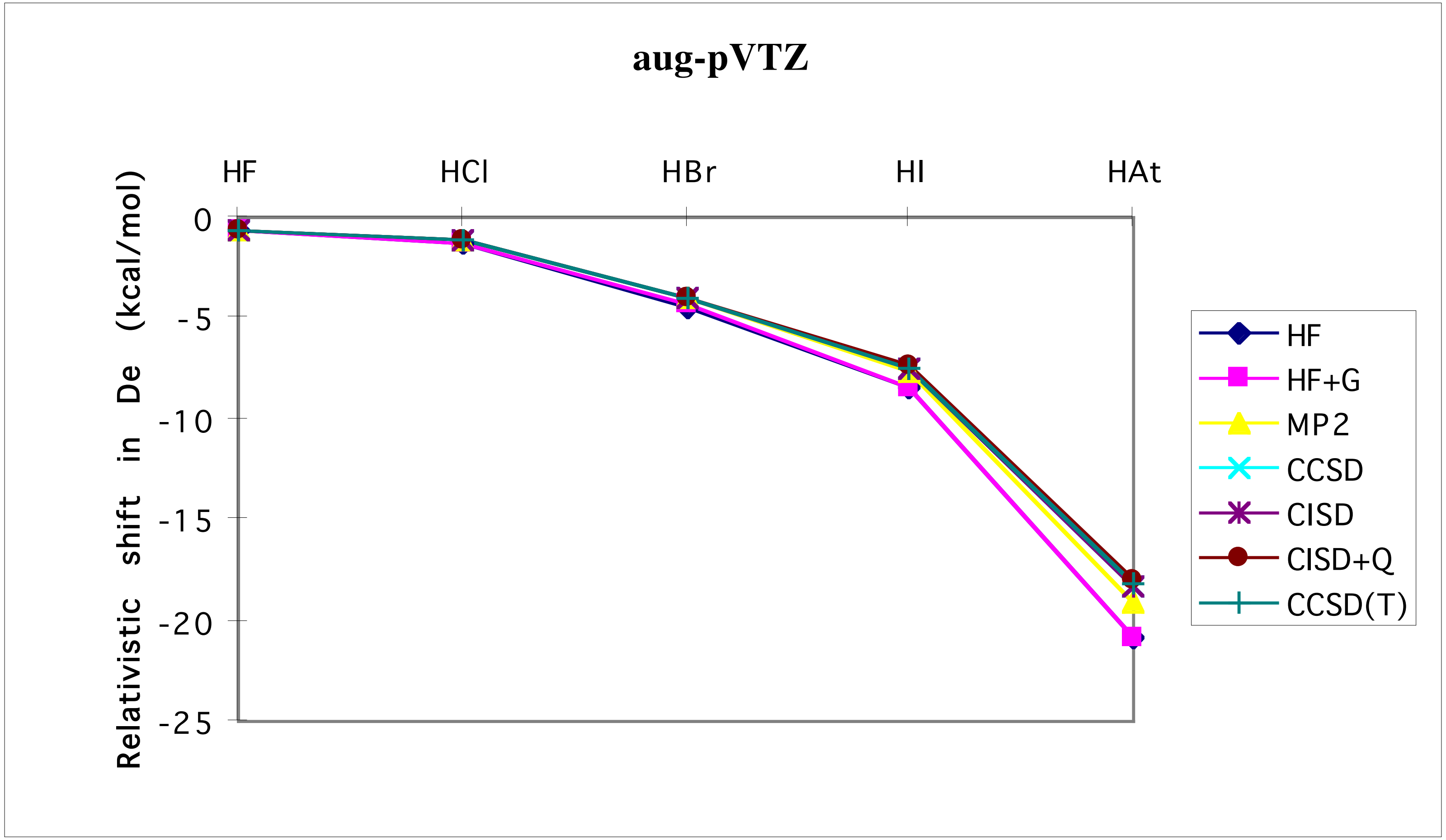
Important and slightly method dependent for 6p elements

Atomization energies

- Example: Hydrogen halides
- SO-coupling is mostly quenched in the molecule
- First order perturbation theory
- Strong sigma-pi mixing in ultra-relativistic H117

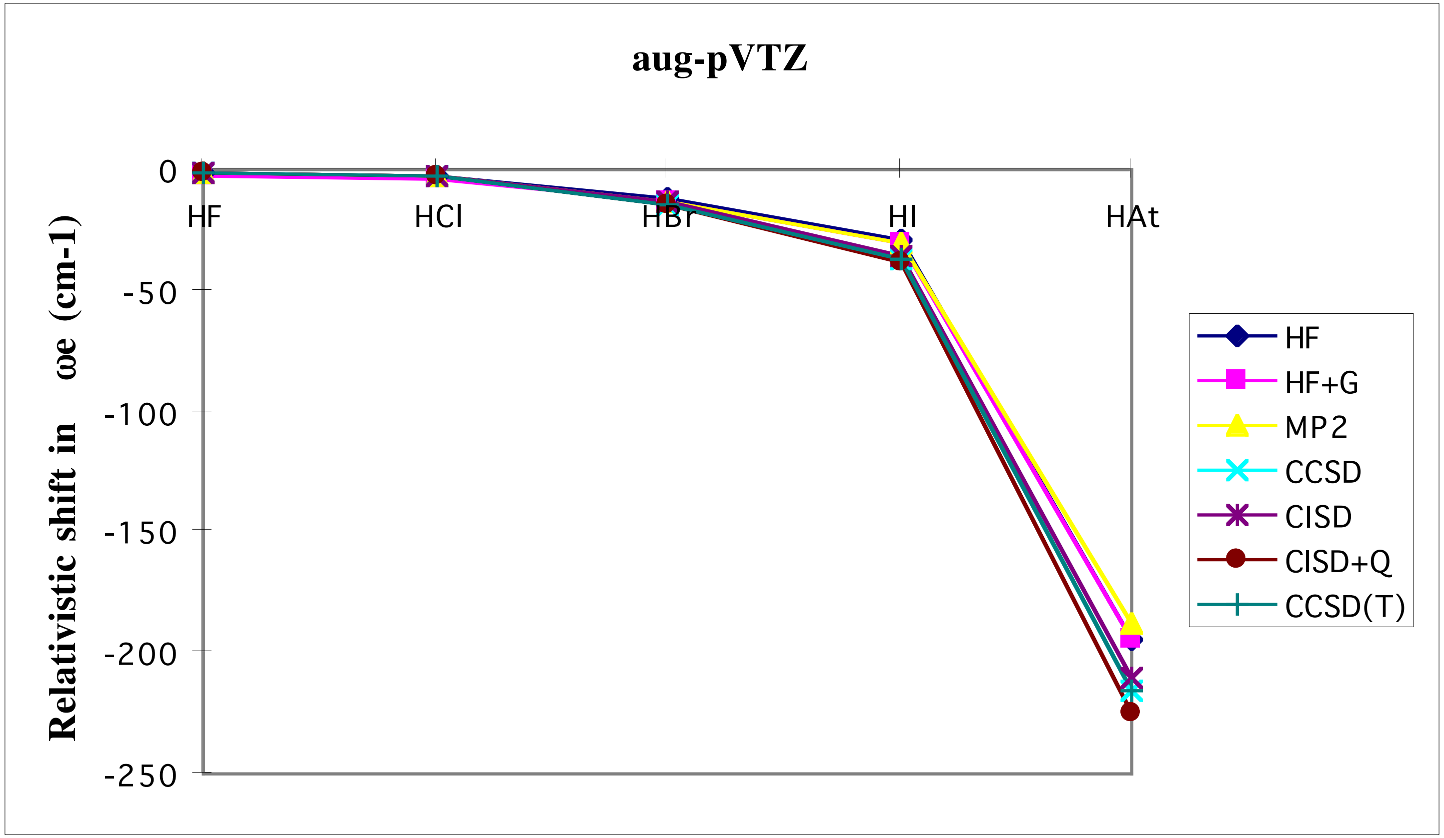


Atomization Energies



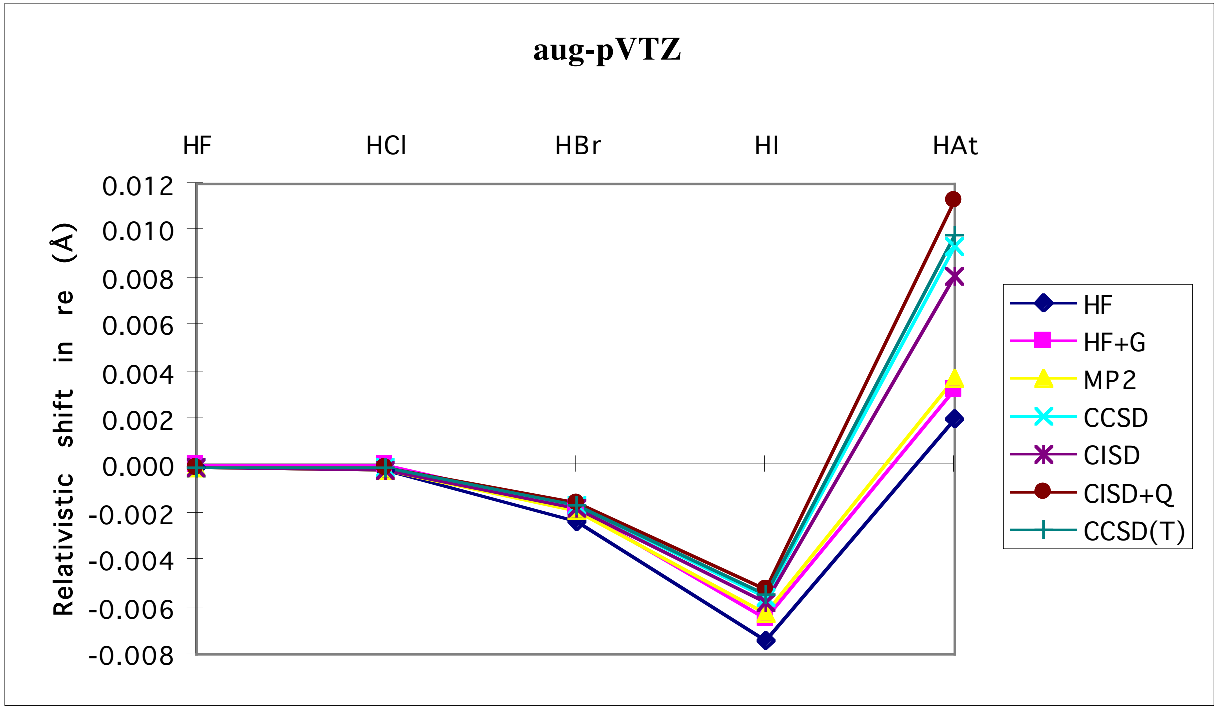
SO-coupling : a good estimate for atomization energies can be obtained by correcting only the asymptote

Vibrational Frequencies



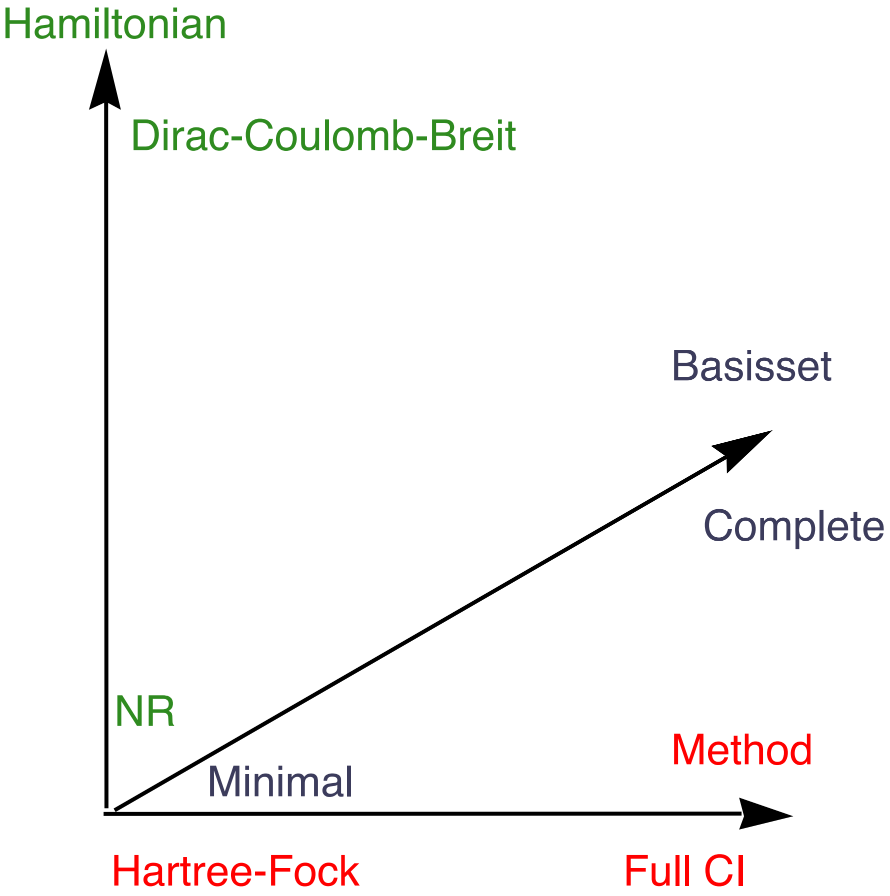
Bond weakening due to loss of sigma-character in bonding orbital. HAt requires inclusion of scalar and SO-effects in the calculation of the frequency.

Bond Lengths



Competition between scalar and spin-orbit effects
Total effect is small (< 0.01 Å) and can be neglected for most practical cases.

The extra dimension



Hamiltonian

Dirac-Coulomb-Breit

Basisset

Complete

NR

Method

Minimal

Hartree-Fock

Full CI

Development of relativistic molecular electronic structure theory

Expansion of the energy expression

- The exact Hydrogen energy expression

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

- Can be expanded to

$$\boxed{(1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^2 - \ldots}$$

$$E = mc^2 - \frac{Z^2}{2n^2} + \frac{Z^4}{2n^4c^2}\left\{\frac{3}{4} - \frac{n}{j+\frac{1}{2}}\right\} + O\left(\frac{Z^6}{c^4}\right)$$

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Approximate Hamiltonians

- Find 2-component operators that describe these scalar relativistic and spin-orbit coupling energy corrections in molecular systems
- Start by decoupling the large and small component equations

$$V\psi^L + c\,\sigma\cdot\mathbf{p}\,\psi^S = E\psi^L$$

$$c\,\sigma\cdot\mathbf{p}\,\psi^L + \left(V - 2mc^2\right)\psi^S = E\psi^S$$

- Rewrite the lower equation as

$$\psi^S(\mathbf{r}) = \left(1 - \frac{E-V}{2mc^2}\right)^{-1} \frac{\sigma\cdot\mathbf{p}}{2mc}\psi^L(\mathbf{r})$$

$$= K(E,\mathbf{r})\frac{\sigma\cdot\mathbf{p}}{2mc}\psi^L(\mathbf{r})$$

$$\boxed{K(E,\mathbf{r}) = \left(1 - \frac{E-V}{2mc^2}\right)^{-1}}$$

Approximate Hamiltonians

- Substitute in the upper equation

$$\left\{\frac{1}{2m}(\sigma\cdot\mathbf{p})K(E,\mathbf{r})(\sigma\cdot\mathbf{p})+V\right\}\psi^{L}(\mathbf{r})=E\psi^{L}(\mathbf{r})$$

- Unnormalized Elimination of the Small Component (ESC)
  - The full spinor is normalized to 1, so the large component only must have a norm < 1
  - Large component spinors are not orthogonal to each other (only the full spinors)

- Exact relation: is used as starting point for approximations

Pauli Hamiltonian

$$\boxed{K(E,\mathbf{r}) = \left(1 - \frac{E - V}{2mc^2}\right)^{-1}}$$

- Crudest approximation : $K(E,\mathbf{r}) \approx 1$

$$\left\{\frac{1}{2m}(\sigma\cdot\mathbf{p})(\sigma\cdot\mathbf{p}) + V\right\}\psi^L(\mathbf{r}) = E\psi^L(\mathbf{r})$$

$$\left\{\frac{p^2}{2m} + V\right\}\psi^L(\mathbf{r}) = E\psi^L(\mathbf{r})$$ Schrödinger equation

- Take K=1 but include also a magnetic field

$$\left\{\frac{1}{2m}(\sigma\cdot\pi)(\sigma\cdot\pi) + V\right\}\psi^L(\mathbf{r}) = E\psi^L(\mathbf{r})$$ Pauli equation

Breit-Pauli Hamiltonian

$$\boxed{\psi^S = K\frac{\sigma\cdot\mathbf{p}}{2mc}\psi^L}$$

- Find an operator that normalizes the wave function :

$$\psi = N\psi^L$$

$$N = \sqrt{1 + \frac{1}{4m^2c^2}(\sigma\cdot\mathbf{p})K^2(\sigma\cdot\mathbf{p})}$$

- Multiply the UESC equation by *N^{-1}*

$$N^{-1}\left\{\frac{1}{2m}(\sigma\cdot\mathbf{p})K(E,\mathbf{r})(\sigma\cdot\mathbf{p}) + V\right\}N^{-1}N\psi^L(\mathbf{r}) = N^{-1}E\psi^L(\mathbf{r})$$

$$N^{-1}\left\{\frac{1}{2m}(\sigma\cdot\mathbf{p})K(E,\mathbf{r})(\sigma\cdot\mathbf{p}) + V\right\}N^{-1}\psi(\mathbf{r}) = EN^{-2}\psi(\mathbf{r})$$

Breit-Pauli Hamiltonian

- Use series expansions and keep terms up to order c^{-2}

$$\hat{N}^{-1} = \left[1 + \frac{1}{4m^2c^2}(\sigma\cdot\mathbf{p})K^2(\sigma\cdot\mathbf{p})\right]^{-1/2}$$

$$= 1 - \frac{1}{8m^2c^2}(\sigma\cdot\mathbf{p})K^2(\sigma\cdot\mathbf{p}) + \ldots$$

$$= 1 - \frac{p^2}{8m^2c^2} + O(c^{-4})$$

$$\hat{N}^{-2} = \left[1 + \frac{1}{4m^2c^2}(\sigma\cdot\mathbf{p})K^2(\sigma\cdot\mathbf{p})\right]^{-1}$$

$$= 1 - \frac{p^2}{4m^2c^2} + O(c^{-4})$$

$$\boxed{K^2 = \left(1 - \frac{E-V}{2mc^2}\right)^{-2} = 1 + O\left(c^{-2}\right)}$$

Breit-Pauli Hamiltonian

- Expansion of K

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

- Substitute everything and keep only terms to order c^{-2}

$$\hat{N}^{-1}\left[\hat{V}+\frac{1}{2m}(\sigma\cdot\mathbf{p})K\left(\sigma\cdot\mathbf{p}\right)\right]\hat{N}^{-1}\psi=EN^{-2}\psi$$

$$\left(\hat{V}+\hat{T}+\frac{-Ep^{2}+\left(\sigma\cdot\mathbf{p}\right)V\left(\sigma\cdot\mathbf{p}\right)-Tp^{2}-\frac{1}{2}\left[p^{2},V\right]_{+}}{4m^{2}c^{2}}\right)\psi=\left[E-\frac{Ep^{2}}{4m^{2}c^{2}}\right]\psi$$

Breit-Pauli Hamiltonian

- The energy dependent term on the lhs is cancelled by the rhs

$$\hat{H}^{BP} = \hat{T} + \hat{V} + \frac{(\sigma\cdot\mathbf{p})V(\sigma\cdot\mathbf{p}) - T\mathbf{p}^2 - \frac{1}{2}\left[\mathbf{p}^2, V\right]_+}{4m^2c^2}$$

- Further simplify the equation using

$$(\sigma\cdot\mathbf{p})V(\sigma\cdot\mathbf{p}) = \cancel{(\mathbf{p}V)\cdot\mathbf{p}} + \cancel{V\mathbf{p}^2} + i\sigma\cdot(\mathbf{p}V)\times\mathbf{p}$$

$$-\frac{1}{2}\left[\mathbf{p}^2, V\right]_+ = -\frac{1}{2}\left(\mathbf{p}^2 V\right) - \cancel{(\mathbf{p}V)\cdot\mathbf{p}} - \cancel{V\mathbf{p}^2}$$

- Result : The Breit-Pauli equation

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

Darwin Mass-Velocity Spin-Orbit

Expectation values for the hydrogen atom

$$< \hat{H}^{Darwin} >= \frac{Z^4}{2n^3c^2} \quad (l = 0)$$

← Positive: reduces nuclear attraction

$$< \hat{H}^{Darwin} >= 0 \quad (l > 0)$$

← Operator is delta-function for V = -Z/r

$$< \hat{H}^{MV} >= \frac{Z^4}{2n^4c^2}\left\{\frac{3}{4} - \frac{n}{l + \frac{1}{2}}\right\}$$

← Always negative: decreases kinetic energy

$$< \hat{H}^{SO} >= \frac{Z^4}{2n^3c^2}\frac{l}{l(2l+1)(l+1)} \quad \left(j = l + 1/2\right)$$

Splitting larger for small n and/or l and large Z

$$< \hat{H}^{SO} >= \frac{Z^4}{2n^3c^2}\frac{-l-1}{l(2l+1)(l+1)} \quad \left(j = l - 1/2\right)$$

Approximate relativistic Hamiltonians

Can we improve upon the Breit-Pauli Hamiltonian ?

