An introduction to Relativistic Quantum Chemistry

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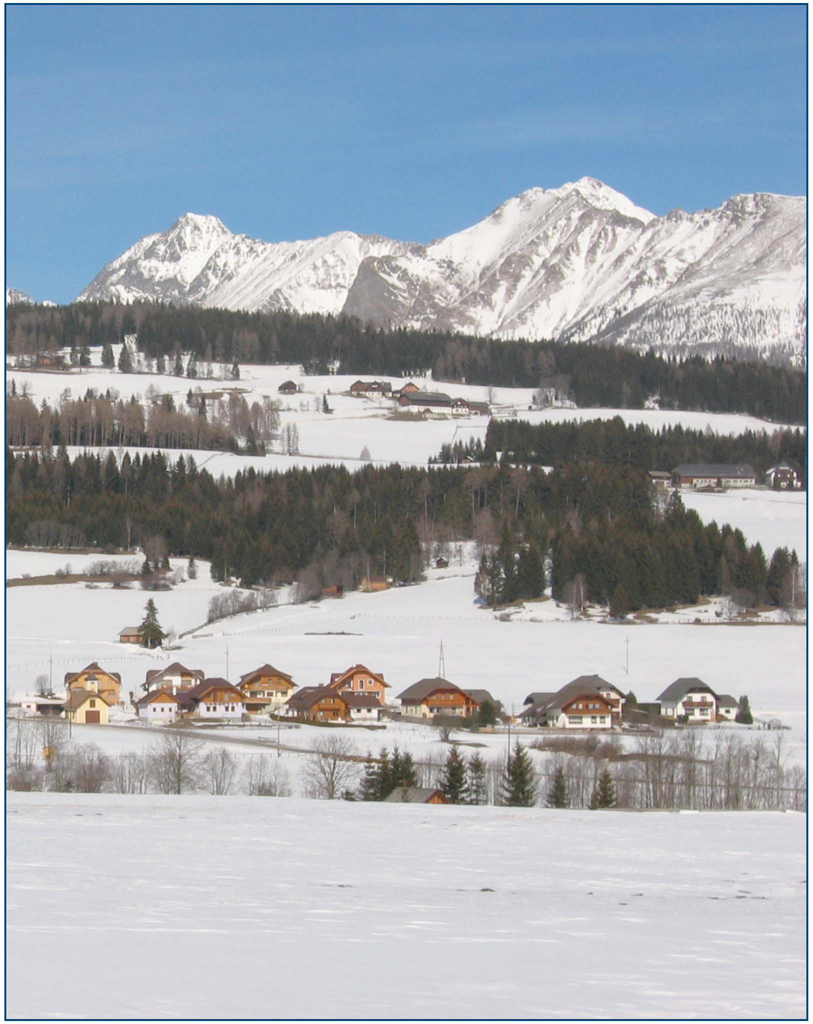
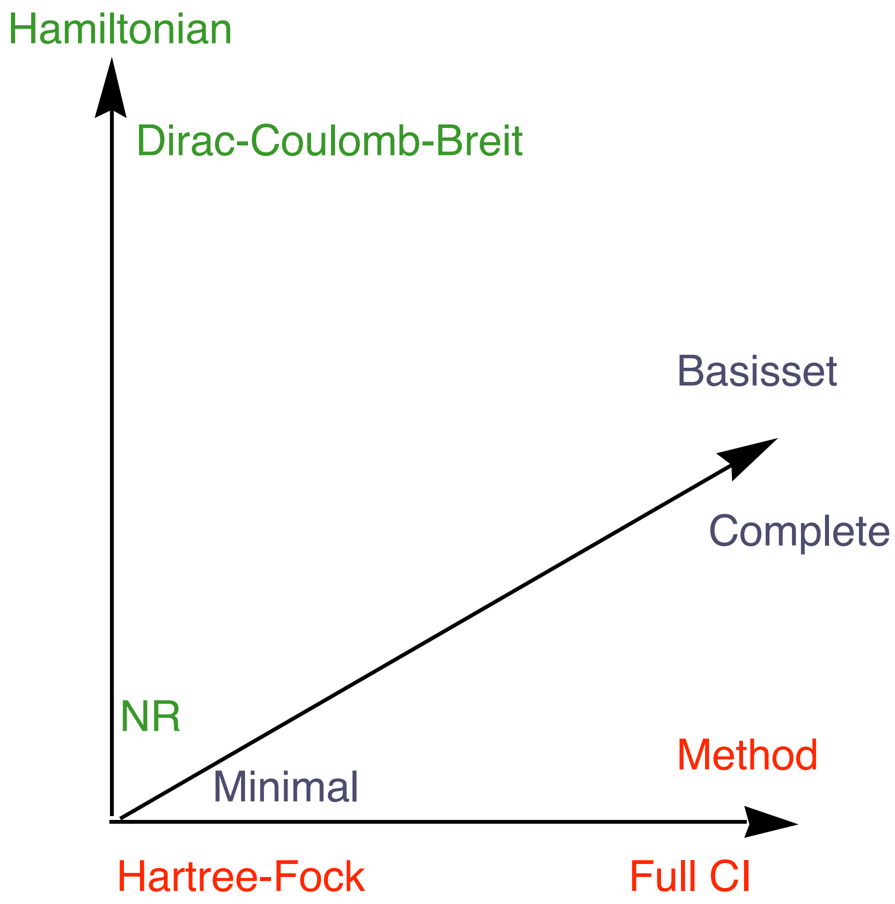
The extra dimension





Course outline: lecture 1+2

- Relativistic Quantum Chemistry
  - Special Relativity
  - The Dirac equation
    - Free particles
    - *Second quantization and QED : a short detour*
    - Hydrogenic atom

- Approximate Hamiltonians
  - Breit-Pauli perturbation theory
  - The regular approximation (ZORA)
  - The Douglas-Kroll-Heß method
  - Four-component methods
  - Direct perturbation theory

Course outline: lecture 3

- Effective Core Potentials
  - Basic assumptions
  - Ab initio Model Potentials
  - Energy-Consistent Pseudopotentials
  - Shape-Consistent Pseudopotentials

- Computational aspects
  - All-electron or valence-only ?
  - Wave Function Theory or Density Functional Theory ?
  - Spin-orbit or scalar relativistic ?

- Relativistic effects in chemistry
  - Dissociation energies
  - Bond lengths and bond strengths
  - Dipole moments
  - NMR shieldings
  - Electric Field Gradients

Coordinate transformation

- Galilean transformation

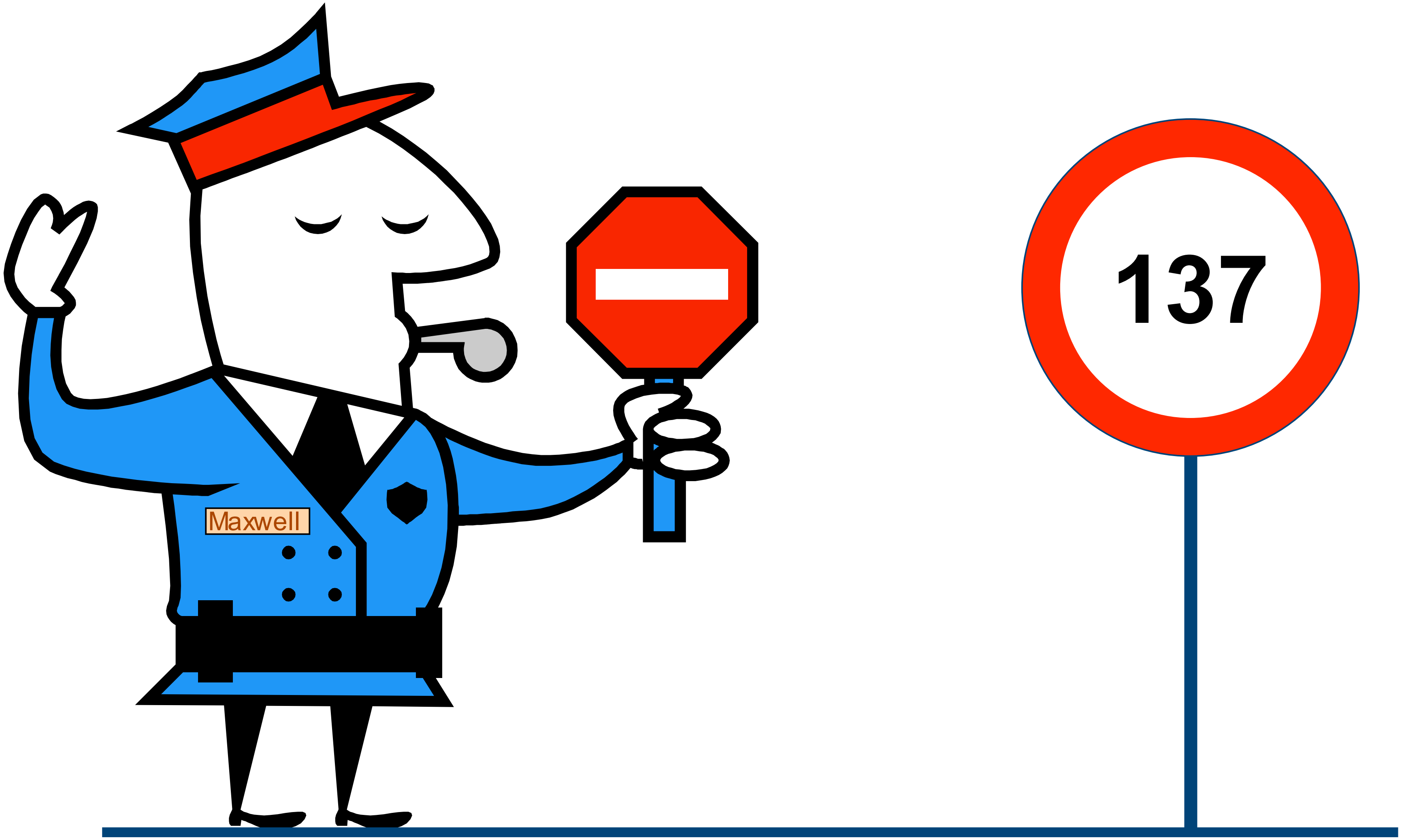
$$x = x' + vt$$

$$y = y'$$

$$z = z'$$

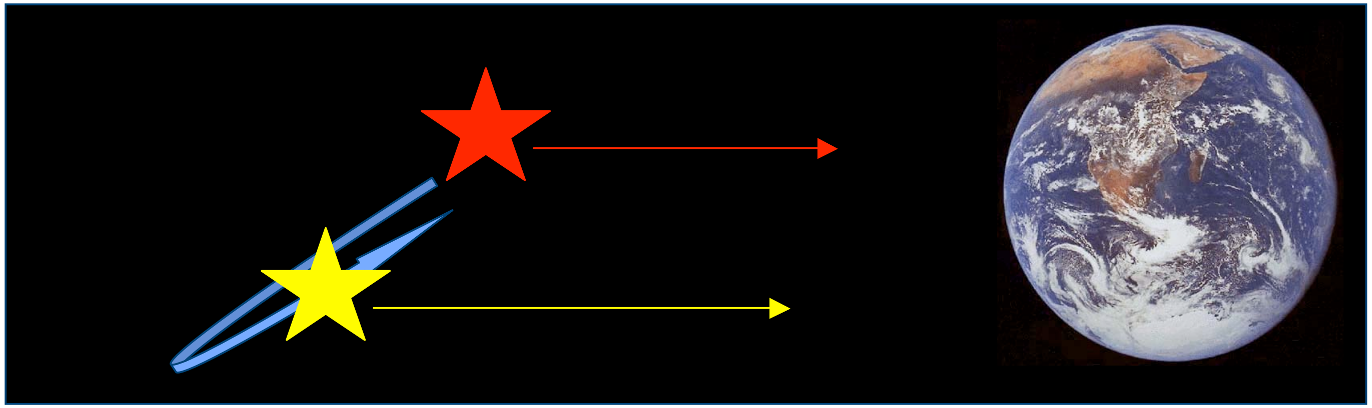
$$w = \frac{dx}{dt} = \frac{d(x' + vt)}{dt} = \frac{dx'}{dt} + v = w' + v$$

- Simple addition of velocities, no speed limit


Maxwell
137

Thought experiment 1

- 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 theory of mechanics

Thought experiment 2

- Take two observers inside and outside a moving train
- The train passes the stationary observer, waiting for the railroad sign, on its way to a nearby tunnel...
- They both know the speed of light and wonder when the light of the railroad sign will illuminate the tunnel

- The observer outside has an easy job : t = distance / c
- The observer inside needs to correct for the fact that the tunnel is moving towards him (and the light) and gets a slightly smaller t

- Their conclusion: with c constant, t needs to be relative

Special relativity

c constant and t variable gives

$$x^2 + y^2 + z^2 = c^2 t^2$$

$$x'^2 + y'^2 + z'^2 = c^2 t'^2$$

Galileo

$$x = x' + vt$$

$$y = y'$$

$$z = z'$$

We need a new transformation

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

Scaling factor

$$y = y'$$

$$z = z'$$

No dependence on y and z since clocks in the yz plane would disagree (reciprocal relation between the frames)

$$t = \alpha\left(t' + \beta x'\right)$$

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

$$x = \gamma\left(x' + vt'\right)$$
$$y = y'$$
$$z = z'$$
$$t = \gamma\left(t' + \frac{vx'}{c^2}\right)$$

Generalize to 3d

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

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

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

The nonrelativistic Hamiltonian function

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

$$\pi = \mathbf{p} - q\mathbf{A}$$

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 also write the the Hamiltonian function as

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

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

← Kronecker delta and Levi-Civita tensor

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

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

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

$$\boxed{\begin{aligned}\hat{\nabla}\times\mathbf{A}(\mathbf{r})f(\mathbf{r})&=\hat{\nabla}\times\left(f(\mathbf{r})\mathbf{A}(\mathbf{r})\right) &&\longleftarrow \text{A is a multiplicative operator}\\&=\left(\hat{\nabla}f(\mathbf{r})\right)\times\mathbf{A}(\mathbf{r})+f(\mathbf{r})\hat{\nabla}\times\mathbf{A}(\mathbf{r}) &&\longleftarrow \text{chain rule}\\&=-\hat{\mathbf{A}}\times\left(\hat{\nabla}f(\mathbf{r})\right)+\mathbf{B}f(\mathbf{r}) &&\longleftarrow \text{Use definition of B}\end{aligned}}$$

$$\hat{H}=\hat{T}+q\hat{\phi}+iq\hat{\mathbf{A}}\cdot\hat{\nabla}+\frac{q^{2}}{2}\hat{\mathbf{A}}^{2}-\frac{q}{2}\sigma\cdot\mathbf{B}\quad\longleftarrow\text{in atomic units}$$

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 magnetic moment to the intrinsic angular momentum) is not well explained

☹ No spin-orbit coupling

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

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

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 prior to quantization

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

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 is used for mesons (that have no spin)

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

☺ Can be shown to be Lorentz invariant

Alpha and Beta are conventionally represented by the following set of 4-component matrices

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

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 : why ?

1) Spin doubles the components

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

Densities

- Charge density

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

- Current density

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

- Conservation 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 (Born-Oppenheimer 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

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

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

$$\boxed{k_\pm = k_x \pm i k_y}$$

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$_-$

$$a_4 = 0$$

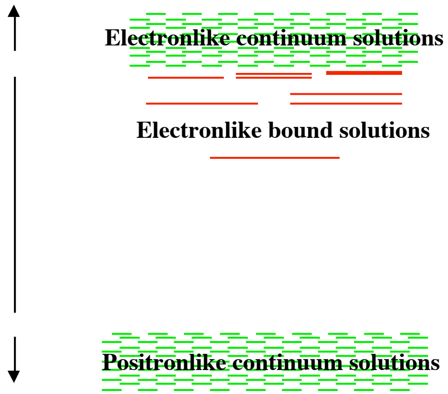
$$a_1 = a_3 \frac{c\hbar k_z}{E_- - mc^2} \approx a_3 \frac{p_z}{-2mc}$$

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

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

💣 Variational Collapse

Dirac sea of electrons



Electronlike continuum solutions

Electronlike bound solutions

Positronlike continuum solutions

- ● 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

Second Quantization

- 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

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

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

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

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

- 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

- Add quantized EM-field and interaction term

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

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

- 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

Dirac-Coulomb-Breit Hamiltonian

- Second quantization is merely convenient for our purposes, but becomes essential when going beyond the No-Pair approximation
- Page 68 of Book 1 has everything we need:

$$\hat{H} = \sum_{i,j} h_{ij}^{D} a_i^{\dagger} a_j + \frac{1}{2} \sum_{i,j,k,l} \left(g_{ijkl}^{C} + g_{ijkl}^{B} \right) a_i^{\dagger} a_k^{\dagger} a_l a_j$$

- Matrix elements are complex and (therefore) have less permutational symmetry
- We want to compute these matrix elements, so we need to go back to first quantization and basis set expansion techniques.....

MO-integrals in quaternion form

L. Visscher, J. Comp. Chem. ***23*** *(2002) 759.*

$$G^{VW,XY}_{\mu\nu,\kappa\lambda} = \iint \frac{\chi^{V\dagger}_{\mu}(r_1)\,\chi^{W}_{\nu}(r_1)\,\chi^{X\dagger}_{\kappa}(r_2)\,\chi^{Y}_{\lambda}(r_2)}{r_{12}}\, d\mathbf{r}_1 d\mathbf{r}_2$$

$$B^{XX,\Lambda_{12}}_{\mu\nu,pq}\, e_{\Lambda_{12}} = \sum_{\Lambda_1=0}^{3}\sum_{\Lambda_1=0}^{3} c^{X,\Lambda_1}_{\mu p}\, c^{X,\Lambda_2}_{\nu q}\, e^{*}_{\Lambda_1} e_{\Lambda_2}$$

$$G^{Dirac-Coulomb\ \Lambda_{12}\Lambda_{34}}_{pqrs} = \sum_{X}^{L,S}\sum_{Y}^{L,S}\sum_{\mu,\nu}^{N_X}\sum_{\kappa,\lambda}^{N_Y} B^{XX,\Lambda_{12}}_{\mu\nu,pq}\, G^{XXYY}_{\mu\nu\kappa\lambda}\, B^{YY,\Lambda_{34}}_{\kappa\lambda,rs} \quad \left(\Lambda_{12}, \Lambda_{34} = 0,1,2,3\right)$$

$$G^{Lévy-Leblond}_{pqrs} = \sum_{\mu,\nu}^{N_L}\sum_{\kappa,\lambda}^{N_L} B^{LL,0}_{\mu\nu,pq}\, G^{LLLL}_{\mu\nu\kappa\lambda}\, B^{LL,0}_{\kappa\lambda,rs}$$

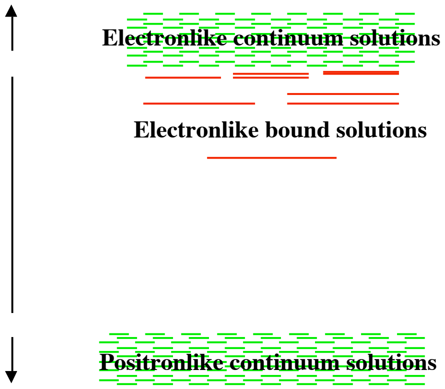
$$G^{\text{spinfree}}_{pqrs} = \sum_{X}^{L,S}\sum_{Y}^{L,S}\sum_{\mu,\nu}^{N_X}\sum_{\kappa,\lambda}^{N_Y} B^{XX,0}_{\mu\nu,pq}\, G^{XXYY}_{\mu\nu\kappa\lambda}\, B^{YY,0}_{\kappa\lambda,rs}$$

$$G^{Two-spinor\,\Lambda_{12}\Lambda_{34}}_{pqrs} = \sum_{\mu,\nu}^{N_L}\sum_{\kappa,\lambda}^{N_L} B^{LL,\Lambda_{12}}_{\mu\nu,pq}\, G^{LLLL}_{\mu\nu\kappa\lambda}\, B^{LL,\Lambda_{34}}_{\kappa\lambda,rs} \quad \left(\Lambda_{12}, \Lambda_{34} = 0,1,2,3\right)$$

Discussed in Lecture 1

$$\left(\beta mc^{2} + c\,\boldsymbol{\alpha}\cdot\hat{\boldsymbol{\pi}} + q\phi\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Dirac equation



Electronlike continuum solutions

Electronlike bound solutions

Positronlike continuum solutions

Lorentz invariance

Renormalization (QED)

Choosing the reference Dirac Hamiltonian in QED: we need orbitals

No-Pair approximation and second quantized Hamiltonian

Breit interaction

One more exact solution of the Dirac equation

- The hydrogenic atom

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

- This equation can be solved exactly by separating the radial and angular variables
- The derivation and energy is found in various textbooks.

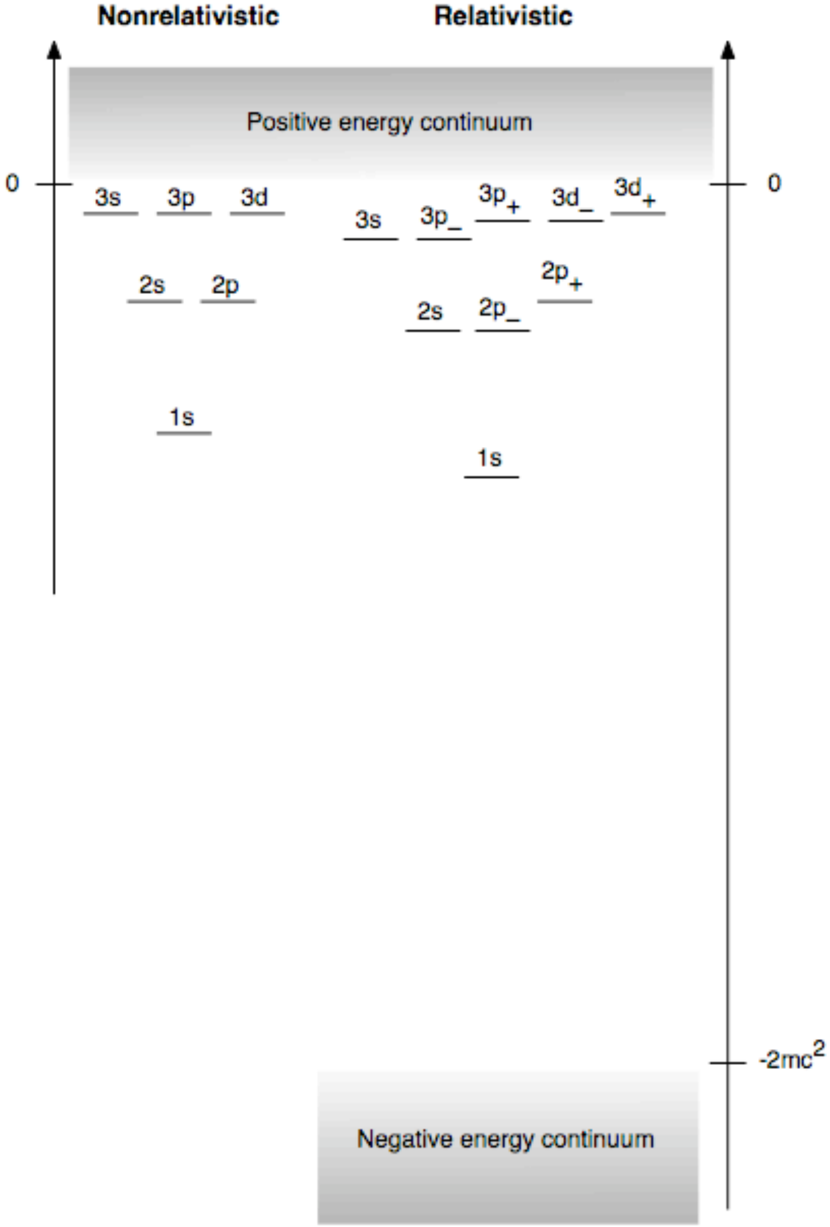
The hydrogenic atom

- The exact energy expression

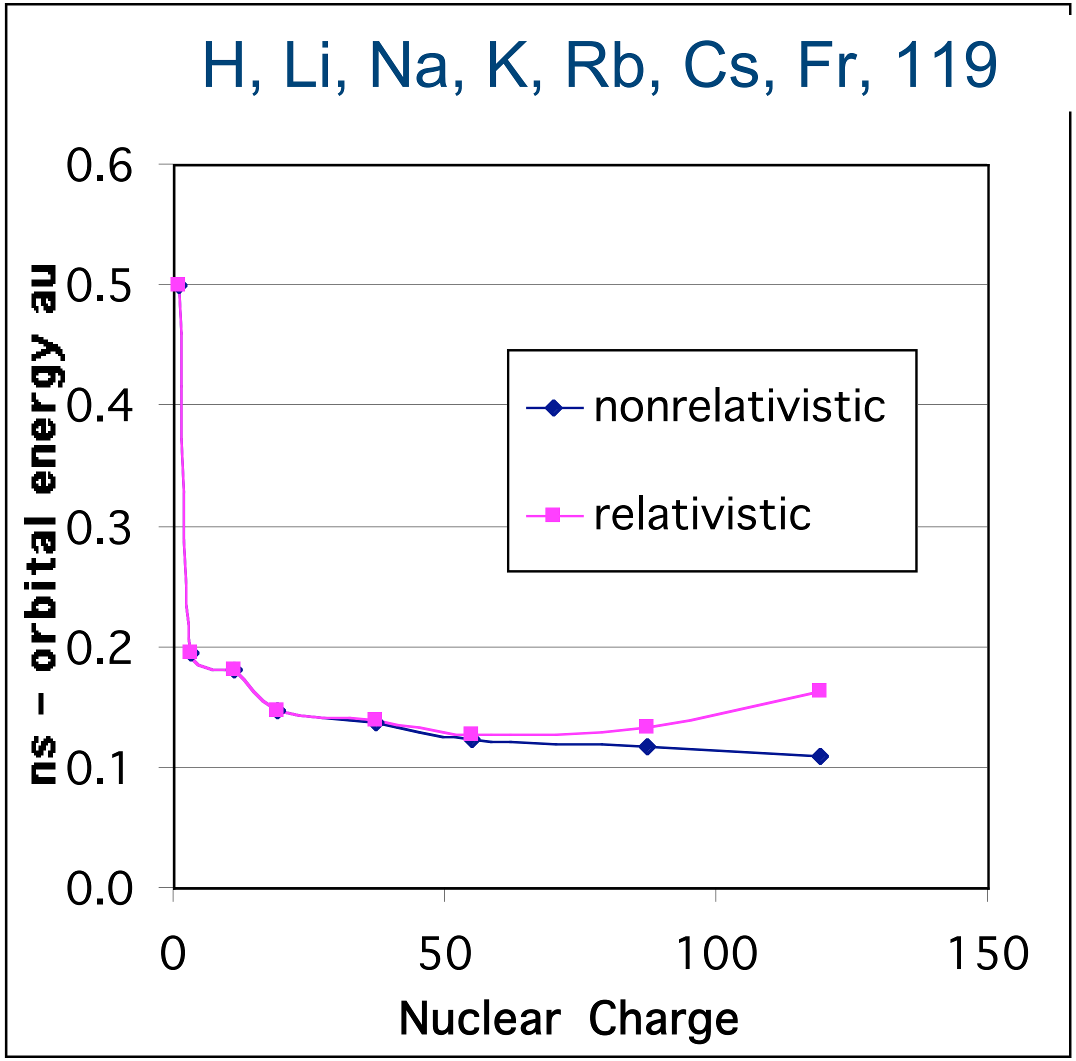
$$E = mc^2 / \sqrt{1 + \left\{ \frac{Z/c}{n - j - \frac{1}{2} + \sqrt{(j + 1/2)^2 - \frac{Z^2}{c^2}}} \right\}^2}$$

- Scalar relativistic corrections : $\boxed{E^{NR} = -\frac{Z^2}{2}}$

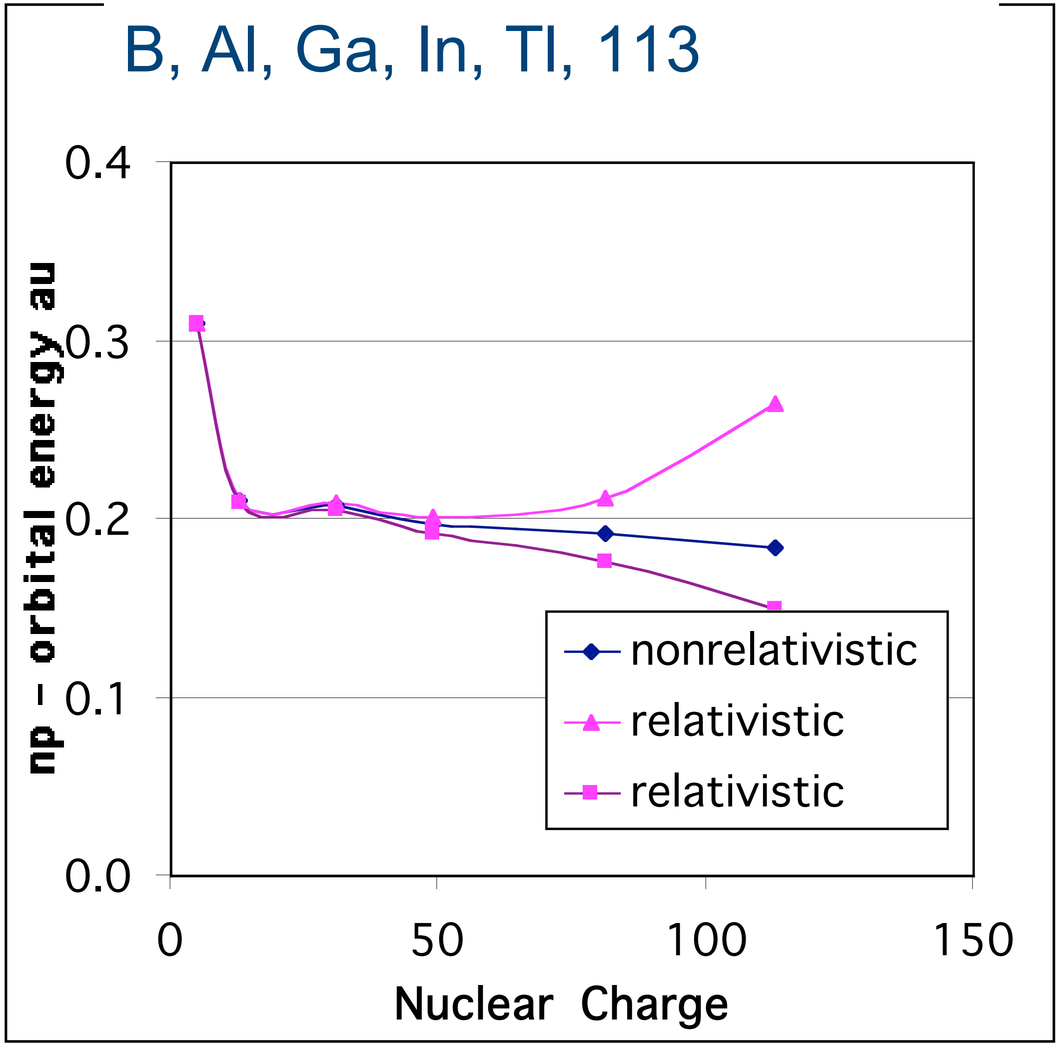
- Spin-orbit couping : $\boxed{j = l \pm s}$