A short wish list :

1. It should describe the scalar relativistic effects
2. It should describe the spin-orbit coupling effect
3. It should be variationally stable
4. Interpretation: comparison with Schrödinger picture
5. Implementation: easy integrals, efficient coding
6. Errors should be small and systematically improvable

7. It should be well-named....

Regular Approximation

- What did we do wrong ? Check the expansion parameter

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

- E should be small relative to $2mc^2$
  - 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 $2mc^2$
  - 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^{th} order regular approximation: ZORA

- Can we find a better expansion parameter ? Yes !

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

- 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

$$\left\{\frac{1}{2m}(\sigma\cdot\mathbf{p})\left(1 - \frac{V}{2mc^2}\right)^{-1}(\sigma\cdot\mathbf{p}) + V\right\}\psi^{ZORA}(\mathbf{r}) = E\psi^{ZORA}(\mathbf{r})$$

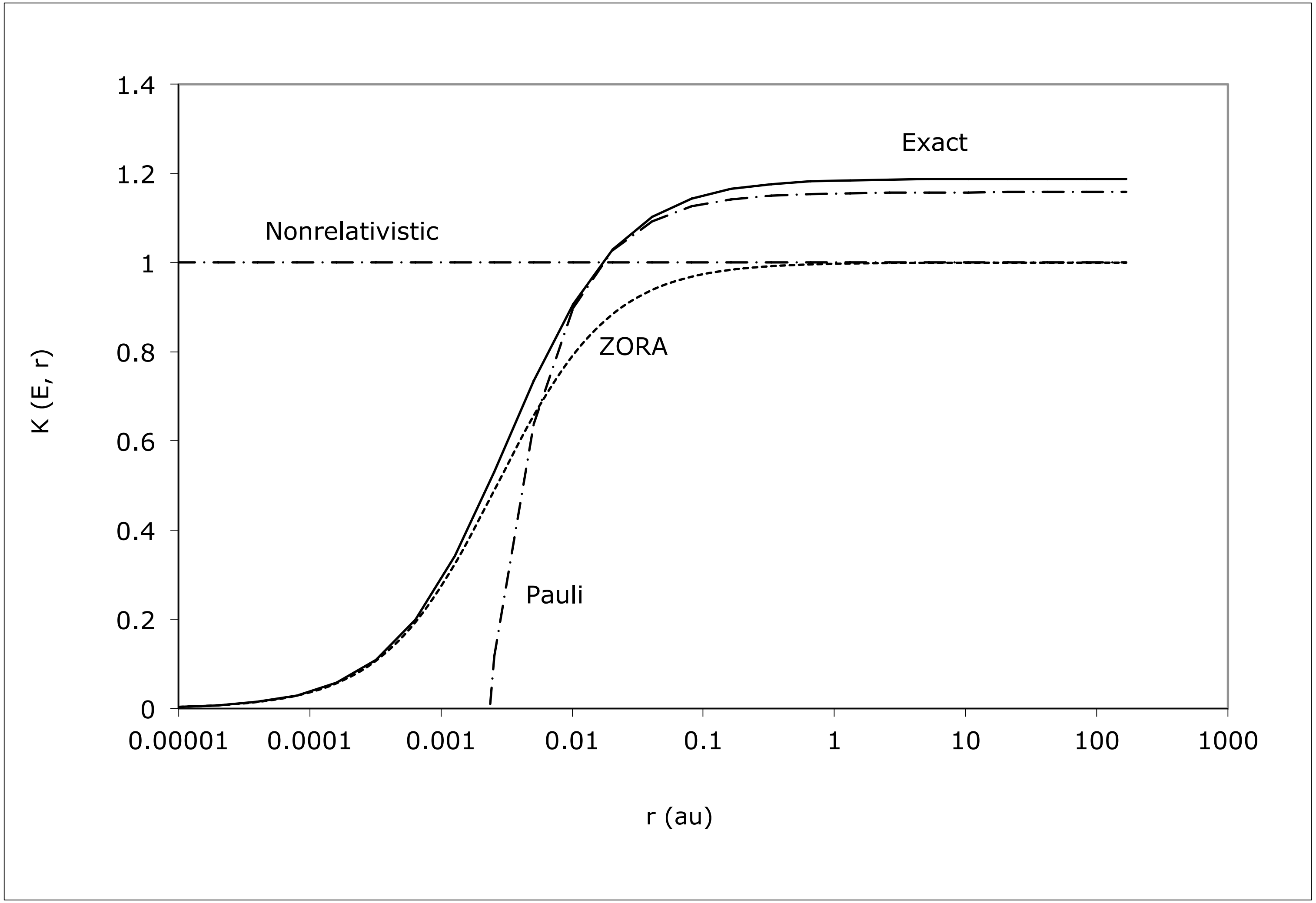
☺ Zeroth order equation does describe SO-coupling and scalar relativistic corrections

☹ Gauge dependence of the energy

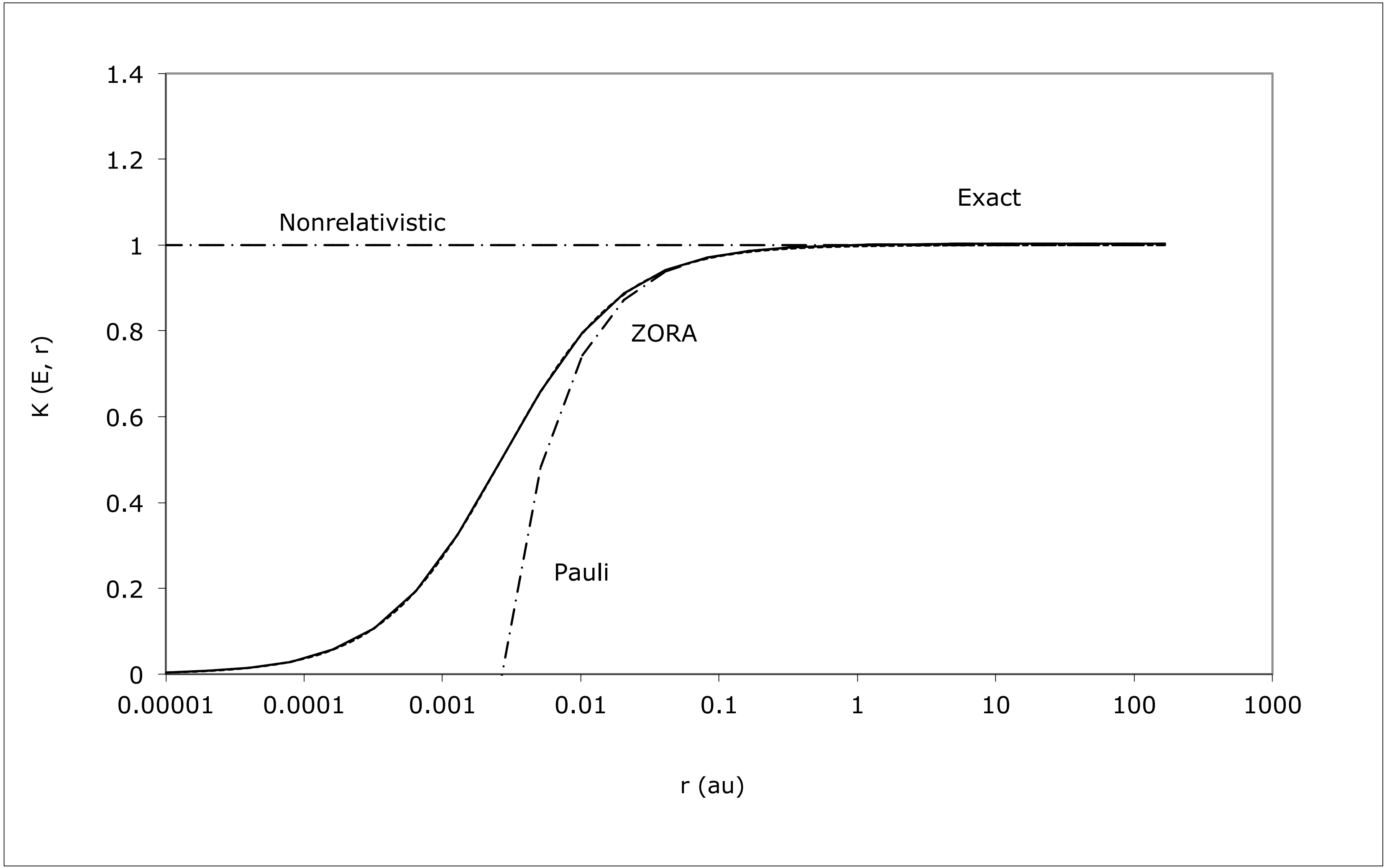
$$\boxed{V \rightarrow V + C \quad E \rightarrow E + C - \frac{EC}{2mc^2}}$$

- Affects ionization energies, structures
- Gauge independence can be achieved in various ways

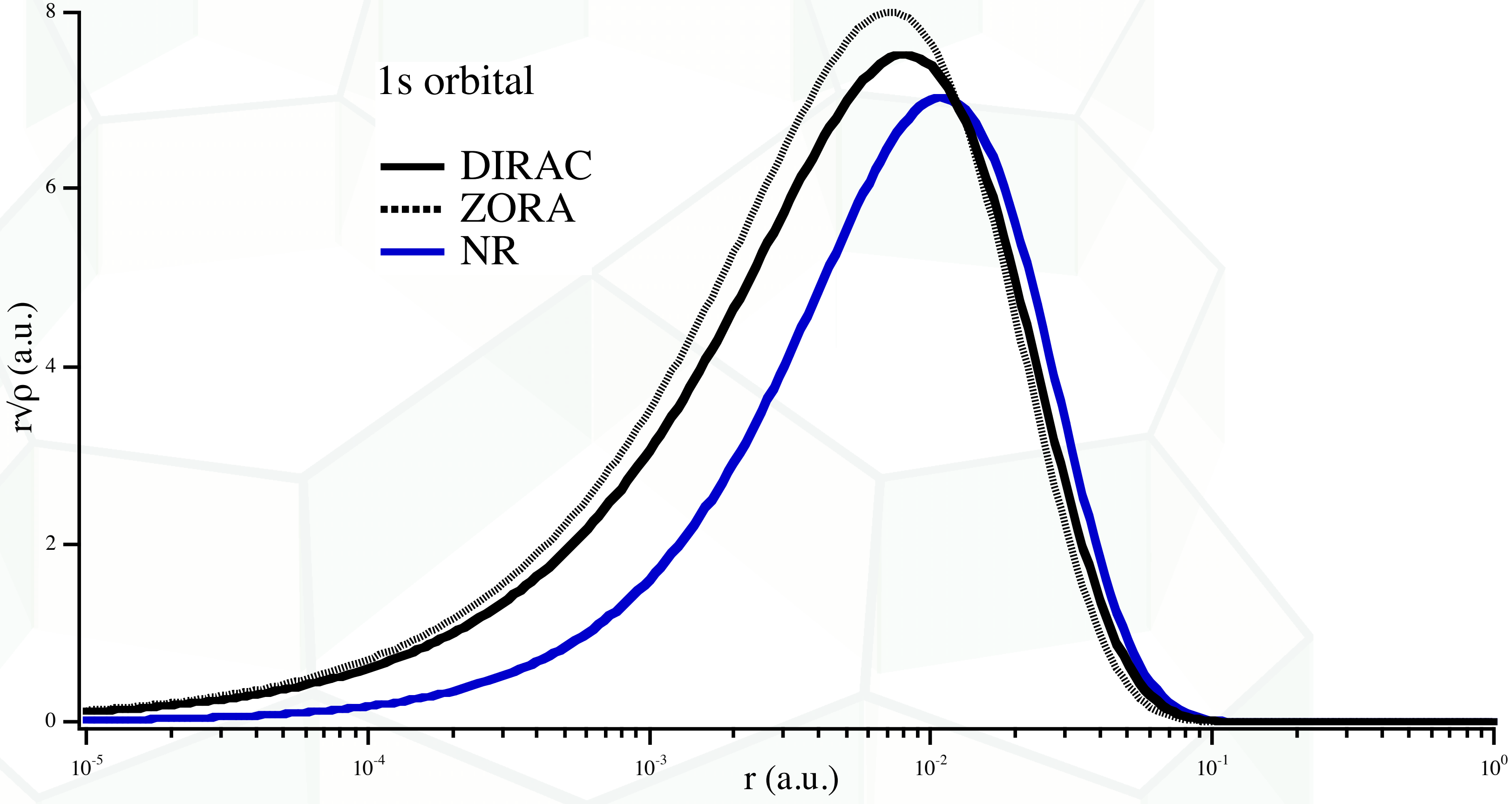
Approximations to K(E,**r**) for the 1s orbital of Fm^{99+}



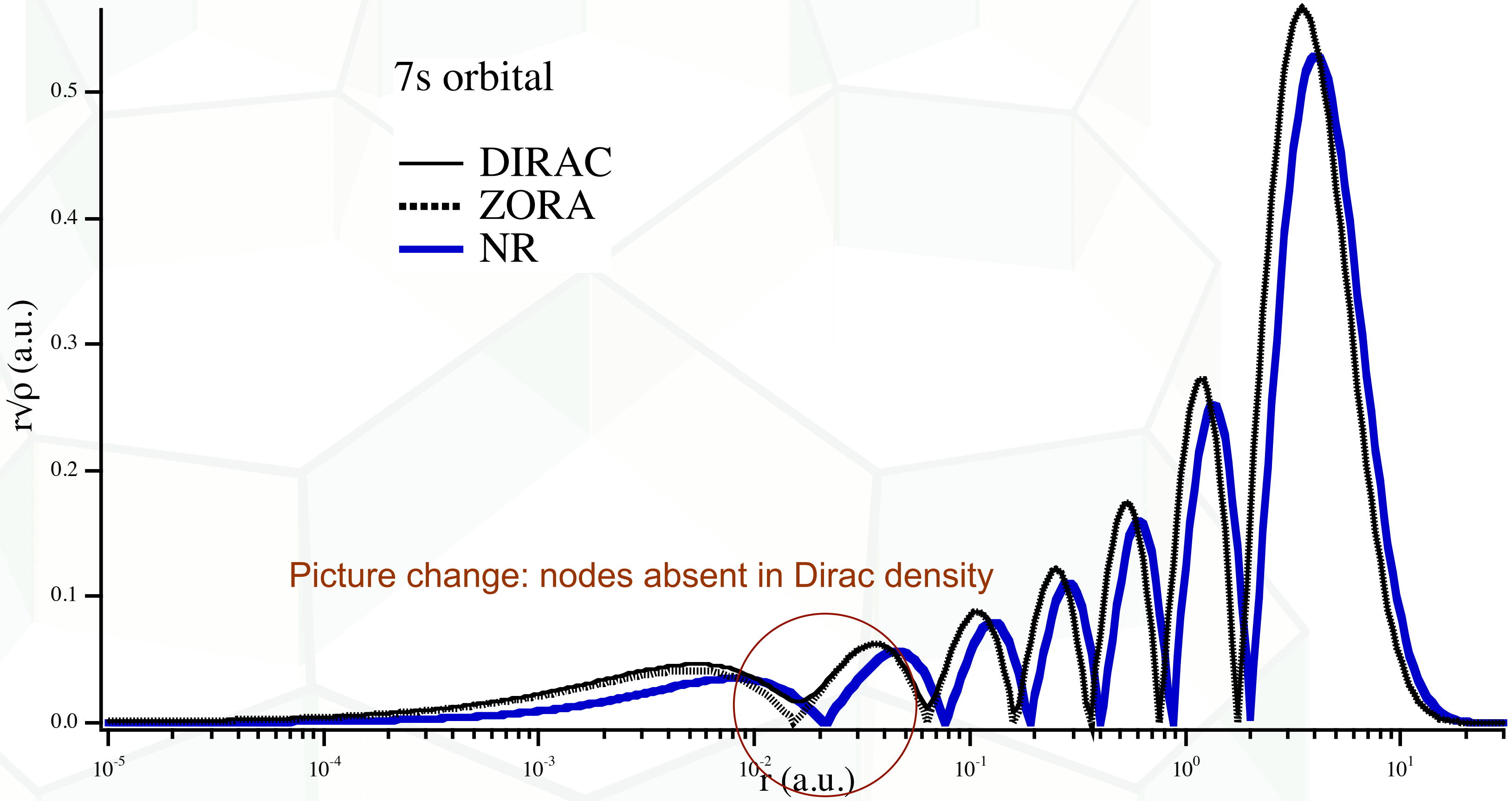
Approximations to K(E,**r**) for the 7s orbital of Fm^{99+}



Uranium atom



Uranium atom



Picture change: nodes absent in Dirac density

Scientific Computing & Modelling

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

Basis set expansion

- Use different expansion sets for the large and small component parts of the wave function

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^{N^L} \begin{pmatrix} \chi_\mu^L(\mathbf{r}) \\ 0 \end{pmatrix} c_{\mu i}^L + \sum_{\nu=1}^{N^S} \begin{pmatrix} 0 \\ \chi_\nu^S(\mathbf{r}) \end{pmatrix} c_{\nu i}^S$$

- Kinetic balance condition

$$\chi^S(\mathbf{r}) = \frac{\sigma \cdot \mathbf{p}}{2mc} \chi^L(\mathbf{r}) \quad \text{or} \quad \{\chi^S(\mathbf{r})\} = \left\{ \frac{\partial \chi^L(\mathbf{r})}{\partial x}, \frac{\partial \chi^L(\mathbf{r})}{\partial y}, \frac{\partial \chi^L(\mathbf{r})}{\partial z} \right\}$$