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

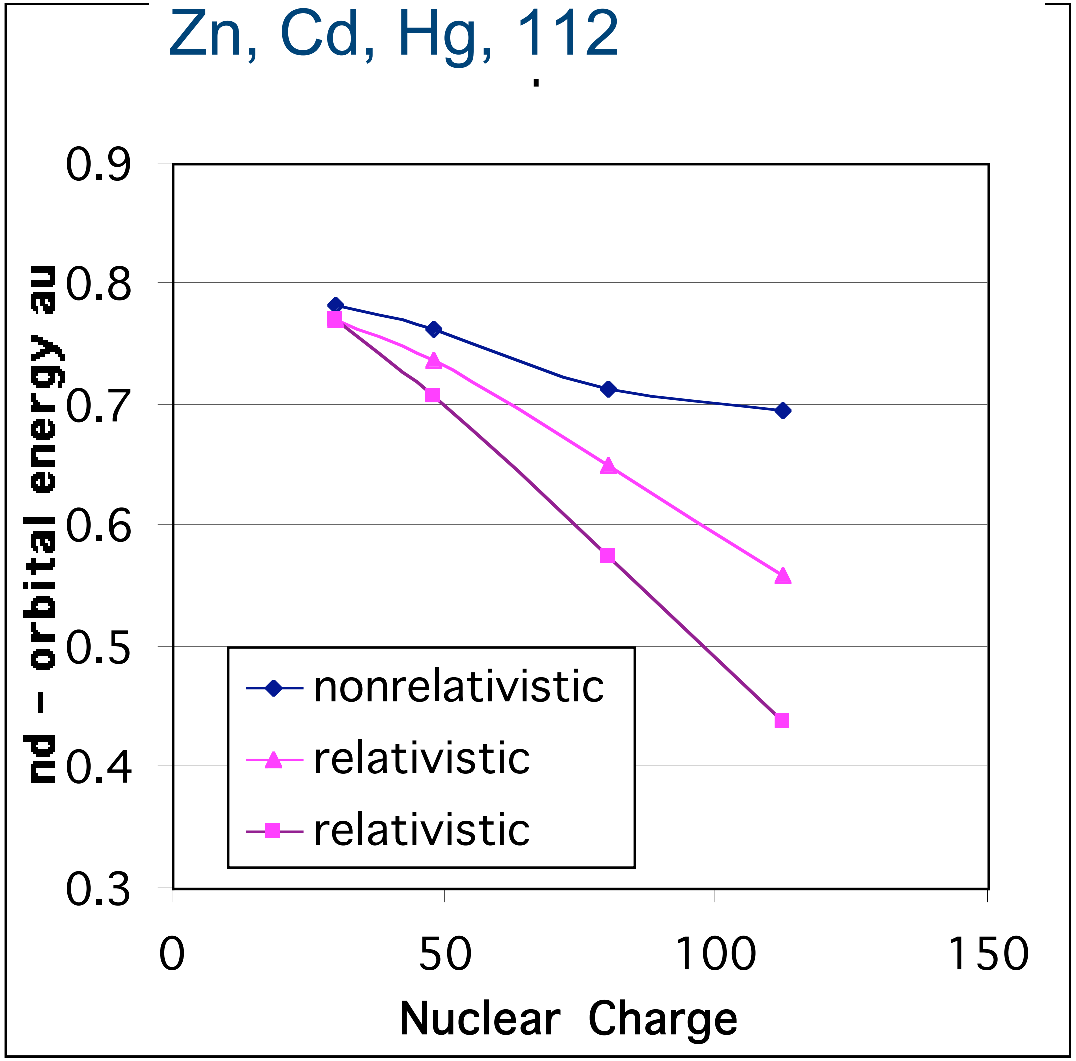
Orbital stabilisation



Spin-orbit splitting

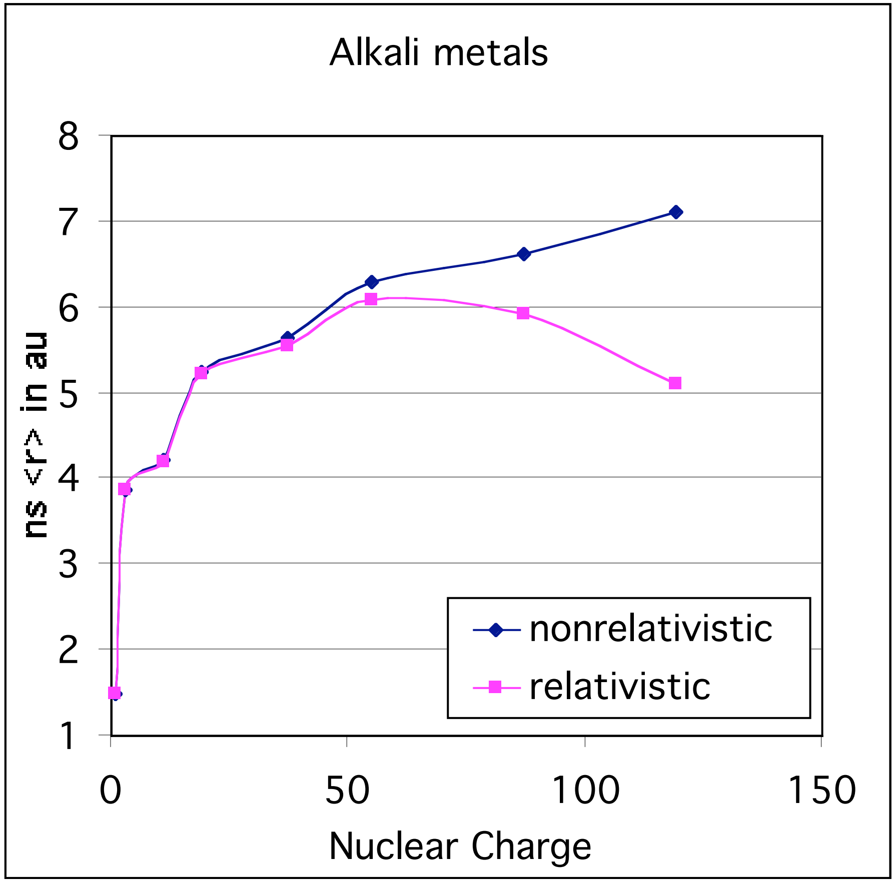


Orbital destabilisation



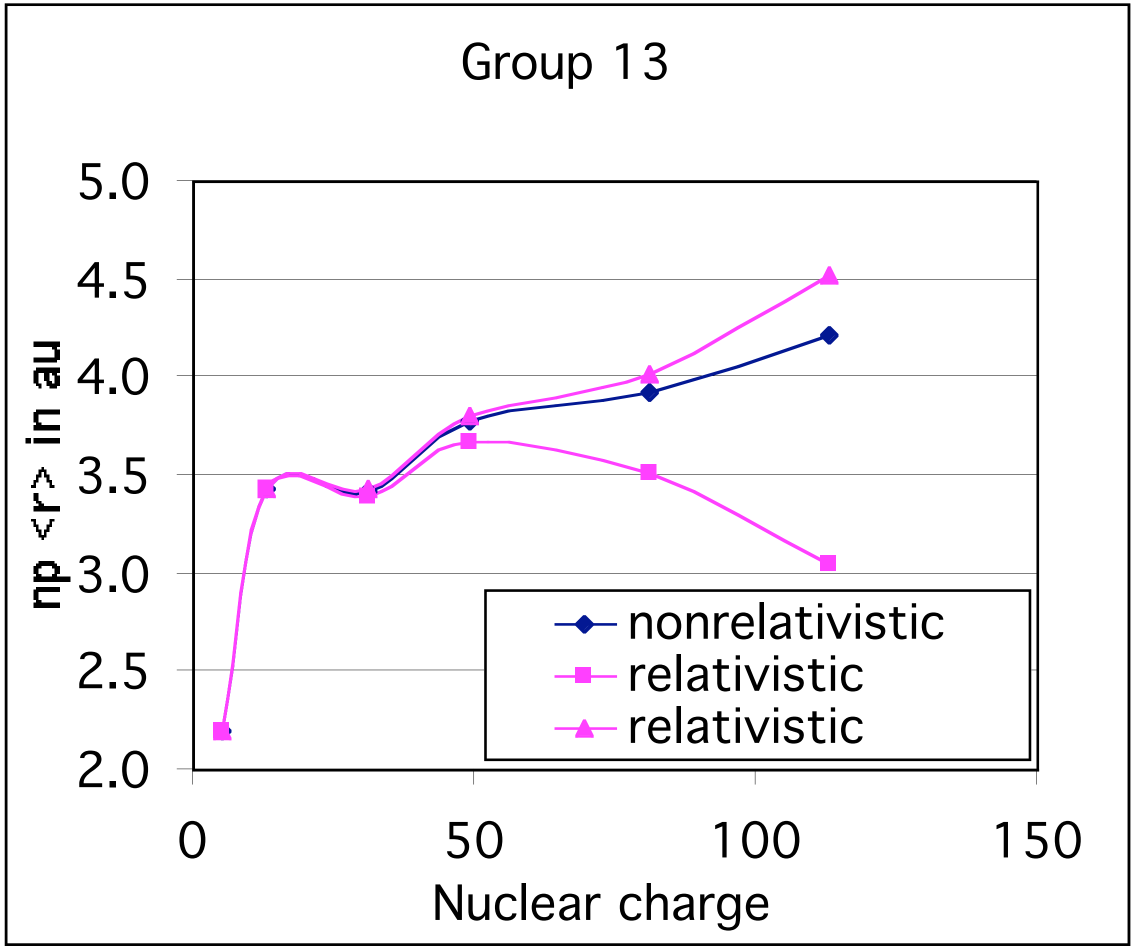
Orbital contraction

- <r> of the outermost s-orbital



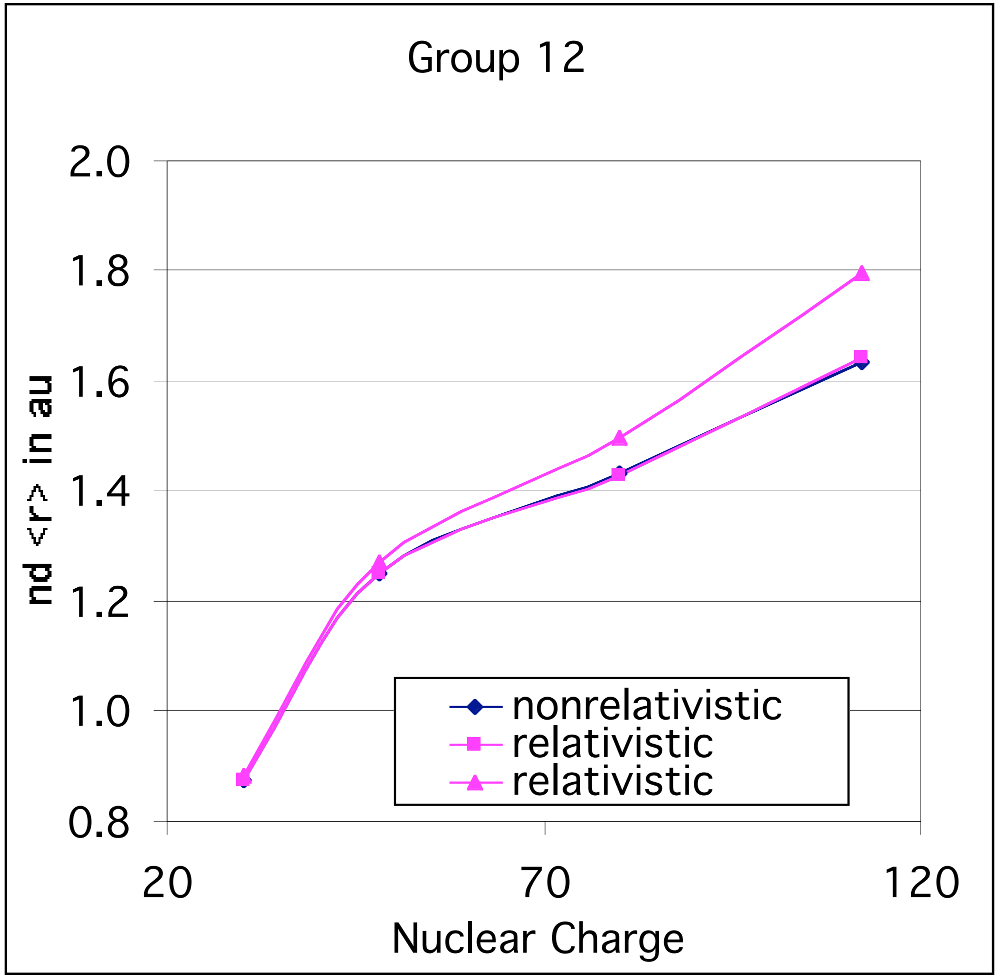
Orbital contraction

- <r> of the outermost p-orbital



Orbital expansion

- <r> of the outermost d-orbital



The hydrogenic atom

- The exact energy expression

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

- Can be expanded to

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

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

Approximate Hamiltonians

- Find operators that can describe these scalar relativistic and spin-orbit coupling 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

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

Pauli Hamiltonian

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

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

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

- Take K=1 but keep the magnetic field

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

Breit-Pauli Hamiltonian

- 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}

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

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

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

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

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

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

Breit-Pauli Hamiltonian

- Expansion of K

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

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

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

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

Breit-Pauli Hamiltonian

- The energy dependent term on the lhs was 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

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

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

- Result : The Breit-Pauli equation

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

Darwin Mass-Velocity Spin-Orbit

Expectation values for the hydrogen atom

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

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

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

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

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

Approximate relativistic Hamiltonians

Can we improve upon the Breit-Pauli Hamiltonian ?

A short wish list :

1. The Hamiltonian should resemble the Schrödinger Hamiltonian as much as possible
2. It should describe the scalar relativistic effects
3. It should describe the spin-orbit coupling effect
4. It should be variationally stable
5. It should be easy to implement
6. Errors relative to the Dirac solutions should be small and systematically improvable

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

Regular approximations

- 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 RMS radius is 4.7 10^{-5} au for C.

Regular approximations

- 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

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

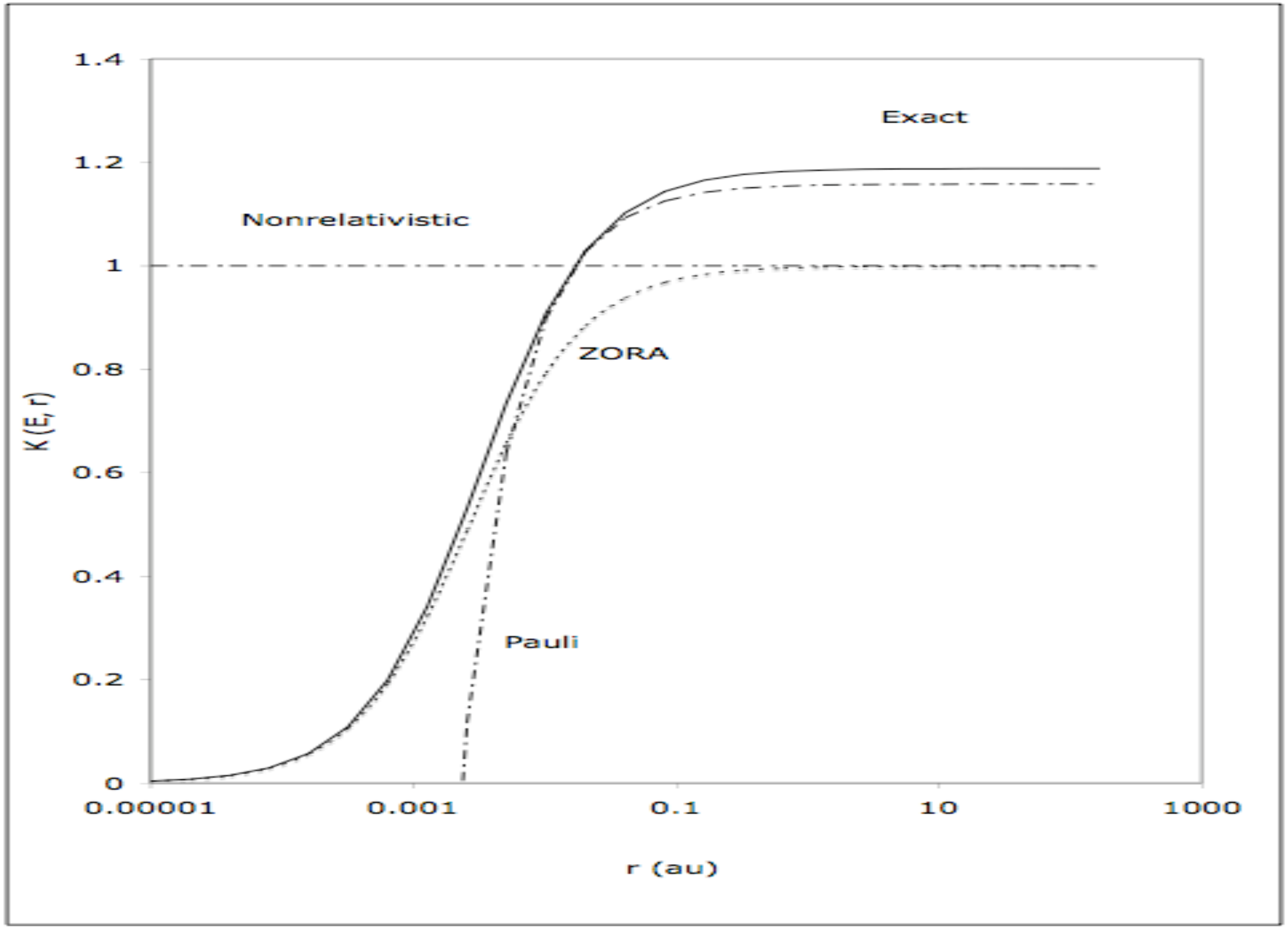
☺ Zeroth order equation does describe SO-coupling and scalar relativistic corrections

☹ Gauge dependence of the energy

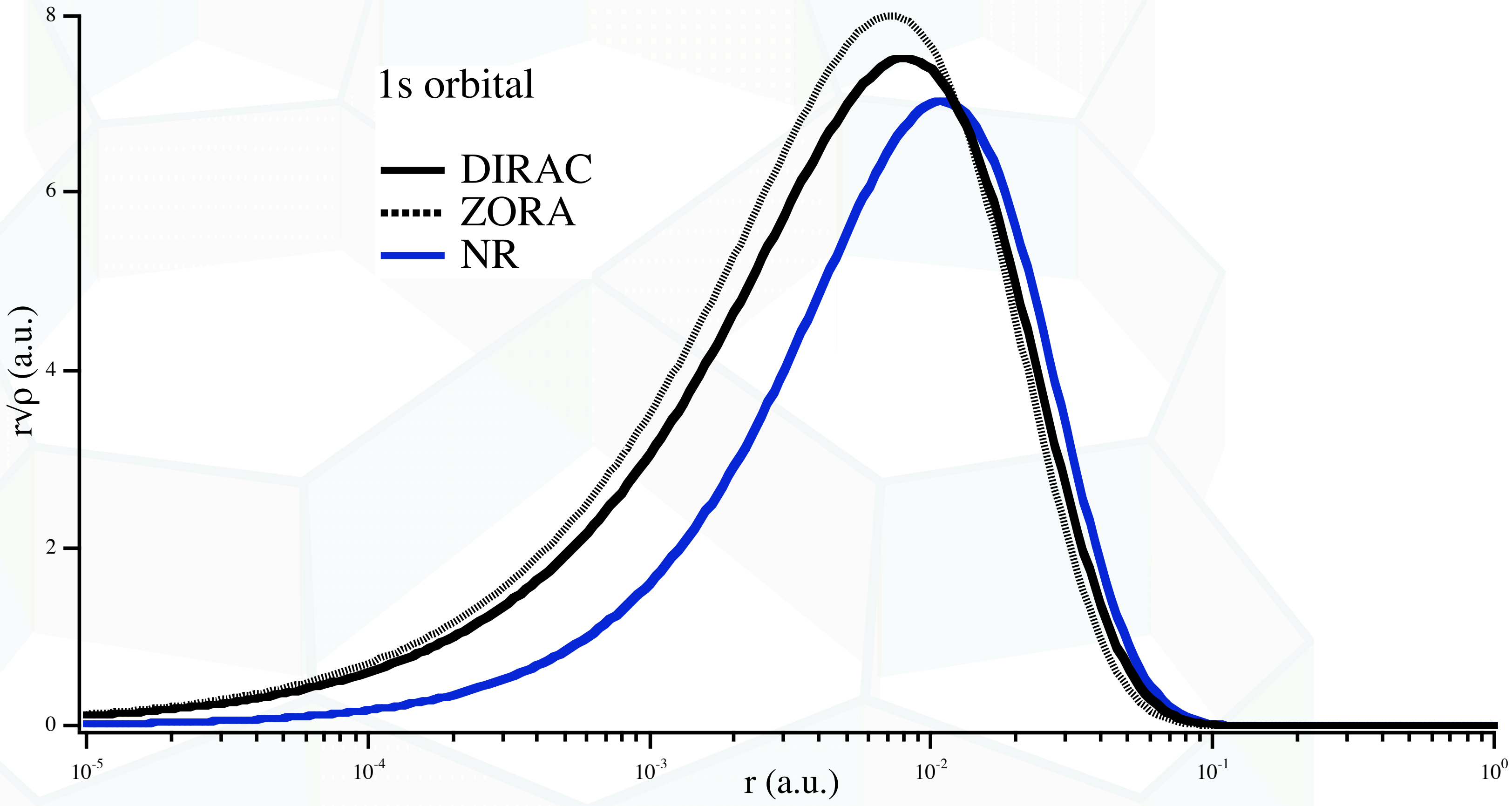
- Affects ionization energies, structures
- Gauge independence can be achieved various ways

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

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

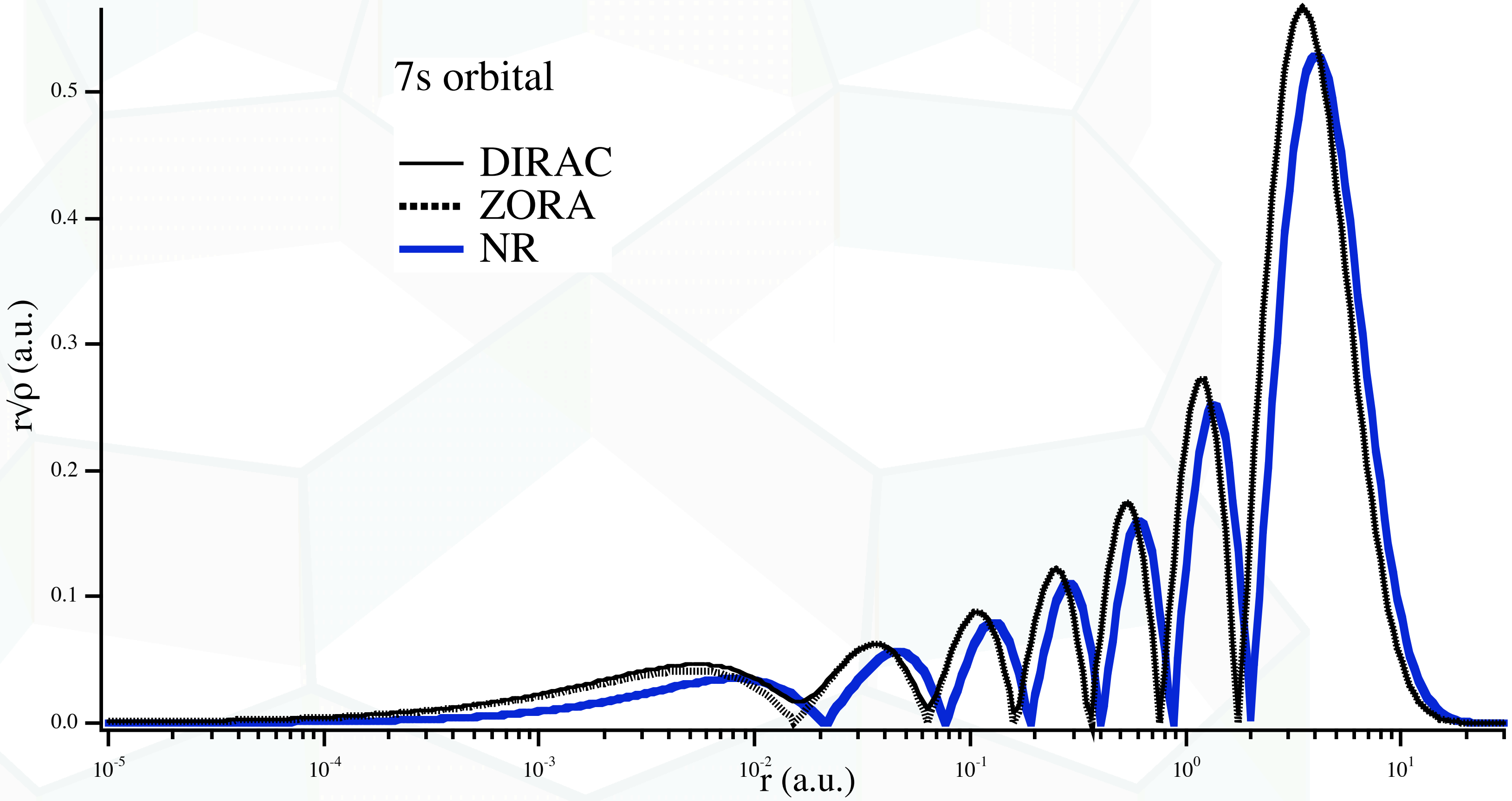


Uranium atom



Scientific Computing & Modelling

Uranium atom



Scientific Computing & Modelling

Foldy-Wouthuysen transformations

- Use an 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

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

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

- Exact expressions are only known for the free particle problem

Douglas-Kroll-Hess method

- Idea
  - Transform “bare-nucleus Hamiltonian” with the known free-particle tranformation 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

$$H^{DKH2} = E_p + A_p\left(V + (\boldsymbol{\sigma}.\mathbf{P}_p)V(\boldsymbol{\sigma}.\mathbf{P}_p)\right)A_p + W_1E_pW_1 + \frac{1}{2}W_1{}^2E_p + \frac{1}{2}E_pW_1{}^2$$

$$\boxed{E_p = \sqrt{m^2c^4 + c^2p^2}} \longleftarrow$$ Free particle energy operator

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

$$\boxed{R_p = \frac{c\alpha \cdot \mathbf{p}}{E_p + mc^2} = \alpha \cdot \mathbf{P}_p} \qquad \boxed{W_1 = \frac{A_pR_pV(\mathbf{p},\mathbf{p}')A_{p'} - A_pV(\mathbf{p},\mathbf{p}')R_{p'}A_{p'}}{E_p + E_{p'}}}$$

Higher order approaches

- General operator transformations
  - Barysz-Sadlej-Snijders (1997)
  - Reiher (200X)
  - van Wüllen (200X)

- Higher order two electron effects
  - Samzow, Hess, Jansen (1992)
  - Park and Almlöf (1994)
  - Hirao (2003-present)

- Infinite order via matrix representations
  - Ilias and Jensen (2005)

Four-component methods

- Idea
  - Expand Dirac equation in separate basis sets for the large and small components
  - 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 need to be handled
  - ☹ The Fock matrix is twice as large
  - ☺ No picture change problems

Hartree-Fock Self Consistent Field

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

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

Fock operator

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

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

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

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

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

$$\chi^S(\mathbf{r}) = \frac{\sigma \cdot \mathbf{p}}{2mc} \chi^L(\mathbf{r})$$

- Recovers the non-relativistic limit

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

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

← Resolution of identity

Choice of expansion functions

- Large component
  - Atoms : Sturmians, Slaters or Gaussians
  - Molecules : Spherical or Cartesian Gaussians
- Small component
  - Same type as large component
  - Should fulfill kinetic balance relation

$$\left\{\chi_P^S\right\} = \left\{(\sigma \cdot \mathbf{p})\chi_P^L\right\}$$

Restricted KB

$$\left\{\chi_P^S\right\} = \left\{\frac{\partial \chi_P^L}{\partial x}, \frac{\partial \chi_P^L}{\partial y}, \frac{\partial \chi_P^L}{\partial z}\right\}$$

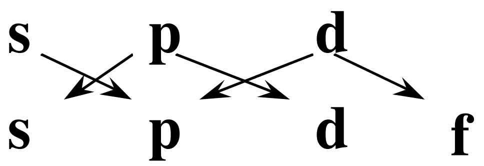
Unrestricted KB

Kinetic Balance

Dirac equation $\xrightarrow{c \to \infty}$ **Schrödinger equation**

Condition : $(\sigma \cdot p)(\sigma \cdot p) = p^2$

Cartesian Gaussian basis



Large Component s p d

Small Component s p d f

The small component density

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

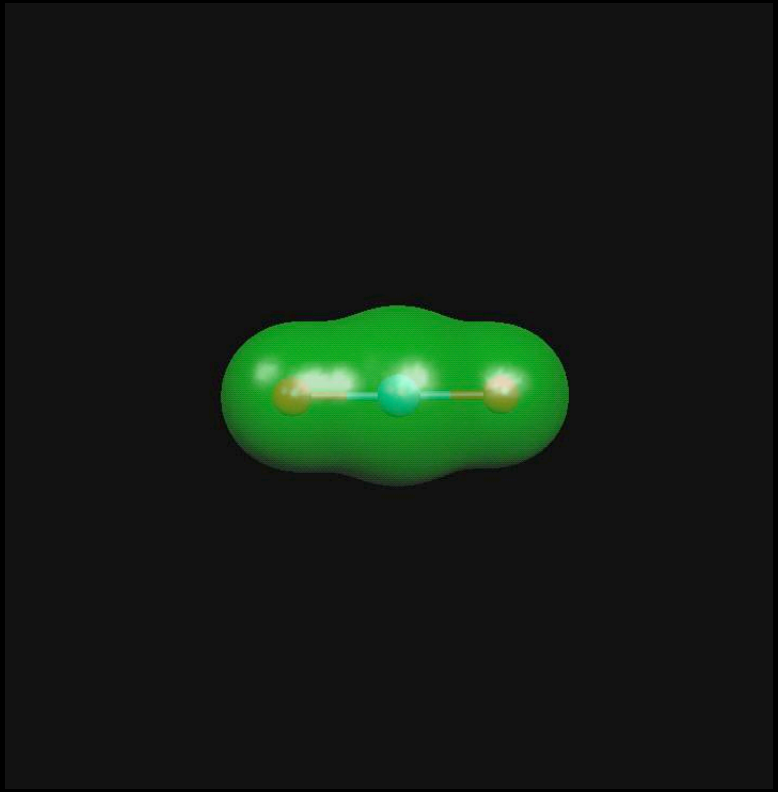
$$\breve{\psi}^S = \frac{-1}{2c}\left(1 + \frac{E - V}{2c^2}\right)^{-1} \breve{\nabla}\breve{\psi}^L$$

- Small component wave function is related to the first derivative of large component wave function
- The small component density is an

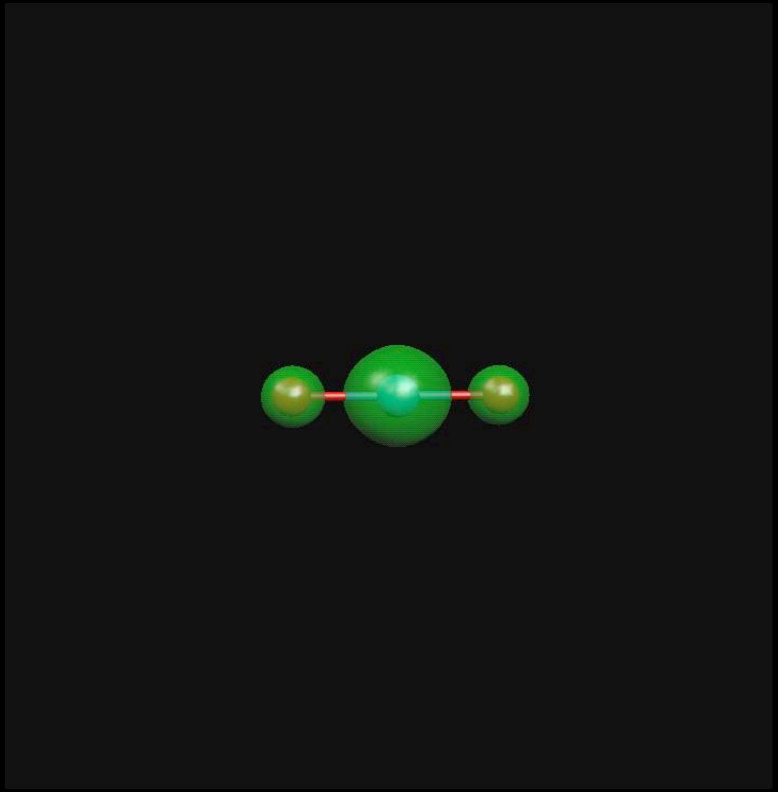
  embarrassingly **local** quantity !