- Recovers the non-relativistic limit

$$\int \chi_\kappa^{L^*}(\mathbf{r}) T \chi_\lambda^L(\mathbf{r}) d\mathbf{r} = \frac{1}{2} \sum_{\mu=1}^{N^S} \int \chi_\kappa^{L^*}(\mathbf{r})(\sigma \cdot \mathbf{p}) \chi_\mu^S(\mathbf{r}) d\mathbf{r} \times \int \chi_\mu^{S^*}(\mathbf{r})(\sigma \cdot \mathbf{p}) \chi_\lambda^L(\mathbf{r}) d\mathbf{r}$$

$$\boxed{\mathbf{T}^{LL} = \frac{1}{2}(\sigma \cdot \mathbf{p})^{LS}(\sigma \cdot \mathbf{p})^{SL}} \longleftarrow \text{Resolution of identity}$$

Self Consistent Field: Hartree-Fock

1. Construct Fock operator $F = \beta' c^2 + c\alpha \cdot \mathbf{p} + V + \sum_j^{occupied\ orbitals} J_j - K_j$
2. Find eigensolutions $F\psi(\mathbf{r}_1) = \varepsilon\psi(\mathbf{r}_1)$
3. Check convergence $\{\psi^{new}\} = \{\psi^{old}\}$?
4. Compute energy $E^{HF} = E^{Kinetic} + E^{Potential} + E^{Elec.Rep.}$

$$E^{HF} = \sum_i^{occupied\ orbitals} < i \mid \beta' c^2 + c\alpha \cdot \mathbf{p} \mid i > + \sum_i^{occupied\ orbitals} < i \mid V \mid i > + \frac{1}{2} \sum_{i,j}^{occupied\ orbitals} < i \mid J_j - K_j \mid i >$$

Fock operator

$$F = \begin{pmatrix} V + \sum_j J_j - K_j & c(\boldsymbol{\sigma}.\mathbf{p}) - \sum_j K_j \\ c(\boldsymbol{\sigma}.\mathbf{p}) - \sum_j K_j & V - 2c^2 + \sum_j J_j - K_j \end{pmatrix}$$

$$J_j(\mathbf{r}_1) = \int \frac{\psi_j^{L^\dagger}(\mathbf{r}_2)\psi_j^L(\mathbf{r}_2) + \psi_j^{S^\dagger}(\mathbf{r}_2)\psi_j^S(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 = \int \frac{\rho_j(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2$$

$$\begin{aligned} K_j \psi_i^L(\mathbf{r}_1) &= K_j^{LL}\psi_i^L(\mathbf{r}_1) + K_j^{SL}\psi_i^L(\mathbf{r}_1) \\ &= \int \frac{\psi_j^{L^\dagger}(\mathbf{r}_2)\psi_i^L(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \psi_j^L(\mathbf{r}_1) + \int \frac{\psi_j^{L^\dagger}(\mathbf{r}_2)\psi_i^L(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \psi_j^S(\mathbf{r}_1) \end{aligned}$$

$$\begin{aligned} K_j \psi_i^S(\mathbf{r}_1) &= K_j^{LS}\psi_i^S(\mathbf{r}_1) + K_j^{SS}\psi_i^S(\mathbf{r}_1) \\ &= \int \frac{\psi_j^{S^\dagger}(\mathbf{r}_2)\psi_i^S(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \psi_j^L(\mathbf{r}_1) + \int \frac{\psi_j^{S^\dagger}(\mathbf{r}_2)\psi_i^S(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \psi_j^S(\mathbf{r}_1) \end{aligned}$$

Choice of expansion functions

- Large component
  - Atoms: Slaters or Gaussians
  - Molecules: Spherical, Cartesian or Hermite Gaussians

- Small component
  - Same type as large component
  - Should fulfill kinetic balance relation

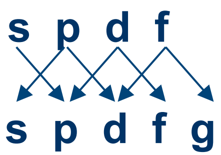
$$\left\{\chi_P^S\right\} = \left\{(\sigma\cdot\mathbf{p})\chi_P^L\right\} \qquad \left\{\chi_P^S\right\} = \left\{\frac{\partial\chi_P^L}{\partial x},\frac{\partial\chi_P^L}{\partial y},\frac{\partial\chi_P^L}{\partial z}\right\}$$

Restricted KB Unrestricted KB

Kinetic Balance realizations

$$(\vec{\sigma}\cdot\vec{p})(\vec{\sigma}\cdot\vec{p}) = p^{2} \Rightarrow \left\{(\vec{\sigma}\cdot\vec{p})\chi^{L}\right\} \subset \left\{\chi^{S}\right\}$$

Scalar functions

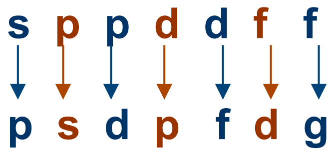


Large component **s p d f**

Small component **s p d f g**

Typically 4-5 times…

2-spinor functions



s p p d d f f

p s d p f d g

Exactly 4 times …

…as many basisfunctions as in NR calculation

Conventional integral code

Specialized integral code

The small component density

- The large component wave function resembles the non-relativistic wave function
- Exact relation between large and small component wave functions

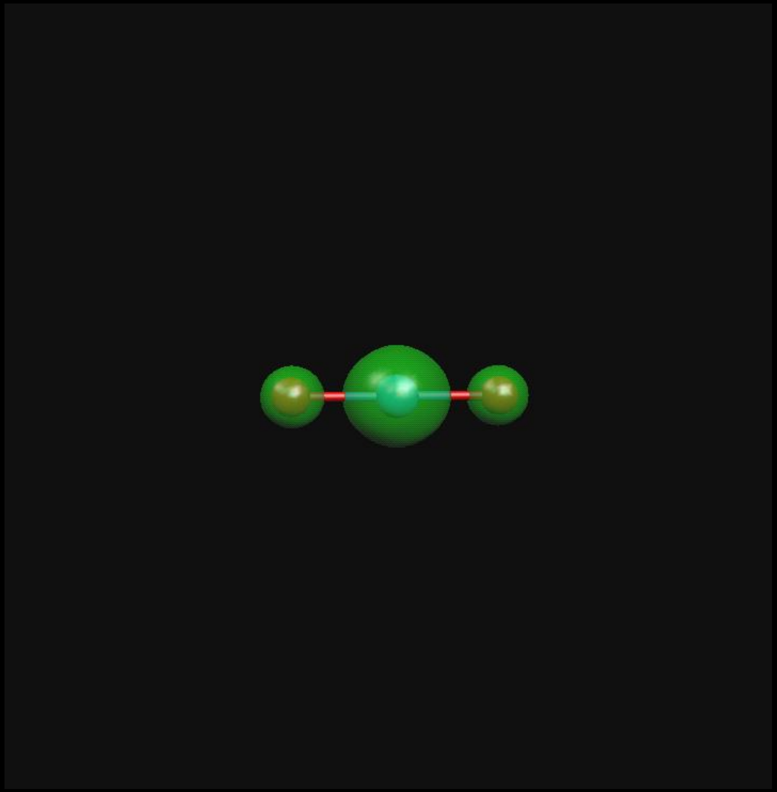
$$\psi^S = \frac{-i}{2c}\left(1+\frac{E-V}{2c^2}\right)^{-1}\sigma\cdot\left(\nabla\psi^L\right)$$

- Small component wave function is related to the first derivative of large component wave function
- The small component density is an embarrassingly **local** quantity !

Electron Density of Uranyl

Large component

Small component



Modified Dirac equation

- Define an auxilliary function such that

$$\psi^S = \frac{1}{2mc}(\sigma \cdot \mathbf{p})\phi^L \longleftarrow \text{Relation holds by definition}$$

- Transform the Dirac equation accordingly

$$\begin{pmatrix} V & T \\ T & \frac{(\sigma \cdot \mathbf{p})V(\sigma \cdot \mathbf{p})}{4mc^2} - T \end{pmatrix} \begin{pmatrix} \psi^L \\ \phi^L \end{pmatrix} = E \begin{pmatrix} 1 & 0 \\ 0 & \frac{T}{2mc^2} \end{pmatrix} \begin{pmatrix} \psi^L \\ \phi^L \end{pmatrix}$$

- Separate scalar and spin-dependent part and neglect the spin-dependent terms if desired

Direct perturbation theory

- Consider the modified Dirac equation

$$\begin{pmatrix} V & T \\ T & \frac{(\sigma\cdot\mathbf{p})V(\sigma\cdot\mathbf{p})}{4mc^2} - T \end{pmatrix}\begin{pmatrix} \psi^L \\ \phi^L \end{pmatrix} = E\begin{pmatrix} 1 & 0 \\ 0 & \frac{T}{2mc^2} \end{pmatrix}\begin{pmatrix} \psi^L \\ \phi^L \end{pmatrix}$$

- Non-relativistic limit is related to the Lévy-Leblond equation

$$\begin{pmatrix} V & T \\ T & -T \end{pmatrix}\begin{pmatrix} \psi^L \\ \phi^L \end{pmatrix} = E^{NR}\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} \psi^L \\ \phi^L \end{pmatrix} \qquad \begin{pmatrix} V & (\sigma\cdot\mathbf{p}) \\ (\sigma\cdot\mathbf{p}) & -2m \end{pmatrix}\begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = E^{LL}\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix}$$

- Define perturbation theory with as first order perturbations

$$\boxed{H^{(1)} = \begin{pmatrix} 0 & 0 \\ 0 & -Vc^{-2} \end{pmatrix}} \qquad \boxed{S^{(1)} = \begin{pmatrix} 0 & 0 \\ 0 & c^{-2} \end{pmatrix}}$$

Foldy-Wouthuysen transformations

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

$$UH^{D}U^{-1}U\psi_i^{D} = EU\psi_i^{D}$$

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

$$\psi_i^{FW4(+)} = U\psi_i^{D(+)} = \begin{pmatrix} \psi_i^{FW} \\ 0 \end{pmatrix}$$

Picture change

$$\hat{U} = \begin{pmatrix} \left(1 + X^{\dagger}X\right)^{-\frac{1}{2}} & \left(1 + X^{\dagger}X\right)^{-\frac{1}{2}}X^{\dagger} \\ -\left(1 + XX^{\dagger}\right)^{-\frac{1}{2}}X & \left(1 + XX^{\dagger}\right)^{-\frac{1}{2}} \end{pmatrix}$$

$$X = \frac{1}{2mc}K(\boldsymbol{\sigma}.\mathbf{p})$$

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

Douglas-Kroll-Hess method

- Idea
  - Transform “bare-nucleus Hamiltonian” with the known free-particle transformation matrix, followed by additional transformations to reduce size of remaining off-diagonal elements to some order in the potential

- Assumptions
  - The transformation is based on the Furry picture: potential does not include mean-field of electrons
  - The conventional implementations neglect the transformation of the two-electron interaction and often also the SO-coupling terms

- Advantages-Disadvantages
  - ☺ Method is variationally stable
  - ☺ Slight modification of existing code required (replacement of one-electron nuclear attraction integrals), fast implementation
  - ☺ Good results in practice, significant improvement over Breit-Pauli
  - ☹ Complicated operators, matrix elements can not be calculated analytically
  - ☹ Two-electron terms are hard to evaluate
  - ☹ Interactions with external field need to be represented by transformed operators (picture change)

Douglas-Kroll-Hess method

- The second-order Hamiltonian

$$H^{(2)} = \begin{pmatrix} H^{DKH2} & H_{12}^{(2)} \\ H_{21}^{(2)} & H_{22}^{(2)} \end{pmatrix}$$

- The Douglas-Kroll-Hess Hamiltonian

$$H^{DKH2} = E_p + A_p\left(V + \left(\boldsymbol{\sigma}\cdot\mathbf{P}_p\right)V\left(\boldsymbol{\sigma}\cdot\mathbf{P}_p\right)\right)A_p + W_1 E_p W_1 + \frac{1}{2}W_1^2 E_p + \frac{1}{2}E_p W_1^2$$

$$\boxed{E_p = \sqrt{m^2c^4 + c^2p^2}}$$

← Free particle energy operator

$$\boxed{A_p = \sqrt{\frac{E_p + 2mc^2}{2E_p}}}$$

← Kinematical factor

$$\boxed{R_p = \frac{c\alpha\cdot\mathbf{p}}{E_p + mc^2} = \alpha\cdot\mathbf{P}_p}$$

$$\boxed{W_1 = \frac{A_p R_p V(\mathbf{p},\mathbf{p}')A_{p'} - A_p V(\mathbf{p},\mathbf{p}')R_{p'}A_{p'}}{E_p + E_{p'}}}$$

Iterative decoupling schemes

- Write Foldy-Wouthuysen decoupling transformation (U) as product of normalization (V) and decoupling (W)

$$\hat{U} = \begin{pmatrix} \left(1+\hat{X}^\dagger\hat{X}\right)^{-\frac{1}{2}} & \left(1+\hat{X}^\dagger\hat{X}\right)^{-\frac{1}{2}}\hat{X}^\dagger \\ -\left(1+\hat{X}\hat{X}^\dagger\right)^{-\frac{1}{2}}\hat{X} & \left(1+\hat{X}\hat{X}^\dagger\right)^{-\frac{1}{2}} \end{pmatrix}$$

$$= \begin{pmatrix} \left(1+\hat{X}^\dagger\hat{X}\right)^{-\frac{1}{2}} & 0 \\ 0 & \left(1+\hat{X}\hat{X}^\dagger\right)^{-\frac{1}{2}} \end{pmatrix}\begin{pmatrix} 1 & \hat{X}^\dagger \\ -\hat{X} & 1 \end{pmatrix}$$

$$= \hat{V}\hat{W}$$

- The decoupling requirement provides equations for X

$$\left(\hat{W}\hat{H}^D\hat{W}^\dagger\right)^{SL} = 0$$

$$\hat{h}^{SL} + \hat{h}^{SS}\hat{X} - \hat{X}\hat{h}^{LL} - \hat{X}\hat{h}^{LS}\hat{X} = 0$$ ← Quadratic equation for X

Iterative decoupling schemes

- All Foldy-Wouthuysen transformed solutions should only have two non-zero components

$$\begin{pmatrix} 1 & \hat{X}^{\dagger} \\ -\hat{X} & 1 \end{pmatrix} \begin{pmatrix} \psi_{+}^{L} & \psi_{-}^{L} \\ \psi_{+}^{S} & \psi_{-}^{S} \end{pmatrix} = \begin{pmatrix} \phi_{+} & 0 \\ 0 & \phi_{-} \end{pmatrix}$$

$$\psi_{+}^{S} - \hat{X}\psi_{+}^{L} = 0$$

$$\psi_{-}^{L} + \hat{X}^{\dagger}\psi_{-}^{S} = 0$$

← Linear equations for X

- Equation for X can be solved if all analytical solutions of the Dirac equation can be written in a simple form. This was possible in the free-particle case .

- For atoms and molecules the potential operator is too complicated to work with the exact solutions, but it is possible to derive iterative decoupling schemes (Barysz, Reiher, Hirao) that provide nearly exact (but very complicated) operator expressions based on solutions of the hydrogenic atom.

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)

Exact two-component theory

- A matrix representation of the Dirac matrix is formed and diagonalized: eigenvectors gives access to the exact decoupling *matrix* X in this basis

$$\begin{pmatrix} \mathbf{h}^{LL} & \mathbf{h}^{LS} \\ \mathbf{h}^{SL} & \mathbf{h}^{SS} \end{pmatrix} \begin{pmatrix} \mathbf{y}_{+}^{L} & \mathbf{y}_{-}^{L} \\ \mathbf{y}_{+}^{S} & \mathbf{y}_{-}^{S} \end{pmatrix} = \begin{pmatrix} \mathbf{e}_{+} & 0 \\ 0 & \mathbf{e}_{-} \end{pmatrix} \begin{pmatrix} \mathbf{y}_{+}^{L} & \mathbf{y}_{-}^{L} \\ \mathbf{y}_{+}^{S} & \mathbf{y}_{-}^{S} \end{pmatrix}$$

- Write the equations for X in matrix form

$$\mathbf{y}_{+}^{S} - \mathbf{X}\mathbf{y}_{+}^{L} = 0$$
$$\mathbf{y}_{-}^{L} + \mathbf{X}^{\dagger}\mathbf{y}_{-}^{S} = 0$$

- Manipulate to get an equation of the form AX = B that can be solved by Cholesky decomposition (A is Hermitian and positive definite)

$$\left[\mathbf{y}_{-}^{S}\mathbf{y}_{-}^{S^{\dagger}}\right]X = \left[\mathbf{y}_{-}^{S}\mathbf{y}_{-}^{L^{\dagger}}\right]$$

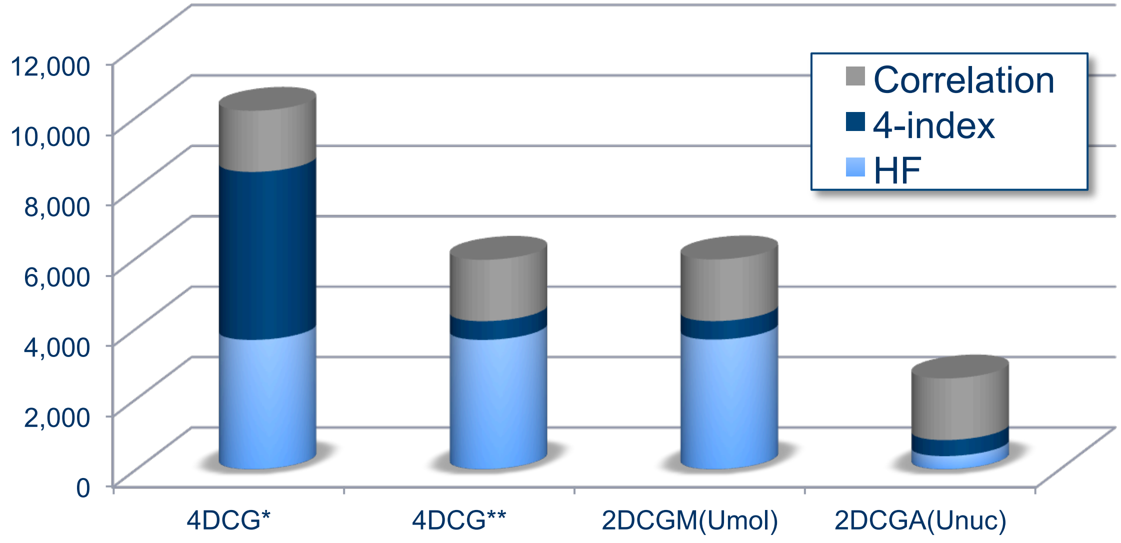
- See Ilias & Saue (JCP **126** (2006) 064102) for details