Electron Density of Uranyl

Large component



Small component



Spinfree Dirac equation

- Define an auxilliary function

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

- Transform the Dirac equation accordingly

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

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

Direct perturbation theory

- Consider the modified Dirac equation

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

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

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

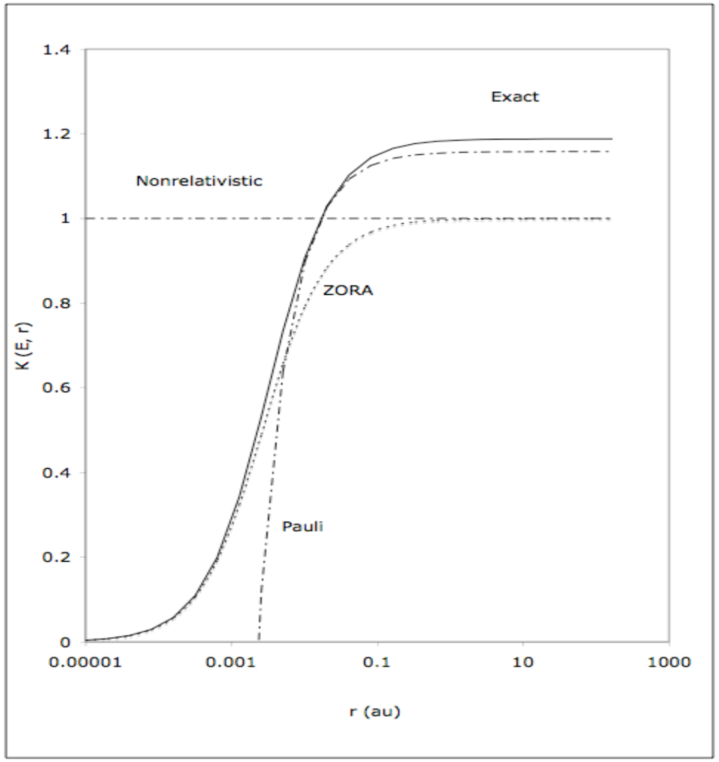
- Define a perturbation theory with as first (or second) order perturbations

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

Discussed in Lecture 2

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

Two-component methods



Breit-Pauli perturbation theory

Regular approach (ZORA)

Douglas-Kroll-Hess method

4-component methods

Direct Perturbation Theory

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
  5. Model frozen core by a Relativistic Effective Core Potential

- Error correction and additional features
  1. Estimate higher order correlation effects in another basis set
  2. Use a core correlation potential
  3. Use a core polarization potential
  4.
  5. Include valence relativistic effects in RECP

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 $\boxed{Z_A^* = Z_A - Z_{Core}}$

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

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

V_{Coulomb} V_{Exchange}

- Coulomb potential goes to zero at large distance, contains correction due to imperfect screening of nuclei at short distance
- Exchange contribution depends on the overlap : short range
- Approximation made : atomic core orbitals are not allowed to change upon molecule formation

Core polarization and overlap

- Polarizability of the core can modeled by a classical core polarization potential (see also book II, formula 45.9)

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

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 and thus neglects the exchange repulsion and nuclear attraction between neighbour cores
- 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

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

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

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

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

Resolution of identity with non-orthogonal functions

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

Level shift that enforces orthogonality to the core

Ab Initio Model Potentials

😐 No freely adjustable parameters

😐 Keeps nodal structure of the valence orbitals

😐 Core orbitals in the virtual space

☺ Relativistic effects can be included in the reference Fock operator

- Cowan-Griffin Hamiltonian
- Wood-Boring Hamiltonian
- Douglas-Kroll-Hess Hamiltonian

☺ Can also be used to generate “no-valence” MPs

- Improves description of ions in crystals
- May require iterative generation scheme
- See example from the work of Seijo in the green hand-out

Effective Core Potentials

Reduce the basis set used to describe the valence orbitals

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

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

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

Make nodeless pseudo-orbitals

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

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 *pseudopotentials* are determined via a fitting procedure. They take 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 orbital in the bonding region

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

Original orbital in the outer region

Smooth polynomial expansion in the inner region

  - Absolute correlation energy may be overestimated relative to correlation calculations done with the real orbitals
  - Fit is sometimes done to the large component of Dirac wave function (picture change error)
  - Reasonable accuracy for bond lengths and frequencies
  - Available in many program packages

Energy consistent ECPs

- “German school” : Stoll, Preuss, Dolg
- Semi-empirical or 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 due to nodeless valence orbitals is automatically included in the fit
  - Small cores are often necessary to obtain stable results
  - Available in many program packages

Methods to treat relativity

- "Best" method depends on system studied
- See exercise (and answer) 10

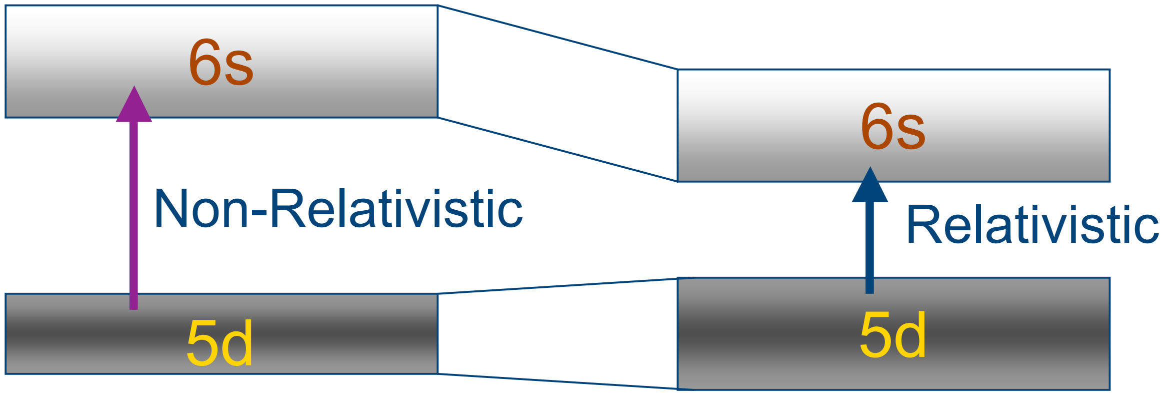
- Closed shells and simple open shells
  - Use a size-extensive and economical method
  - SOC-inclusive method may be required

- Complicated open shells, bond breaking
  - MCSCF, 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

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 scalar relativistic effects



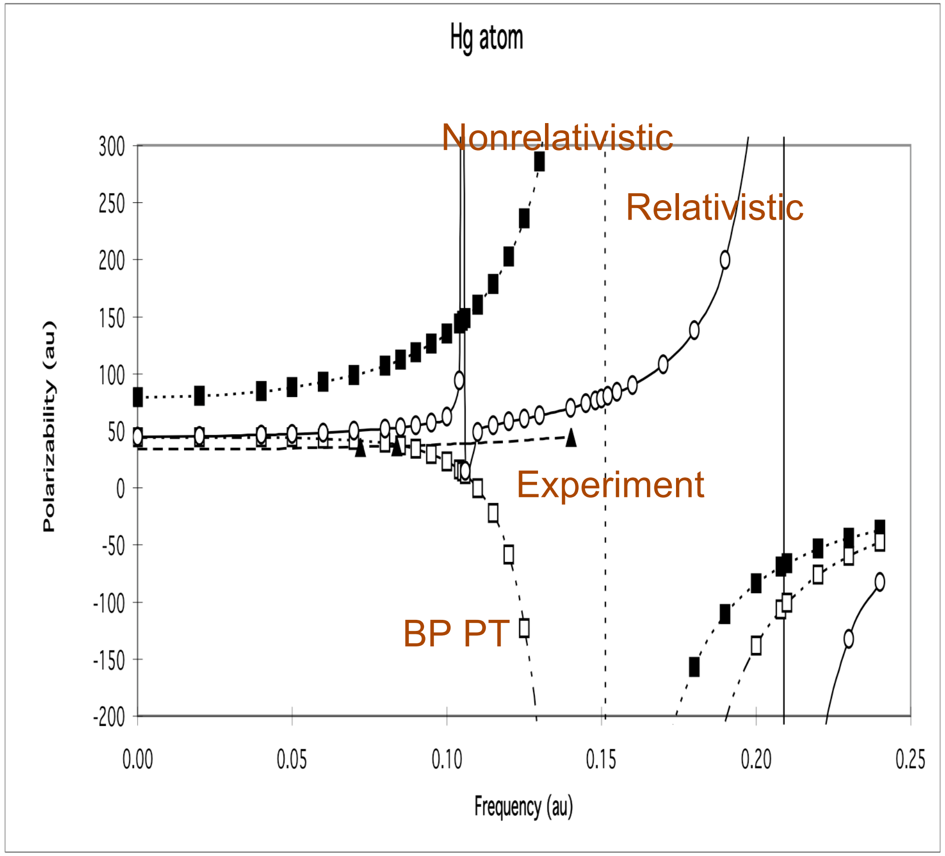
- Phosphorescence
  - Singlet-triplet transitions are allowed because the non-relativistic quantum numbers are not exact

Mercury: Dipole polarizability

- Calculation via 4-component time-dependent Hartree-Fock (4c TD-DFT is nowadays also possible)

A. Relativistic
B. Nonrelativistic
C. Breit-Pauli Pert. Theory

- 6s→6p transitions
- "Forbidden" $^1S_0 \rightarrow {}^3P_1$
- "Allowed" $^1S_0 \rightarrow {}^1P_1$



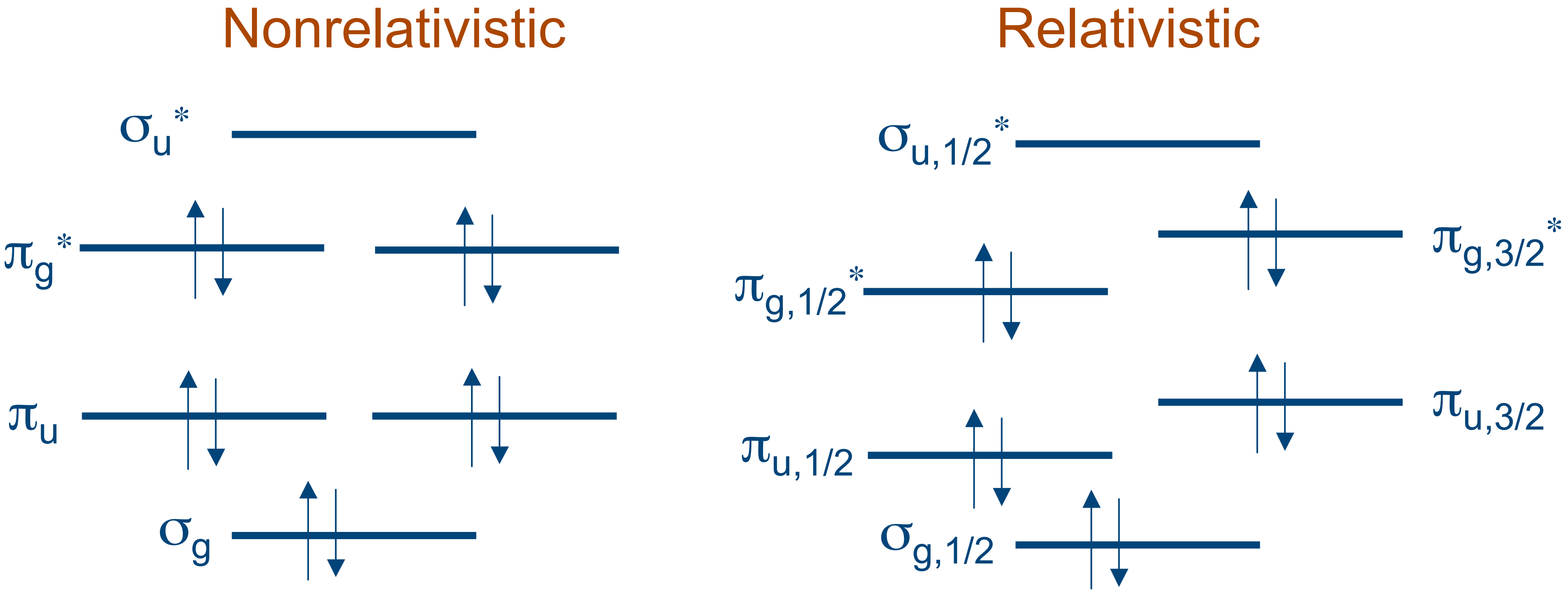
Closed shell molecules

- Some studies with all-electron single reference methods

- Analyze relativistic effects for diatomic molecules

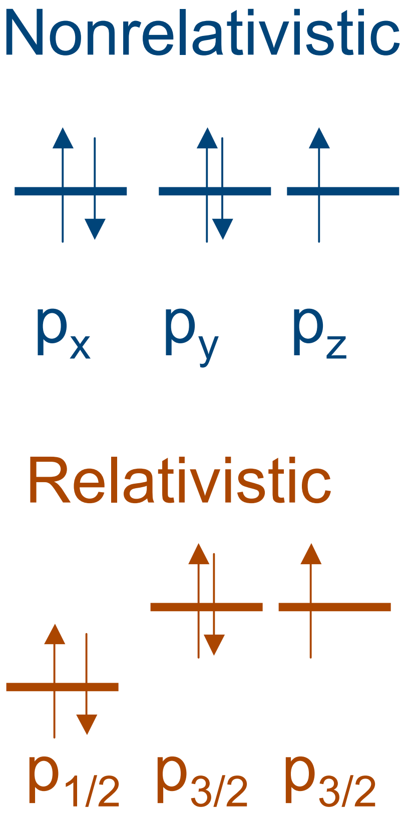
Atomization energies

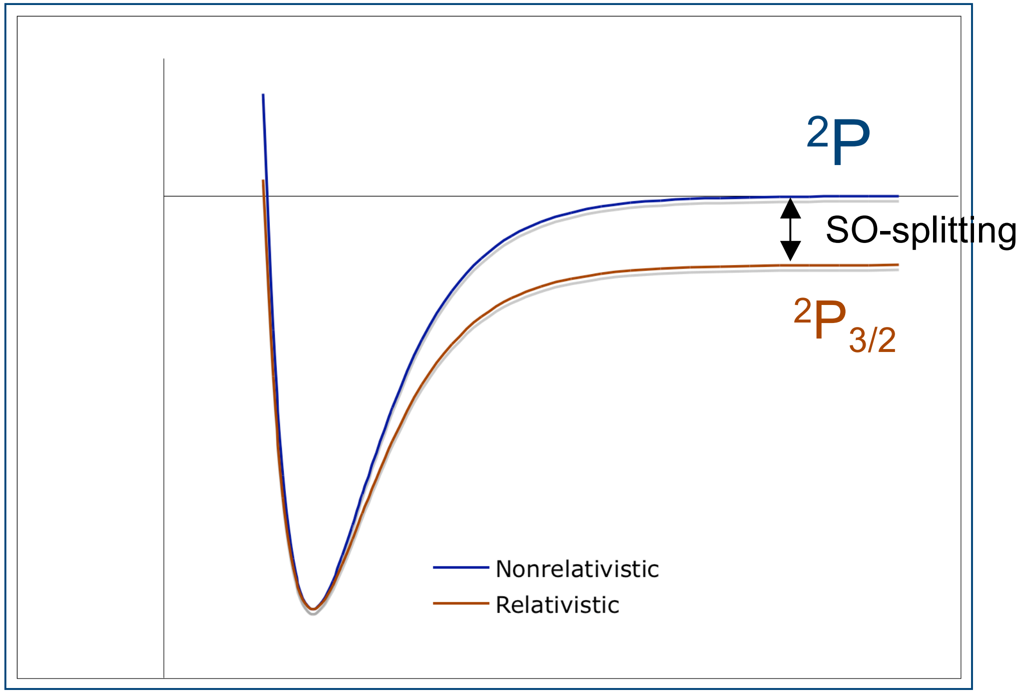
- Example: Halogen molecules
- Molecular energy is hardly affected by SO-coupling (SO quenching)
- First order perturbation theory