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

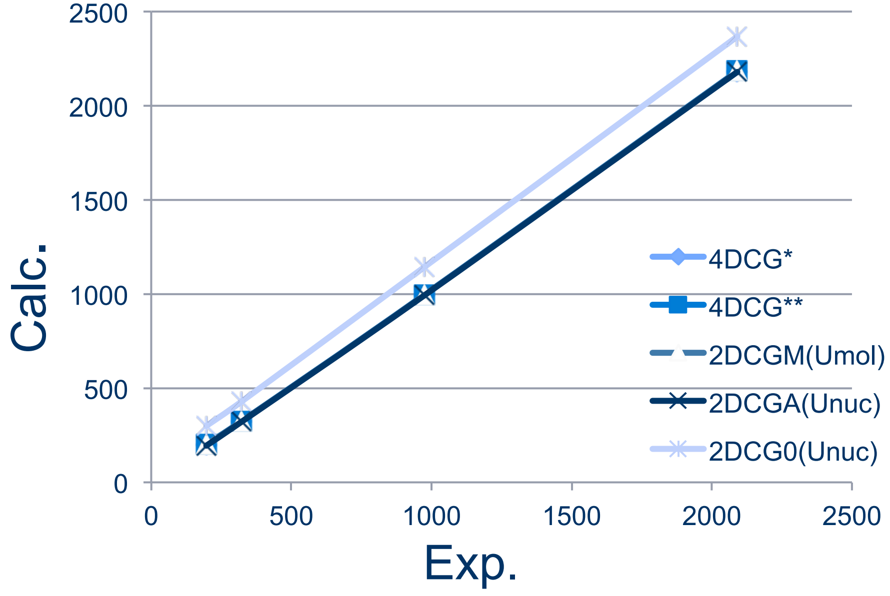
- 😐 The necessary diagonalization and other matrix manipulations are done before the SCF procedure
- 😐 Decoupling from molecular Hartree-Fock solutions: molecular mean-field (X2C-MMF) approach
- 😐 4-component property matrices can be readily transformed to the 2-c picture

X2C: computational efficiency



CPU-times in s

SO-spitting in cm^{-1}



Errors in SO relative to ^{4}DCG* (cm^{-1})

	^{4}DCG**	^{2}DCG^{M}(U$_{mol}$)
FO	1.38	1.35
ClO	0.80	0.75
BrO	0.97	0.73
IO	1.22	0.61

Valence-Only approaches

- All-electron calculations are not always feasible or necessary

- Hierarchy of approximations for “core” electrons
  1. Correlate the core electrons at a lower level of theory (e.g. MP2)
  2. Include core electrons only at HF level of theory
  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 or NLPP)
  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. Can be used in density-only DFT calculations

Frozen Core approximation

- Consider the Fock operator

$$F = h^{kinetic} - \sum_{A}^{Nuclei} \frac{Z_A}{r_A} + \sum_{j}^{\substack{occupied\\orbitals}} \left(J_j - K_j\right)$$

- Identify localized (atomic) core orbitals and partition $\boxed{Z_A^* = Z_A - Z_{Core}}$

$$F = h^{kinetic} - \sum_{A}^{Nuclei} \frac{Z_A}{r_A} + \sum_{A}^{Nuclei} \sum_{c}^{core} J_c^A - K_c^A + \sum_{v}^{valence} J_v - K_v$$

$$F = h^{kinetic} - \sum_{A}^{Nuclei} \frac{Z_A^*}{r_A} + \sum_{v}^{valence} J_v - K_v + \underbrace{\boxed{\sum_{A}^{Nuclei} \left(- \frac{Z_A^{core}}{r_A} + \sum_{c}^{core} J_c^A \right)}}_{V_{Coulomb}} - \underbrace{\boxed{\sum_{A}^{Nuclei} \sum_{c}^{core} K_c^A}}_{V_{Exchange}}$$

- 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 modeled by a classical core polarization potential (see also book II, formula 41.9)

$$V_{CPP}^{A} = -\frac{1}{2}\sum_{A} \mathbf{f}_A^T \boldsymbol{\alpha}_A \mathbf{f}_A$$

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

Polarizability 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 this requires a correction

Ab Initio Model Potentials

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

$$V^A_{\mathit{Frozen\ core}} = \sum_{c}^{\mathit{core}}\left(J_c^A - Z_A^{\mathit{core}}\right) - \sum_{c}^{\mathit{core}} K_c^A \approx V^A_{\mathit{Coul}} + V^A_{\mathit{Exch}} + P^A_{\mathit{Core}}$$

$$\boxed{V^A_{\mathit{Coul}} = \frac{1}{r_A}\sum_i c_i^A e^{-\alpha_i^A r_A^2}}$$

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

$$\boxed{V^A_{\mathit{Exch}} = -\sum_{c}^{\mathit{core}} \sum_{r,s,t,u}^{\substack{\mathit{primitive} \\ \mathit{basis\ on}\ A}} |r\rangle S^{-1}_{rs}\langle s|K_c^A|t\rangle S^{-1}_{tu}\langle u|}$$

Resolution of identity with non-orthogonal functions

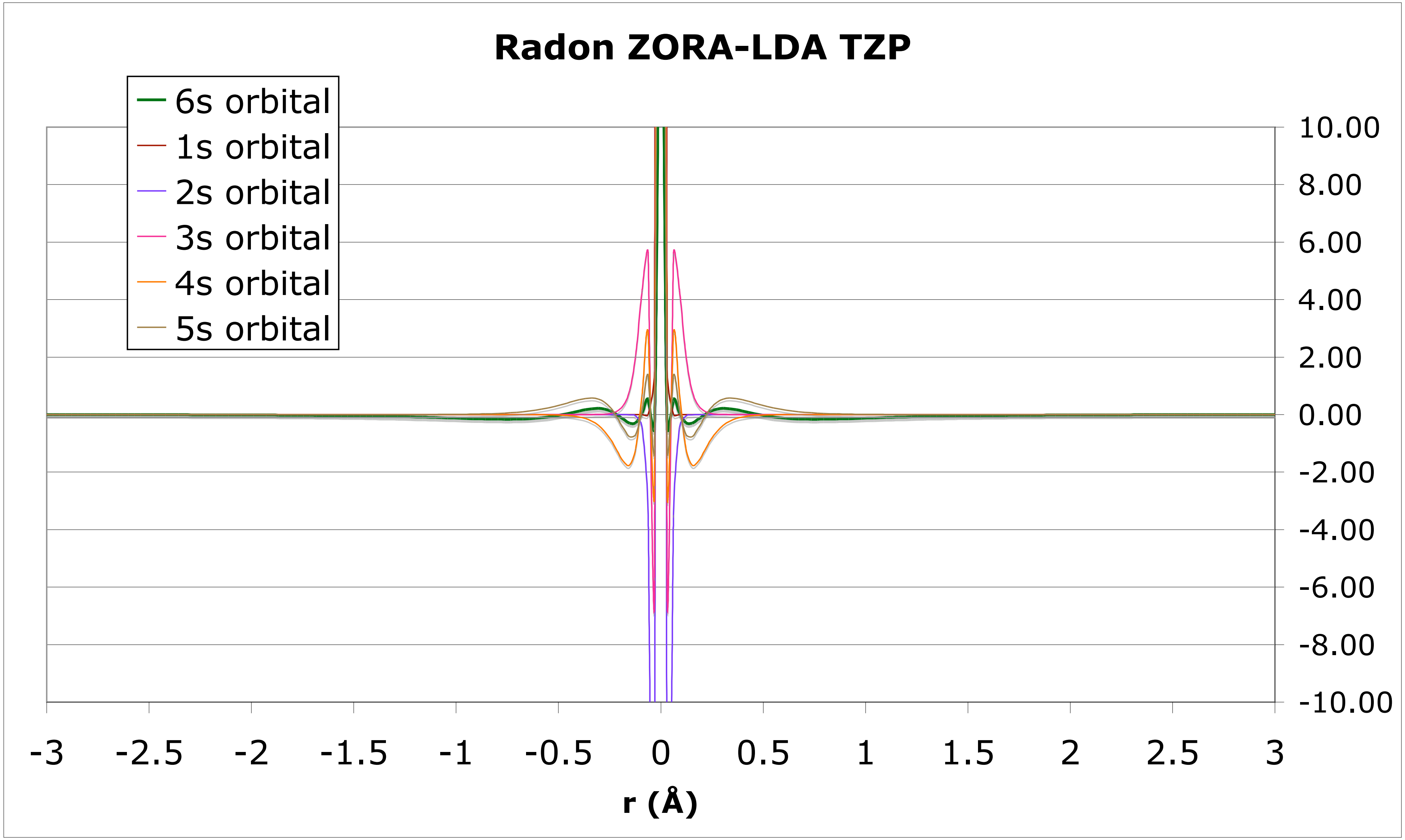
$$\boxed{P^A_{\mathit{Core}} = \sum_{c}^{\mathit{core}} |c\rangle B_c^A \langle c|}$$

Level shift that shifts the core solutions to high energies

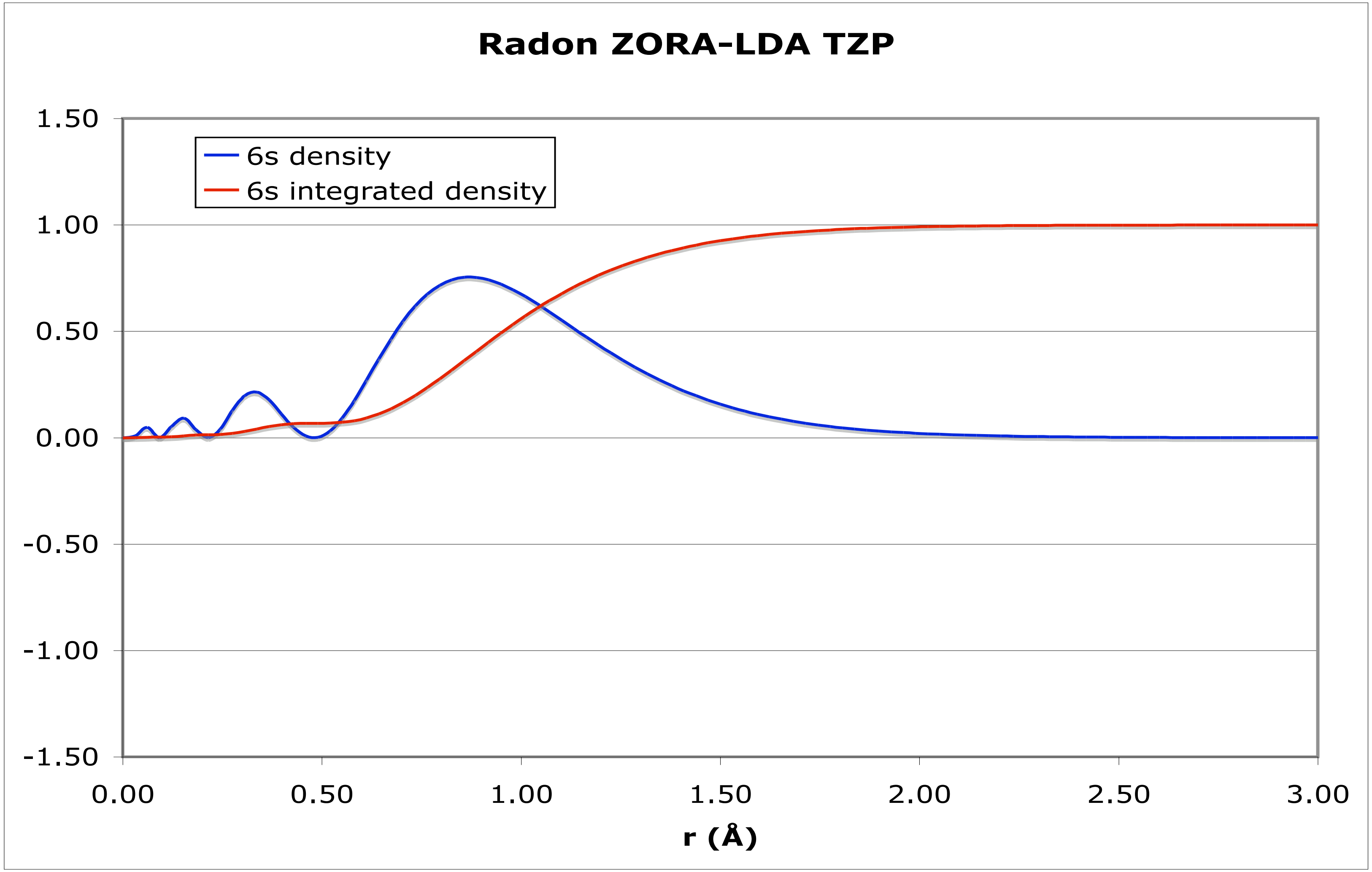
Ab Initio Model Potentials

- 😐 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

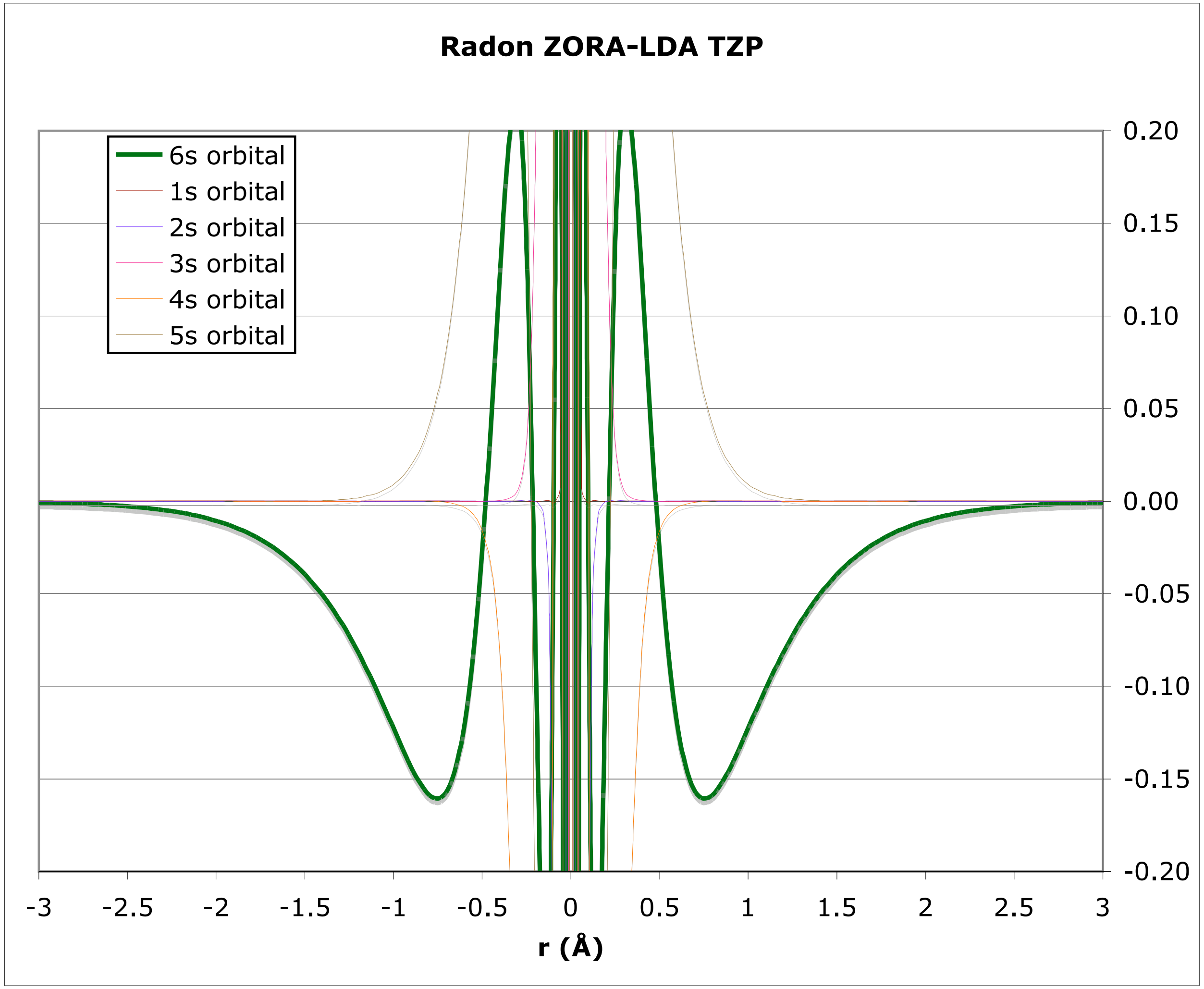
Nodal structure



Valence density



Valence orbitals



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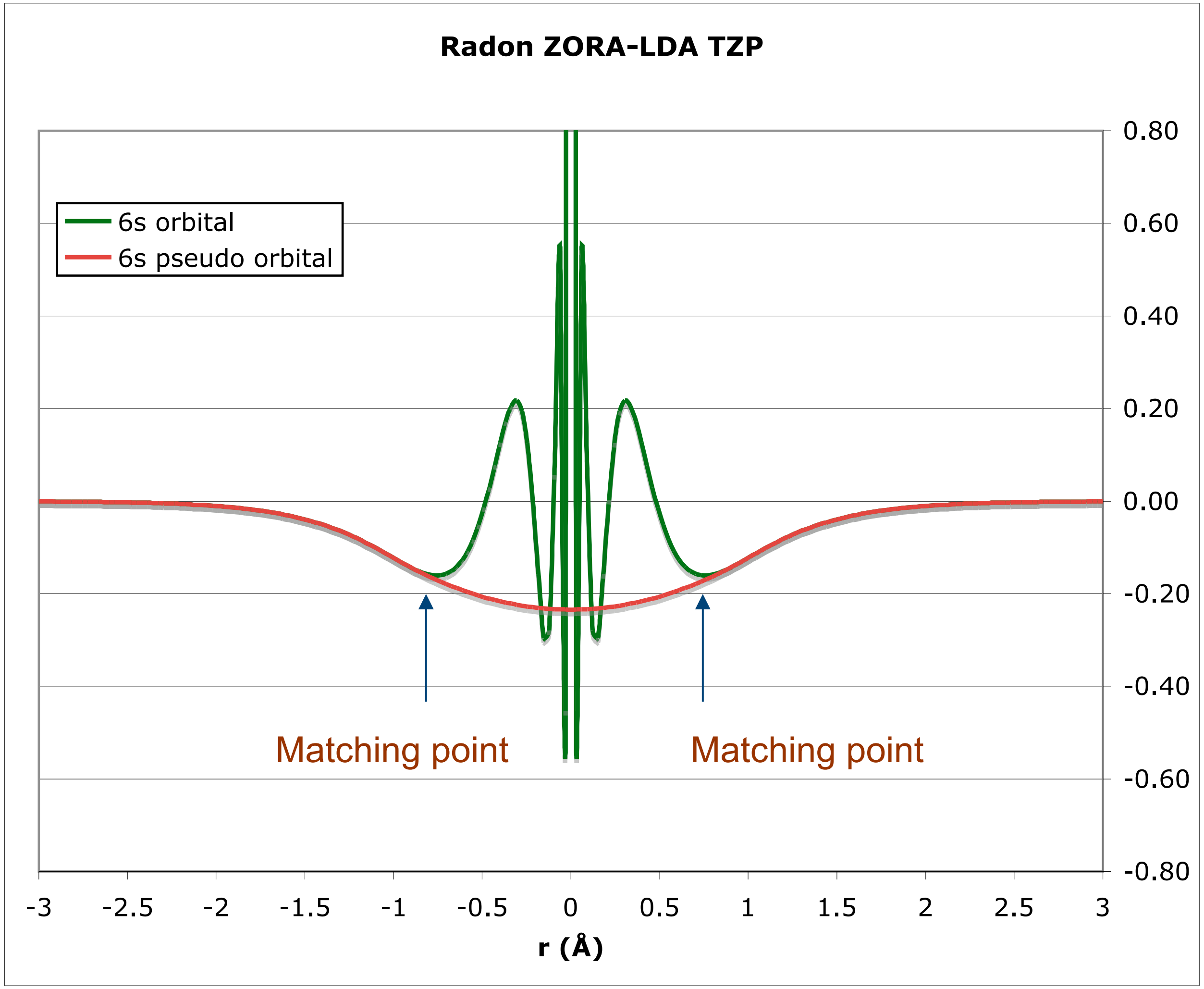
Pseudo orbitals