Atomization energies

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

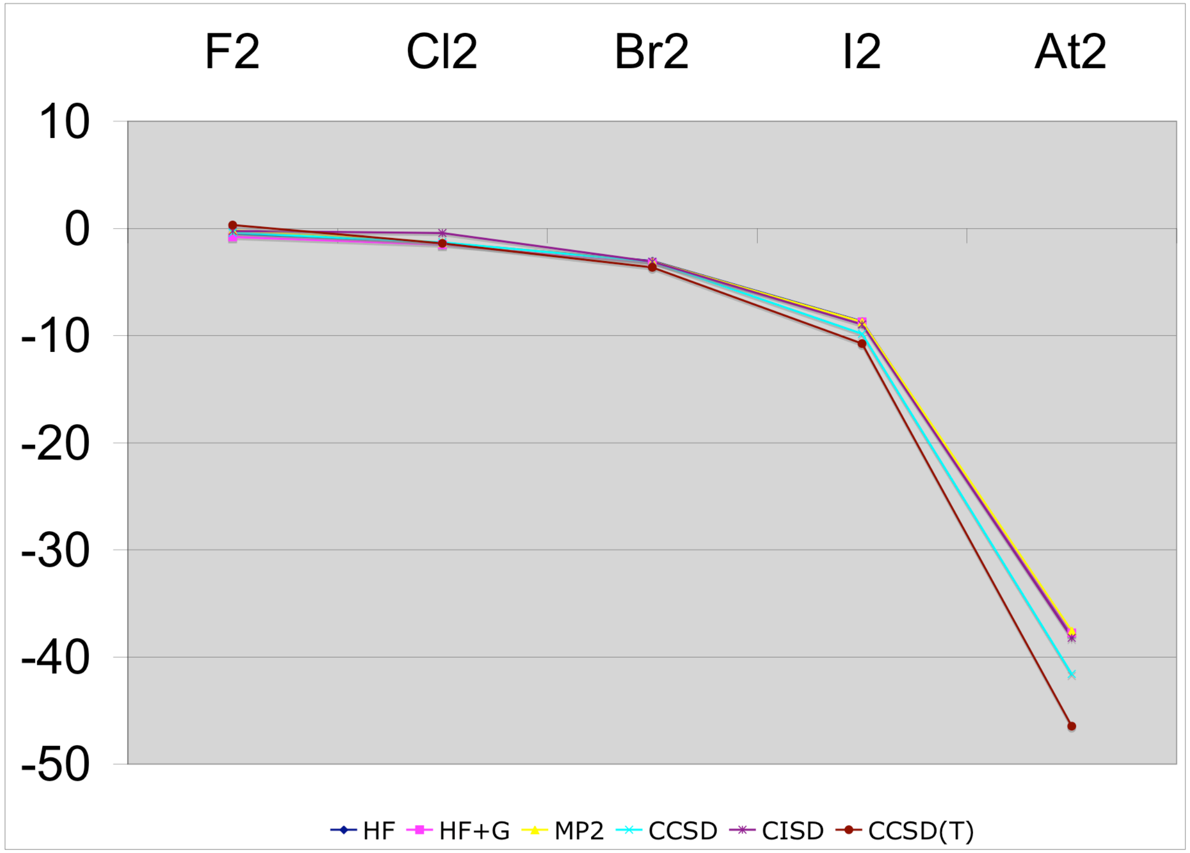




Relativistic effect on atomization energies (kcal/mol)

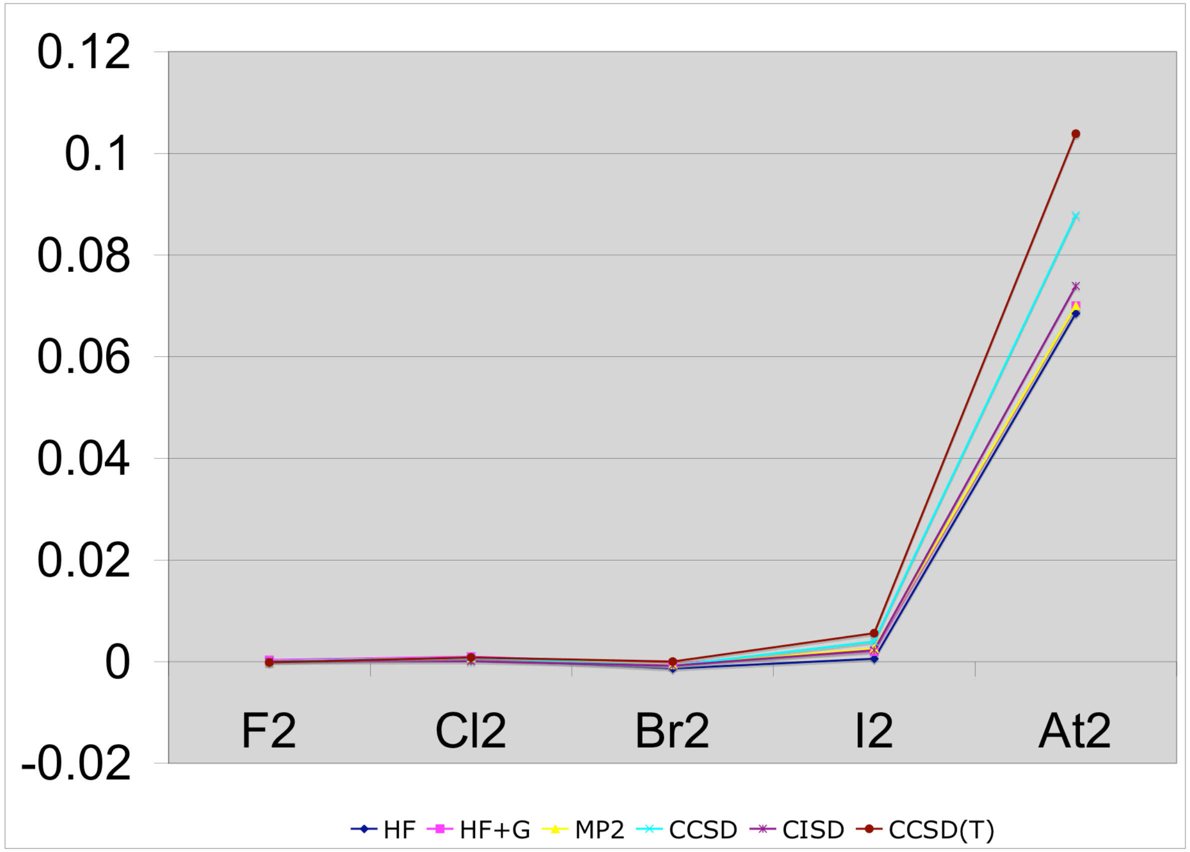
Mainly SO-coupling : relativistic effect on atomization energies can be estimated by correction to the asymptote

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



Bond weakening due to admixture of the antibonding sigma orbital. This is a second order spin-orbit effect

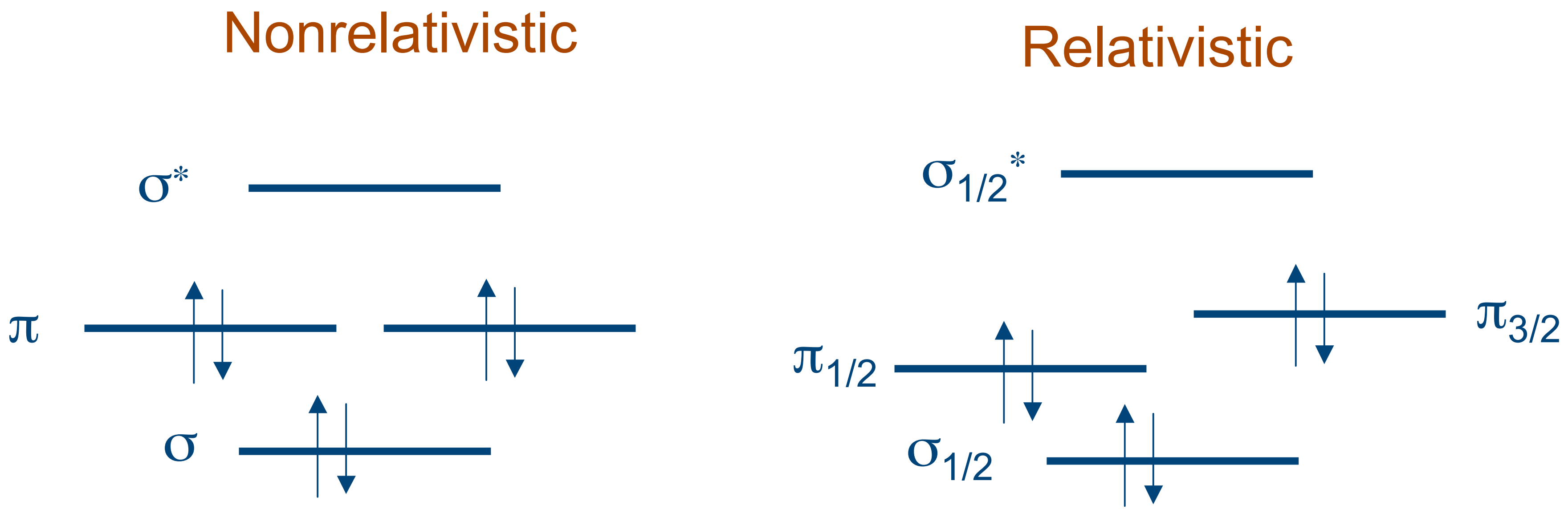
Relativistic effect on equilibrium distances (Å)



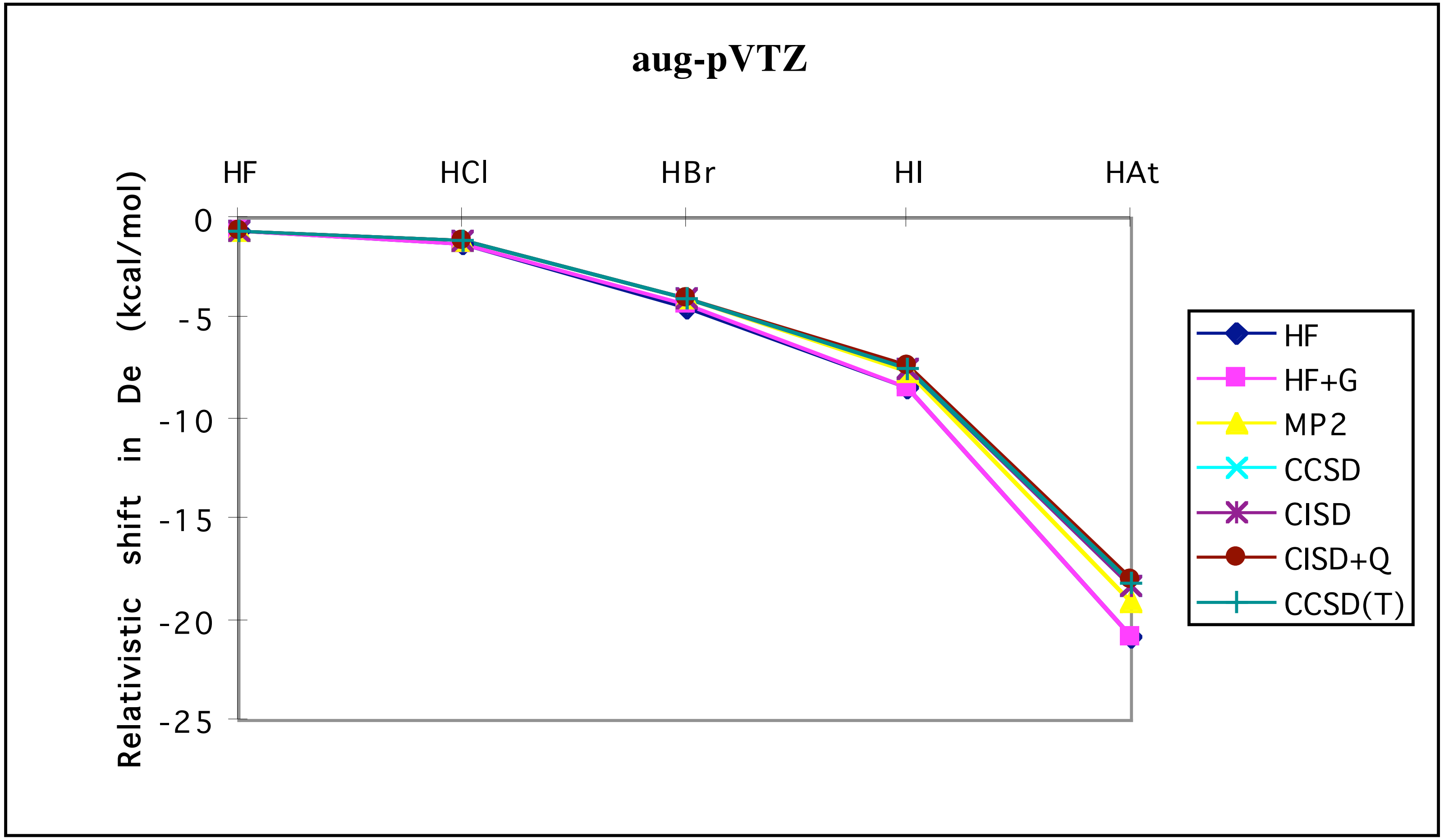
Note the underestimation by Hartree-Fock in At_2

Atomization energies

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

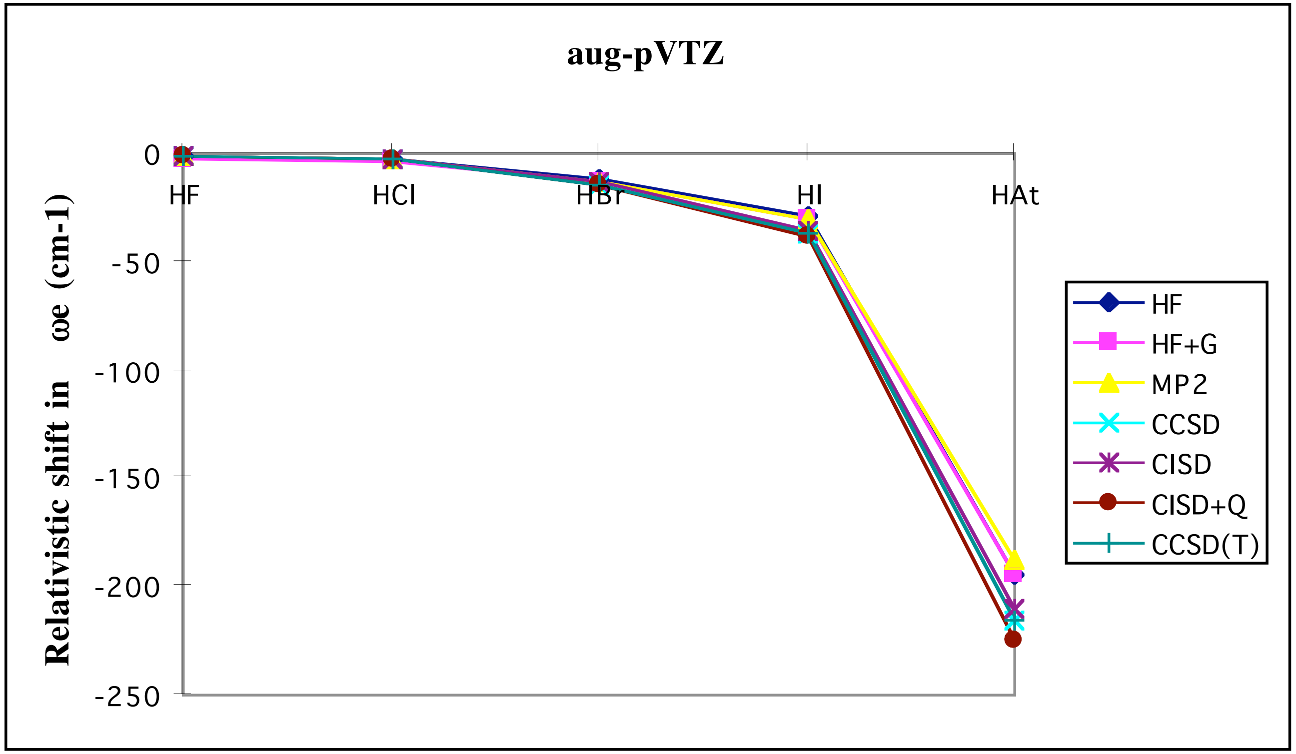


Dissociation Energies



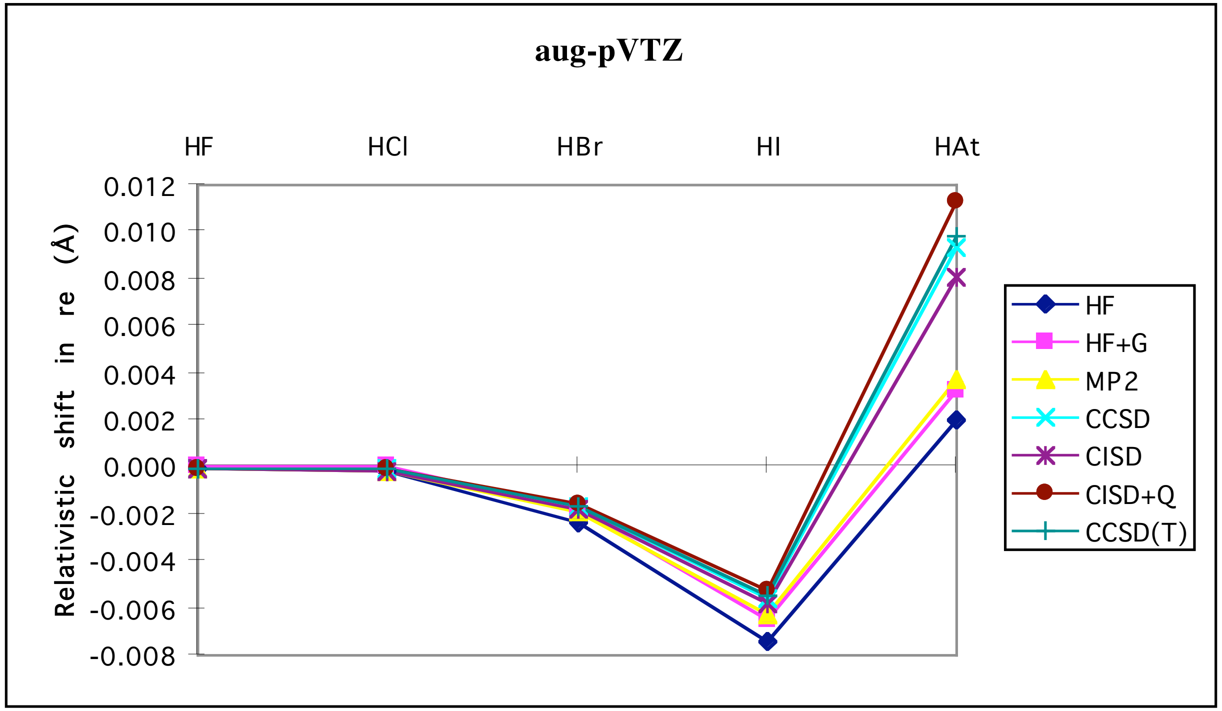
Mainly SO-coupling : a good estimate for atomization energies can be obtained by correcting only the asymptote

Vibrational Frequencies

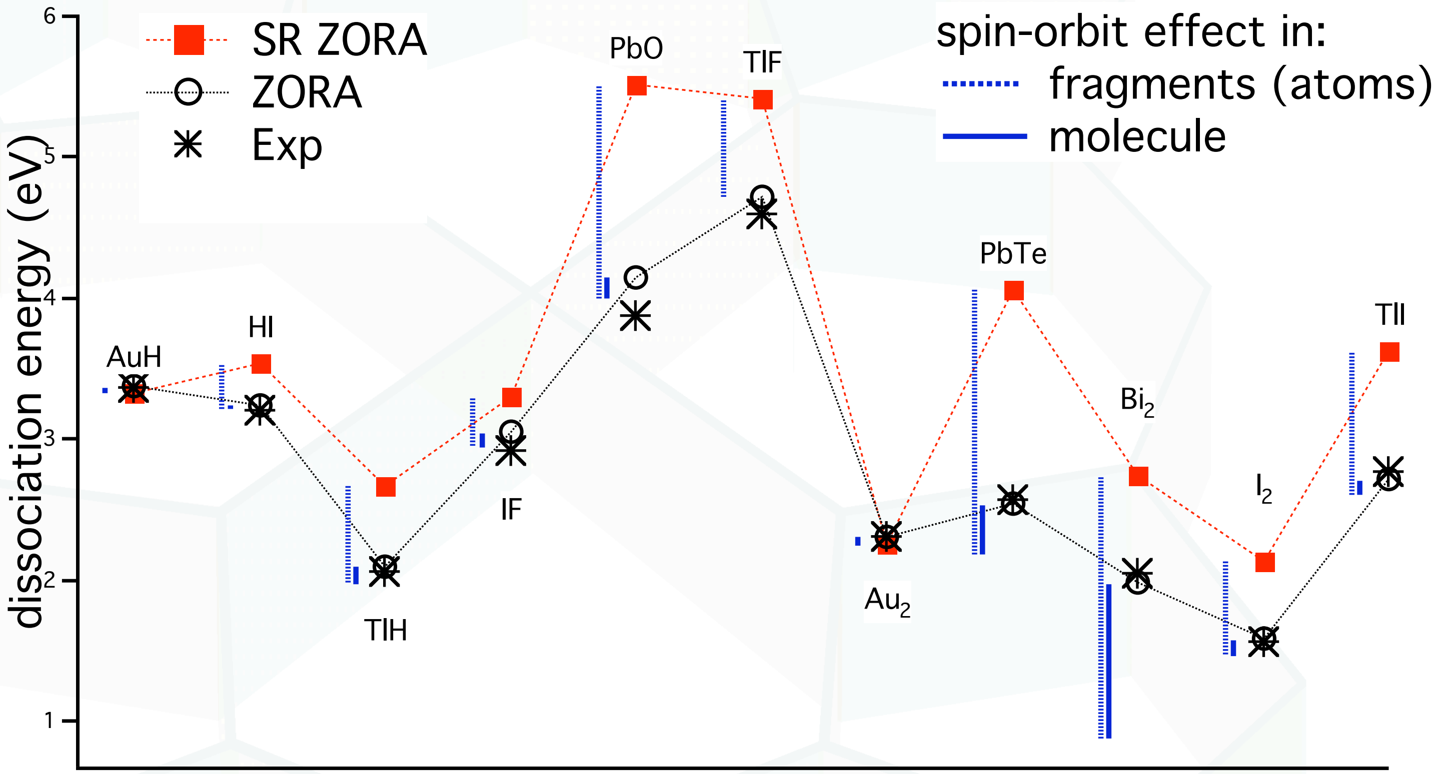


Bond weakening due to admixture of the antibonding sigma orbital

Bond Lengths



Competition between scalar and spin-orbit effects
Total effect is small (< 0.01 Å) in this case



Scientific Computing & Modelling

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

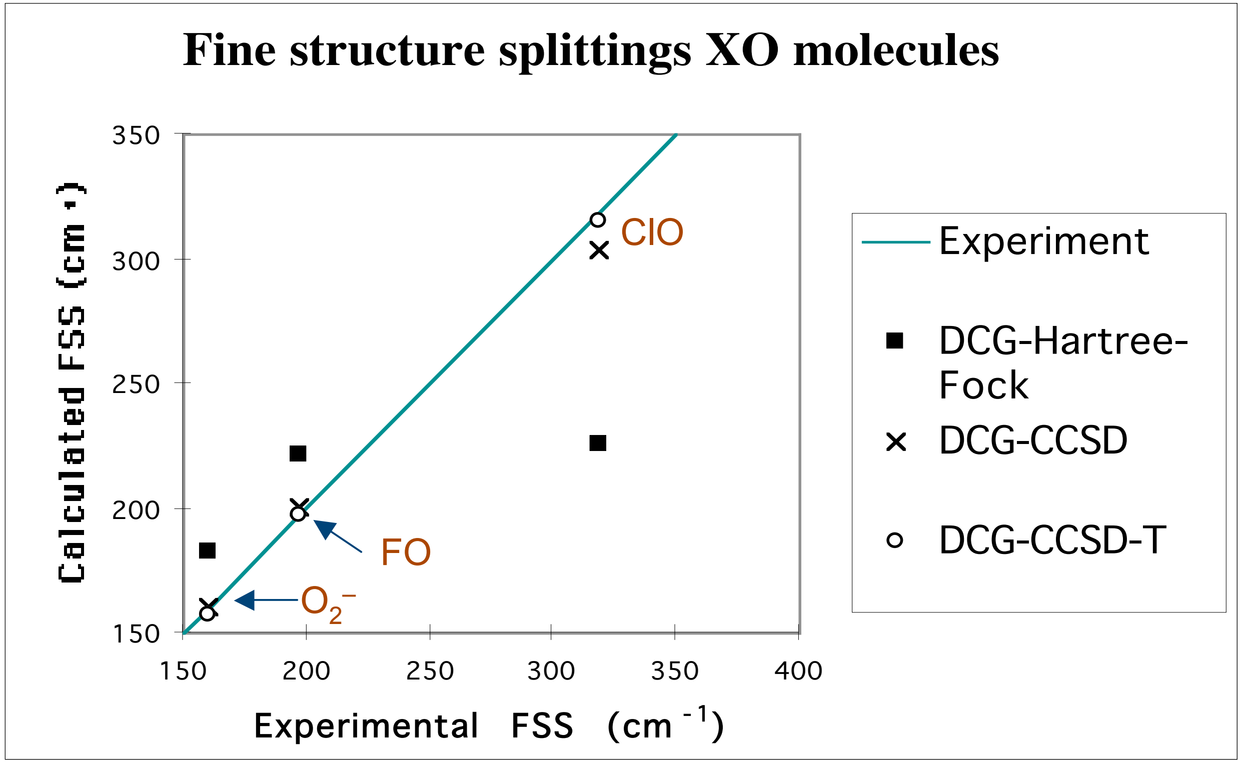
*Seth, Schwerdtfeger and Faegri (1999) calculations with contracted basis sets.

Open shell molecules

- Two studies with all-electron single and multireference methods
- Analyze relativistic effects

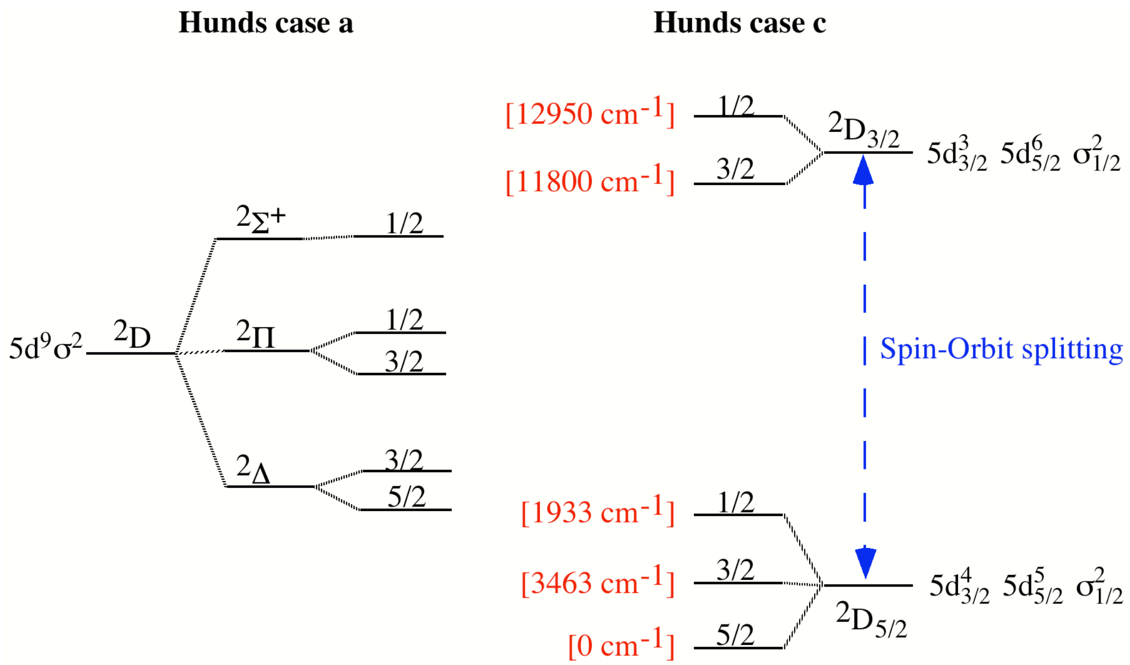
Fine structure splitting in radicals

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



Platinumhydride

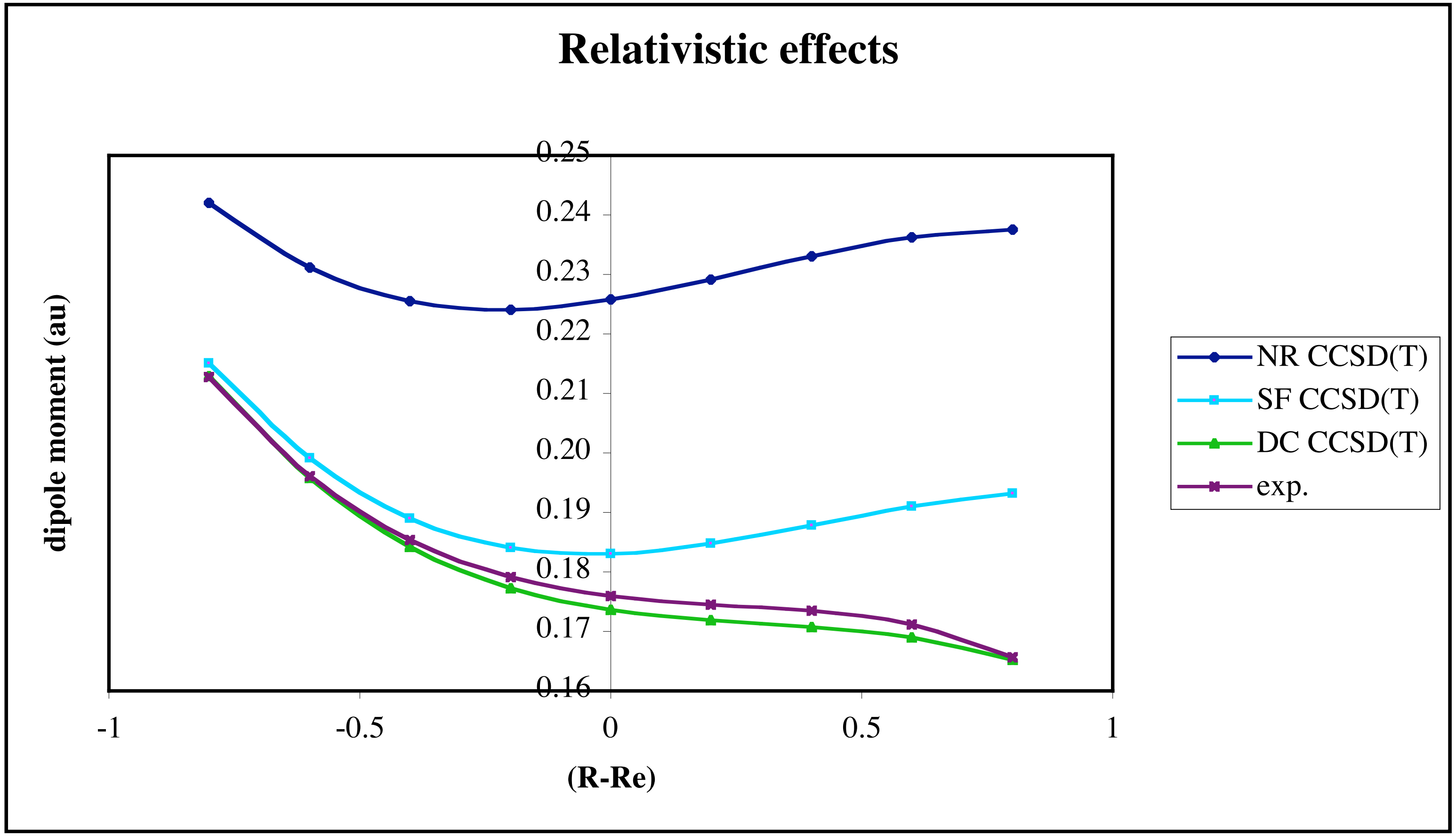
- PtH molecule : jj-coupling instead of LS-coupling scheme
- Pt ($5d^96s^1$) + H ($1s^1$) → PtH ($5d^9\sigma^2$)