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Pseudopotentials in DFT

Easier to consider pseudo-orbitals in Density Functional Theory

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

Reference atomic calculation

$$\left(\hat{T} + \hat{V}_A^{eff}\right)\psi_i^A\left(\mathbf{r}\right) = \varepsilon_i^A \psi_i^A\left(\mathbf{r}\right)$$

Orbitals are solution of a local effective potential

$$\hat{V}_A^{eff}\left(\mathbf{r}\right) = \varepsilon_i^A - \frac{\nabla^2 \psi_i^A\left(\mathbf{r}\right)}{2\psi_i^A\left(\mathbf{r}\right)}$$

Potential can be constructed if the orbitals are known

$$\left(\hat{T} + \hat{V}_A^{PP}\right)\phi_i^A\left(\mathbf{r}\right) = \varepsilon_i^A \phi_i^A\left(\mathbf{r}\right)$$

Equation that is to be fulfilled by the pseudo-orbital

$$\hat{V}_A^{PP}\left(\mathbf{r}\right) = \varepsilon_i^A - \frac{\nabla^2 \phi_i^A\left(\mathbf{r}\right)}{2\phi_i^A\left(\mathbf{r}\right)}$$

Construction of the pseudopotential

PP depends on a specific ε and ϕ
Representation in terms of grid in $\mathbf{r}$

Nonlocal normconserving pseudopotentials

Define a local and a *nonlocal* potential

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

V^L takes care of the long range (screened) nuclear attraction, is identical to V^{eff} for $r > R$

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

Wavefunction that is only non-zero for $r < R$

$$\hat{V}_A^{NL}=\frac{\left|\chi_i^A\right\rangle\left\langle\chi_i^A\right|}{\left\langle\chi_i^A\middle|\phi_i^A\right\rangle}$$

V^{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

$$Q_{ij}=\left\langle\psi_i^A\middle|\psi_j^A\right\rangle_R-\left\langle\phi_i^A\middle|\phi_j^A\right\rangle_R=0$$

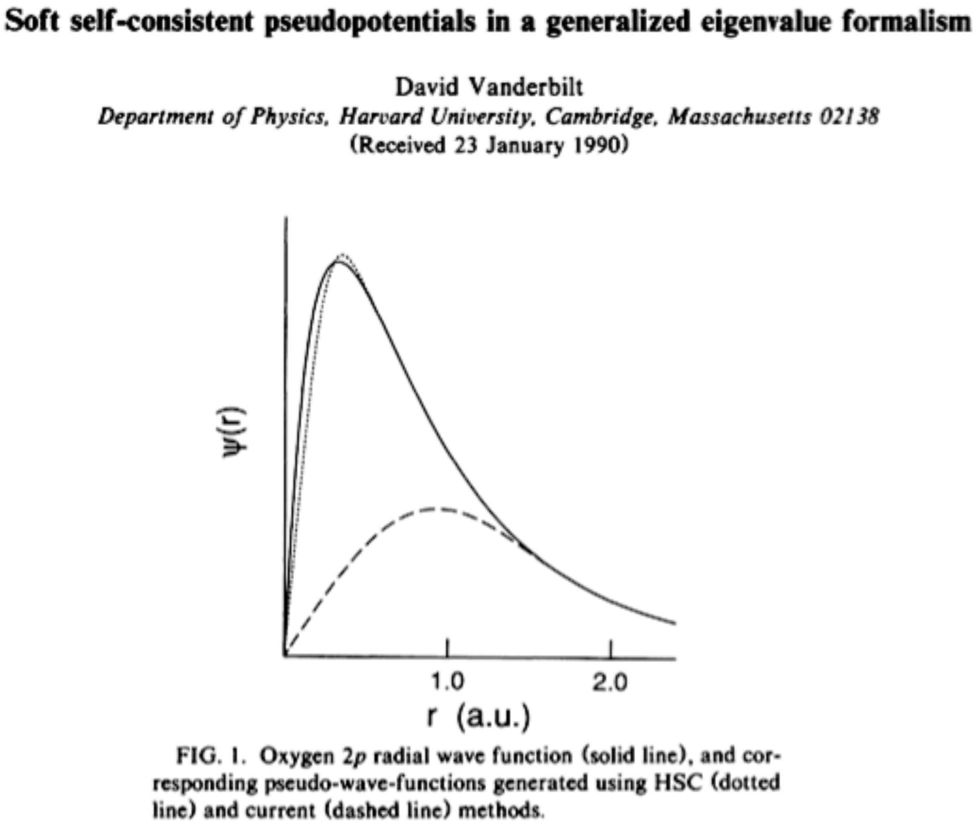
Makes sure orthonormality of the original orbitals is also obeyed by the pseudo-orbitals

$$\hat{V}_A^{NL}=\sum_{i,j}B_{ij}^{-1}\left|\chi_i^A\right\rangle\left\langle\chi_j^A\right|$$

$$\boxed{B_{ij}=\left\langle\phi_i^A\middle|\chi_j^A\right\rangle}$$

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.



Soft self-consistent pseudopotentials in a generalized eigenvalue formalism

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(Received 23 January 1990)

FIG. 1. Oxygen 2*p* radial wave function (solid line), and corresponding pseudo-wave-functions generated using HSC (dotted line) and current (dashed line) methods.

- 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

$$F_v \to F_v + \sum_c (\varepsilon_v - \varepsilon_c)|c\rangle\langle c|$$

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

$$\{\psi_v\} \to \{\tilde{\psi}_v\}$$

Make nodeless pseudo-orbital by mixing core and valence spinors

$$V^A_{Frozen\ core}(\mathbf{r}_A) \approx M^A_L(r_A) + \sum_{l=0}^{L-1} \sum_{m_l=-l}^{l} |lm_l\rangle f_l^A(r_A)\langle lm_l|$$

Scalar

$$V^A_{Frozen\ core}(\mathbf{r}_A) \approx M^A_L(r_A) + \sum_{l=0}^{L-1} \sum_{j=|l-1/2|}^{l+1/2} \sum_{m_l=-l}^{l} |ljm_j\rangle f_{lj}^A(r_A)\langle ljm_j|$$

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

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

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

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

$$\langle ij \| ab \rangle^{pseudo} - \langle ij \| ab \rangle^{original} \neq 0$$

$$\varepsilon_i^{original} - \varepsilon_a^{original} > \varepsilon_i^{pseudo} - \varepsilon_a^{pseudo}$$

- 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)

$$\min\left(\sum_{I}^{\substack{Lowlying\\Levels}} w_I\left(E_I^{PP} - E_I^{Reference}\right)^2\right)$$

- 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”)

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)

How to include an SO-operator in CI (CC)

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 usually not explictly 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

Relativistic electron correlation

- Many-Body Perturbation Theory
    - Integral-direct implementation of MP2
- Configuration Interaction
    - Full CI to about 10,000 determinants
    - Direct CI to about 5,000,000 determinants
    - Spinfree CI to 1,000,000,000 determinants
- Coupled Cluster
    - CCSD(T) to a few million amplitudes
    - Fockspace (MR) CCSD (EA, IE.EE)
- Multi-Configuration Self Consistent Field
    - CI to about a few million determinants

- Computational bottlenecks
    - Transformation of 2-e. integrals to the molecular spinor basis
    - Memory use in the CI and CC modules

Second quantization

- Hamilton operator

$$\hat{H} = \sum_{PQ}^{2m_e} Z_P^Q \hat{E}_Q^P + \frac{1}{2} \sum_{PQRS}^{2m_e} G_{PQ}^{RS} \hat{E}_{RS}^{PQ}$$

- Fock operator

$$\hat{F} = \sum_{PQ} \left(Z_P^Q + U_P^Q \right) \hat{E}_Q^P = \sum_{PQ} F_P^Q \hat{E}_Q^P = \sum_P \varepsilon_P \hat{E}_P^P$$

- Mean field $$U_P^Q = \sum_I^{M_{occ.}} V_{PI}^{QI} \qquad \left(V_{PQ}^{RS} = G_{PQ}^{RS} - G_{PQ}^{SR} \right)$$

Many-Body Perturbation Theory

- Perturbation

$$\hat{H}^{1} = \hat{H} - \hat{F} = \frac{1}{4}\sum_{PQRS} V_{PQ}^{RS}\hat{E}_{RS}^{PQ} - \sum_{PQ} U_{P}^{Q}\hat{E}_{Q}^{P}$$

- First order energy

$$E^{1} = \langle 0|\hat{H}^{1}|0\rangle = \frac{1}{4}\sum_{PQRS}^{M} V_{PQ}^{RS}\langle 0|\hat{E}_{RS}^{PQ}|0\rangle - \sum_{PQ}^{M} U_{P}^{Q}\langle 0|\hat{E}_{Q}^{P}|0\rangle$$

$$= \frac{1}{2}\sum_{IJ}^{N} V_{IJ}^{IJ}\langle 0|\hat{E}_{IJ}^{IJ}|0\rangle - \sum_{I}^{N} U_{I}^{I}\langle 0|\hat{E}_{I}^{I}|0\rangle = \frac{1}{2}\sum_{IJ}^{N} V_{IJ}^{IJ}$$

Many-Body Perturbation Theory

- Second order energy

$$E^2 = \sum_{\mu} \frac{\left|\langle 0|\hat{H}^1|\mu\rangle\right|^2}{\langle 0|\hat{H}^0|0\rangle - \langle \mu|\hat{H}^0|\mu\rangle} = \frac{1}{4}\sum_{IJAB}^{N} \frac{\left|V_{AB}^{IJ}\right|^2}{\varepsilon_{IJ}^{AB}}$$

- Definitions

$$\varepsilon_I^A = \varepsilon_I - \varepsilon_A$$

$$\varepsilon_{IJ}^{AB} = \varepsilon_I + \varepsilon_J - \varepsilon_A - \varepsilon_B$$

Direct Configuration Interaction

- Write wave function as linear combination of determinants

$$\left|i\right\rangle = \sum_{\mu}^{N} \left|\mu\right\rangle c_{\mu i}$$

- Define sigma and error vector

$$\boldsymbol{\sigma}_i^{(n)} = \mathbf{H}\mathbf{c}_i^{(n)} \qquad \mathbf{d}_i^{(n)} = \boldsymbol{\sigma}_i^{(n)} - E_i^{(n)}\mathbf{c}_i^{(n)}$$

- Obtain sigma vector directly from MO-integrals

$$\sigma_{\mu i}^{(n)} = \sum_{\nu}^{N} c_{\nu i}^{(n)} \left[\sum_{PQ}^{M_e} Z_P^Q \gamma_Q^P(\mu,\nu) + \frac{1}{4} \sum_{PQRS}^{M_e} V_{PQ}^{RS} \gamma_{RS}^{PQ}(\mu,\nu) \right]$$

Coupling Coefficients

- Without SOC use of spin-adapted schemes is possible. Distinguish between spin-conserving and non-conserving excitations.
- Insert resolution of identity to work with one-electron coupling coefficients

$$\gamma^{PQ}_{RS}(\mu,\nu) = \sum_{\lambda} \gamma^{P}_{R}(\mu,\lambda)\gamma^{Q}_{S}(\lambda,\nu) - \gamma^{P}_{S}(\mu,\nu)\delta^{Q}_{R}$$

- Use graphical techniques to index determinants and evaluate coupling coefficients (+/-1 or 0)
- Use Abelian point group symmetry if possible

Kramers-restricted CI

- Rewrite Hamiltonian in terms of Kramers' pairs

$$\hat{H} = \sum_{pq}^{m_e} Z_p^q \hat{X}_q^p(0) + \frac{1}{2}\sum_{pq}^{m_e} Z_p^{\bar{q}} \hat{X}_q^p(1) + \frac{1}{2}\sum_{pq}^{m_e} Z_{\bar{p}}^q \hat{X}_q^p(-1)$$

$$+ \frac{1}{2}\sum_{pqrs}^{m_e} G_{pq}^{rs} \hat{X}_{rs}^{pq}(0,0) + \frac{1}{2}\sum_{pqrs}^{m_e} G_{pq}^{\bar{r}s} \hat{X}_{rs}^{pq}(1) + \frac{1}{2}\sum_{pqrs}^{m_e} G_{\bar{p}q}^{rs} \hat{X}_{rs}^{pq}(-1)$$

$$+ \frac{1}{4}\sum_{pqrs}^{m_e} G_{\bar{p}q}^{r\bar{s}} \hat{X}_{rs}^{pq}(0,1) + \frac{1}{8}\sum_{pqrs}^{m_e} G_{pq}^{\bar{r}\bar{s}} \hat{X}_{rs}^{pq}(2) + \frac{1}{8}\sum_{pqrs}^{m_e} G_{\bar{p}\bar{q}}^{rs} \hat{X}_{rs}^{pq}(-2)$$

- Block CI-vector by counting the number of "unpaired" electrons
- Use modified non-relativistic CI algorithms

Kramers-restricted CI

- X-operators are defined as linear combinations of the original excitation operators, e.g.

$$\hat{X}_{q}^{p}(0) = \hat{E}_{q}^{p} + \hat{E}_{\bar{p}}^{\bar{q}}$$

$$\hat{X}_{rs}^{pq}(0,0) = \hat{E}_{rs}^{pq} + \hat{E}_{\bar{p}s}^{\bar{r}q} + \hat{E}_{r\bar{q}}^{p\bar{s}} + \hat{E}_{\bar{p}\bar{q}}^{\bar{r}\bar{s}}$$

$$\hat{X}_{rs}^{pq}(0,1) = \hat{E}_{r\bar{s}}^{\bar{p}q} - \hat{E}_{p\bar{s}}^{\bar{r}q} - \hat{E}_{r\bar{q}}^{\bar{p}s} + \hat{E}_{p\bar{q}}^{\bar{r}s}$$

$$\hat{X}_{rs}^{pq}(1) = \hat{E}_{\bar{r}s}^{pq} - \hat{E}_{\bar{p}s}^{rq} + \hat{E}_{\bar{r}\bar{q}}^{p\bar{s}} - \hat{E}_{\bar{p}\bar{q}}^{r\bar{s}}$$

- Reduces memory that is needed for the algorithm
- Facilitates approximations and use of spin-orbitals

Coupled Cluster

- Write wave function in exponential form

$$\left|g\right\rangle = e^{\hat{T}}\left|0\right\rangle$$

- CCSD : Restriction to single & double excitations

$$\hat{T} = \sum_{I}\sum_{A} T_{I}^{A}\hat{E}_{I}^{A} + \sum_{I<J}\sum_{A<B} T_{IJ}^{AB}\hat{E}_{IJ}^{AB}$$

- Energy expression (I,J : occupied, A, B virtual)

$$E^{CCSD} = \sum_{IA} F_{A}^{I} T_{I}^{A} + \sum_{I<J,A<B} V_{AB}^{IJ}\tau_{IJ}^{AB}$$

The CCSD equations

- Equations for T_1 and T_2 amplitudes

$$F_I^A - 2\sum_{K,C} F_C^K T_K^A T_I^C + \sum_C H_C^A T_I^C - \sum_K H_I^K T_K^A + \sum_{K,C} H_C^K \left(T_{IK}^{AC} + T_K^A T_I^C\right) + \\ + \sum_{K,C} V_{IC}^{AK} T_K^C + \sum_{K,C<D} V_{CD}^{AK} \tau_{IK}^{CD} - \sum_{K<L,C} V_{IC}^{KL} \tau_{KL}^{AC} = 0$$

$$V_{IJ}^{AB} + P_{AB}\left(\sum_C G_C^A T_{IJ}^{CB} - \sum_K V_{IJ}^{AK} T_K^B\right) - P_{IJ}\left(\sum_K G_I^K T_{KJ}^{AB} - \sum_C V_{IC}^{AB} T_J^C\right) + \\ \sum_{K<L} A_{IJ}^{KL} \tau_{KL}^{AB} + \boxed{\sum_{C<D} B_{CD}^{AB} \tau_{IJ}^{CD}} + P_{IJ} P_{AB}\left(\sum_{K,C} H_{IC}^{AK} T_{JK}^{BC} - \sum_{K,C} V_{IC}^{AK} T_J^C T_K^B\right) = 0$$

The CCSD intermediates

- Intermediates used in T_1 and T_2 equations

$$H_A^C = F_A^C - \sum_{K<L,D} V_{CD}^{KL} \tau_{KL}^{AD} \qquad H_I^K = F_I^K + \sum_{L,C<D} V_{CD}^{KL} \tau_{IL}^{CD}$$

$$H_C^K = F_C^K + \sum_{LD} V_{CD}^{KL} T_L^D$$

$$G_A^C = H_A^C - \sum_{K} F_C^K T_K^A + \sum_{KD} V_{CD}^{AK} T_K^D \qquad G_I^K = H_I^K + \sum_{K} F_C^K T_I^C + \sum_{KC} V_{IC}^{KL} T_L^C$$

$$A_{IJ}^{KL} = V_{IJ}^{KL} + P_{IJ} \sum_{C} V_{IC}^{KL} T_J^C + \sum_{C<D} V_{CD}^{KL} \tau_{IJ}^{CD} \qquad \boxed{B_{AB}^{CD} = V_{AB}^{CD} - P_{AB} \sum_{C} V_{CD}^{AK} T_K^B}$$

$$H_{IC}^{AK} = V_{IC}^{AK} + \sum_{L} V_{IC}^{KL} T_L^A - \sum_{D} V_{CD}^{AK} T_I^D + \sum_{LD} V_{CD}^{KL} \left(\tfrac{1}{2} T_{IL}^{AD} - T_I^D T_L^A \right)$$

Evaluation of the <vv||vv> integral contribution

- Contribution to be evaluated

$$S_{IJ}^{AB} \leftarrow \sum_{C<D} B_{CD}^{AB} \tau_{IJ}^{CD}$$

- Use point group symmetry

$$\Gamma_A^* \otimes \Gamma_B^* \otimes \Gamma_C \otimes \Gamma_D = 1 \qquad \Rightarrow \quad \Gamma_{AB} = \Gamma_{CD} = \Gamma_{IJ}$$

- Write contraction as BLAS DGEMM or ZGEMM

$$S(AB,IJ) = \sum_{CD}^{\Gamma_{CD}=\Gamma_{IJ}} B(AB,CD) \times TAU(CD,IJ)$$

- Parallelize over integral batches

$$S(AB,IJ) = \sum_{node}^{all\ \ nodes} S^{node}(AB,IJ) = \sum_{node}^{all\ \ nodes} \sum_{CD\ \ on\ \ node}^{\Gamma_{CD}=\Gamma_{IJ}} B(AB,CD) \times TAU(CD,IJ)$$

Kramers-restricted CC

- For closed shells systems one can define

$$T_{i}^{a} = T_{\bar{i}}^{\bar{a}\,*} \qquad T_{i}^{\bar{a}} = -T_{\bar{i}}^{a\,*}$$

$$T_{ij}^{ab} = T_{\bar{i}\bar{j}}^{\bar{a}\bar{b}\,*} \qquad T_{ij}^{\bar{a}\bar{b}} = T_{\bar{i}\bar{j}}^{ab\,*} \qquad T_{i\bar{j}}^{a\bar{b}} = T_{\bar{i}j}^{\bar{a}b\,*} \qquad T_{ij}^{a\bar{b}} = -T_{\bar{i}\bar{j}}^{\bar{a}b\,*}$$

- Rewrite equations in terms of unique quantities
  - Reduction of factor 2 in number of amplitudes
  - Reduction by factor 8 in number of operations necessary

- Comparison with optimal spinfree algorithm
  - KRCCSD is max. 32 times more expensive than NR SR-CCSD

Fock Space Coupled Cluster

Single reference CC

$$\left|\Psi^{CC}\right\rangle = e^{\hat{T}}\left|\Psi^{0}\right\rangle$$

$$E\left|\Psi\right\rangle = \hat{H}\left|\Psi\right\rangle$$

$$E^{CC}e^{\hat{T}}\left|\Psi^{0}\right\rangle = \hat{H}e^{\hat{T}}\left|\Psi^{0}\right\rangle$$

$$E^{CC} = \left\langle\Psi^{0}\middle|\hat{H}e^{\hat{T}}\middle|\Psi^{0}\right\rangle$$

Fock space CC

$$\left|\Psi_i^{CC}\right\rangle = \hat{\Omega}\left|\Psi_i^{0}\right\rangle$$

$$E_i\left|\Psi_i\right\rangle = \hat{H}\left|\Psi_i\right\rangle$$

$$E_i^{CC}\hat{\Omega}\left|\Psi_i^{0}\right\rangle = \hat{H}\hat{\Omega}\left|\Psi_i^{0}\right\rangle$$

$$\hat{H}^{eff} = \hat{P}\hat{H}\hat{\Omega} = \hat{P}\hat{H}\hat{\Omega}\hat{P}$$

The states in the model space correspond to

- Annihilation of an electron from an active occupied orbital
  (1h,0e) sector Ionization energy
- Creation of an electron in an active virtual orbital
  (0h, 1e) sector Electron Affinity
- Creation and excitation of an electron: Excitation energy

Intruder states may require introduction of buffer space (IH-FSCC)

High accuracy: relativity and electron correlation

- “Best” method depends on system studied

- Closed shells and simple open shells
  - Use a size-extensive economical method (include SOC for p-block elements)

- Complicated open shells, bond breaking
  - CASSCF/PT2, MRCI or MR-CC
  - SOC-inclusive methods for heavier elements

- Use “best practice” and experience from calculations on light elements
  - Combine methods: structure optimization // energies

  - Check basis set dependence (DZ -> TZ -> QZ, DZ -> aug-DZ)
  - Check frozen core approximations (Large Core -> Small Core)
  - Check Hamiltonian (NR -> X2C -> 4C)

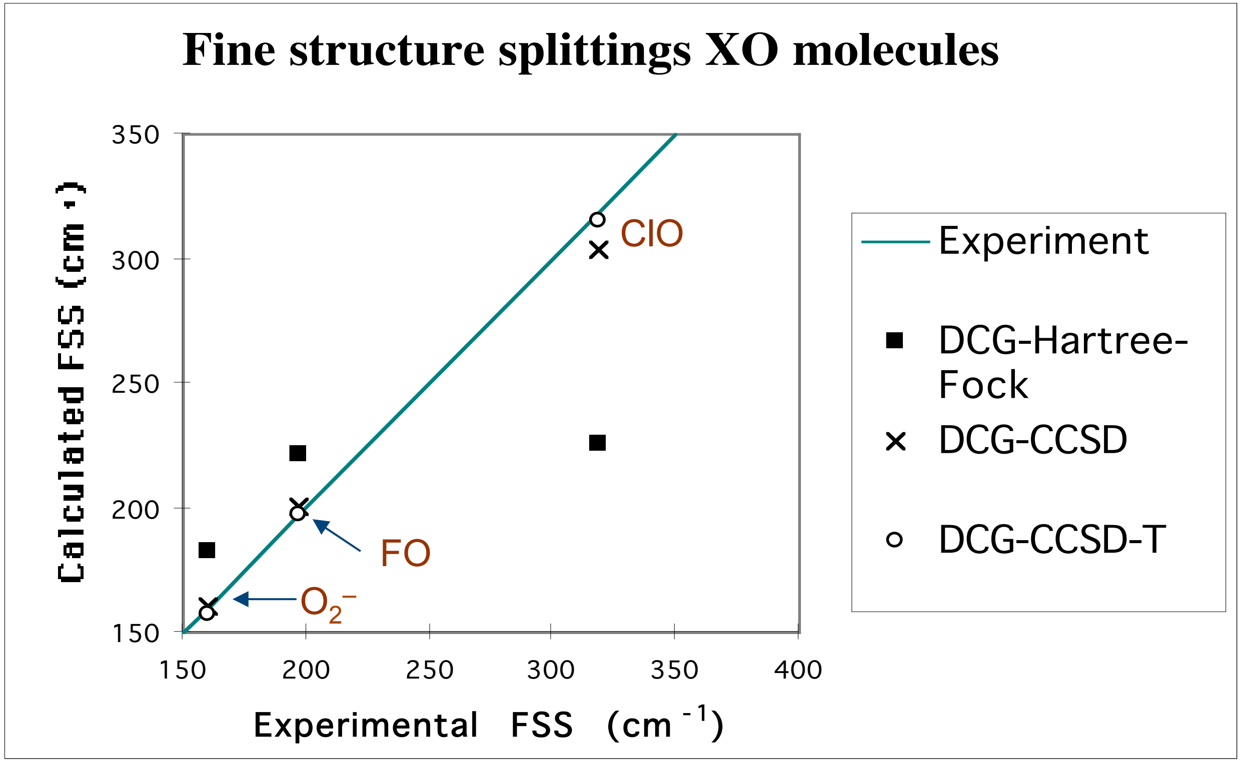
- Some examples...

Sample applications

1. Accurate calculations on diatomic molecules
2. Can mercury loose 4 electrons ?
3. The unrivaled precision of aluminum
4. Can TD-DFT handle uranium ?

Spin-orbit splitting in atmospheric molecules

- Valence iso-electronic systems O_2^-, FO, ClO
- Breit interaction and correlation should be included for accurate results



Groundstate of thalliumhydride

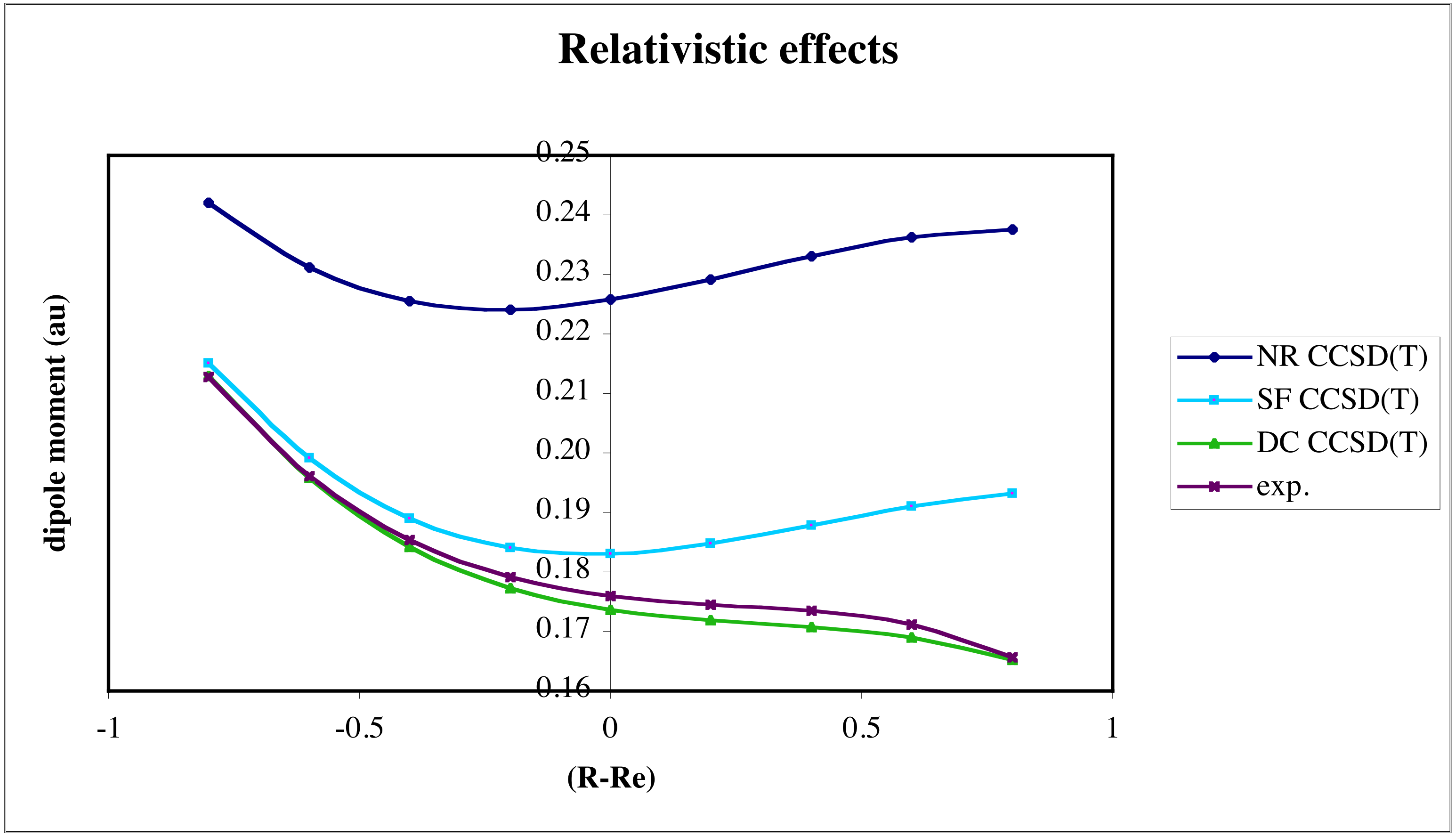
K. Faegri Jr.. and L. Visscher, Theor. Chem Acc. ***105*** *(2001) 265.*

- Goal : Provide benchmark values for this standard testcase
- Hamiltonian : Dirac-Coulomb-(Gaunt)
- Correlation space : up to 36 electrons (6s, 6p; 4f, 5s, 5p, 5d)

Method and	# electrons corr.	Re (pm)	Ke (N/m)	ω (cm-1)	De (eV)
MP2*	14	186.2	121	1437	1.83
DC-CCSD(T)*	14	188.5	111	1376	2.07
DC-CCSD(T)	14	187.6	113.3	1385	2.00
DC-CCSD(T)	20	187.4	112.1	1378	1.98
DC-CCSD(T)	36	187.4	111.1	1371	1.98
DCG-CCSD(T)	36	187.7	111.9	1376	2.06
experiment		186.8	114.4	1391	2.06

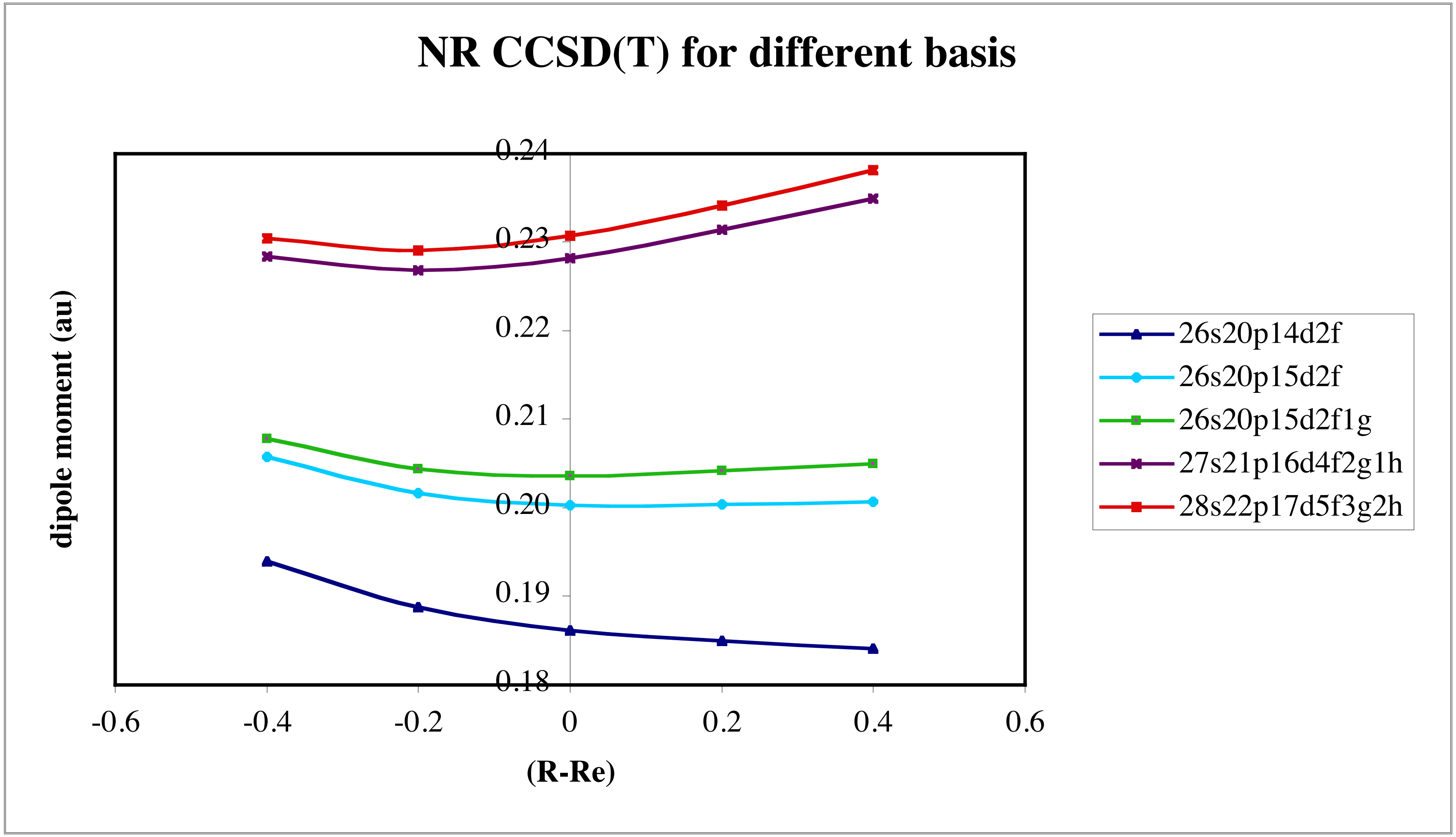
*Seth, Schwerdtfeger and Faegri (1999) calculations with contracted basis sets.

Dipole moment of HI



Be ware of error cancellation: basis set incompleteness & relativity errors have different signs in this case

Basis set convergence



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Nuclear-electron interaction

$$E_{eN}^{\text{int}} = \iint \frac{\rho_N(\mathbf{R})\rho_e(\mathbf{r})}{|\mathbf{r}-\mathbf{R}|} d\mathbf{r}\,d\mathbf{R}$$

Electronic structure calculations

$$E_{eN}^{\text{int}} = \int V_N(\mathbf{r})\rho_e(\mathbf{r})\,d\mathbf{r}$$

$$V_N(\mathbf{r}) = \frac{Z_N}{|\mathbf{r}-\mathbf{R}_N|}$$

$$V_N(\mathbf{r}) = Z_N \int \frac{N_N e^{-a_N(\mathbf{R}-\mathbf{R}_N)^2}}{|\mathbf{r}-\mathbf{R}|} dR$$

Point or Gaussian nuclear model

Decomposition in nuclear moments

$$E_{eN}^{\text{int}} = \int V_e(\mathbf{R})\rho_N(\mathbf{R})\,d\mathbf{R}$$

$$V_e(\mathbf{R}) \approx V_e(\mathbf{R}_N) - \mathbf{E}_e(\mathbf{R}_N)\cdot\mathbf{R} - \frac{1}{2}\mathbf{R}^T\cdot\mathbf{F}_e(\mathbf{R}_N)\cdot\mathbf{R}$$

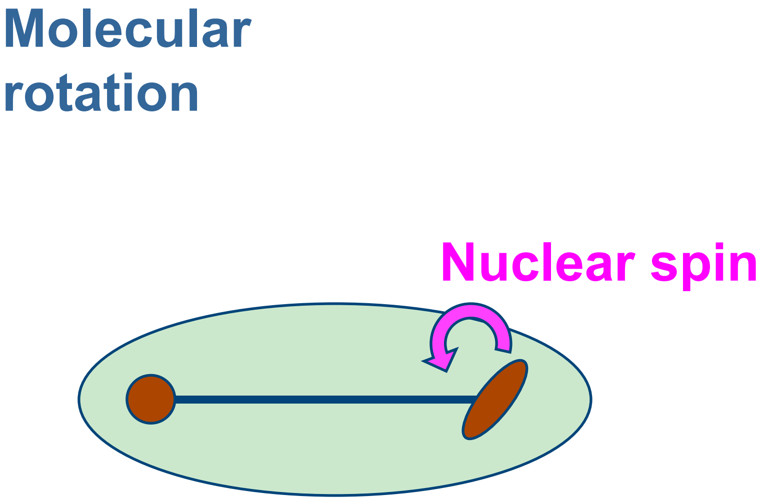
$$E_{eN}^{\text{int}} \approx E_{eN}^{0} + E_{eN}^{1} + E_{eN}^{2,\,isotropic} + E_{eN}^{2,\,anisotropic}$$

Taylor expansion of the electronic potential

Extracting nuclear structure information from Spectroscopy & Quantum Chemistry

Nuclear Quadrupole Moments

- The coupling between the nuclear quadrupole moment Q and the electric field gradient (EFG) at the nucleus q gives an energy splitting that depends on the orientation of the nuclear spin. This can be observed with high precision in microwave (rotational) spectroscopy on diatomic molecules.
- Quantum chemistry gives q and can thus be used to obtain accurate values of Q or to predict and rationalize NQR or NMR observations.