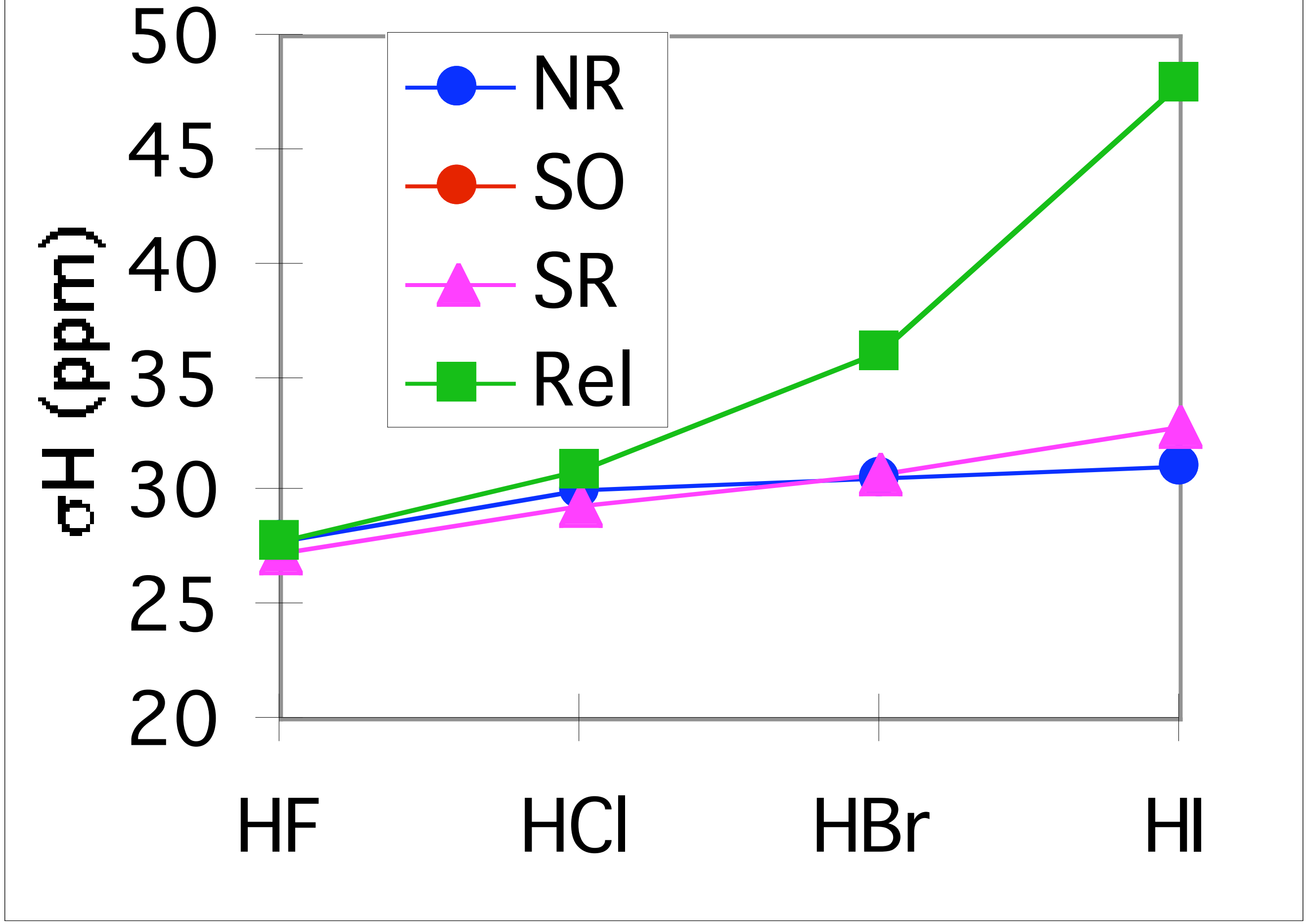
Molecular properties

- Relativistic effects on some molecular properties

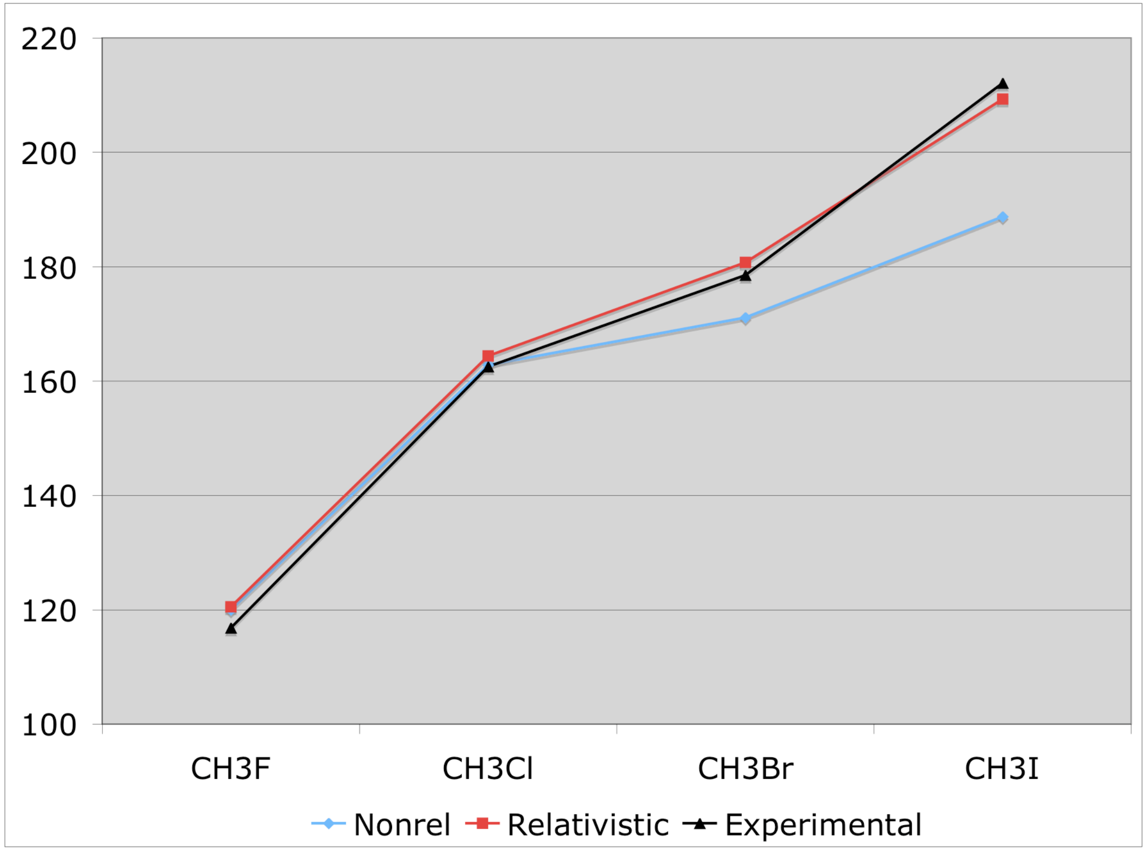
Dipole moment of HI



NMR: ^{1}H shielding trends



NMR: ^{13}C shielding trends

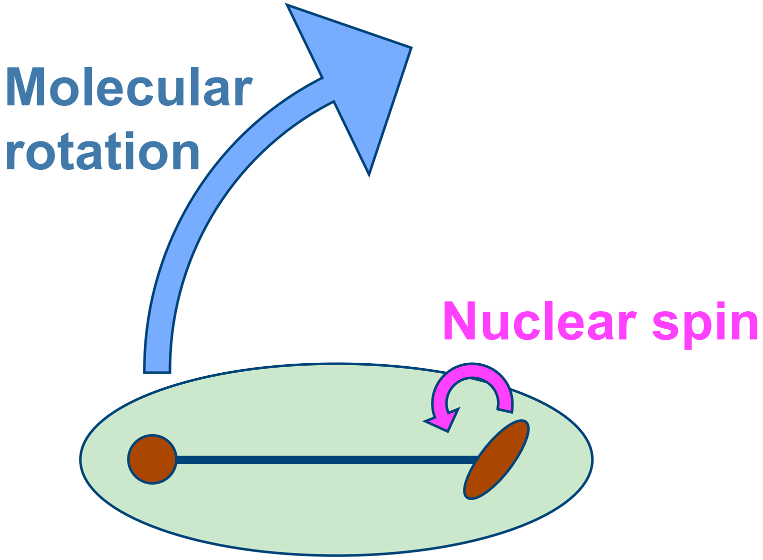


Data from Malkina et al., Chem. Phys. Lett. 1998
Mean-field SO method employed.

Extracting nuclear structure information from Spectroscopy & Quantum Chemistry

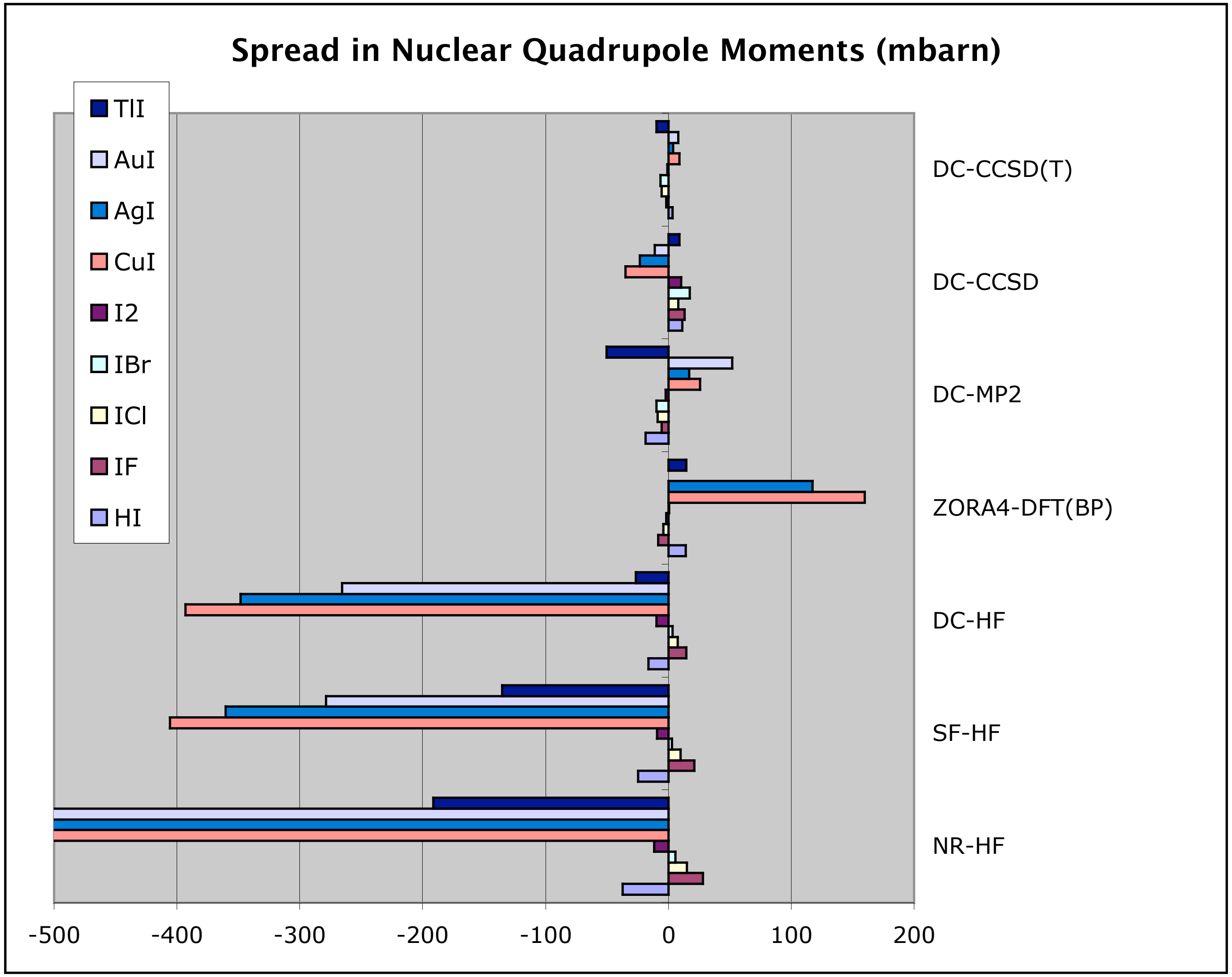
Nuclear Quadrupole Moments

- 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.



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

Iodine


Spread in Nuclear Quadrupole Moments (mbarn)
TlI
AuI
AgI
CuI
I2
IBr
ICl
IF
HI
DC-CCSD(T)
DC-CCSD
DC-MP2
ZORA4-DFT(BP)
DC-HF
SF-HF
NR-HF
-500
-400
-300
-200
-100
0
100
200

Further reading

- Relativistic Quantum Mechanics
  - 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, A'dam, 2002).
  - *Theoretical chemistry and physics of heavy and superheavy elements*, ed. U. Kaldor and S. Wilson (Kluwer, Dordrecht, 2003.
  - *Relativistic Effects in Heavy-Element Chemistry and Physics*, edited by B. A. Hess (Wiley, Chichester, 2003).
- Applications
  - *Relativistic Electronic Structure Theory - Part 2 : Applications*, ed. P. Schwerdtfeger (Elsevier, Amsterdam, 2004).

Typographical errors

- Page 601 & Formula 4 (answer to question 3) : c missing

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

- Page 604 : division symbol missing

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

- Answer to question 2

$$\begin{aligned}(\sigma\cdot\mathbf{X})(\sigma\cdot\mathbf{Y}) &= \sigma_i\sigma_j X_i Y_j \\ &= \frac{1}{2}\left[\sigma_i,\sigma_j\right]_+ X_i Y_j + \frac{1}{2}\left[\sigma_i,\sigma_j\right]_- X_i Y_j \\ &= \delta_{ij} X_i Y_j + i\varepsilon_{ijk}\sigma_k X_i Y_j \\ &= \mathbf{X}\cdot\mathbf{Y} + i\sigma\cdot(\mathbf{X}\times\mathbf{Y})\end{aligned}$$