$$E_Q = \frac{e^2 q_{zz} Q\left[3m_I^2 - I(I+1)\right]}{4I(2I-1)}$$

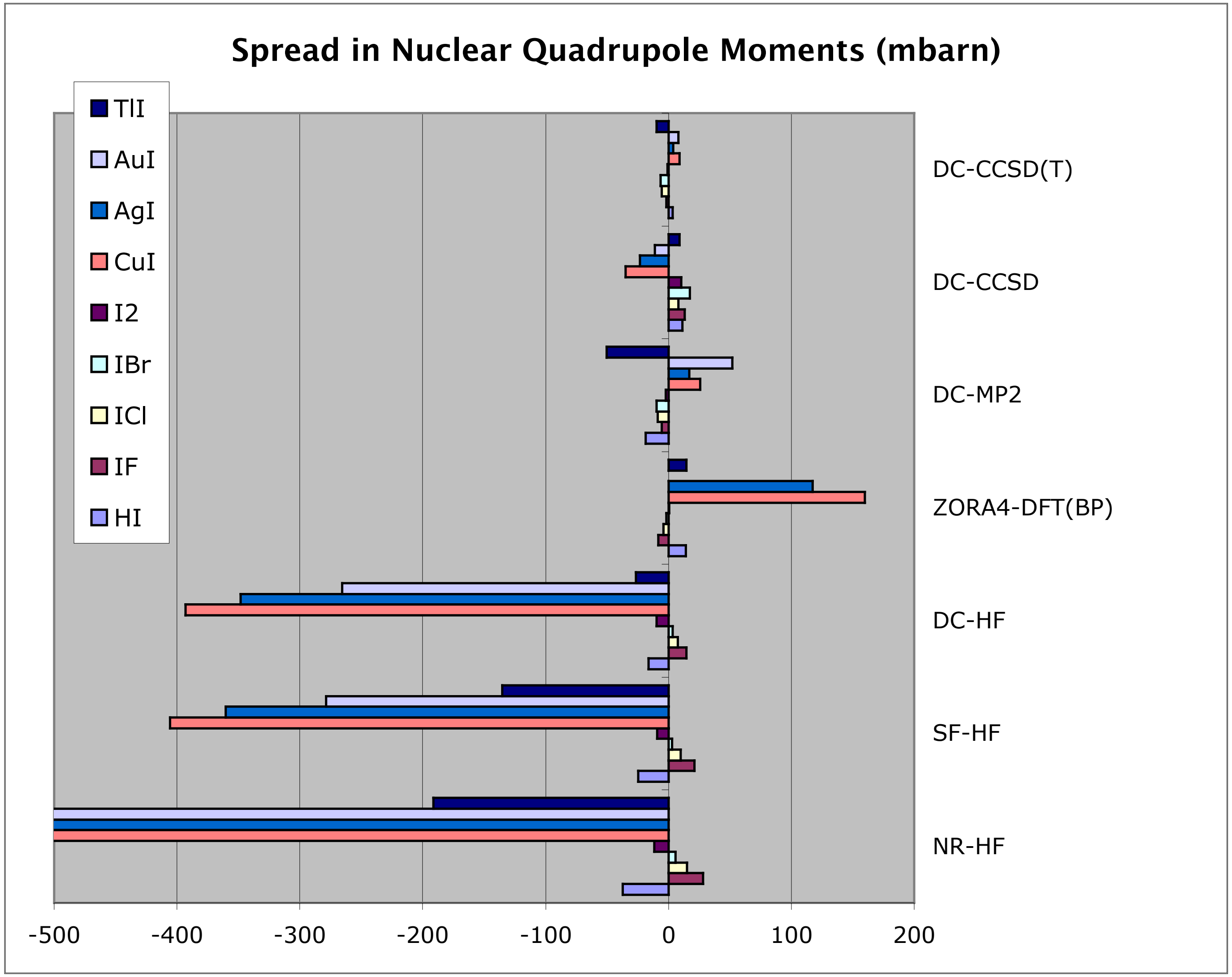
NQM ^{121}Sb (mbarn)

Isotope	Method	SbN	SbP	SbF	SbCl	Average(1)	Error(1)	Average(2)	Error(2)
^{121}Sb	DC-HF*	-527.2	-427.6	-569.1	-579.4	-525.8	49.1	-477.4	49.8
	DC-B3LYP*	-503.0	-513.0	-	-	-	-	-508.0	5.0
	DC-BPW91*	-510.0	-533.7	-	-	-	-	-521.9	11.9
	DC-CCSD	-521.8	-511.4	-628.9	-707.3	-592.4	75.8	-516.6	5.2
	DC-CCSD(T)	-562.2	-540.9	-546.4	-505.3	-538.7	16.7	-551.6	10.7
	DC-CCSD-T	-542.5	-543.2	-559.8	-528.3	-543.4	8.2	-542.9	0.4

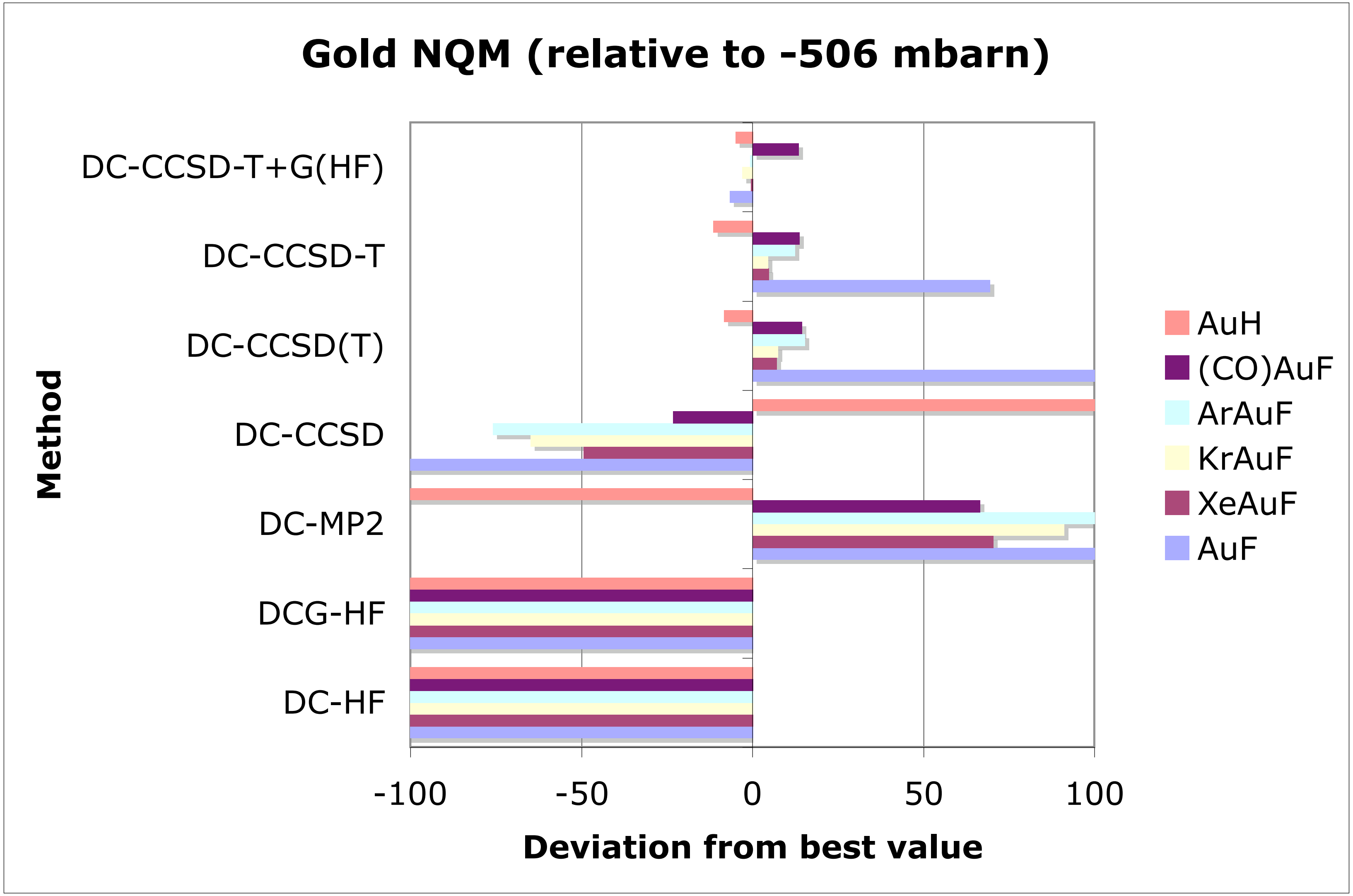
With only SbN, SbP

Buchholz, et al., Z. Phys. A **288** (1978) 247 (Current standard Value)	^{121}Sb=-360(40) mb
Demovic *et al.* JCP **124** (2006)184308 (IOTC CCSD(T))	^{121}Sb=-556(24) mb
Haiduke *et al.* JCP **124** (2006) (this work)	^{121}Sb=-543(11) mb

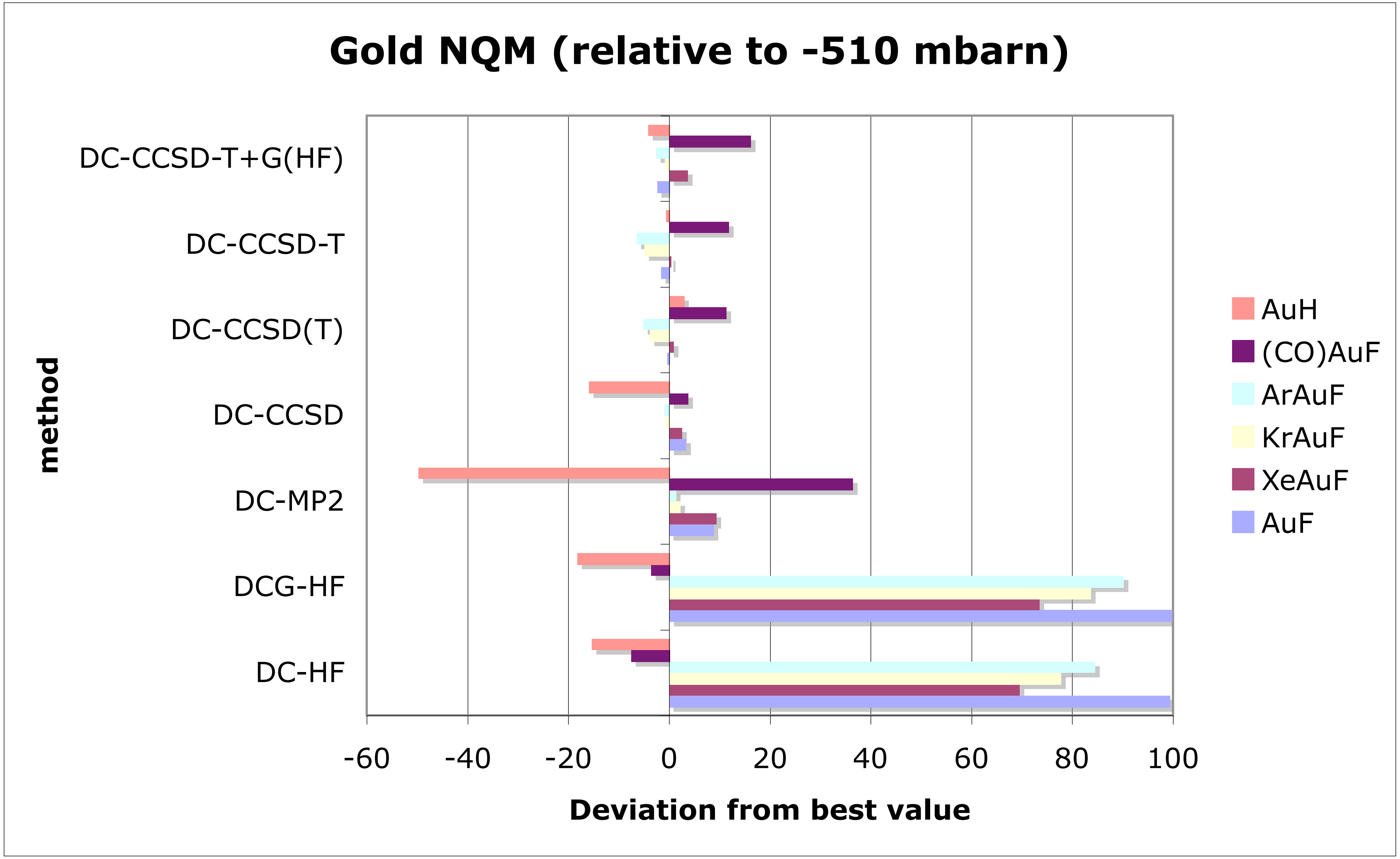
NQM ^{127}I (mbarn)



Gold : direct method



Gold : indirect method



L. Belpassi, F. Tarantelli, A. Sgamellotti, H. M. Quiney, J. N. P. van Stralen, L. Visscher, *J. Chem. Phys.* **126** (2007) 064314.

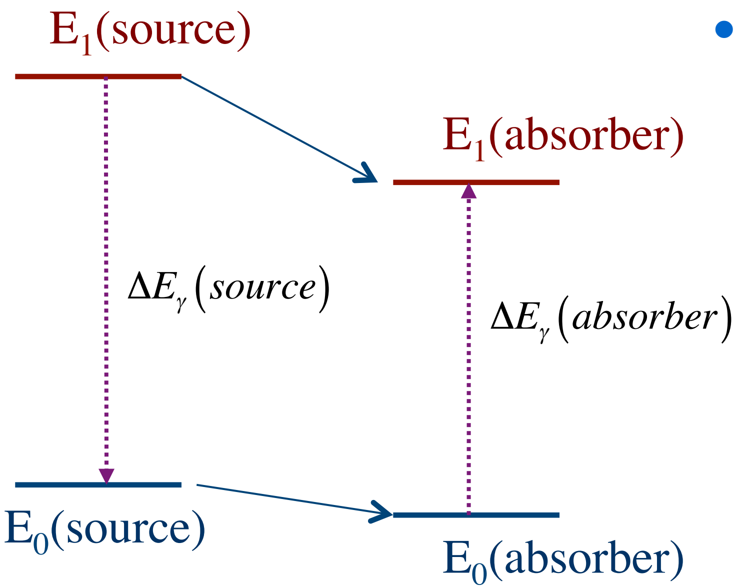
Reaction energies: $HgF_2 + F_2 \rightarrow HgF_4$

Hamiltonian	Basis	Method	Reaction energy (kJ/mol)
sc-ECP	aug-QZ	MP2	–76
sc-ECP		CCSD	–3
sc-ECP		CCSD(T)	–34
DC	aug-TZ	MP2	–67
DC		CCSD	–1
DC		CCSD(T)	–31
DCG		CCSD(T)	–29

sc-ECP calculations: S. Riedel, M. Straka, M. Kaupp, PCCP 6 (2004) 1122.

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

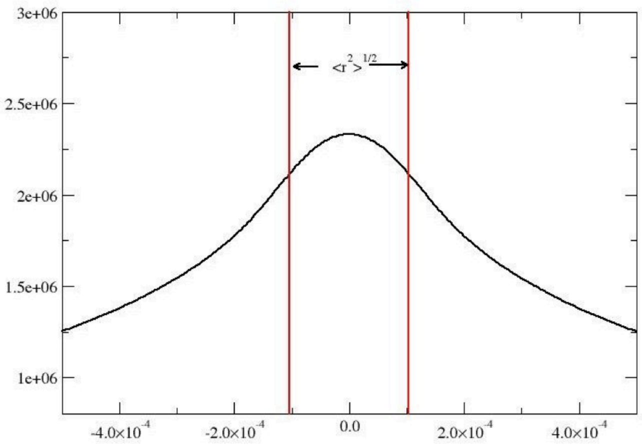
Mössbauer Isotope Shift



- Change in electron-nuclear attraction energy due to changing nuclear radius

$$\Delta E_\gamma = E^{n-e}(R_1) - E^{n-e}(R_0)$$
$$\approx \left.\frac{\partial E_\gamma}{\partial R}\right|_{R=R_0} \Delta R$$

$$\left.\frac{\partial E_\gamma}{\partial R}\right|_{R=R_0} = \left.\int \rho_e(\mathbf{r}_e;\mathbf{R})\frac{\partial \phi_n(\mathbf{r}_e,\mathbf{R})}{\partial R} d^3\mathbf{r}_e\right|_{R=R_0}$$
$$+\left.\int \frac{\partial \rho_e(\mathbf{r}_e;\mathbf{R})}{\partial R}\phi_n(\mathbf{r}_e,\mathbf{R})\, d^3\mathbf{r}_e\right|_{R=R_0}$$



- Second term is not relevant[1] for δ: chemical information from environmental influence on this shift

$$\delta = c\,\frac{\Delta E_\gamma(source) - \Delta E_\gamma(absorber)}{\Delta E_\gamma}$$

- Further approximations:
  - proton charge density is constant inside the nuclear volume
  - electron charge density is approximated by contact density

[1] B. Fricke, J. Waber, *Phys. Rev. B* **5** (1972), 3445.

Implementation in DIRAC

- Finite-size nucleus
    - Has nothing to do with relativity !
    - Realistic charge distribution of the nucleus
    - Removes cusp condition at the origin
    - Nuclear excitation can be modeled directly (but be careful with numerical precision)

- Relativistic (4-component) electron densities
    - Large and small component contribution
    - Difference with non-relativistic density most prominent near nuclei
    - Mössbauer shift: analysis in terms of orbitals

- Implementation
    - HF and DFT: expectation value
    - CC: HF value + finite differences of electron correlation energy

S. Knecht, S.Fux, R. van Meer, L. Visscher, M. Reiher, T. Saue,. Theor. Chem. Acc. **129** (2011), 631.

Mercury atom: orbital contributions

Orbital	Contact density	Eff. density correction
1s1/2	1,951,311.50	-194,467.78
2s1/2	294,993.24	-29,548.24
3s1/2	67,814.71	-6,798.36
4s1/2	17,035.79	-1,708.17
5s1/2	32,65.26	-327.42
6s1/2	276.32	-27.71
2p1/2	21,856.04	-2,107.28
3p1/2	5,638.93	-544.14
4p1/2	1,398.44	-134.96
5p1/2	237.17	-22.89
2p3/2	0	0.51
3p3/2	0	0.14
4p3/2	0	0.03
5p3/2	0	0.01
Total	2,363,827.39	-235,685.57

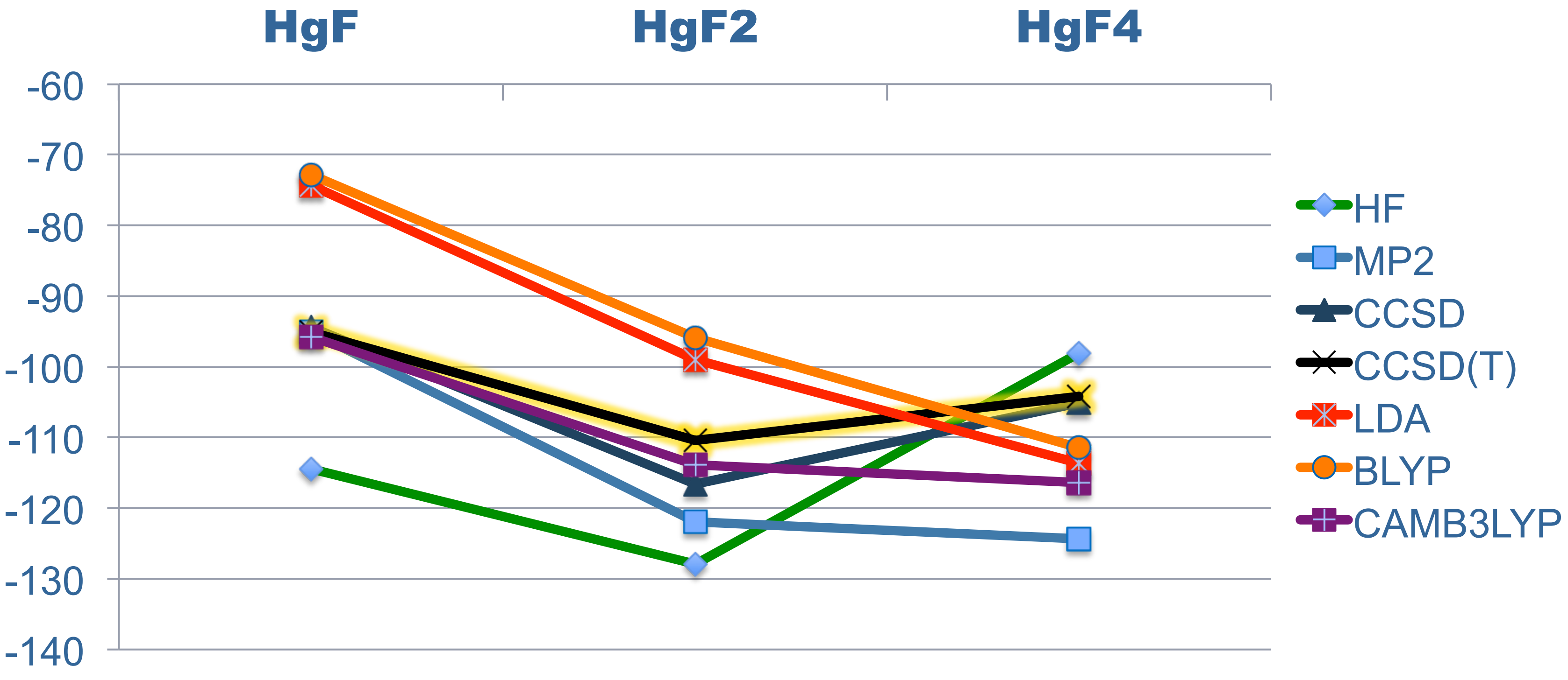
units: a_0^{-3}

Non-relativistic
361,818.93

Mercury halides: Hg_n (n=1,2,4)

units: a_0^{-3}

Molecule	Contact density	Effective density	Difference
HgF	-114.54	-103.05	-10.0%
HgF2	-127.58	-115.01	-9.9%
HgF4	-98.09	-88.22	-10.1%



Mercury Fluorides: conclusions

- Contact density approximation in Mössbauer calculations
  - Significant overestimation of effective density
  - Scaling relation can be applied for relativistic wave function

- Interpretation of HF vs. LDA result
  - LDA gives more compact 6s ➔ larger effect of electron withdrawal
  - LDA gives smaller polarizability ➔ smaller effect of ligands

◆ Is this really Hg(IV) ? Charge analysis gives:

	HgF	HgF2	HgF4
HF	0.88	1.51	2.47
LDA	0.55	1.12	1.89

S. Knecht, S.Fux, R. van Meer, L. Visscher, M. Reiher, T. Saue,. Theor. Chem. Acc. **129** (2011), 631.

Al^+ atomic clock

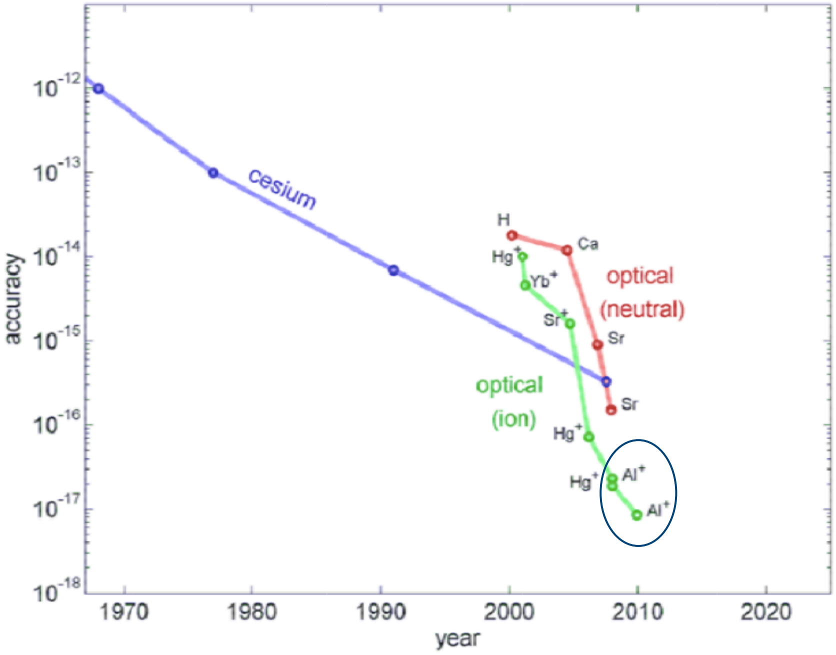


Fig. 1: Accuracy of atomic clocks based on different species of atoms.

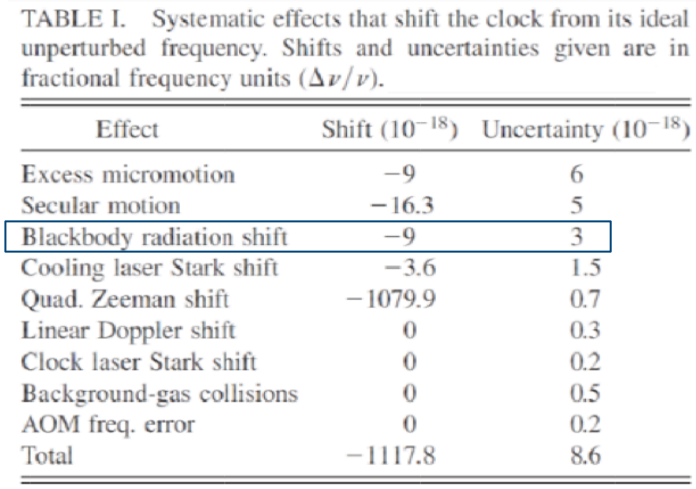


TABLE I. Systematic effects that shift the clock from its ideal unperturbed frequency. Shifts and uncertainties given are in fractional frequency units ($\Delta\nu/\nu$).

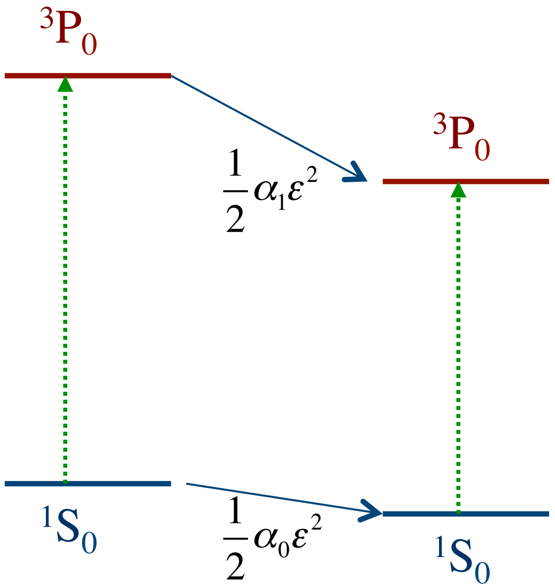
Effect	Shift (10^{-18})	Uncertainty (10^{-18})
Excess micromotion	−9	6
Secular motion	−16.3	5
Blackbody radiation shift	−9	3
Cooling laser Stark shift	−3.6	1.5
Quad. Zeeman shift	−1079.9	0.7
Linear Doppler shift	0	0.3
Clock laser Stark shift	0	0.2
Background-gas collisions	0	0.5
AOM freq. error	0	0.2
Total	−1117.8	8.6

T. Rosenband, C. W. Chou, D. B. Hume, D. J. Wineland, *Laser Science* (2010);C. W. Chou, D. B. Hume, J. C. J. Koelemeij, D. J. Wineland, T. Rosenband, *Phys. Rev. Lett.*, **104** (2010) 070802.

- Based on $^1S_0 \longrightarrow {}^3P_0$ transition in Al^+
- Relative accuracy 8.6 10^{-18} (3.7 seconds / age of the universe)
- Blackbody radiation shift (BBRS) responsible for 35% of this uncertainty

- Precise calculation of BBR shift using relativistic coupled cluster approach

Blackbody Radiation Shift



Energy levels of the Al$^+$ ion:

State		Excitation energy [cm^{-1}]
$3s^2$	$^1S_0$	–
$3s3p$	$^3P_0$	37393
$3s3p$	$^3P_1$	37454
$3s3p$	$^3P_2$	37578

Clock transition: $3s^2\,{}^1S_0 \rightarrow 3s3p\,{}^3P_0$

- BBR shift is calculated from the difference in polarizabilities of the ground and excited state:

$$\Delta E_{ij}^{BBR} = -\frac{1}{2}(831.9\,V/m)^2\left(\frac{T(K)}{300}\right)^4\left(\alpha_i-\alpha_j\right)$$

- Finite field differentiation for the DC contribution

$$\alpha_i^{DC} = \frac{2}{\varepsilon^2}\left[E_i^{CC}(\hat{H}^{DC}+\varepsilon\hat{z}) - E_i^{CC}(\hat{H}^{DC})\right]$$

- Breit + QED correction from numerical relativistic MCSCF calculation

$$\Delta\alpha_{ij} = \left(\alpha_i^{DC}-\alpha_j^{DC}\right)+\left(\alpha_i^{BQED}-\alpha_j^{BQED}\right)$$

Results and convergence

Basis set	α ($^1S_0$)	α ($^3P_0$)	$\Delta\alpha$	$\Delta\Delta\alpha$
DZ	24.203	24.261	0.058	
TZ	24.143	25.040	0.897	0.839
QZ	24.273	24.700	0.427	0.470
5Z	24.251	24.656	0.406	0.021
CCSD	24.251±0.044	24.656±0.88	0.406±0.042	

Correlation+QED	α ($^1S_0$)	α ($^3P_0$)	$\Delta\alpha$
CCSD	24.251±0.044	24.656±0.088	0.406±0.042
ΔT	-0.126±0.011	-0.061±0.015	0.065±0.026
ΔQ	-0.002±0.005	0.001±0.002	0.003±0.007
ΔBQED	0.015±0.015	0.018±0.018	0.003±0.003
Total	24.137±0.075	24.614±0.123	0.477±0.078

M. Kallay, H. S. Nataraj, B. K. Sahoo, B. P. Das, L. Visscher, Phys. Rev. A, **83** (2011) 030503.

Actinide spectroscopy by TD-DFT ?

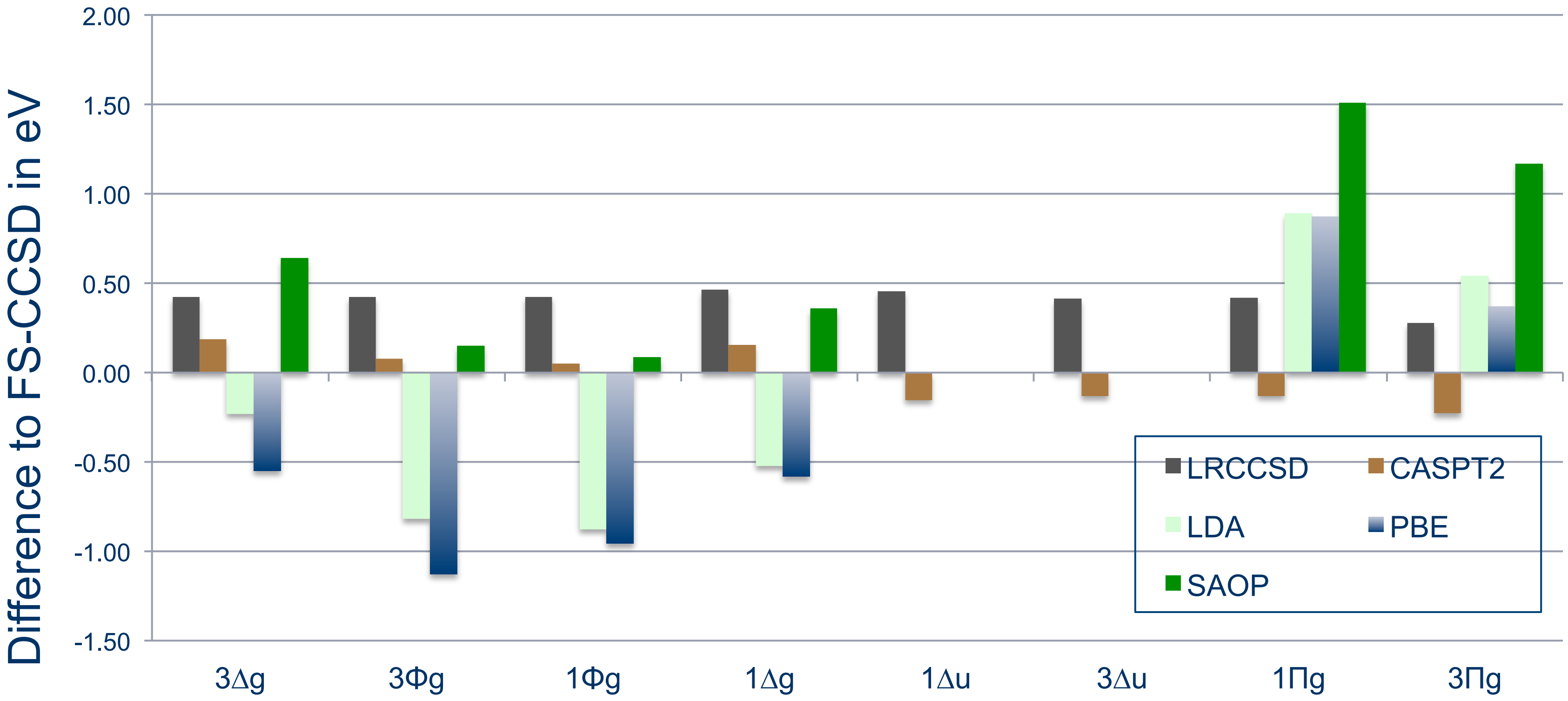
- CASPT2 (MOLCAS)
    - ✓ Versatile treatment of multideterminant reference wave functions
    - ✓ Electron correlation to second order
    - ✓ Douglas-Kroll-Hess Hamiltonian
    - ✓ Spin-Orbit coupling in two-step procedure

- Coupled Cluster (DIRAC)
    - ✓ Restricted by need for single determinant reference
    - ✓ Electron correlation to infinite order but limited by excitation level
    - ✓ (Intermediate Hamiltonian) Fock Space CCSD
    - ✓ DC and/or ^{2}DCG^{A}

- Time-Dependent Density Functional Theory (ADF & DIRAC)
    - ✓ Assessment of functionals
    - ✓ Study influence of ALDA approximation

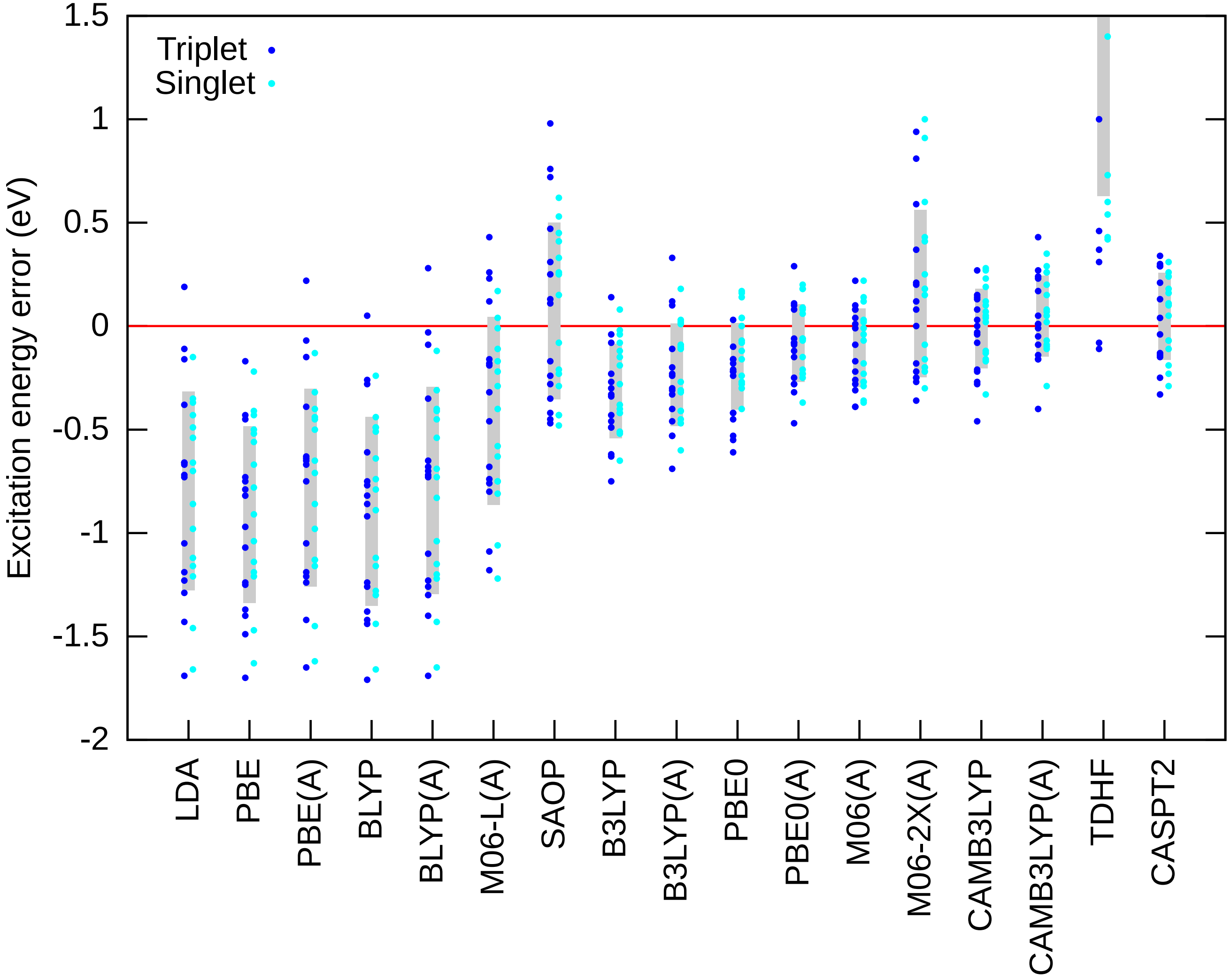
Excited states of Uranyl

- LR-CCSD consistently higher than FS-CCSD, CASPT2 close.
- TD-DFT: no functional gives a consistent picture. Influence Hamiltonian (ZORA) small but ALDA approximation has significant effect.



F. Réal, A. S. P. Gomes, V. Vallet, L. Visscher, E. Eliav, J. Phys. Chem. A **113** (2009) 12504–12511

OUO^{2+}, NUO^{+} and NUN



P. Tecmer, A. S. P. Gomes, U. Ekström, L. Visscher, 13**6** (2011) 6249.
Automatic differentation for XC functionals: Ekström *et al.* J. Chem. Theory Comput. **6** (2010) 1971.

Further reading for RQC

Relativistic Quantum Mechanics

- M. Reiher and A. Wolf, Relativistic Quantum Chemistry, (Wiley, 2009)
- K. G. Dyall and K. Faegri Jr, Relativistic Quantum Chemistry, (Oxford University Press, 2007)
- R. E. Moss, *Advanced molecular quantum mechanics*. (Chapman & Hall, London, 1973).
- P. Strange, *Relativistic Quantum Mechanics*. (Cambridge University Press, Cambridge, 1998).

Relativistic Quantum Chemical methods

- *Relativistic Electronic Structure Theory - Part 1 : Fundamentals*, ed. P. Schwerdtfeger (Elsevier, Amsterdam, 2002).
- *Theoretical chemistry and physics of heavy and superheavy elements*, ed. U. Kaldor and S. Wilson (Kluwer, Dordrecht, 2003.

Applications

- *Relativistic Electronic Structure Theory - Part 2 : Applications*, ed. P. Schwerdtfeger (Elsevier, Amsterdam, 2004).